Interfacial Properties of Graphene and 2D Materials Heterostructures Investigated by

Scanning Probe Microscopy

by

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David Mitzi

Dissertation submitted in partial fulfillment of
the requirements for the degree of
Doctor of Philosophy in the Department of
Mechanical Engineering and Materials Science
in the Graduate School of Duke University

2017
ABSTRACT

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Abstract

2D materials, e.g., graphene, and heterostructures have extraordinary properties compared to their 3D counterparts, and have great potential for a broad range of applications, including flexible electronic devices, nanocomposites, and transistors. However, in most of these applications the 2D materials need to interface with other materials such as substrates or other 2D heterostructures for not only device functionality but also mechanical stability. The interfacial properties of 2D materials and heterostructures greatly affect the performance of these 2D materials-based devices and thus call for further investigation.

In this dissertation, advanced scanning probe microscopy (SPM) techniques, including contact resonance atomic force microscopy (CR-AFM) and piezoresponse force microscopy (PFM), are applied to study the interfacial mechanical and piezoelectrical properties of graphene and 2D materials heterostructures. For the first time, CR-AFM is demonstrated with the sensitivity to local stiffness changes that arise from a single atomic layer of a van-der-Waals-adhered material. To this end, a new approach, combining CR-AFM with first-principles calculations and continuum mechanics modeling, is introduced, which can yield a quantitative subsurface atomic structure fingerprint for 2D materials and heterostructures, as demonstrated on an ideal model system – epitaxial graphene on SiC (0001). This model system is further investigated with PFM, which revealed a new
source of piezoelectricity in graphene layers that arises from the presence of interfacial dipole moments induced by the polarization in the substrate. The last part of the dissertation discusses the interfacial mechanical properties of graphene deposited onto self-assembled-monolayers (SAMs). CR-AFM experiments and molecular dynamics (MD) simulations show that the surface energy of the SAM strongly affects the amount of water molecules present at the graphene-SAM interface, which in turn influences the elastic modulus of these graphene-SAM heterostructures. The SPM methods used in this dissertation can provide rich structure-property information about interfaces and surfaces, and can be used to understand other interfacial problems of fundamental and practical interest in 2D materials and heterostructures, such as nanoconfined water and 2D layered hybrid organic-inorganic perovskites.
Dedication

To my wife.
Contents

Abstract .................................................................................................................................................iv

List of Tables...........................................................................................................................................xi

List of Figures ........................................................................................................................................xiii

Acknowledgements .................................................................................................................................xxi

1. Overview .............................................................................................................................................1

  1.1 Motivation ........................................................................................................................................1

  1.2 Objectives .......................................................................................................................................2

    1.2.1 Interfacial Mechanical Properties as a Quantitative Subsurface Atomic Structure Fingerprint for 2D Materials and Heterostructures (Objective 1) ........................................3

    1.2.2 Interface-Induced Electromechanical Properties of Epitaxial Graphene on SiC (Objective 2) .............................................................................................................................3

    1.2.3 Interfacial Mechanical Properties of Graphene-SAMs Heterostructures (Objective 3) .................................................................................................................................4

    1.2.4 Conclusions and future work ....................................................................................................5

2. Background .........................................................................................................................................6

  2.1. The Structure and Synthesis of Graphene ....................................................................................6

  2.2. Interfaces in 2D Materials Based Devices ...................................................................................10

  2.3. Piezoelectricity of 2D Materials ....................................................................................................12

  2.4. Scanning Probe Microscopy ........................................................................................................15

    2.4.1. Contact Resonance AFM ........................................................................................................17

    2.4.2. Piezoresponse Force Microscopy ............................................................................................21

    2.4.3. PeakForce Quantitative Nanomechanical Property Mapping ..............................................23
2.5. Raman Spectroscopy........................................................................................................... 24

3. Interfacial Mechanical Properties as a Quantitative Subsurface Atomic Structure
Fingerprint for 2D Materials and Heterostructures .......................................................... 27

3.1. Introduction.......................................................................................................................... 27

3.2. Methods .............................................................................................................................. 29

3.2.1. First-Principles-Informed CR-AFM .............................................................................. 29

3.2.2. AFM Measurements........................................................................................................ 33

3.2.3. Hertzian Contact............................................................................................................ 34

3.2.4. Continuum Model for Layered Material Systems ......................................................... 35

3.2.5. Graphene Growth on SiC (0001) ................................................................................ 38

3.2.6. DFT Calculations of Out-of-Plane Mechanical Properties for Epitaxial
Graphene on SiC...................................................................................................................... 40

3.3. Results and Discussion ..................................................................................................... 43

3.3.1. Epitaxial Graphene on SiC Examples ............................................................................ 43

3.3.2. Theoretical Derivation of Reduced Moduli Ratios ....................................................... 47

3.3.3. CR-AFM of Oxygen-intercalated Graphene on SiC ..................................................... 49

3.3.4. Beyond Graphene.......................................................................................................... 52

3.4. Conclusions ....................................................................................................................... 54

4. Interface Induced Electromechanical Properties of Epitaxial Graphene on SiC........ 55

4.1. Introduction........................................................................................................................ 55

4.2. Materials and Methods..................................................................................................... 57

4.3. Results and Discussions.................................................................................................... 59

4.4. Conclusions....................................................................................................................... 67
6.2.3. Piezoelectricity in 2D HOIPs

Appendix

Appendix A. Additional Information for Chapter 3

Section A.I. CR-AFM Procedures

Section A.II. Supplementary SiC Sample Surface Characterization by AFM and Raman Spectroscopy

Appendix B. Additional Information for Chapter 4

Section B.I. PFM setup

Appendix C. Additional Information for Chapter 5

Section C.I. MD setup

Section C.II. SAM Characterization

Section C.III. MD Simulations

Section C.IV. Structural Schematic

Appendix D. Additional Information for Chapter 6

References

Biography
List of Tables

Table 5.1. Surface Characterization of SAMs on Au. ......................................................... 83

Table A1. Cantilever parameters calibrated in each experiment. Cantilevers of type MPP-33220-10 from Bruker were used for CR-AFM. \( f_{i,\text{air}} \) denotes the cantilever’s free resonance frequency of the \( i \)th flexural mode in air. \( k_c \) is the spring constant of the cantilever. \( f_{i,\text{Si}} \) is the contact resonance frequency of the \( i \)th flexural mode when the cantilever is in contact with Si. \( F_{\text{Si}} \) is the total force applied on Si. \( L_i/L \) is the relative tip position of the cantilever. \( R_t \) is the tip radius. For tip radius calibration, we used a silicon wafer, assuming it is isotropic with Young’s modulus \( E_{\text{Si}} = 165 \) GPa and Poisson’s ratio \( \nu = 0.22 \). The uncertainty of the calibrated tip radius by this methodology is about 30% (Section A.I. above) ......... 117

Table A2. Measured contact resonance frequencies and total forces for Fig. 3.3e (ZLG sample) in Chapter 3. The experimental contact stiffness \( k’ \) is derived following the methods in Section A.I (above) and the experimental reduced elastic moduli range is derived via the Hertzian contact model with contact stiffness values and calibrated tip radius (See Table A1 above). The large uncertainty in tip radius results in a wide range of reduced moduli. As explained in Chapter 3, this uncertainty essentially cancels when elastic modulus ratios are formed. ................................................................. 119

Table A3. Measured contact resonance frequencies and total forces for Fig. 3.3h (MLG sample) in Chapter 3. See caption of Table A2 for further explanation. ......................... 119

Table A4. Measured contact resonance frequencies and total forces for Fig. 3.4d (O-intercalated sample) in Chapter 3. See caption of Table A2 for further explanation. ..... 120

Table A5. Entries of the stiffness tensor for 3C-SiC in GPa as calculated by DFT-PBE+TS and employed in this work. \( C_{66}’ = (C_{11} – C_{12}) / 2 \). ............................................................................. 121

Table A6. Entries of the stiffness tensor for graphite in GPa as calculated by DFT-PBE+TS and employed in this work. \( C_{66}’ = (C_{11} – C_{12}) / 2 \). ............................................................................. 122

Table A7. 2D elastic stiffness elements for freestanding layers of graphene, hexagonal boron nitride, molybdenum disulfide, and molybdenum oxide as obtained by DFT-PBE+TS in this work in GPa-nm. ............................................................................. 123

Table A8. Calculated reduced moduli values for Fig. 3.3e (ZLG sample) in Chapter 3. 123
Table A9. Calculated reduced moduli values for Fig. 3.3h (MLG sample) in Chapter 3.

........................................................................................................................................123
List of Figures

Figure 2.1. 2D graphene is the building block for many other nanocrystalline carbon: 0D fullerene, 1D carbon nanotube and 3D graphite[16]. .............................................................. 7

Figure 2.2. Growth of epitaxial graphene on SiC (0001) surface: (A-B) Formation of the $6\sqrt{3}\times 6\sqrt{3} - R30^\circ$ zero-layer (ZL) graphene starting from the SiC terrace edges; (C) the vdW-bonded monolayer (ML) graphene formed from the terrace edges and (D) as this process continues, bilayer (BL) graphene will be formed similarly. Figure modified from Ref[32]. ................................................................................. 9

Figure 2.3. Strategies proposed in the literature to break the inversion symmetry of graphene. (A) Creating non-centrosymmetric simple defects, such as triangular holes, which will cause non-zero polarization when the graphene sheet is deformed (bottom frame), while centrosymmetric circular holes (middle frame) will lead to zero polarization[58]. (B) A more complicated example of symmetry-breaking defects, which can be filled with BN units to further enhance the piezoelectricity[59]. (C) Physical adsorption of Li atoms (red) on one side of graphene[60]. (D) Chemical functionalization of graphene with hydrogen atoms (pink) on one side and fluorine atoms (grey) on the other side, causing a dipole moment across the plane (top frame). For bilayer hydrofluorinated, the polarization can be enhanced (middle frame) or canceled (bottom frame) depending on the stacking of the layers[61]. ..................................................................................... 13

Figure 2.4. Schematic of atomic force microscopy........................................................................ 17

Figure 2.5. Schematic of CR-AFM. (A) Typical CR-AFM feedback loop with indirect ultrasonic driving under the sample. For CR-AFM frequency mapping, the Dual-Actuation Resonance Tracking (DART) function[78] developed by Asylum Research is used. (B) The tip-sample contact can be modeled by a Hertzian contact model. (C) The AFM cantilever can be modeled as an Euler-Bernoulli Beam, and the contact stiffness ($k^*$) can be analytically solved from the CR frequency information. ....................................................... 18

Figure 2.6. Schematic of PFM: (A) PFM resembles conventional contact mode imaging when no bias is applied; when bias is applied, the piezoelectric sample will contract (B) or expand (C) if the applied electric field is inversed or aligned with respect to the orientation of the spontaneous polarization, respectively. .............................................................................. 21

Figure 2.7. DART PFM Mapping on ferroelectric PZT thin film polarized by ± 8V (left to right, side by side): (A) Topographic image (1 μm × 1 μm scan area); (B) PFM amplitude
mapping and (C) PFM phase mapping (scale: -90° to +90°). Imaging is done in air with a Pt/Ir coated conductive probe (spring constant ~ 5 N/m) at a set-point 0.1 V.

Figure 2.8. Raman spectrum of a freshly cleaved sample of highly oriented pyrolytic graphite. The blue arrow indicates the characteristic shoulder in 2D peak for graphite compared to the Raman spectrum of graphene.

Figure 3.1. Overview of our first-principles-informed CR-AFM approach. In CR-AFM (a), the sample is placed on an ultrasonic actuator, and the AFM cantilever, in contact with the sample, is driven and maintained at resonance by dual AC resonance tracking[78] while imaging the sample. Regions on the sample with different mechanical properties (i.e., I and II) have different CR frequencies (f_I and f_{II}) (b). In addition to the resonance frequencies, the applied forces (F^I⊥ and F^II⊥) while imaging the different regions are recorded. The cantilever dynamics is modeled by an Euler-Bernoulli beam (c) with a linear spring k* located at the tip position (L_1). The tip-sample contact is approximated by a Hertzian contact model (d), i.e., an elastic sphere with radius R_t in contact with an elastic half-space. With the experimentally measured frequencies and forces, the calibrated relative tip positions (L_1/L), and invoking a Hertzian contact model, the Euler-Bernoulli beam equation is used to derive the reduced contact modulus ratio (E^II/E^I)_exp. Alternatively, the AFM tip can also be considered as an ultrasonic transducer with a size equal to the contact area (radius a in frame (d)), and the generated acoustic waves (dark arrows) can propagate into the layered materials and across the interfaces (transmission and reflection (light arrows)) (d). This situation can be described by a continuum model, for which the stiffness matrix for each material layer (C_{kl}(I,II)) in each of the different regions on the sample is derived from an atomistic structure model (e) via first-principles calculations (f). Using the experimentally measured frequencies, forces, and the AFM tip radius, the continuum model will generate a reduced modulus ratio (E^II/E^I)_th, characteristic of the atomistic structure models used. By comparing the theoretically derived with the experimentally derived reduced modulus ratio, one can test the validity of a particular structure model, revealing detailed subsurface/interface information.

Figure 3.2. DFT calculations of the elastic properties of graphene on SiC (0001). (a) Atomistic models of (left to right) ZLG, MLG, and BLG. The blue carbon layer, G_0, indicates the buffer layer. The first G_1 and second G_2 vdW-bonded graphene layers are shown in light green and red, respectively. Silicon atoms at the interface are shown in brown and carbon atoms in gray. (b) Schematic illustration of the linear spring model. Layers with layer-dependent stiffness tensor elements C_{33,l} are connected by individual springs with spring constant k_l. (c) Layer-dependent stress-strain curves for a 6√3×6√3-R30° BLG interface model are shown in the inset. S_n denotes SiC bilayers; G_0, G_1, G_2, and
$G_3$ refer to the buffer layer, first, second, and third graphene layer respectively. The $C_{33,i}$ elements are obtained from fits to the linear part of the stress-strain curves.

Figure 3.3. CR-AFM exemplified for epitaxial graphene grown on 6H-SiC (0001). (a, b) Raman spectra of the ZLG and the MLG samples, respectively. (c) 2D peak of the MLG sample, fitted by a single Lorentzian peak ($\text{fwhm} \sim 45 \pm 2 \text{ cm}^{-1}$). (d, e) AFM height image and corresponding first flexural mode contact-resonance frequency mapping over a terrace on the ZLG sample. (f) AFM height image and (g) corresponding CR-AFM first flexural mode contact resonance frequency mapping on the MLG sample. The blue arrows indicate MLG growth fingers extending to the BLG region of the sample. (h) High-resolution CR-AFM frequency map of the region shown in red in (g). Other types of fingers (referred to as region “O” finger) with much higher CR frequency than that of the MLG domains are identified, and one of them is circled by a white dashed line. (i) Average height cross-sectional profiles (direction: from left to right) for the regions indicated in (h). For averaged $f$ and $F_\perp$ of the domains identified in (e) and (h), see Appendix A, Tables A2 and A3.

Figure 3.4. Calculation of the elastic properties of graphene on SiC (0001). (a) Calculated layer-dependent stiffness values $C_{33,i}$ for the 6$\sqrt{3}\times6\sqrt{3}-R30^\circ$ ZLG, MLG, and BLG interface models (Fig. 3.2a). (b) Reduced moduli ratios $(E_{II}^*/E_{I}^*)_{th}$ predicted for different atomic structure models compared with experimentally measured modulus ratios $(E_{II}^*/E_{I}^*)_{th}$ on the ZLG and MLG samples in Figs. 3.3e, h, respectively. The error bar for $(E_{II}^*/E_{I}^*)_{th}$ is calculated by considering the uncertainty in tip radius $R_t$ (See Appendix A, Section A.1). The experimentally measured ratio $(E_0^*/E_{MLG}^*)_{exp}$ is compared to the predicted modulus ratio $(E_{ZLG}^*/E_{MLG}^*)_{th}$, but the actual structure of region O is unknown.

Figure 3.5. CR-AFM image on an oxygen-intercalated MLG sample reveals distinct subsurface regions. (a) Height and (b) corresponding CR frequency mapping of the first flexural mode. (c,d) Zoom-in height and frequency images, respectively, of the area shown in the red box in (b). CR-AFM reveals three distinct regions marked “I”, “II”, and “III” in (d). (e) Comparison of reduced moduli ratios using various models to the experimental ratio of region “II” to “III”. The white area reflects the experimental error range. (f) Atomistic structure models of the -OH interface (left) and Si:O3 interface (right). O atoms are shown in red. For domain-averaged $f$ and $F_\perp$ in subfigure (d), see Appendix A, Table A4.

Figure 3.6. Calculated reduced elastic moduli ratios $E_{II,th}^*/E_{I,th}^*$ for different 2D layer models (II = graphene, h-BN, MoS$_2$, or MoO$_3$) suspended on H-QF-MLG vs. the bare H-
The QF-MLG model surface as reference (area I). Assumed tip parameters: radius $R_t = 100$ nm; force $F^\perp = 200$ nN; frequency $f = 200$ kHz.

Figure 4.1. Piezoelectricity measurement on the MLG sample. (A) Topographic AFM images of the sample and (B) zoom-in height image of the blue box marked in (A). (C) Corresponding contact resonance frequency mapping, and (D) the intrinsic piezoresponse mapping. (E) Piezoresponse as a function of applied AC voltage by PFM-point measurements at both MLG and BLG regions.

Figure 4.2. Piezoelectricity measurement on the ZLG sample. (A) Topographic AFM and (B) corresponding piezoresponse mapping across a few terraces on the sample with ZLG and MLG regions marked in the image. (C) Piezoresponse plotted as a function of the applied AC voltage, measured by PFM at randomly-picked points on both ZLG and MLG regions. (D) Schematic of the SiC-graphene interfacial structure. The additional dipole moment $\delta P$ exists across the $G_1$ and $G_0$ layer due to the spontaneous polarization of SiC. Pseudo-charges in $G_0$ and $G_1$ layers are marked with red and blue circles, respectively.

Figure 4.3. Piezoelectricity of oxygen-intercalated MLG sample. (A) Schematics of the interfacial structure of the QF-BLG region after the oxygen intercalation. The $G_0$ layer now is vdW-bonded to the substrate and a thin SiO$_x$ layer is formed at the interface. The original MLG region now becomes a BLG region. Note the real structure of the oxide at the interface can be different from that shown in the schematic. (B) Topographic AFM and piezoresponse mapping (CB) across a QF-BLG and QF-TLG region. (D) Piezoresponse vs. applied AC voltage relation measured by PFM at randomly-picked points on both regions.

Figure 4.4. Piezoelectricity of F4-TCNQ doped MLG sample. (A) Schematic of F4-TCNQ doped MLG region. The pseudo-negative charges in $G_1$ layer is neutralized and the additional interfacial dipole moment $\delta P$ becomes zero. The F4-TCNQ molecules are vertical on graphene layer for schematic purpose. (B) the piezoresponse vs. applied AC voltage relation measured by PFM at points randomly picked on MLG and BLG regions.

Figure 5.1. Schematic of the CR-AFM setup. The AFM tip can be approximated as a sphere with radius $R$ indenting the sample.

Figure 5.2. (a) Optical microscopy and (b) AFM topographic images of a typical few layer graphene on UDT. The red arrows indicate the region where point measurements were made. (c) Raman spectra of graphene on CH$_3$-(black, UDT) and NH$_2$-SAMs (blue, AUT).
Figure 5.3. Contact resonance frequencies of FLG-CH₃-SAM (black) and FLG-NH₂-SAM (blue) heterostructures: (a) for as-prepared samples and (b) for samples after vacuum annealing. (c) and (d) are the corresponding Raman 2D peak position for both samples before and after vacuum annealing, respectively.

Figure 5.4. (a) Representative MD snapshots of FLG on SAM with –NH₂ (top) and –CH₃ (bottom) head groups (water molecules are colored in dark blue). (b) Number of water molecules and (c) temporal profile of the non-bonded interaction energy between FLG and SAM with –NH₂ (blue) and –CH₃ (black) head groups. Average values over the last 10 ns of the simulations are inserted as bar graphs.

Figure 5.5. (a) Simulated stress – strain curves for FLG-NH₂-SAM and FLG-CH₃-SAM heterostructures in ambient (top) and vacuum conditions (bottom). (b) Estimated Young’s modulus for each case. (c) Representative snapshots of steered MD simulations. The images from top to bottom correspond to regimes I, II and III of a FLG-CH₃-SAM heterostructure in vacuum.

Figure 5.6. (a) Schematic showing the components of non-bonded interactions that are present in the SAM-FLG system: Interfacial non-bonded interactions between FLG and SAMs (green), inter-chain interactions among SAMs (blue), inter-chain interactions with only the alkyl chains (i.e., without head groups, orange), graphene (bottom layer only) – water interactions (gray), and interactions between water and the SAM (red). Deconvolution of the non-bonded interaction energy determined for (b) the FLG-CH₃-SAMs and for (c) the FLG-NH₂-SAMs in compression regime I.

Figure 5.7. Histogram of the nearest neighbor distances (head group to head group) in compression Regime I, for a CH₃-SAM in (a) ambient conditions, and (b) in vacuum, and for a NH₂-SAM in (c) ambient conditions, and (d) in vacuum. The red-dashed lines illustrate average values of the nearest neighbor distances between the well-aligned SAM head groups used as an initial structure in the simulations. The red dotted circles in the representative snapshots represent regions with lower molecular order, in (b) disruption at the edge and in (d) local aggregations.

Figure 6.1. Schematics of water adlayer formed on mica surface when it is exposed to ambient environment (A). The adlayers are in dynamic equilibrium with the water vapor in the environment. (B) The graphene transferred to mica surface under ambient
condition will thus forms a coating layer on the water adlayer, which enables subsequent AFM characterization. Figures are modified from Ref. [241].

Figure 6.2. AFM characterization of water confined at graphene-mica interface. (A) Topographic image and (B) corresponding Peakforce QNM DMT modulus mapping. The tip radius is not calibrated; thus the absolute modulus value is not shown and only modulus contrast is presented. The red arrow indicates some small nanodrops of water formed on top of the first water adlayer. (C) and (D) topographic images of the same regions taken at different times (~ 40 mins).

Figure 6.3. CR-AFM characterization of the water adlayer confined at graphene-mica interfaces. (A) Large area topographic images and (B) zoom-in topographic image of the region marked by the red box in (A). (C) CR-AFM second flexural mode frequency mapping and (D) corresponding Q factor mapping.

Figure 6.4. (A) Schematic of the 2D layered HOIP structure (modified after Ref.[251]). A is an organic ammonium cation, M is a divalent metal cation, and X is a halogen anion. The dashed line indicates the vdW interface. (B) schematic of AFM nanoindentation on suspended 2D HOIP layer to extract in-plane modulus and strength of the material (modified after Ref.[5]). (C) Optical image of a mechanically exfoliated 2D (PEA)2PbI4 flakes on Au substrate, where PEA = 2-phenylethylamine. HOIP flakes on Au substrate. The transparency of the flakes indicates the thickness. (D) AFM topographic image of mechanical exfoliated 2D HOIP flakes on Au.

Figure 6.5. CR-AFM characterization of a 3D CH3NH3PbI3 single crystal in ambient environment. (A) Topographic image and (B) the first flexural mode CR frequency map.

Figure 6.6. PFM characterization of (PMA)2PbCl4 (A and B) and (NMA)2PbCl4 (C and D). (A) and (C) are topographic AFM images. (C) and (D) are PFM point measurements. The linear relationship between piezoresponse and applied AC voltage indicates the presence of piezoelectricity.

Figure A1. Frequency histogram (blue) and Gaussian distribution fit (red line) for Fig. 3.3e (ZLG sample) in Chapter 3. (a) ZLG region and (b) MLG region. The frequencies are taken from the entire labeled region and the Gaussian distribution fitting parameters are specified in Table A2.

Figure A2. Characterization of terraces on the “ZLG sample” and the “MLG sample” by topographic and tapping mode AFM. Tapping mode AFM is operated in the repulsive...
regime (\textit{i.e.}, driving frequency \( f < \) free resonance frequency \( f_0 \), phase lag < 90\(^\circ\))[263, 264]. (a) Height, (b) the corresponding phase lag image of the ZLG sample, globally offset by 80\(^\circ\). On the SiC terrace edges, some MLG is formed. (c) Height, (d) the corresponding phase lag image of the MLG sample region shown in Fig. 3.3h in Chapter 3, globally offset by 82\(^\circ\).

Figure A3. Time-dependent change of height of the region O ("finger") features on the MLG sample discussed in Chapter 3 (See Fig. 3.3h). For two different preparations of "MLG samples" ("Batch 1" and "Batch 2"), topographic AFM images at different positions were taken within 1.5 months of preparation (samples stored in air), and again within 4-12 months after preparation. Average step heights are shown either between BLG and region O ("finger") or between BLG and MLG domains. Each column is averaged by over 20 data points measured on 10 different locations on the samples. The step height difference between BLG and MLG remains unchanged, consistent with the chemical inertness of graphene. In contrast, the relative height of the region O "fingers" changes significantly within this time period, indicating that a slow adhesive or corrosive process affects the "region O" domains.

Figure A4. Raman spectrum of the oxygen intercalated MLG sample. No apparent D peak is found, indicating the absence of the "buffer layer" feature in the investigated region.

Figure B1. Schematic of piezoresponse force microscopy setup. The sample is glued to a backelectrode by silver paste. The back electrode is grounded and the AC voltage is sent to the conductive AFM probe.

Figure B2. XPS F 1s of epitaxial graphene on SiC after the sample has been immersed in F4-TCNQ solution overnight, showing that the molecules has been adsorbed to the graphene surface.

Figure C1. Partial charge information on (a) 1-undecanethiol (-CH\(_3\)), (b) 11-amino-1-undecanethiol (-NH\(_2\)), and (c) protonated 11-amino-1-undecanethiol (-NH\(_3^+\)) used in this study.

Figure C2. Elastic modulus as a function of indentation speed (\( v \)), 0.05, 0.001, and 0.00001 pN/time step. (a) Stress – strain curve in compression regime I. For each indentation rate, the left figure is in ambient environment and right figure is in vacuum. Black and grey are FLG-CH\(_3\) heterostructures; blue and light blue are FLG-NH\(_2\) heterostructures. The negative strain in the beginning part of some of the curves is due to FLG-SAM force fluctuations when the applied stress is low. (b) Elastic modulus values with...
corresponding $R^2$ values (number inside the bar graphs) obtained from the slopes in the linear compression regime for three different indentation speeds, and (c) comparison between reduced modulus values from the experiment and averaged modulus values from SMD simulations.

Figure C3. Temporal profiles of the overall interfacial interaction energy between (a) FLG and CH$_3$ terminated SAMs and (b) FLG and NH$_2$ terminated SAMs in compression regime I. Dark colored and light colored bars with step value (t) illustrate the approximate yield point. Temporal profiles of inter-chain interactions among (c) CH$_3$ and (d) NH$_2$ terminated SAMs. The dotted lines represent the profiles of inter-chain interactions of alkyl chains without head groups.

Figure C4. High resolution N 1s XPS shows the protonation of amine groups in the NH$_2$-SAM.

Figure C5. Time evolution of the non-bonded interaction energy between SAMs and interfacial water (red), SAMs and surrounding water (water molecules within 4.5 Å of head groups excluding interfacial water, blue), the bottom layer of FLG and water (gray), and the entire SAM and water molecules (black).

Figure C6. (a) Representative simulation snapshot of FLG on NH$_3^+$-SAMs in water. In this snapshot, water molecules are omitted. (b) Average number of water molecules and (c) average non-bonded interaction energy between FLG and –NH$_3^+$ head groups.

Figure C7. Non-bonded interaction energy between FLG and –CH$_3$ head groups, –NH$_2$ head groups, and –NH$_3^+$ head groups in vacuum condition.

Figure C8. Schematic showing the presence of water in the vicinity of the FLG-CH$_3$-SAM interfaces in real systems: (A) The SAM is a polycrystalline structure, with grain boundaries and defects (The image is modified from a STM image of a CH$_3$-terminated alkanethiol SAM on Au (111)[268]). The MD simulations simplify this complex scenario into a patch of the FLG-SAM heterostructure with periodic boundary conditions. (B) Due to defects of the SAM and the roughness of the underlying substrate, small water clusters (blue) can present between graphene and the CH$_3$-terminated SAM when graphene is transferred to the SAM surface in ambient conditions. (b) Top view, showing that water (blue) can be present at the grain boundaries and defects, which is represented by the surrounding water in MD simulations.
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1. Overview

1.1 Motivation

Since the first isolation of graphene in 2004[1], two-dimensional (2D) materials, belonging to the family of van-der-Waals (vdW)-bonded, atomically-thin layered materials, have attracted tremendous research interest[2-4]. These 2D materials have extraordinary materials properties that are quite different from their 3D counterparts[2-4]. For instance, graphene, a 2D sp\(^2\) carbon layer, has a combination of exceptional mechanical, electrical, thermal, and optical properties, including extremely high mechanical modulus (~ 1TPa) and intrinsic mechanical strength (~ 130 GPa)[5], room-temperature electron mobility reaching theoretical predicted limits (~ 2.5 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})[6, 7], and very high thermal conductivity (> 3000 W mK\(^{-1}\))[8], which endow graphene with huge application potentials in high performance devices[2, 9].

However, to realize 2D-materials-based device applications, 2D materials usually sit on a substrate to enhance the stability of the atomically thin layers. Thus, the interfaces between 2D materials and substrates can directly alter the mechanical and electronic properties of the 2D materials and thus affect the long-term stability and performance of the devices. It is critically important to understand the influence of the 2D materials-substrate interface on the mechanical property and electromechanical property of the 2D layers for both the as-grown and transferred 2D-materials on a substrate.
However, many existing interface or subsurface characterization techniques are either destructive (e.g., cross-section transmission electron microscopy (TEM)[10]), and/or requires restrictive experimental environment (e.g., low-energy electron diffraction (LEED)[10-13]) or sample preparation conditions (e.g., tip-enhanced raman spectroscopy (TERS)[14]), or only provides area-integrated information of the interface with low lateral resolution (e.g., Raman spectroscopy[15], x-ray photoelectron spectroscopy[12, 13]). On the other hand, many atomic force microscopy (AFM)-based advanced scanning probe microscopy techniques, which are designed for high lateral resolution, non-destructive, interface and subsurface characterization, have surprisingly not been widely used to study the interfacial and subsurface properties of 2D materials. The need to further understand interfaces in 2D materials-based devices and the advantages of advanced AFM techniques motivates the current study on the interfacial mechanical and electromechanical properties of graphene and 2D materials heterostructures by scanning probe microscopies.

1.2 Objectives

The plan and objectives of this dissertation are described below. While throughout the dissertation, I will mostly use graphene as an example of a 2D material, the techniques used here are not limited to graphene, and I demonstrate the extension to other 2D
materials and 2D materials either by collaborative simulations (by Dr. Bjoern Lange and Prof. Volker Blum) or some preliminary results in the future work part.

**Objective 1: Interfacial Mechanical Properties as a Quantitative Subsurface Atomic Structure Fingerprint for 2D Materials and Heterostructures**

Chapter 3 presents the first application of contact resonance AFM (CR-AFM) to study the interfacial mechanical properties of graphene. CR-AFM is a dynamic AFM technique that is extremely sensitive to changes in the local elastic properties. Epitaxial graphene on 6H-SiC (0001) serves as a model sample because the structure and bonding of each atomic plane are well understood in terms of strain-free \((6\sqrt{3} \times 6\sqrt{3}) - R30^\circ\) interface models. The specific aims of this chapter are i) to demonstrate the capability of CR-AFM to detect stiffness differences arising from a single atomic layer; ii) to develop a theoretical approach – by combining continuum modeling of acoustic wave propagation in the layered materials with first-principles calculations of each materials layer and interface – to quantitatively correlate the nanomechanical measurement by CR-AFM to the underlying atomic structure and thus, iii) to establish a first-principles-calibrated CR-AFM approach for quantitative subsurface atomic structure fingerprint characterization for 2D materials and heterostructures.

**Objective 2: Interface-Induced Electromechanical Properties of Epitaxial Graphene on SiC**

Chapter 4 presents a piezoresponse force microscopy (PFM) study of epitaxial graphene on 6H-SiC (0001). Graphene is intrinsically non-piezoelectric due to its
centrosymmetric crystal structure. However, it would be very attractive to have piezoelectricity in graphene to add another dimension of functionality to this “wonder material.” While many theoretical strategies have been proposed to break the inversion symmetry and to engineer graphene into piezoelectric material, only few experimental studies are reported to demonstrate piezoelectric graphene in very special cases. Epitaxial graphene grown on a piezoelectric SiC substrate has its symmetry broken in the out-of-plane direction, which might cause piezoelectricity in graphene. The specific aims of this chapter are: i) to investigate the presence of piezoelectricity in epitaxial graphene on 6H-SiC (0001); ii) to study how piezoelectricity changes as a function of graphene thickness; and iii) to identify the origin of this piezoelectricity by systematically-designed experiments.

**Objective 3: Interfacial Mechanical Properties of Graphene-SAMs Heterostructures**

Chapter 5 presents a CR-AFM study of the mechanical property of non-ideal, transferred graphene-substrate interfaces. Self-assembled monolayers (SAMs) have been widely used to engineer the electronic properties of substrate-supported graphene devices while little is known how the surface chemistry of the SAMs affects the interfacial mechanical properties of graphene supported on SAMs. The out-of-plane elastic modulus of the graphene-SAM heterostructure reflects the change in the graphene-SAM interfacial mechanical property. The specific aims of this chapter are: i) to investigate the effect of SAM surface chemistry (i.e., hydrophobic vs. hydrophilic head groups) on the elastic
modulus of graphene-SAM heterostructure in ambient environment; ii) to study how the SAM surface chemistry affect the elastic modulus with and without vacuum annealing; and iii) to understand the mechanism of this surface energy effect by combining other surface characterization (e.g., Raman spectroscopy) and molecular dynamics simulations.

1.2.4 Conclusions and future work

Chapter 6 summarizes the salient outcomes of the research and provides a few future research studies of the 2D materials interfaces by scanning probe microscopies. Overall, this research demonstrates, for the first time, the interfacial mechanical and electromechanical properties of graphene and 2D materials heterostructures characterized by advanced AFM techniques such as CR-AFM and PFM. These techniques can be applied to many other 2D materials heterostructures systems and the findings in the current research can provide new insights for interfacial engineering of substrate-supported, 2D materials-based devices.
2. Background

The study of Interfacial properties of graphene and 2D materials requires the understanding of the structure and synthesis of graphene, the interfaces in graphene-based devices, piezoelectricity of 2D materials, and a variety of characterization tools. Each section of this chapter is intended to introduce an essential concept or characterization tool.

2.1. The Structure and Synthesis of Graphene

Graphene is the first, extensively studied 2D material. It is a monolayer of carbon atoms arranged in hexagonal crystal structure, which essentially forms the fundamental building block for many other carbon-based, nanocrystals[16]. The hexagonal 2D layer can be wrapped up into 0D fullerene, or rolled into 1D carbon-nanotubes, or stacked into 3D graphite. Inside the graphene layers, each carbon atom is bonded to neighboring atoms through strong covalent bonds, while out-of-plane, graphene layers interacting with other graphene layers or other materials through weak van-der-Waals (vdW) interactions. The weak vdW interactions between graphene layers enable the isolation of individual atomic layers and/or their stacking onto other, vdW-bonded, 2D crystals, to form heterostructures, in which the strong in-plane covalent bonds ensures the crystal integrity[3].
Figure 2.1. 2D graphene is the building block for many other nanocrystalline carbon materials: 0D fullerene, 1D carbon nanotube and 3D graphite[16].

Theoretical studies of graphene can be dated back to the 1940s[17]. However, for a long time, graphene was just a toy model until 2004, when K. Novoselov and A. Geim mechanical exfoliated 3D graphite into 2D graphene layer using a sticky tape[1]. This experiment ignited the “gold rush” in graphene. Since then, extraordinary properties of graphene have been unveiled, and many of these properties are record high and close to theoretical limits, including: A Young’s modulus of 1 TPa and an intrinsic strength ~ 130
GPa [5] (theoretically predicted ~ 1.05 TPa and ~ 120 GPa for modulus and strength, respectively [18]); impermeable to any gas molecules[19]; a room temperature electron mobility of $2.5 \times 10^5$ cm$^2$ V$^{-1}$ s$^{-1}$ [6] (theoretical prediction: $\sim 2 \times 10^5$ cm$^2$ V$^{-1}$ s$^{-1}$ [7]); record-high thermal conductivities ranging from ~ 2000 to 5300 W m$^{-1}$ K$^{-1}$ [8]; an ability to withstand extremely high current density (> million times that of copper [20]) and so on. Because of these unique properties, graphene holds great potential in various application areas, such as transistors, composites, transparent conductors, super-capacitors, etc.[2]

Although many approaches have been developed to produce large quantities, high quality graphene[2, 21], dry exfoliation, including the tape exfoliation method developed by Geim and Novoselov[1], still provides graphene flakes with the highest quality of 2D graphene crystal albeit at very low quantity. Although liquid exfoliation of graphite[22] as well as the reduction of graphene-oxide[23] can be used to scale up the graphene production, the resulting graphene has a high defect density compared to that obtained by dry exfoliation. Chemical vapor deposition[24, 25] can grow graphene on metallic catalyst surfaces on the wafer-scale and with relatively low defect density, but for device application, this will require transferring graphene to an insulating substrate.

Epitaxial graphene (EG) can be grown on SiC (0001) via high temperature sublimation of Si atoms[10, 12]. This growth technique can produce high quality graphene on the wafer scale[26]. The SiC substrate is semiconducting, which can be directly used for prototyping applications without additional transfer procedures[27]. This growth
process has been well-studied[10, 12, 28-30]. The structure and bonding of each plane are also well understood in terms of a strain-free \((6\sqrt{3} \times 6\sqrt{3}) - R30^\circ\) interface model (Fig. 2.2)[30, 31]. When subjected to high temperature, the Si atoms will be sublimated and the C atoms left behind on the surface re-arrange into a graphene-like, hexagonal crystal. Stoichiometrically, the sublimation of almost exactly 3 SiC-bilayers is required to form one C layer[12, 29].

Figure 2.2. Growth of epitaxial graphene on SiC (0001) surface: (A-B) Formation of the \((6\sqrt{3} \times 6\sqrt{3}) - R30^\circ\) zero-layer (ZL) graphene starting from the SiC terrace edges; (C) the vdW-bonded monolayer (ML) graphene formed from the terrace edges and (D) as this process continues, bilayer (BL) graphene will be formed similarly. Figure modified from Ref[32].

At the initial stage of the growth (Fig. 2.2 A), a partially \(\sigma\)-bonded, honeycomb carbon plane will be formed on top of the SiC. This layer is not graphene yet, as about 1/3 of the carbon atoms are covalently bonded to the underlying SiC, and it is usually referred
to as “buffer layer” or “zero-layer” graphene (ZLG). The growth is usually initiated from the edges of the SiC terraces and extends towards the inner part of the terraces (Figs. 2.2 A and B)\[10, 28, 32\]. As the growth continues, a new ZLG can be formed underneath and the original ZLG now becomes a vdW-bonded monolayer graphene (MLG) (Fig. 2.2C). Similarly, bilayer (BL) (Fig. 2.2D), or even thicker layers of graphene can thus be formed. By controlling the growth conditions, one can obtain samples that are predominantly covered by graphene of a certain thickness, with some thicker graphene layers along the terrace edges. Foreign atoms (e.g., hydrogen\[33\], oxygen\[13, 34\], fluorine\[35\], etc.) can be used to intercalate ZLG-SiC interface to break the covalent bonds and passivate Si dangling bonds, which will turn n layers of vdW-bonded graphene on ZLG into (n+1) layers of quasi-freestanding graphene.

### 2.2. Interfaces in 2D Materials Based Devices

In practice, the atomically-thin graphene and 2D materials are quite fragile and substrates are usually used to support the 2D materials not only for device function but also to increase the mechanical stability of the 2D materials themselves. The interface between the substrate and a 2D material, and interfaces between layers of the 2D-materials thus play a critical role for device performance. For example, the surface morphology of the substrate can affect the stress-strain state of the 2D material, while a 2D layer trying to conform to the underlying substrate, can cause inhomogeneity in the electronic properties
of the devices\cite{36}. The charged impurities\cite{37} and/or adsorbates\cite{36, 38} on the substrate surface can act as dopants of the 2D material layers and significantly alter the carrier density and carrier mobility. Small molecules, such as H$_2$O and O$_2$, can be trapped at the interfaces\cite{39} during the fabrication process and/or migrate into and out of the interfaces\cite{40, 41}, causing large hysteresis in the device performance and affecting the long-term stability of these devices\cite{42}.

A widely-used method to mitigate these unwanted, interfacial issues is to use a self-assembled monolayer (SAM) of organic molecules, such as silanes and thiols, as an interfacial layer to modify the substrate surfaces. The long alkyl chain of a SAM layer can separate a 2D materials from direct contact with charge impurities on the substrate surface\cite{43}. Furthermore, hydrophobic SAMs can greatly reduce the hysteresis of the devices when working in an environment with changing relative humidity\cite{44}. Furthermore, these SAMs can be used as controllable dopants to intentionally alter the electronic property of these 2D layers, by selecting the chemical identity of the SAM head groups and/or dipole moments of the molecules\cite{45-47}.
2.3. Piezoelectricity of 2D Materials

Piezoelectricity is an electromechanical coupling phenomenon, in which the mechanical deformation of piezoelectric materials creates an electrical field in the materials and vice versa[48]. Piezoelectricity can only exist in non-centrosymmetric materials[49, 50]. Many 2D materials have been reported to be intrinsically piezoelectric due to the break of inversion-symmetry in the crystal structure[2, 51, 52], including trigonal prismatic transition metal dichalcogenides (e.g., MoS$_2$ and WS$_2$)[51, 53], hexagonal Boron Nitride (h-BN)[54, 55], and group-IV monochalcogenides (e.g., SnS, GeS, SnSe, and GeSe)[51, 56]. For instance, bulk MoS$_2$ is non-piezoelectric because the 3D crystal structure is centrosymmetric[53]. This centro-symmetry will be broken when MoS$_2$ exists as a monolayer, which leads to piezoelectricity in MoS$_2$[53, 57]. Furthermore, piezoelectric property depends on the layer number. Odd numbers of layers break the inversion symmetry of the 2D crystal, and lead to piezoelectric behavior. A finite and zero piezoresponse were observed in MoS$_2$ with odd and even layers, respectively, due to the breaking and recovery of the inversion symmetry of the 2D crystals[53, 57]. Finally, for odd layer numbers of MoS$_2$, the piezoelectric coefficients decrease as the layer number increases, which eventually converges to the zero value of the bulk crystal[53, 57].
Figure 2.3. Strategies proposed in the literature to break the inversion symmetry of graphene. (A) Creating non-centrosymmetric simple defects, such as triangular holes, which will cause non-zero polarization when the graphene sheet is deformed (bottom frame), while centrosymmetric circular holes (middle frame) will lead to zero polarization[58]. (B) A more complicated example of symmetry-breaking defects, which can be filled with BN units to further enhance the piezoelectricity[59]. (C) Physical adsorption of Li atoms (red) on one side of graphene[60]. (D) Chemical functionalization of graphene with hydrogen atoms (pink) on one side and fluorine atoms (grey) on the other side, causing a dipole moment across the plane (top frame). For hydrofluorinated bilayers, the polarization can be enhanced (middle frame) or canceled (bottom frame) depending on the stacking of the layers[61].

Both graphite and graphene have centrosymmetric crystal structures[49, 53], and are therefore intrinsically non-piezoelectric[49, 60]. However, many symmetry breaking strategies have been proposed theoretically to engineer graphene into a piezoelectric material. In general, these approaches involve the selective introduction of defects into graphene. Creating holes with the correct symmetry in graphene, e.g., triangular rather
than circular holes (Fig. 2.3 A), has been proposed as an effective way to break the centrosymmetric crystal structure and “coax” graphene into becoming piezoelectric[49]. This type of defect is believed to be the source of the experimentally observed anomalous piezoelectric property in graphitic-carbon-nitride[58]. More complex symmetry-breaking defects can be introduced strategically (e.g., Fig. 2.3 B), and further functionalization of these defects with piezoelectric BN units can result in a piezoelectric response of graphene that is larger than that of pure BN[59]. In addition, selective surface adsorption of atoms, such as Li, K, H, and F, on one side of graphene can break the inversion symmetry of the graphene sheet and generate piezoelectric effects (Fig. 2.3 C)[60]. Furthermore, dipole moments could be introduced across the graphene 2D layer by selectively functionalizing graphene with fluorine on one side and hydrogen on the other side (Fig. 2.3 D top frame)[50, 61]. First principles calculations for this hydrofluorinated graphene show that piezoelectricity is maximal for a bilayer configuration where the dipole moments of the layers are aligned (Fig. 2.3 D middle frame), and decreases with increasing layer number due to the electron and hole carriers on the top and bottom layers induced by the depolarization field[61]. Certain types of oxide defects[62], as well as periodic topographical engineering[63], can also lead to graphene piezoelectricity. The theoretically-predicted piezoelectric coefficients of these strategically engineered graphene are comparable to those found in 3D piezoelectric crystals such as ZnO and Quartz[49, 50, 60].
Despite the various strategies proposed by theoretical calculations, very few experimental observations of piezoelectricity in graphene have been reported. Strong out-of-plane piezoelectricity is observed in SiO$_2$/Si supported monolayer CVD graphene[64]. The origin of this piezoelectricity likely arises from the dipole moments formed at the graphene-SiO$_2$ interfaces due to C-O bond formation and symmetry breaking in the out-of-plane direction[64]. However, whether graphene transferred to SiO$_2$ can form covalent bonds to the underlying substrate at room temperature is yet unknown[65], and thus the real mechanism of this strong piezoelectricity in graphene is still under debate[65, 66]. In addition to the polarization piezoelectricity discussed above, another type of piezoelectric effect in graphene, termed “band piezoelectricity”, is experimentally reported. This band piezoelectricity occurs across the boundary where graphene is suspended on one side and substrate-supported on the other side[67], and is due to the charge transfer across the boundary arising from the different response of the suspended graphene and supported graphene to strain, which induces a work function gradient across the junction. Band piezoelectricity has been utilized to build a prototype nanogenerator[67].

2.4. Scanning Probe Microscopy

Scanning probe microscopy (SPM) is branch of microscopy techniques that use a physical probe scanning the surface of the sample to form images. SPM can reliably measure pico-Newton forces with nanometer scale spatial resolution[68, 69]. One of the
most widely used SPM techniques is atomic force microscopy (AFM) [68]. In AFM, a typically 100-µm-long cantilever is used as a force sensor, which deflects through the interaction force between the AFM cantilever probe tip and the sample surface while it scans over the sample surface (Figure 2.4). The cantilever deflection is recorded by a laser-photodiode system. For imaging, there are two basic modes[70]: 1) Contact Mode, in which the cantilever maintains in contact with the sample surface at constant set-point force (deflection) while the cantilever scans over the sample surface; and 2) Tapping Mode, in which the cantilever is driven to resonance through application of a high frequency excitation, and the cantilever only touches the surface in part of each oscillation cycle. Over the years, various additional AFM modes have been developed to provide more information about the samples investigated than just topography [71-74]. Here, I only review in detail the modes used in the current study: contact resonance AFM (CR-AFM), piezoresponse force microscopy (PFM), and peak-force quantitative nanomechanical mapping (PeakForce-QNM).
2.4.1. Contact Resonance AFM

Contact resonance AFM (CR-AFM) belongs to an AFM technique family called acoustic AFM, in which additional ultrasonic vibration is coupled into the cantilever-sample contact[75]. In CR-AFM, this ultrasonic vibration is implemented either indirectly through an additional ultrasonic actuator under the sample[74, 75] or directly through electromagnetic field generated by a solenoid (magnetic modification to the cantilever...
required)[76], or photo-acoustically by a focused laser[77]. The latter setup works both in air and liquid[76, 77], but requires additional instrumental accessories. Although the indirectly driven operation mode only works well in air or vacuum[74, 76], it is easier to implement and thus is used in the current study (Fig. 2.5).

Figure 2.5. Schematic of CR-AFM. (A) Typical CR-AFM feedback loop with indirect ultrasonic driving under the sample. For CR-AFM frequency mapping, the Dual-Actuation Resonance Tracking (DART) function[78] developed by Asylum Research is used. (B) The tip-sample contact can be modeled by a Hertzian contact model. (C) The AFM cantilever can be modeled as an Euler-Bernoulli Beam, and the contact stiffness \( k^* \) can be analytically solved from the CR frequency information.

In CR-AFM, the AFM cantilever will adopt certain flexural modes depending on the driving frequency and the contact resonance frequency, \( f_c \), of the cantilever in contact
with a sample. \( f \) is directly related to the local tip-sample contact stiffness \( k^* \)[74, 75]. For the same flexural mode, a higher resonance frequency indicates a higher local tip-sample contact stiffness[74]. The tip-sample contact can be modeled by classical Hertzian contact theory between an elastic plane (sample surface) and a sphere (cantilever tip with radius \( R \)) (Fig. 2.5B)[74, 79, 80], and the contact stiffness \( k^* \) will be:

\[
k^* = \frac{3}{\sqrt{6}} F R^{*2},
\]

(2.1)

where \( F \) is the total normal force applied to the sample, and \( E^* \) is the reduced modulus of the tip-sample contact. For an isotropic, homogeneous material, \( E^* \) is given by:

\[
\frac{1}{E^*} = \frac{1-v_s^2}{E_s} + \frac{1-v_t^2}{E_t},
\]

(2.2)

where \( E_s \) and \( E_t \) are the Young’s moduli, and \( v_s \) and \( v_t \) are the Poisson’s ratios of the sample and the tip material, respectively. The \( f-k^* \) relation can be derived by modeling the AFM cantilever in contact with the sample as an Euler-Bernoulli beam (Fig. 2.5 C)[74, 81], i.e., a cantilever beam made of a homogeneous, isotropic material, extending parallel to the sample surface:

\[
E_t I \frac{\partial^4 y}{\partial x^4} + \rho A \frac{\partial^2 y}{\partial t^2} = 0,
\]

(2.3)

where \( \rho \) is the mass density, \( A = ab \) denotes the beam cross section (\( a \) is width and \( b \) is height) and \( I = \frac{ab^3}{12} \) describes the beam’s moment of inertia. The variables \( x \) and \( y \) denote the longitudinal distance along the beam and the deflection from the rest position, respectively. From Equation (2.3), one can derive the dispersion relation:

\[
E_t I \alpha_n^4 - \rho A \omega_n^2 = 0,
\]

(2.4)
where \( \omega_n \) is the angular frequency of the \( n \)th mode cantilever resonance and \( \alpha_n \) is the wave number. The resonance frequencies are given by:

\[
f_n = \frac{(\alpha_n L)^2}{2\pi} \sqrt{\frac{E_l}{\rho A L^3}},
\]

where \( f_n \) is the free and/or contact resonance frequency of the cantilever. When the cantilever is in the free state, the characteristic equation[74]:

\[
1 + \cos(\alpha_n L) \cosh(\alpha_n L) = 0,
\]

(2.6)
can be used to calculate the wave number \( \alpha_n \). The solutions to the Equation (2.6) are \( \alpha_n L = 1.8751, 4.6941, 7.8547 \) for \( n = 1, 2, 3 \), respectively. When the cantilever is in contact with the sample, \( i.e. \), the cantilever has an additional constraint at the tip position (Fig. 2.5C), the characteristic equation becomes[74]:

\[
\frac{k^*}{k_c} \left[ -[\cosh(\alpha_n L_1) \sin(\alpha_n L_1) - \sinh(\alpha_n L_1) \cos(\alpha_n L_1)] \times [1 + \cos(\alpha_n L') \cosh(\alpha_n L')] \right] + \\
[\cosh(\alpha_n L') \sin(\alpha_n L') - \sinh(\alpha_n L') \cos(\alpha_n L')][1 - \cos(\alpha_n L_1) \cosh(\alpha_n L_1)] = 2 \left( \frac{\alpha_n L_1}{3} \right)^3 [1 + \cos(\alpha_n L) \cosh(\alpha_n L)],
\]

(2.7)

where \( k_c \) is the spring constant of the free cantilever and \( L_1 \) and \( L' \) are shown in Fig. 2.5C. The relative tip position \( L'/L \) can be calibrated by the mode-equivalence method on a known sample, \( i.e. \), \( L'/L \) can be obtained by equating the contact stiffnesses derived from two flexural modes of the same cantilever with the same experimental conditions[82, 83].

More complex analytic models for the cantilever beam dynamics can be found elsewhere to take into account a sample’s viscoelasticity, lateral forces and damping on the cantilever and/or the relative position of the cantilever with respect to the sample surface[74].
2.4.2. Piezoresponse Force Microscopy

Piezoresponse force microscopy (PFM) is a contact mode AFM technique used to characterize the electromechanical coupling properties in a material, i.e., piezoelectricity or ferroelectricity[84, 85]. In PFM, through contact with a conductive AFM probe tip, an AC electric field is applied to the sample surface while the tip scans over the sample surface (Fig. 2.6). If the sample is piezoelectric, i.e., it contains a spontaneous polarization, the sample will expand or contract depending on whether the electric field applied by the AFM is aligned with the spontaneous polarization or not (Figs. 2.6A and B).

![Figure 2.6. Schematic of PFM: (A) PFM resembles conventional contact mode imaging when no bias is applied; when bias is applied, the piezoelectric sample will contract (B) or expand (C) if the applied electric field is inversed or aligned with respect to the orientation of the spontaneous polarization, respectively.](image)

The mechanical deformation in the sample induced by the AC field is measured by the first harmonic response of the AFM cantilever. For piezoelectric materials, due to the converse piezoelectric effect, the field-induced strain $s_j$ is[85]:

$$s_j = d_{ij}E_i ,$$

(2.8)

where $d_{ij}$ are components of the piezoelectric tensor (in Voigt form), and $E_i$ is the applied electric field. The field-induced displacement measured by the AFM will be
\[ A_{PR} = d_{eff} V_{AC}, \]  

(2.9)

where \( d_{eff} \) is the effective, converse piezoelectric coefficient, which depends on the piezoelectric tensor \( d_{ij} \) \[85, 86\], and where \( V_{AC} \) is the applied AC voltage. Thus piezoelectricity will result in a frequency-independent PFM amplitude when the frequency of the AC field is away from the cantilever resonance\[87\], and the piezoresponse signal \( A_{PR} \) should depend linearly on the strength of the driving AC electric field\[58, 88\]. The frequency of the AC electric field can be tuned to coincide with the contact resonance frequency of the AFM cantilever, which largely enhances the PFM signal (>100 times)\[89\]. For PFM point measurements, the cantilever response is recorded as a function of driving frequency, and can be fitted to a damped simple harmonic oscillator (DSHO) model to extract the piezoresponse signal\[58, 89\]:

\[ A(\omega) = \frac{A_{PR}\omega_0^2}{\sqrt{(\omega^2-\omega_0^2)^2-(\omega\omega_0/Q)^2}}, \]  

(2.10)

where \( A, \omega, \omega_0, Q \) and \( A_{PR} \) are the amplitude, the driving frequency, the contact resonance frequency of the AFM cantilever, quality factor of the resonance peak and the piezoresponse signal, respectively. The DART function of the AFM can be used to maintain the AFM cantilever at contact resonance while the AFM tip scans over the sample surface to extract the piezoresponse signal\[78\]. DART-PFM mapping can provide qualitative contrast of regions with different piezoelectric properties, such as the piezoelectric coefficient (by piezoresponse mapping) and the piezoelectric polarization direction (by PFM phase mapping)\[78, 90\]. Figure 2.7 is an example of a ferroelectric PZT
thin film that was polarized side-by-side with +8V and −8V. The same polarization bias in the two domains results in a similar, piezoelectric spontaneous polarization (i.e., both domains have the same piezoelectric coefficient) as shown by the piezoresponse mapping (Fig. 2.7B). The upward vs. downward polarization direction, however, yields a 180° difference across the two domains in phase mapping (Fig. 2.7C). A quantification of the piezoelectrical coefficient of the sample by PFM is complicated and requires careful calibration of the AFM cantilever both in lateral and vertical direction, as well information of the tip geometry[84-86].

Figure 2.7. DART PFM Mapping on ferroelectric PZT thin film polarized by ±8V (left to right, side by side): (A) Topographic image (1 µm × 1 µm scan area); (B) PFM amplitude mapping and (C) PFM phase mapping (scale: -90° to +90°). Imaging is done in air with a Pt/Ir coated conductive probe (spring constant ~ 5 N/m) at a set-point 0.1V.

### 2.4.3. PeakForce Quantitative Nanomechanical Property Mapping

PeakForce Quantitative Nanomechanical Property Mapping (PeakForce-QNM)[91, 92] is another type of nanomechanical mapping technique which is based on
peakforce tapping mode[93], a pulsed force mode. PeakForce-QNM performs a nano-indentation at each pixel of the scan area and analyzes the obtained force-distance curve using the Derjaguin-Muller-Toporov (DMT) model[91, 92]. Other than topographical images, PeakForce-QNM can concurrently provide measure for adhesion, deformation, elastic modulus, and dissipation with the same lateral resolution as the height image. Unlike other contact mode based nanomechanical property mapping, PeakForce-QNM can better preserve the sample and the tip due to less force applied and less wear[91, 92]. PeakForce-QNM has been used to qualitatively show Young’s Modulus contrast patterns arising from the commensurate-incommensurate transition in graphene-h-BN heterostructures [94].

### 2.5. Raman Spectroscopy

Raman spectroscopy is an inelastic light scattering technique for materials characterization based on vibrational and rotational modes of molecules in different states[95, 96]. Raman spectroscopy measures the frequency shift of the scattered phonons compared to the monochromatic incident phonons, which contains fingerprint information on a materials’ structure and electronic states[95]. Because of its non-destructiveness and information-rich character, Raman spectroscopy has been widely used for the chemical characterization of surfaces, including graphene. A typical graphite Raman spectrum within 1000 ~ 3000 cm⁻¹ with two prominent features is shown in Figure...
2.8: i) the “G” peak at ~ 1580 cm⁻¹, which arises from a first order Raman scattering originating from the in-plane C-C bond stretching and bending; and ii) the “2D” peak at ~2700 cm⁻¹, which is the “D” peak overtone[15, 97, 98]. Unlike the “D” peak (~1350 cm⁻¹), which is due to the breathing modes of the hexagonal ring in graphene and requires a defect for its activation[98-100], the “2D” peak does not require a defect and thus is always present[101, 102]. The absence of the D peak indicates the presence of essentially defect-free graphene layers in the graphite sample. The shoulder in the 2D peak (blue arrow in Fig. 2.8) is a characteristic feature of graphite[100, 101].

Raman spectroscopy on graphene samples can provide tremendous information on the total number of graphene layers[101, 103], doping[104, 105], defects[106], strain state[107], chemical functionalization[108], electrical mobility[109], etc. of graphene. For instance, the intensity ratio of the D peak to the G peak (I(D)/I(G)) can be used to evaluate the relative defect density and the grain size of a graphene sample[110]. The 2D peak position is very sensitive to the doping of graphene samples[105]. The full-width at half maximum (FWHM) of the 2D peak is a good indicator of the total number of graphene layers[103, 111]. However, the 2D peak will be indistinguishable from that of graphite when the sample has 5 or more layers of graphene[101]. For more details about the mechanism and the interpretation of Raman spectroscopy on graphene samples, the readers are deferred to the two comprehensive reviews by A. C. Ferrari etc.[15], and M. S. Dresselhaus[97].
Figure 2.8. Raman spectrum of a freshly cleaved sample of highly oriented pyrolytic graphite. The blue arrow indicates the characteristic shoulder in 2D peak for graphite compared to the Raman spectrum of graphene.
3. Interfacial Mechanical Properties as a Quantitative Subsurface Atomic Structure Fingerprint for 2D Materials and Heterostructures

3.1. Introduction

Two-dimensional van der Waals (vdW)-bonded materials, including graphene, hexagonal boron nitride (h-BN), and transition metal dichalcogenides (MX₂), possess extraordinary electrical, optical, and mechanical properties, holding great promise for high-performance device applications[2]. Harnessing the unique properties of 2D materials and heterostructures for nanoscale device applications requires precise control over the interface to the growth substrate[11, 13, 34, 112, 113], the layer number[114-116], the lateral arrangement of different domains[117, 118], and the nature of subsurface structure elements[3]. Interfaces between these 2D materials are critical for device applications[2, 3, 119]. For example, in vertical heterostructures, interactions through interfaces and/or intentional or unintentional intercalations[11] can chemically change or mechanically distort the 2D material layers, altering their electrical[119, 120], optical[111, 120, 121], and mechanical properties[94]. It is thus critical to obtain precise information

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1 This chapter is based on Qing Tu, Björn Lange, Zehra Parlak, Joao Marcelo J. Lopes, Volker Blum, and Stefan Zauscher, Quantitative Subsurface Atomic Structure Fingerprint for 2D Materials and Heterostructures by First-Principles Calibrated Contact-Resonance Atomic Force Microscopy, ACS Nano, 2016, 10 (7), pp 6491-6500. The first-principles calculations and part of the continuum simulations were performed by Dr. Björn Lange. The SiC graphene samples are prepared by Dr. Joao Marcelo J. Lopes
about the identity and the in- and out-of-plane arrangement of material domains in layered 2D material heterostructures[122].

Many existing surface and interface characterization techniques are destructive (e.g., cross-sectional transmission electron microscopy[10]), require restrictive experimental environments (e.g., low-energy electron diffraction (LEED)[10-13, 30], low-energy electron microscopy (LEEM)[10-12, 30, 123], grazing incidence X-ray diffraction[124], X-ray standing waves[119]), or provide only area integrated information (e.g., X-ray photoelectron spectroscopy[12, 13] and Raman spectroscopy[12, 111, 121]).

Several atomic force microscopy (AFM)-based nondestructive techniques have been developed to indirectly probe interfaces and/or subsurface structures. For instance, scattering-type scanning near-field optical microscopy[125] provides insights into lateral defect structures by measuring the plasmonic response of a surface layer. However, this technique demands the existence of high momenta plasmons and is therefore not suitable for a large range of materials. Tip-enhanced Raman spectroscopy (TERS) can provide nanoscale chemical analysis of a sample surface[14, 126, 127], but the stringent prerequisites for the tips and sample substrates limit the application of TERS[14]. Peakforce tapping AFM has been used to detect the commensurate-incommensurate transition in graphene-h-BN heterostructures by analyzing qualitative out-of-plane Young’s modulus contrast patterns[94]. Recently, contact resonance atomic force microscopy (CR-AFM) in liquid has been used to characterize the out-of-plane mechanical
properties of 2D Ti$_3$C$_2$T$_x$ (MXene)-based electrodes in situ during alkaline cation intercalation and extraction[128]. In this case, the film studied was micrometers thick and the measured mechanical property changes reflect the cumulative effects of the interfaces in the film.

Here we report an innovative approach that synergistically combines CR-AFM[81] – a nondestructive, dynamic scanning probe microscopy method that can be employed in a wide range of environmental conditions – with first-principles atomistic calculations and a continuum mechanics model to provide quantitative, atomic-layer-resolved nanomechanical information. This approach yields a nanomechanical, subsurface-sensitive “fingerprint” of the atomic structure of an interface, demonstrated here for heterostructures involving graphene and other 2D materials. Fast continuum simulations, informed by databases[129] of elastic properties of 2D and 3D materials, will enable the rapid identification of experimentally observed structure fingerprints.

3.2. Methods

3.2.1. First-Principles-Informed CR-AFM

Figure 3.1 summarizes our combined approach. CR-AFM is based on a conventional contact mode AFM but uses an additional actuator – typically mounted beneath the sample – that drives the coupled cantilever-sample system (Fig. 3.1a) at
resonance. CR-AFM is thus able to map structure-dependent differences via the contact resonance frequency $f$ of different regions (Fig. 3.1b), reflecting nanoscale changes in the elastic and interfacial properties of thin, layered materials systems[74, 81]. We show that these measured changes can be quantitatively compared to the structure theoretically expected response from domains of different structure. Remarkably, our approach is sensitive to changes in the atomic structure of single layers and their sequence in the investigated region.

In CR-AFM, the AFM cantilever can be considered as an Euler-Bernoulli cantilever beam (Fig. 3.1c). The tip-sample contact is represented by an elastic spring[81], whose spring constant reflects the effective tip-sample contact stiffness $k^*$

$$k^* = \frac{dF}{d\delta} |_{F^\perp}$$

(3.1)

where $\delta$ is the indentation depth of the probe and $F^\perp$ is the total force applied normal to the surface and includes both the set point force applied through the AFM cantilever and the local interaction between the AFM cantilever tip and sample surface determined by force-distance “pull-off” curves. $k^*$ can be related to the cantilever flexural resonance frequencies, $f$, the primary observable of CR-AFM, by solving the beam dynamics analytically (see Chapter 2, Section 2.4.1). For a given flexural vibration mode, a higher contact stiffness will result in a higher resonance frequency[74]. The contact stiffness thus reflects the elastic properties of (i) each atomic layer in the sample, of (ii) each interface, and of (iii) the probe tip. The Hertzian contact model (Fig. 3.1c), widely accepted to
describe the AFM tip-sample contact for elastic materials[74, 79, 80], connects \( k^* \) to the reduced elastic modulus of the tip-sample contact, \( E^* \), via

\[
k^* = \sqrt{\frac{3}{6} F_{\perp} R_t E^{*2}}.
\]  

(3.2)
with the sample, is driven and maintained at resonance by dual AC resonance tracking [78] while imaging the sample. Regions on the sample with different mechanical properties (i.e., I and II) have different CR frequencies ($f_I$ and $f_{II}$) (b). In addition to the resonance frequencies, the applied forces ($F_I^\perp$ and $F_{II}^\perp$) while imaging the different regions are recorded. The cantilever dynamics is modeled by an Euler-Bernoulli beam (c) with a linear spring $k^*$ located at the tip position ($L_1$). The tip-sample contact is approximated by a Hertzian contact model (d), i.e., an elastic sphere with radius $R_t$ in contact with an elastic half-space. With the experimentally measured frequencies and forces, the calibrated relative tip positions ($L_1/L$), and invoking a Hertzian contact model, the Euler-Bernoulli beam equation is used to derive the reduced contact modulus ratio ($E_{II}^*/E_I^*$)\text{exp}. Alternatively, the AFM tip can also be considered as an ultrasonic transducer with a size equal to the contact area (radius $a$ in frame (d)), and the generated acoustic waves (dark arrows) can propagate into the layered materials and across the interfaces (transmission and reflection (light arrows)) (d). This situation can be described by a continuum model, for which the stiffness matrix for each material layer ($C_{k_{II}}(I,II)$) in each of the different regions on the sample is derived from an atomistic structure model (e) via first-principles calculations (f). Using the experimentally measured frequencies, forces, and the AFM tip radius, the continuum model will generate a reduced modulus ratio ($E_{II}^*/E_I^*$)\text{th}, characteristic of the atomistic structure models used. By comparing the theoretically derived with the experimentally derived reduced modulus ratio, one can test the validity of a particular structure model, revealing detailed subsurface/interface information.

See Section 3.2.3 below for details. $R_t$ is the effective radius for the assumed spherical tip in contact with a flat surface. In practice, both $R_t$ and $F^\perp$ are determined experimentally along with $k^*$. Importantly, Equation (3.2) shows that the dependence on $R_t$ can be eliminated by focusing on ratios of the reduced elastic moduli, $E_{II}^*/E_I^*$, of two different surface regions I and II:

$$\frac{E_{II}^*}{E_I^*} = \sqrt{\frac{k_{II}}{k_I}} \frac{F_I^\perp}{F_{II}^\perp}. \quad (3.3)$$
The central point of this paper is that, by our approach, the reduced elastic moduli, measured for different surface regions on a given sample, can be related quantitatively to the specific surface and subsurface atomic structure(s) of these regions. As shown in Figure 3.1, $E_{II}^*/E_{I}^*$ can be inferred either purely from experimental data (via the Euler-Bernoulli beam model) or independently from theory by postulating surface and subsurface atomic structure models for different regions (Fig. 3.1e). The elastic properties of each atomic layer are calculated from first principles and passed into a continuum mechanical model (see Section 3.2.4) that predicts the reduced elastic modulus for the AFM tip-sample system. The measured ratios $(E_{II}^*/E_{I}^*)_\text{exp}$ can be compared to first-principles-based ratios $(E_{II}^*/E_{I}^*)_\text{th}$ to establish the consistency between experiment and the postulated structure models. The result is a quantitative, nanomechanical “fingerprint” of the surface and subsurface atomic structure of the different regions on a sample.

### 3.2.2. AFM Measurements

All AFM measurements were conducted with an Asylum MFP-3D AFM (Oxford Instrument, CA) in dry ambient environment (20% ≤ RH ≤ 28%, T ~ 297 ± 1 K). Prior to any measurement, the deflection sensitivity was calibrated by engaging the cantilever on a silicon surface. The spring constant, $k_c$, of the cantilever was determined from the power spectral density of the thermal noise fluctuations in air\[130\] by fitting the first free resonant peak to the equations for a simple harmonic oscillator\[131\] (See Appendix A,
Table A.1 for calibration details). For CR-AFM mapping, the built-in dual actuation
resonance tracking approach of the Asylum MFP-3D AFM was used to track the contact-
resonance frequency while scanning the sample surface[78]. Ultrasonic actuation was
implemented by gluing the sample on a small ultrasonic transducer (see Fig. 3.1a) with a
broadband resonance of 2.25 MHz (V133-RM, Olympus NDT). The driving signal sent
from the AFM controller ranged between 100 to 200 m and yield 10 – 30 mV of contact-
resonance amplitude in air. The local interaction between the AFM tip and the sample
surface was determined from adhesion measurements on the region of interest in the
sample. The relative tip position \( L_1/L \) (see Figure 3.1c) was determined by measuring the
first and second flexural mode resonance frequencies of the cantilever in constant force
contact with a silicon surface. The tip radius \( R_t \) was determined by measuring the contact
stiffness on a silicon wafer using the known bulk material properties of Si[132] and
applying a Hertzian contact model (see Section 2.4.1 and below). The average CR
frequency of a region in the image is the mean value of the Gaussian fit to the frequency
distribution of the entire region (see Appendix A, Figure A.1 for instance).

### 3.2.3. Hertzian Contact

Hertzian contact theory describes the elastic contact of a sphere with a plane (Fig.
3.1d) and is often used to approximate an AFM tip indenting a sample surface with a force
\( F^\perp \). The contact radius, \( a \), and the contact stiffness, \( k^* \), are given by[74]
\[ a = \sqrt[3]{\frac{3F^4R^*}{4E^*}}, \quad k^* = \frac{3}{6F^4R^*E^*}, \quad E^* = \frac{k^*}{2a}, \quad (3.4) \]

where \( R^* \) and \( E^* \) are the reduced radius and the reduced modulus, respectively, and are given by

\[
\frac{1}{R^*} = \frac{1}{R_t} + \frac{1}{R_s}, \quad (3.5)
\]

\[
\frac{1}{E^*} = \frac{1}{E_t^*} + \frac{1}{E_s^*}, \quad (3.6)
\]

\( R_t \) and \( R_s \) are the curvature radii of the AFM tip and the sample surface, respectively. As \( R_s \to \infty \), \( R^* \to R_t \). \( E_t^* \) and \( E_s^* \) are the reduced moduli of the AFM tip and the sample, respectively, which are related to the mechanical properties of the materials. The reduced modulus of an isotropic material \( E_i^* \) is

\[
E_i^* = \frac{E_i}{1-v_i^2}, \quad (3.7)
\]

where \( E_i \) and \( v_i \) are the Young’s modulus and the Poisson ratio of the material, respectively. For anisotropic or layered materials, the reduced modulus of the material is a more complicated expression and can be calculated by the method proposed by Yaralioglu, et al.[80] (see below).

### 3.2.4. Continuum Model for Layered Material Systems

To deconvolute the experimentally measured, reduced elastic moduli and, where possible, to unequivocally assign a layer structure with single-atomic-layer resolution, we calculate elastic moduli ratios \( \left( \frac{E_{ii}^*}{E_{ij}^*} \right)_\text{th} \) by a continuum mechanics modeling approach[80]. This approach combines Hertzian contact theory with the mechanical
impedance of thin, layered materials derived from acoustic wave propagation. The AFM tip-sample contact (Fig. 3.1c) is considered to be a finite-sized transducer (contact radius a) that modulate the layered material surface with ultrasonic pressure fields. When $a \ll \lambda_0$, where $\lambda_0$ is the shortest wavelength in the probed layered solid at the actuator frequency, the radiation loss is very small. Thus, the imaginary part of the effective mechanical radiation impedance, $\text{Im}(Z_{\text{eff}})$, which reflects the elastic system response, dominates.

Here we give a brief sketch of the continuum model. Following the notation in the paper by Yaragioğlu et al.[80], the effective mechanical impedance of a layered materials system is

$$Z_{\text{eff}} = -\frac{\iint_S \sigma_{zz}(x,y) \sigma_{zz}^*(x,y) \, dx \, dy}{\iint_S \sigma_{zz}^*(x,y) V_z(x,y) \, dx \, dy},$$

(3.8)

where $S$ is the size of the ultrasonic source, here the contact area of the AFM probe on the surface. $\sigma_{zz}(x,y)$ is the normal stress over $S$, and $V_z(x,y)$ is the corresponding particle velocity induced by this normal stress. Here the $xyz$ coordinates are set as the following: the $x$-$y$ plane is parallel to the layer plane and the $z$-axis normal to the layer plane. Equation (3.8) can be Fourier-transformed into the frequency domain considering the axial symmetry of the system:

$$Z_{\text{eff}} = -\frac{\int_0^\infty |\sigma_{zz}(k_x)|^2 k_x \, dk_x}{\int_0^\infty \sigma_{zz}(k_x) V_z(k_x) k_x \, dk_x}.$$  

(3.9)
where $k_r$ is the radial wave number and $\tilde{\sigma}_{zz}(k_r)$ is the Fourier transform of $\sigma_{zz}$. We assume that a uniform unit normal stress, $\tilde{\sigma}_{zz}(k_r) = 2\pi a \frac{\mathcal{B}_1(k_r a)}{k_r}$, is applied in the tip-surface contact area $S$, $\mathcal{B}_1(\cdot)$ denotes the Bessel function of the first kind, first order. The stress on the surface perpendicular to the $z$ axis is related to the particle velocity $\tilde{V}$ through the surface impedance tensor $G(k_r, z)$

$$\begin{bmatrix} \tilde{\sigma}_{xz}(k_r) \\ \tilde{\sigma}_{yz}(k_r) \\ \tilde{\sigma}_{zz}(k_r) \end{bmatrix} = G(k_r, z) \begin{bmatrix} \tilde{V}_x(k_r) \\ \tilde{V}_y(k_r) \\ \tilde{V}_z(k_r) \end{bmatrix}. \quad (3.10)$$

For layered material heterostructures, the surface impedance tensor $G(k_r, z)$, is calculated following the methods proposed by Degertekin[133] by considering a Lamb wave with wave number $k_r$ that propagates in each layer, and is partially transmitted and reflected at the interfaces between the layers. In this calculation, the thickness and stiffness matrix of each layer are the input, and the interfacial bonding strength determines the boundary conditions. For covalently-bonded interfaces, $G$ will be continuous across the interface. However, in case of interfaces bonded through secondary bonds, e.g., van der Waals forces, successive plane slip freely so that the shear stress ($\tilde{\sigma}_{xz}, \tilde{\sigma}_{yz}$) can be close to zero, and only the normal force $\tilde{\sigma}_{zz}$ and the normal particle velocity $\tilde{V}_z$ will be continuous across the interface[80, 133, 134]. In this case, only $G_{3,3}$ will be continuous. For few layer graphene on SiC, the bonding between the zero layer and SiC shows covalent character, while the freestanding graphene layers on top of the zero layer are bonded by van der Waals interactions.
Once $G$ is obtained at the top surface of the sample, the effective mechanical impedance will take the final form:

$$Z_{\text{eff}} = -\left(2 \int_0^\infty \frac{b_1(k_r \omega)}{k_r} \mathcal{G}_{3,3}^{-1}(k_r) k_r \, dk_r \right)^{-1},$$

(3.11)

where $\mathcal{G}_{3,3}^{-1}$ is the (3,3) element of the inverse of the surface impedance tensor. This effective impedance, $Z_{\text{eff}}$ can be related to the contact stiffness by Equation (3.12) below. Note that $Z_{\text{eff}}$ is a complex number with both a real and an imaginary part. In the mechanical impedance analogy, the imaginary part of the mechanical impedance corresponds to the elastic response, while the real part corresponds to the viscous response. When the imaginary part dominates (see above), the sample surface stiffness $k_s^*$ is

$$k_s^* = \frac{\text{normal force on contact}}{\text{displacement}} = \text{Im}(2 \pi n^2 a^2 Z_{\text{eff}}).$$

(3.12)

The reduced moduli of the layered material sample would be,

$$E_s^* = \frac{k_s^*}{2a}.$$  

(3.13)

The Matlab code calculating the surface impedance tensor is available in the appendix of Ref. [133]. The continuum model was implemented according to the contact stiffness algorithm depicted in Ref. [80].

### 3.2.5. Graphene Growth on SiC (0001)

Epitaxial graphene was grown on a 6H-SiC (0001) substrate, cut from a nominally on-axis, 2 in., n-doped SiC wafer, polished on the (0001) face. The substrates were
chemically cleaned in n-butylacetate, acetone, and methanol. Hydrogen etching and graphene growth were both performed in an induction heating furnace. Hydrogen etching treatment was carried out at 1673 K for 15 min in a forming gas atmosphere (95% atom % Ar and 5 atom % H) of 900 mbar and a flow rate of 100 sccm. The sample that was predominantly covered by zero-layer graphene (referred to as “ZLG” sample) was then produced[124] by thermally treating the samples in the same system at a temperature of 1723 K for 15 min in an Ar atmosphere of 900 mbar and a flow rate of 100 sccm. The sample predominantly covered by monolayer graphene (referred to as “MLG” sample) was prepared[34, 135] by exposure to 900 mbar Ar atmosphere also, with a flow rate of 500 sccm at 1873 K for 15 min. Oxygen intercalation was achieved[34] by thermally treating the monolayer epitaxial graphene on 6H-SiC (0001) for 40 min at 873 K in air with a preceding heating ramp of 50 K/min. Raman spectra of the samples were acquired with a Horiba Jobin Yvon LabRam Aramis Raman microscope equipped with CCD camera and a HeNe laser (\(\lambda \sim 633\) nm). During the measurement, the laser spot (\(\sim 1\) μm in diameter) was placed inside the SiC terraces to minimize the signal disturbance from the edges. All Raman data were corrected by subtracting the spectrum from that of a H-etched SiC sample obtained from the same wafer[34, 121].
3.2.6. DFT Calculations of Out-of-Plane Mechanical Properties for Epitaxial Graphene on SiC

The continuum model requires as input the atomic-layer-resolved elastic constants of the assumed atomic structure of a given sample region. We calculate in-plane and out-of-plane stiffness tensor elements, $C_{ij}$, from atomist layer models using density functional theory (DFT) based on the Tkatchenko-Scheffler[136] (TS) vdW-corrected Perdew-Burke-Ernzerhof[137] generalized gradient approximation (PBE+TS) and linear response theory[138].

![Diagram of graphene models](image)

Figure 3.2. DFT calculations of the elastic properties of graphene on SiC (0001). (a) Atomistic models of (left to right) ZLG, MLG, and BLG. The blue carbon layer, $G_0$, indicates the buffer layer. The first $G_1$ and second $G_2$ vdW-bonded graphene layers are
shown in light green and red, respectively. Silicon atoms at the interface are shown in brown and carbon atoms in gray. (b) Schematic illustration of the linear spring model. Layers with layer-dependent stiffness tensor elements $C_{33,i}$, are connected by individual springs with spring constant $k_i$. (c) Layer-dependent stress-strain curves for a $(6\sqrt{3}\times6\sqrt{3})$-$R30^\circ$ BLG interface model are shown in the inset. $S_n$ denotes SiC bilayers; $G_0$, $G_1$, $G_2$, and $G_3$ refer to the buffer layer, first, second, and third graphene layer respectively. The $C_{33,i}$ elements are obtained from fits to the linear part of the stress-strain curves.

The structure and bonding of each plane in epitaxial graphene grown by high temperature Si sublimation on SiC are well understood in terms of strain-free $(6\sqrt{3}\times6\sqrt{3})$-$R30^\circ$ interface models (Fig. 3.2a)[30, 31, 139], and also amenable to first-principles calculations of elastic properties. We call structure models (including the SiC substrate) terminated by the buffer layer $G_0$ “zero-layer graphene” (ZLG) (Fig. 3.2a, left). Monlayer graphene (MLG) (Fig. 3.2a, middle) and bilayer graphene (BLG) (Fig. 3.2a, right) structure models are defined by adding vdW-bonded graphene layers $G_1$ and $G_2$, respectively, to the SiC substrate and the “buffer layer” $G_0$.

The in-plane $C_{ij}$ for hexagonal planes ($C_{11}$, $C_{12}$, $C_{22}$, $C_{13}$, $C_{44}$, $C_{55}$, and $C_{66}$) are calculated for equivalent planes in the vdW-bonded bulk materials (using graphite in the case of graphene). The out-of-plane tensor elements $C_{33,i}$, schematically indicated in Fig. 3.2b, depend on the atomic plane number I and are obtained from detailed atomic structure models of each region. Supercells for DFT calculations of $(6\sqrt{3}\times6\sqrt{3})$-$R30^\circ$ models contain six SiC bilayers and up to three layers of graphene. The total number of atoms per supercell is thus 1742, 2080, and 2418 atoms for zerolayer (ZLG), monolayer (MLG) and bilayer (BLG) graphene, respectively. The carbon side of the slab model was
passivated with hydrogen atoms (Fig. 3.1e). The challenging model sizes are handled by
the FHI-aims all-electron code[140, 141] with “tight” numerical settings and the ELPA
eigenvalue solver library[142, 143].

To model bulk-like conditions, the two bottom-most SiC bilayer were kept fixed
during the ionic relaxation. The atomic displacements in the slab model were then
averaged over individual layers. By applying different, fixed external surface stresses $\sigma_3$
to the atoms of the topmost surface plane and taking finite differences of the resulting
displacements, we obtained the layer-dependent, out-of-plane stiffness tensor elements
$C_{33,i}$ by fitting to the linear range of the stress-strain curves (Fig. 3.2c). For continuous
media, Hooke’s law relates the stress $\sigma_3$ and the layer-dependent strain $\epsilon_{3,i}$ in the $z$-
direction via the rank-4 tensor element $C_{33,i}$

$$\sigma_3 = C_{33,i} \epsilon_{3,i} .$$

As shown in Fig. 3.2c, we calculate the $C_{33,i}$ by applying an external surface stress $\sigma_3$ and
averaging the resulting atomic displacements in each plane to obtain the strain, $\epsilon_{3,i} = \frac{\langle \Delta z_i \rangle}{\langle \Delta z_i^0 \rangle} - 1$, where $\langle \Delta z_i \rangle$ and $\langle \Delta z_i^0 \rangle$ are the laterally averaged, strained and unstrained layer
distances, respectively. Interplanar spring constants $k_i$ (Fig. 3.2b) are determined from

$$k_i = \frac{C_{33,i} A}{\langle \Delta z_i \rangle},$$

where $A$ denotes the loaded area.

For computational expediency, we also performed calculations based on a much
smaller ($\sqrt{3} \times \sqrt{3}) - R30^\circ$ interface model for conceptual models of the oxygen (O)-
intercalated surfaces. In order to add commensurate graphene planes to this model, the
graphene planes incur $\approx 8\%$ strain[144]. For MLG and BLG, we verified that the deviations of calculated $C_{33}$ to the full $(6\sqrt{3}\times6\sqrt{3})$-$R30^\circ$ models are small since the lateral $C_{ij}$ continue to be taken from unstrained graphene planes.

### 3.3. Results and Discussion

#### 3.3.1. Epitaxial Graphene on SiC Examples

Epitaxial graphene films, grown by high temperature Si sublimation on SiC[12, 31, 34, 113, 124], are excellent models to demonstrate the power of our first-principles-informed CR-AFM approach. Fig. 3.3 shows AFM images and Raman spectra from two different samples grown at conditions chosen to yield predominantly ZLG and MLG domains (See Section 3.2.5). Their surfaces consist of micrometer-sized terraces arising from the underlying SiC (Fig. 3.3f and Appendix A, Figure A2). Raman spectroscopy confirmed the predominant graphene layer number on the samples.
Figure 3.3. CR-AFM exemplified for epitaxial graphene grown on 6H-SiC (0001). (a, b) Raman spectra of the ZLG and the MLG samples, respectively. (c) 2D peak of the MLG sample, fitted by a single Lorentzian peak (FWHM $\sim 45 \pm 2$ cm$^{-1}$). (d, e) AFM height image and corresponding first flexural mode contact-resonance frequency mapping over a terrace on the ZLG sample. (f) AFM height image and (g) corresponding CR-AFM first flexural mode contact resonance frequency mapping on the MLG sample. The blue arrows indicate MLG growth fingers extending to the BLG region of the sample. (h) High-resolution CR-AFM frequency map of the region shown in red in (g). Other types of fingers (referred to as region “O” finger) with much higher CR frequency than that of the MLG domains are identified, and one of them is circled by a white dashed line. (i) Average height cross-sectional profiles (direction: from left to right) for the regions indicated in (h). For averaged $f$ and $F_\perp$ of the domains identified in (e) and (h), see Appendix A, Tables A2 and A3.
The “ZLG sample” (Fig. 3.3a) shows two broad Raman peaks around 1330 and 1575 cm\(^{-1}\) and one smaller peak around 1480 cm\(^{-1}\). These peaks and the absence of a 2D peak are consistent with ZLG as the predominant domain[121]. CR-AFM imaging additionally shows some MLG, softer than ZLG along the terrace edges (Fig. 3.3e and discussion below). The “MLG” sample (Fig. 3.3b) shows a sharp Raman G peak, a broad D peak, and a 2D peak that can be fitted by a single Lorentzian distribution function (fwhm ~ 45 ± 2 cm\(^{-1}\), Fig. 3.3c), without apparent shoulders. These features are consistent with \(G_1\) coverage[34, 111]. Some bilayer graphene occurs at terrace edges (Fig. 3.3g), in agreement with literature reports[10, 12]. Figure 3.3e, g, h shows that CR-AFM imaging yields an astonishingly clear, mechanical contrast between different regions on the samples. On the ZLG sample, (Fig. 3.3e), the CR frequencies for the first flexural mode in the region labeled “ZLG” are higher than those in the region labeled “MLG”. On the MLG sample (Fig. 3.3 g, h), the region labeled “MLG” has CR frequencies higher than those in the region labeled “BLG”. We show below that these assignments agree quantitatively with results derived theoretically for the corresponding structure models.

In addition to large MLG and BLG regions, some finger-like features and small islands are visible on the MLG sample (Fig. 3.3g). In earlier work[145, 146], such features were explained as remnants left behind during the anisotropic growth of a new graphene layer. Thus, \(G_0\)-terminated “fingers” should extend into newly formed MLG domains, and \(G_1\)-terminated fingers should extend into newly formed BLG domains. Indeed, Figure
3.3g (blue arrows) reveals some features that are consistent with MLG fingers extending into BLG domains because these fingers have contact-resonance frequencies similar to those of MLG domains. However, CR-AFM reveals another group of “fingers” (labeled “O” in Fig. 3.3h) that also extends into the BLG area. These fingers exhibit CR frequencies considerably higher than those in the BLG and MLG regions (Appendix A, Table A4). AFM height measurements show that, on this sample, their height difference to BLG is smaller than the step height between BLG and MLG (Fig. 3.3i). Additionally, after storing the sample in air for several months, regions “O” show height changes that are not observed for MLG and BLG (Appendix A, Figure A3). Thus, the fingers labeled “O” cannot be MLG.

The experimentally derived reduced elastic moduli ratio (Equation 3.3) for the ZLG to MLG regions on the ZLG sample in Figure 3.3e is \((E_{ZLG}^*/E_{MLG}^*)_{exp} = 1.082 \pm 0.024\). For the MLG sample (Fig. 3.3h), \((E_{BLG}^*/E_{MLG}^*)_{exp} = 0.928 \pm 0.012\) and \((E_{O}^*/E_{MLG}^*)_{exp} = 1.140 \pm 0.028\) for the BLG to MLG and the “O” to MLG regions, respectively.

AFM tapping mode phase images (Appendix A, Figs. A2 b and d) also provide layer-number-dependent contrast and qualitatively corroborate the observed stiffness differences[10, 147]. However, in contrast to the CR-AFM procedure summarized in Figure 3.1, it is not possible to deconvolute the phase contrast into quantitative, mechanical property information on the single atomic layer level[10, 79, 148].
3.3.2. Theoretical Derivation of Reduced Moduli Ratios

Figure 3.4a compares the layer-dependent $C_{33,i}$ derived from $(6\sqrt{3}\times 6\sqrt{3})$-R30° ZLG, MLG, and BLG slab models. Three distinct layer stiffness regimes are apparent. The highest $C_{33,i}$ values in the range of 500 – 520 GPa are found for the SiC bilayers ($S_i$). The pristine buffer layer ($G_0$ in ZLG) yields $C_{33,i} \approx 270$ GPa. When graphene is present on the buffer layer, its $C_{33,i}$ decreases to 231 GPa. As expected, the vdW-bonded graphene planes $G_1$ and $G_2$ exhibit the lowest stiffness $C_{33,i} \approx 60$ GPa.

![Figure 3.4a](image)

**Figure 3.4.** Calculation of the elastic properties of graphene on SiC (0001). (a) Calculated layer-dependent stiffness values $C_{33,i}$ for the $(6\sqrt{3}\times 6\sqrt{3})$-R30° ZLG, MLG, and BLG interface models (Fig. 3.2a). (b) Reduced moduli ratios $(E_{II}^*/E_1^*)_{th}$ predicted for different atomic structure models compared with experimentally measured modulus ratios $(E_{II}^*/E_1^*)_{exp}$ on the ZLG and MLG samples in Figs. 3.3e, h, respectively. The error bar for $(E_{II}^*/E_1^*)_{th}$ is calculated by considering the uncertainty in tip radius $R_t$ (See Appendix A, Section A.I). The experimentally measured ratio $(E_0^*/E_{MLG}^*)_{exp}$ is compared to the predicted modulus ratio $(E_{ZLG}^*/E_{MLG}^*)_{th}$, but the actual structure of region O is unknown.
Figure 3.4b compares reduced elastic modulus ratios \((E_{II}*/E_{I}^*)_{th}\), predicted for different atomic structure models, to the experimentally measured ratios \((E_{II}*/E_{I}^*)_{exp}\) on the ZLG and MLG samples (Figs. 3.3e and h). For the ZLG sample, \((E_{ZLG}*/E_{MLG}^*)_{th} = 1.088\) is in excellent agreement with \((E_{ZLG}*/E_{MLG}^*)_{exp} = 1.082 \pm 0.024\), validating our structure assignments of these areas. Likewise, \((E_{BLG}*/E_{MLG}^*)_{th} = 0.936\) agrees nearly perfect with \((E_{BLG}*/E_{MLG}^*)_{exp} = 0.928 \pm 0.012\) on the MLG sample. This leaves the question of the identity of the finger-like structures, labeled “region O” in Fig. 3.3h. The measured ratio \((E_{O}*/E_{MLG}^*)_{exp} = 1.140 \pm 0.028\) is high and could indicate a substrate area not covered by graphene. In Fig. 3.4b, we thus compare \((E_{O}*/E_{MLG}^*)_{exp}\) to the predicted ratio \((E_{ZLG}*/E_{MLG}^*)_{th} = 1.094\) on the MLG sample. The discrepancy between the experimental ratio and the ratio calculated assuming ZLG suggests that “region O” cannot be assigned unequivocally to a simple ZLG surface area. The growth models in refs. [145] and [146] and the occurrence of actual MLG fingers in Figure 3.3g suggest that “region O” could be related to, for example, oxidized former MLG areas no longer covered by graphene after handling the sample in air. While a detailed search for definite atomic structure models for these areas is outside the scope of this paper, the success of our nanomechanical fingerprint is that we can clearly distinguish “region O” fingers from MLG fingers, and that we can rule out a simple ZLG model for “region O” fingers and similar areas on the MLG sample.
3.3.3. CR-AFM of Oxygen-intercalated Graphene on SiC

Next, we demonstrate the power of our approach for graphene with deliberately modified subsurface interfaces, revealing subsurface features and information on atomic structures. By annealing MLG samples in air, oxygen and/or water vapor can passivate the Si dangling bonds and break Si-C bonds at the buffer layer-SiC interface [13, 34, 149-152]. A pristine MLG region can thus be transformed to oxygen-intercalated, quasi-freestanding bilayer graphene (O-QF-BLG) without a buffer layer underneath, as verified by Raman spectroscopy and angle-resolved photoemission spectroscopy (ARPES) [34]. Similarly, pristine ZLG can be transformed to O-QF-MLG [149]. In Figures 3.5a-d, we show topographic and corresponding CR-AFM images of a MLG sample that was oxygen-intercalated as described in ref. 6. Raman spectroscopy confirms the absence of a buffer layer (Appendix A, Figure A4), indicating an essentially defect-free graphene surface layer. Likewise, AFM height images are consistent with homogeneous graphene-covered terraces (Figs. 3.5a, c). In contrast, CR-AFM (Figs. 3.5b, d) reveals a surprising richness of structural features and morphological variability that is not apparent in either AFM height images or Raman spectroscopy. These features are thus very likely located underneath the seemingly intact graphene surface layer. As an example, we focus on the zoomed-in region in Fig. 3.5d. Here, the nanomechanical response helps us to distinguish three different regions, labeled I, II and III. Regions II and III are both extended with similar but not identical CR frequencies and are also seen in topographic AFM. In contrast, region I,
which is readily apparent in CR-AFM and consists of localized islands $\approx 100$ nm in diameter with a much higher CR frequency, is not identifiable in the topography. Visually, Fig. 3.5c suggests that region I is more abundant within region II than within region III. Although (as shown below) a definitive assignment of all three regions by theory alone remains ambiguous without clear starting points for atomistic structure models, the qualitative revelation of abundant, localized subsurface features, not apparent in AFM height images or Raman, is a spectacular accomplishment of CR-AFM.

Figure 3.5. CR-AFM image on an oxygen-intercalated MLG sample reveals distinct subsurface regions. (a) Height and (b) corresponding CR frequency mapping of the first flexural mode. (c,d) Zoom-in height and frequency images, respectively, of the area shown in the red box in (b). CR-AFM reveals three distinct regions marked “I”, “II”, and “III” in (d). (e) Comparison of reduced moduli ratios using various models to the experimental ratio of region “II” to “III”. The white area reflects the experimental error range. (f) Atomistic structure models of the -OH interface (left) and SiO$_2$ interface (right). O atoms are shown in red. For domain-averaged $f$ and $F^\perp$ in subfigure (d), see Appendix A, Table A4.
Considering the growth history of this sample, one would expect the areas near the substrate step edges (region III in Figure 3.5c) to correspond to BLG that was subsequently intercalated with oxygen. Region II, away from the substrate steps, could be MLG, now also intercalated with oxygen. In a simple scenario (supported by ARPES and Raman[34]), region II should therefore now correspond to O-QF-BLG, while region III would correspond to oxygen-intercalated, quasi-freestanding trilayer graphene (O-QF-TLG). CR-AFM shows immediately that the reality is more complex and varied, revealing that region II is in detail inhomogeneous and includes large numbers of localized region I defects where oxidation has likely progressed further. However, for a quantitative comparison to theory, we do not have sufficient information about the oxidized structure formed underneath the apparently intact surface graphene planes. As shown in Fig. 3.5e, the experimentally observed reduced moduli ratio \( \left( \frac{E_{II}^*}{E_{III}^*} \right)_{\text{exp}} = 1.044 \pm 0.031 \). Assuming areas II and III to be MLG and BLG supported by a buffer layer \( \mathcal{G}_0 \), we predict \( \left( \frac{E_{II}^*}{E_{III}^*} \right)_{\text{th}} = 1.11 \pm 0.01 \), that is, significantly higher than experiment. As an example of an oxide-supported model, we consider an intercalated two dimensional \((\sqrt{3} \times \sqrt{3})\)-R30° SiO₃ (“silicate”) layer, connected by a linear Si-O-Si bond to SiC. If not covered by graphene, this model is identical to an experimentally established SiO₅ superstructure on SiC(0001) (Fig. 3.5f)[153]. However, with 1.09 ± 0.01, the theoretically predicted modulus ratio of BLG supported by silicate (BLG\(_{\text{SiO}_3}\)) to TLG supported by silicate (TLG\(_{\text{SiO}_3}\)) is still higher than experiment (Fig. 3.5e). As long as the interface underneath the BLG and TLG is kept
identical (shown for hypothetical OH-terminated interface models and $G_0$ buffer layer interfaces in Fig. 3.5e), the predicted $(E_{II}^*/E_{III}^*)_{th}$ values are similarly high. Thus, the interfaces under regions II and III in Fig. 3.5d are likely not identical. Two different interface combinations for II/III ($\text{BLG}_{\text{Si}_2\text{O}_5}/\text{TLG}_{G_0}$ and $\text{BLG}_{\text{OH}}/\text{TLG}_{\text{Si}_2\text{O}_5}$) that would be compatible with the experimentally observed elastic modulus ratio are shown as examples in Fig. 3.5e. Another simple possibility is suggested by observing that, in our calculations, the silicate adlayer is softer than SiC itself. Thus, the experimental modulus ratio could be explained by a SiO$_2$ film underneath the O-QF-BLG of region II thicker than that of III. This assignment would be consistent with the observed occurrence of further oxidized region I embedded in region II. The observed enhanced stiffness of region I could then be due to a slightly volume expanded, localized three-dimensional oxidized domain “pushing” against the covering, suspended bilayer graphene from underneath. However, in all cases, further evidence from other methods or from the growth process itself would be required to reveal definitive atomistic structure models for regions II and III.

3.3.4. Beyond Graphene

Finally, we show in Figure 3.6 that CR-AFM is able to resolve differences between other well-defined 2D material domains. Specifically, we consider conceptual ($\sqrt{3} \times \sqrt{3}$)-$R30^\circ$ interface models for 2D hexagonal boron nitride, molybdenum disulfide, and molybdenum trioxide on hydrogen-intercalated, quasi-freestanding monolayer graphene.
To mimic typical CR-AFM experimental input parameters (Figure 3.1), we use \( R_t = 100 \) nm, \( F^\perp = 200 \) nN, and \( f = 200 \) kHz. Figure 3.6 shows that the different models yield distinctly different ratios \( (E''_{II}/E''_I)_{th} \). This sensitivity does not originate from different \( C_{33,ij} \) values alone. Rather, the elastic moduli also reflect different in-plane \( c_{ij} \) and distinct interplanar spacings in the different materials that enter the continuum model described above.

Figure 3.6. Calculated reduced elastic moduli ratios \( E''_{th,II}/E''_{th,II} \) for different 2D layer models (II = graphene, h-BN, MoS\(_2\), or MoO\(_3\)) suspended on H-QF-MLG vs. the bare H-QF-MLG model surface as reference (area I). Assumed tip parameters: radius \( R_t = 100 \) nm; force \( F^\perp = 200 \) nN; frequency \( f = 200 \) kHz.
3.4. Conclusions

In this chapter, we showed that CR-AFM, combined with first-principles theory and modeling, is a powerful experimental tool to investigate the interfaces and subsurface layers of 2D material and heterostructures. CR-AFM enables the nondestructive and quantitative characterization of structural, compositional, and/or interfacial bonding changes in lateral and vertical material heterostructures. Remarkably, CR-AFM is exquisitely sensitive to the stiffness changes that arise from even a single atomic layer of a vdW-adhered material. If likely atomistic structure model candidates are available, a combined DFT and continuum modeling approach can be used to analyze the experimentally obtained contact resonance frequency maps quantitatively to yield subsurface-sensitive, structural fingerprints of different regions of interest on the sample. CR-AFM is able to detect subsurface defects easily and with high lateral resolution even if these are not apparent in other surface-sensitive techniques such as AFM height imaging or Raman spectroscopy. In combination with first-principles-calculated elastic stiffness parameters of 2D interfaces and atomic layers, the continuum mechanics model can be readily solved without expensive computational resources. For cases where well-defined structure models of individual surface domains are known, our approach thus constitutes a versatile nanomechanical technique to resolve and interpret surface and subsurface structure across the wide field of 2D materials and their heterostructures.
4. Interface Induced Electromechanical Properties of Epitaxial Graphene on SiC

4.1. Introduction

Graphene, a two-dimensional (2D) $sp^2$ carbon layer, exhibits unique mechanical, optical and electrical properties, and has great potential for high-performance device applications[2, 9]. The recent discovery of piezoelectricity in some other 2D materials[52], including monolayer MoS$_2$[53, 57] and BN[54, 55], has triggered interest in engineering this property also into graphene and thus further extending graphene’s application potential for stretchable electronics[154], nanogenerators[53, 155], actuators[154, 156] and other nano-electromechanical-systems[2]. However, pristine graphene, unlike these other piezoelectric 2D materials, has a centrosymmetric crystal structure and is thus intrinsically non-piezoelectric[49, 60]. Theoretically, several symmetry-breaking strategies have been proposed to turn non-piezoelectric graphene into a piezoelectric material. These strategies include non-symmetric chemical functionalization[50, 157], adsorption of foreign atoms[60], or creating special types of in-plane defects that can cause flexoelectricity due to non-symmetric strain gradients in graphene when it is mechanically deformed[49]. The theoretically-predicted piezoelectric coefficients for such engineered graphene materials

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are comparable to those of 3D piezoelectric crystals such as ZnO and Quartz[49, 50, 60, 157], suggesting a promising potential for graphene in piezoelectric materials applications.

However, until now, only a few experimental studies on graphene piezoelectricity have been reported. Following the idea of creating non-centrosymmetric defects, Zelisko et al. demonstrated the existence of piezoelectricity in graphitic-carbon-nitride (g-C₃N₄)[58], which is a 2D layer with non-centrosymmetric triangular holes in the crystal structure. The piezoelectricity in g-C₃N₄ is due to flexoelectricity, i.e., a polarization, induced by a non-uniform strain gradient associated with the crystal structure under deformation. Another type of piezoelectric effect in graphene, termed “band-piezoelectricity”, was reported[67]. Band-piezoelectricity arises from the charge transfer between a strained and unstrained graphene junction, and is due to the work function gradient along the junction. Furthermore, strong out-of-plane piezoelectricity was observed by piezoresponse force microscopy (PFM) in SiO₂/Si supported monolayer graphene, and interpreted as an effect of the dipoles formed at the graphene-SiO₂ interfaces due to C-O bond formation[64]. However, whether transferred graphene can form a C-O bond to the underlying SiO₂ substrate at room temperature is unclear[65] and thus the real mechanism of this observed, strong piezoelectricity is still under debate[65, 66].
Here, we report the discovery of piezoelectricity in epitaxial graphene on silicon carbide (SiC). PFM shows a distinctive out-of-plane piezoresponse contrast between monolayer- (MLG) and bilayer- (BLG) graphene regions. The MLG region produces a larger piezoelectric response than the BLG region. This piezoresponse difference vanishes after i) oxygen intercalation that breaks the covalent bonds between the zero-layer graphene (ZLG) and silicon carbide, and/or after ii) neutralizing the n-doping in graphene by tetrafluoro-tetracyanoquinodimethane (F4-TCNQ). Our results suggest that this out-of-plane piezoelectricity in graphene is due to the charge transfer across the interface between SiC and graphene, which results in an interfacial dipole moment. Furthermore, our findings provide a new route to engineer piezoelectricity into graphene via manipulation of the graphene-substrate interface to create asymmetry in the out-of-plane direction.

4.2. Materials and Methods

Large area graphene films can be grown epitaxially on 6H-SiC (0001) via high temperature sublimation of Si[12, 34]. The graphene layer formed by this method is of very high quality[26] and the underlying SiC substrate is an insulator that obviates the need for transferring graphene to another insulator[27]. The structure and bonding of each atomic plane is well understood in terms of a strain-free \((6\sqrt{3} \times 6\sqrt{3}) - R30^\circ\) interface model[30, 31]. Between the vdW-bonded graphene layer and the SiC substrate, a partially
σ-bonded, honeycomb carbon plane exists, which is usually referred to as “buffer layer” or “zero-layer graphene” (ZLG, not yet graphene). By controlling the growth conditions, one can get samples with predominant coverage of a specific thickness of graphene (e.g., monolayer graphene or bilayer graphene), as shown in our previous work[30, 34, 124, 135, 158] (See also Chapter 3, Section 3.2.5 for more details). We verified the graphene thicknesses on the samples used in the current study by Raman spectroscopy (See Chapter 3, Section 3.3.1). In the following, we will refer to the partially σ-bonded, the first and the second vdW-bonded carbon layers as G₀, G₁, G₂, respectively, and define the regions terminated by zero-layer, monolayer and bilayer graphene as ZLG, MLG and BLG regions, respectively.

We investigated the piezoelectricity of epitaxial graphene on SiC by piezoresponse force microscopy (PFM). See Chapter 2, Section 2.4.2 and Appendix B, Section B.I, for more details. For a piezoelectric material, an electric field applied through the conductive AFM tip can induce measurable AFM cantilever deflection[72]. However, the AFM cantilever contact resonance enhances the piezoresponse signal by over 100 times[89]. The dual resonance frequency tracking (DART)-PFM mode, available on our AFM, is used to map the piezo signal on the sample over the scanned area[78]. For both, DART mapping and point measurements, the intrinsic piezoresponse signal is extracted by treating the AFM cantilever-sample system as a damped, simple harmonic oscillator to remove the enhancement effect from the cantilever resonance (See Chapter 2, Section 2.4.2)[58, 78, 89].
4.3. Results and Discussions

Figure 4.1A shows a typical AFM topographic image of a SiC surface that is mostly covered by MLG (referred to as MLG sample). The surface consists of \( \mu \text{m-sized} \) terraces, which arise from the underlying SiC substrate[12]. The growth of a new graphene layer will usually initiate from the terrace edges[10, 28]. In agreement with results from the literature[12, 158], some BLG regions on our sample can be found along the terrace edges (Figs. 4.1A and B), which is confirmed by the \(-420\) pm height difference between the two regions[12, 29], and the lower contact resonance frequencies in the BLG region compared to that of the MLG region (Fig.4.1C)[158]. Unlike in previous experimental studies on graphene piezoelectricity, here the SiC substrate itself is a piezoelectric material[159-161]. Considering the graphene layers as an electrode on top of SiC, which resembles a typical capacitor structure in PFM applications[162], one would intuitively expect the intrinsic piezoresponse signal to be uniform across the scanning area, regardless of the graphene thickness. However, as shown in Figure 4.1D, the MLG region has a higher piezoelectric response than the BLG region. To further verify the difference in piezoelectricity between the two regions, we conducted point measurements with different driving voltages, at points randomly picked in each region. The measured intrinsic piezoresponse signals are plotted as a function of the applied AC voltage in Figure 4.1E. The linear dependence of the measured, intrinsic piezoresponse on the applied AC voltage confirms the piezoelectricity of the sample[58, 64, 72]. Furthermore, for each driving voltage, the
piezoresponse from the MLG region is stronger than that from the BLG region, and the steeper slope of the piezoresponse of the MLG region suggests that the MLG region has a higher effective, converse piezoelectric coefficient[72].

Figure 4.1. Piezoelectricity measurement on the MLG sample. (A) Topographic AFM images of the sample and (B) zoom-in height image of the blue box marked in (A). (C) Corresponding contact resonance frequency mapping, and (D) the intrinsic piezoresponse mapping. (E) Piezoresponse as a function of applied AC voltage by PFM-point measurements at randomly-picked points on both MLG and BLG regions.
Figure 4.2. Piezoelectricity measurement on the ZLG sample. (A) Topographic AFM and (B) corresponding piezoresponse mapping across a few terraces on the sample with ZLG and MLG regions marked in the image. (C) Piezoresponse plotted as a function of the applied AC voltage, measured by PFM at randomly-picked points on both ZLG and MLG regions. (D) Schematic of the SiC-graphene interfacial structure. The additional dipole moment $\delta P$ exists across the $G_1$ and $G_0$ layer due to the spontaneous polarization of SiC. Pseudo-charges in $G_0$ and $G_1$ layers are marked with red and blue circles, respectively.

These observations suggest that the thickness of the graphene layer does influence the overall piezoresponse of the graphene-SiC sample. To test this notion, we conducted PFM on a sample mostly covered by ZLG (referred to as ZLG sample), with some MLG
stripes along the terrace edges (Fig. 4.2A). The intrinsic piezoresponse mapping shows a higher piezoelectric effect in the MLG regions compared to that in the ZLG regions (Fig. 4.2B). The piezoresponse at each driving voltage as well as the linear slope of the piezoresponse-AC voltage relation are also higher in the MLG regions compared to those in the ZLG regions (Fig. 4.2C). Thus adding the first vdW-bonded graphene G₁ layer increases the overall piezoelectric effect of graphene/SiC sample and this increment decreases with additional, vdW-bonded graphene layers added to the stack (Figs. 4.1D and E). A spontaneous, negative polarization $P_s$ exists in 6H-SiC (polarization vector opposing the conventional $\vec{c}$-axis direction for hexagonal SiC, Fig. 4.2D), which has been reported both experimentally and theoretically[159, 161], and is partially due to the relative elongation of the longitudinal Si-C bonds along the $\vec{c}$-axis and the contraction of the bonds transverse to it[160, 163]. This non-zero spontaneous polarization is in fact the source of piezoelectricity in SiC. Because of this negative $P_s$, the Si-terminated (0001) surface has a negative effective polarization charge, which will result in some positive charges in ZLG (Fig. 4.2D). Hence, a vdW-bonded graphene layer will be negatively charged when it sits on ZLG. This spontaneous polarization-induced charge transfer to graphene through the interface layer G₀ has been widely accepted as the underlying mechanism of the experimentally observed n-type doping in epitaxial graphene on 6H-SiC (0001)[30, 160, 164]. Consequently, a small, negative interfacial dipole moment $\delta P$ between the G₁ and G₀ will be formed, which is aligned to $P_s$ (Fig. 4.2D) and will lead to a
larger piezoelectric effect in the MLG regions compared to that in the ZLG regions (Figs. 4.2B and C). For BLG on 6H-SiC (0001), the n-doping density is almost the same as that in MLG[164, 165]. However, the charge is distributed over a thicker graphene layer[165] and thus leads to a smaller interfacial dipole moment density. Hence, the intrinsic piezoresponse in the BLG regions is weaker than that in the MLG regions (Figs. 4.1D and E). This decrease in piezoelectricity as the thickness increases has also been reported for other 2D piezoelectric materials, and is consistent with a decay towards the bulk piezoelectricity of zero[52, 53, 57].

To test the hypothesis that the charge transfer to graphene through the interfacial G₀ layer, induced by the spontaneous polarization in SiC, is responsible for the observed piezoresponse contrast, we measured the piezoelectricity of oxygen-intercalated graphene on SiC. By annealing the epitaxial MLG sample in ambient environment (Chapter 3, Section 3.2.5), the synergistic oxidation effect of H₂O and O₂ will break the covalent bonding between ZLG and SiC and passivate the Si dangling bonds[13, 34, 149, 150, 152]. After this oxygen intercalation, the G₀ layer will become a graphene layer and the original n layer graphene will become quasi-freestanding (QF-) (n+1) layer (Fig. 4.3A), i.e., the pristine MLG and BLG regions will become QF-BLG and QF-trilayer graphene (TLG) regions, respectively. Raman spectroscopy shows that after annealing, the ZLG related signal disappears and intact (almost no defects) quasi-freestanding graphene is formed (Appendix A, Figure A4)[34]. Figure 4.3B shows a typical oxygen-intercalated
height image inside a terrace across QF-BLG and QF-TLG region. Finger-like features were identified, where the underlying structure is still unknown[146, 158]. The interfacial oxide layer formed in the oxygen intercalation process is inhomogeneous and depends on the thickness of graphene on top of G[149, 152, 158, 166], which is also reflected by the circular, low-piezoresponse features which appear at low density in the QF-TLG region and at higher density in the QF-BLG region (Fig. 4.3C), corroborating our previous finding with mechanical property mapping[158]. Despite these features, the intrinsic piezoresponse in QF-BLG and QF-TLG regions are identical within the instrument sensitivity (Fig. 4.3C). PFM point measurements show comparable, linear piezoresponse slopes as a function of applied AC voltage (Fig. 4.3D) regardless of some lower responses in the QF-BLG regions under high voltage, likely due to electrical-breakdown given the high electrical field in the vicinity of the sharp probe used in the experiment (Fig. 4.3D)[167]. The oxygen-intercalated quasi-free-standing graphene is p-doped with a reported p-doping density ~1.0 x 10^{13}/cm^2[34], which is larger than the p-doping density in hydrogen-intercalated quasi-free-standing graphene (~ 5 x 10^{12}/cm^2)[160, 164], where the doping is solely induced by the spontaneous polarization in SiC. This suggests that the origin of the p-doping in oxygen-intercalated graphene is a combined effect of both P from SiC and the interfacial SiO_x layer[168, 169]. With such high doping density, for multilayer graphene, the screening length will be short and most of the hole carriers will be distributed in the first two layers of graphene that are closer to the substrate[165].
Therefore, the new interfacial polarization would be comparable in QF-BLG and QF-TLG regions. In short, oxygen-intercalation dissociates the $G_0$ from SiC and disrupt the interfacial polarization $\delta P$, which causes a uniform piezoresponse in QF-BLG and QF-TLG regions.

Figure 4.3. Piezoelectricity of oxygen-intercalated-MLG sample. (A) Schematics of the interfacial structure of the QF-BLG region after the oxygen intercalation. The $G_0$ layer now is vdW-bonded to the substrate and a thin SiO$_x$ layer is formed at the interface. The original MLG region now becomes a BLG region. Note the real structure of the oxide at the interface can be different from that shown in the schematic. (B) Topographic AFM and piezoresponse mapping (C) across a QF-BLG and QF-TLG
region. (D) Piezoresponse vs. applied AC voltage relation measured by PFM at randomly-picked points on both regions.

Furthermore, we neutralized the charge in pristine, epitaxial graphene via F4-TCNQ, a p-type molecular dopant[118]. To p-dope the graphene to charge neutrality, i.e., $\delta P = 0$ (Fig. 4.4A)[170], we immersed a pristine MLG sample in F4-TCNQ DMSO solution[170] (4mg/mL, incubated overnight). The adsorption of F4-TCNQ is verified by XPS (Figure B2, Appendix B). With only the spontaneous polarization from the bulk SiC, the piezoresponse should now be uniform across the sample surface. Due to weakly bonded organic molecules on the graphene surface, PFM mapping is difficult because the AFM tip-sample contact will be disturbed during the scan in contact mode. Instead, we first used tapping-mode imaging to identify the SiC terraces and the BLG region along the terrace edges, and then conducted PFM point measurements. The measured piezoresponse is highly linear with respect to the applied AC voltage, and the MLG region has piezoresponses that are similar to those in the BLG region. This observation strongly suggests that the discovered piezoelectricity contrast between different graphene layers is due to the additional piezoelectricity across the graphene-SiC interface arising from the charge transfer induced by the spontaneous polarization of SiC.
Figure 4.4. Piezoelectricity of F4-TCNQ doped MLG sample. (A) Schematic of F4-TCNQ doped MLG region. The pseudo-negative charges in G1 layer is neutralized and the additional interfacial dipole moment δP becomes zero. The F4-TCNQ molecules are vertical on graphene layer for schematic purpose. (B) The piezoresponse vs. applied AC voltage relation measured by PFM at points randomly picked on MLG and BLG regions.

4.4. Conclusions

In conclusion, through converse piezoelectric measurement by PFM, we found that the unexpected piezoresponse contrast on graphene epitaxially grown on 6H-SiC (0001) depends on the graphene layer number. When the first vdW-graphene G1 layer is formed on top of G0, the piezoresponse increases. It decreases as the second vdW-graphene G2 was formed. This piezoelectricity contrast can be explained by the interfacial dipole moment across graphene and the zero-layer, which is due to the charge transfer induced by the spontaneous polarization of the SiC substrate. This explanation is
supported by the uniform piezoresponse found on both oxygen-intercalated quasi-freestanding graphene and F4-TCNQ-coated graphene, both yielding charge neutralized epitaxial graphene on SiC. Our results thus suggest a new route to render graphene piezoelectric through substrate polarization-induced, out-of-plane symmetry breaking, and thus yield graphene for many piezoelectricity-related applications.
5. Interfacial Mechanical Properties of Graphene-Self-Assembled-Monolayer Heterostructures\(^1\)

In previous chapters, the interfacial properties of as-grown 2D materials are studied by scanning probe microscopies. In this chapter, the non-ideal interfaces between transferred graphene and the supporting substrate are studied.

5.1. Introduction

Graphene, a two-dimensional, atomically thin layer of sp\(^2\) bonded carbon, has exceptional electrical, mechanical, and thermal properties\([2, 171]\), which make graphene an exciting material for a variety of devices, including field effect transistors (FET), biosensors, touch screens, and flexible electronics\([2, 9]\). In these devices, graphene is usually supported by a substrate which enables device function and enhances the mechanical stability of graphene. The substrate surface morphology\([36]\), charge impurities\([37]\), and/or adsorbates\([36, 38]\), can interact with graphene and have strong influence on its properties, such as chemical reactivity\([172]\), carrier density\([45]\) and carrier mobility\([173]\), which might adversely affect the electronic performance of the devices.

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\(^1\) This chapter is based on Qing Tu, Ho Shin Kim, Thomas J. Oweida, Zehra Parlak, Yaroslava G. Yingling and Stefan Zauscher, Interfacial Mechanical Properties of Graphene on Self-Assembled Monolayers: Experiments and Simulations, *ACS Applied Materials & Interfaces*, 2017, 9(11), 10203-10213. The Molecular Dynamics simulations are performed by Ho Shin Kim, Thomas J. Oweida and Prof. Yaroslava G. Yingling.
Therefore, it is of great interest to carefully engineer and characterize the graphene-substrate interfaces.

Self-assembled monolayers (SAMs) are used as an effective interfacial layer to modify a substrate surface to mitigate unwanted substrate effects. For instance, hydrophobic alkyl SAMs can screen the charge impurities on a substrate surface[173, 174]. Furthermore, SAMs are used as dopants in graphene-based devices to intentionally alter graphene’s electronic properties. By selecting SAMs with different specific surface energy and dipole moment, graphene can be p- or n-doped, and the doping level can be tuned[45-47], which allows for fabrication of a graphene-based p-n junction via patterned SAMs[175, 176]. However, different SAMs will have different interactions with graphene. For example, the adhesion energy depends on the SAM head group identity[177], the interfacial layer formed between graphene and the SAM during the preparation process, and the graphene-SAM separation distance. Furthermore, interfacial interactions will influence the stress transfer across the interface between graphene and the substrate, and thus impact the electrical properties of graphene[178]. However, how SAMs, and especially their surface energy, affect the mechanical properties at the interface between graphene and a substrate is not yet known.

Although graphene’s in-plane elasticity is an intrinsic property[5], its out-of-plane elasticity depends, for example, on the number of graphene layers and the interactions at the graphene-graphene and graphene-substrate interfaces. Moreover, the out-of-plane
elastic modulus of a layered graphene heterostructure is interrelated with graphene’s thermal, electrical, tribological, and optical properties[128], and it can be manipulated by small changes in the interfacial interactions. Hence, characterization of the out-of-plane elastic modulus is important for both fundamental research and practical applications. However, to date little is known about the out-of-plane elastic modulus of graphene and other 2D materials, as the measurement of modulus changes due to differences in 1~2 atomic or molecular layers, remains challenging.

Contact resonance AFM (CR-AFM) is a nondestructive, dynamic AFM technique that is exquisitely sensitive to changes in local elastic modulus[74]. CR-AFM has been widely used to measure the elastic modulus of polymeric and crystalline nanoscale thin films[74, 75], to probe subsurface defects[74, 75], and to determine the mechanical properties of SAMs both in air[179] and liquid[76]. We recently demonstrated that CR-AFM is sensitive to differences in the out-of-plane Young’s modulus of 2D heterostructures that arise from differences in the identity and interactions of one single atomic layer[158]. Furthermore, we showed that CR-AFM can be used to identify underlying atomic structures[158].

Molecular dynamics (MD) simulations have been widely used to describe the structure and mechanical properties of a wide range of materials[180-182]. Furthermore, many important mechanical and structural properties measured by AFM techniques, including the stiffness of polymers[183], mechanical functions of proteins[184], and the
shear strength of graphene oxide surfaces[185], have been interpreted and validated by MD simulations.

Here we report a combined experimental and computational study of the effect of SAM surface chemistry on the mechanical properties of SAM-graphene interfaces. The out-of-plane elastic moduli of graphene on hydrophobic and hydrophilic SAMs were measured by CR-AFM, and MD simulations were used to produce a mechanistic and atomistic description of the interfacial mechanics in terms of SAM head group chemistry and the environmental conditions used during the measurements. Our study thus provides an important and practical perspective on the use of SAMs for interfacial engineering of graphene and other 2D materials-based electronic devices.

5.2. Materials and Methods

5.2.1. Preparation of SAMs on Au

1-undecane thiol (98%) (UDT) and 11-Amino-1-undecanethiol hydrochloride (99%) (AUT) were purchased from Sigma Aldrich and stored at 4 °C. These two SAMs were chosen because they have the same carbon chain length but two different head-groups (-CH₃ vs. –NH₂), bestowing significantly different surface energetic properties to these SAMs. Furthermore, CH₃-terminated and NH₂-terminated SAMs have been widely used to engineer the electronic properties of graphene-based devices[45, 46, 173-176, 186].
A silicon wafer (<100>, Virginia Semiconductor) was cleaned by freshly prepared Piranha solution (Volume ratio 3:1 for 98% H₂SO₄ and 35% H₂O₂), then rinsed thoroughly by DI water and blown dry by N₂ flow. 10 nm Cr followed by 100 nm Au were coated onto the freshly cleaned silicon wafer by E-beam evaporation (Kurt Lesker PVD 75, Pressure: 4E-6 torr; Rate: 1 Å/s for Cr and 2 Å/s for Au). The Au-coated wafer was then cut into 0.5 cm × 0.5 cm pieces and stored in air. Prior to SAM formation, the Au substrates were cleaned sequentially as described next: sonicate in 0.5% sodium dodecyl sulfate (Sigma Aldrich) solution for 5 min, rinse thoroughly in DI water, sonicate in DI water for 5 min, sonicate in ethanol for 5 mins, blow dry with N₂ flow and then oxygen plasma clean for 2 min (medium RF level, plasma cleaner PDC-32G, Harrick Plasma). After cleaning, Au substrates were immediately immersed into 1.7 mM ethanolic thiol solutions and kept overnight. This concentration and exposure time is sufficient to form saturated, closely packed self-assembled monolayers on Au[187, 188]. The SAM samples were then taken from solution, rinsed with ethanol to remove physisorbed thiol molecules, and blown dry by N₂ flow.

5.2.2. SAM Surface Characterizations

X-ray Photoelectron Spectroscopy (XPS). The elemental composition of the SAM surface was determined with a Kratos Analytical Axis Ultra X-ray photoelectron spectrometer equipped with a monochromatic Al Kα source. The take-off angle was set at
$0^\circ$, i.e., the detector was perpendicular to the sample surface. Survey scans were acquired with a pass energy of 160 eV (resolution 1.0 eV, dwell time 200 ms). Each survey scan reflects the average of 4 sweeps. High resolution scans were acquired with a pass energy of 20 eV (resolution 0.1 eV, 20 sweeps). All XPS data were analyzed by CASA XPS software. The binding energy was calibrated by the position of the Au 4f peak, designated as 84.0 eV. The reported elemental compositions of each sample type were averaged from data taken from 6 to 7 different samples.

**Contact Angle.** All contact angle measurements were conducted with a Rame-Hart model 100 contact angle goniometer. For each measurement, a 10 µL DI water drop was gently placed on the sample surface and the static contact angle was measured from both sides and averaged by the software. The reported contact angle values reflect the average from 8 samples.

### 5.2.3. Graphene Transfer and Characterization

Few-layer graphene (FLG) was mechanically exfoliated from commercially available HOPG (ZYB grade, SPI Supplies / Structure Probe, Inc. and Bruker) and transferred to freshly prepared SAM substrates via Scotch™ tape in ambient environment. The samples were then imaged in an optical microscope to identify thin FLG. Vacuum-annealing of graphene covered SAM samples was accomplished by placing the samples into the E-beam evaporator at ~7E-7 torr, overnight. Raman spectra of the samples were
acquired with a Horiba Jobin Yvon LabRam Aramis Raman microscope equipped with CCD camera and a HeNe laser (λ ~ 633 nm). A 100x lens (laser spot ~ 1 µm in diameter) was used to collect the Raman spectra from small spots on the same few layer graphene flakes identified in the optical microscope before and after vacuum annealing. All Raman data were corrected by subtracting the signal from the corresponding SAM-Au substrate.

5.2.4. AFM and CR-AFM Measurements

All AFM measurements were conducted with an Asylum MFP-3D AFM (Oxford Instrument, CA) in ambient environment. Prior to each CR-AFM measurement, the AFM cantilever deflection sensitivity was calibrated by a force curve on a hard surface (silicon wafer). The spring constant $k_c$ of the cantilever was determined from the power spectral density of the thermal noise fluctuations in air[130], by fitting the first free resonance peak of the cantilever to equations for a simple harmonic oscillator by the AFM software[131]. For CR-AFM, the ultrasonic actuation was implemented by gluing the sample substrate onto a small ultrasonic transducer (Fig. 1) with a broadband resonance of 2.25 MHz (V133-RM, Olympus NDT). Point CR-AFM measurements were performed on randomly picked, SAM supported FLG to obtain the resonance frequencies at different applied forces. The total normal force at each point has two parts: (i) the adhesion force arising from cantilever tip-sample interactions determined by force curves, and (ii) the applied set-point force determined by the contact set point, the cantilever’s deflection sensitivity and $k_c$. The
vacuum-annealed samples were characterized immediately after they were removed from the vacuum chamber. To directly compare the contact resonance frequencies from different sets of measurements, CR-AFM was conducted with the same cantilever, featuring a blunted tip. For the same flexural mode, a higher contact resonance frequency $f$ indicates a higher contact stiffness, $k^*$ [74]. This $f$-$k^*$ relation was quantified by modeling the AFM cantilever as an Euler-Bernoulli beam oscillating with a mechanical constraint at the tip position [74, 75]. When the cantilever is in contact with a stiff material (high Q value) and tip-sample vibration are kept sufficiently small, the vertical damping can be neglected [128] (See Chapter 2, Section 2.4.1 for more details). $k^*$ can be converted to an effective reduced modulus of the sample by contact mechanics models. Here, we used the Hertzian contact model which approximates the AFM tip-sample contact as a spherical indenter with radius $R$ contacting a flat surface with force $F$ (Figure 5.1 inset):

$$k^* = \sqrt{\frac{3}{2} F R E^*},$$

(5.1)

where $E^*$ is the reduced modulus. For an isotropic homogeneous material, $E^*$ is given by,

$$\frac{1}{E^*} = \frac{1-\nu_s^2}{E_s} + \frac{1-\nu_t^2}{E_t},$$

(5.2)

where $E_s$ and $E_t$ are the Young’s moduli, and $\nu_s$ and $\nu_t$ are the Poisson’s ratios of the sample and the tip, respectively. The tip position on the cantilever and the tip radius $R$ can be calibrated by CR-AFM measurements on a sample with known stiffness (see Chapter 2, Section 2.4.1 and Appendix A, Section A.I. for more details).
5.2.5. All-Atom MD Simulations of Graphene-SAMs Heterostructures

A three layered, defect-free graphene sheet with a dimension of 5 nm x 5 nm was created via inorganic builder in the VMD 1.9.1 package[189]. UDT and AUT chains end-grafted on a Au (111) surface were initially built via the Discovery studio visualizer 4.0[190]. Next, the RESP and ESP charge Derive server (R.E.D server)[191] with GAMESS-US[192] and the RESP charge method were used to obtain partial charges for UDT and AUT SAMs (Appendix C, Figure C1). The Generalized Amber Force Field (GAFF)[193] was used for the system and the GOLP-CHARMM force field[194], with parameters from previous simulation studies[195], was used for gold atoms.
It is known that small water molecules can be present at the graphene-substrate interface when graphene is transferred in ambient conditions[39, 196]. The difference in surface chemistry of the SAMs used here can cause significant differences in the number of water molecules present at the graphene-SAM interfaces and the results from our Raman measurements suggest that water might play an important role for graphene’s electronic properties at these interfaces (see below). Thus, we introduced water molecules for the MD simulations of graphene-SAMs heterostructures in “ambient” conditions. To elucidate the dynamics of water molecules at the graphene-SAM interfaces, we performed all-atom MD simulations in an explicit TIP3P[197] water box for the three different material combinations, i.e., graphene on hydrophobic head groups (-CH₃), on hydrophilic head groups (-NH₂), and on protonated hydrophilic head groups (-NH₃⁺). For all MD simulations, including minimizations, equilibrations, and production runs, we used the AMBER 14 package[198]. In these simulations, the overall system was first equilibrated by solvent minimization for 10,000 steps while the heterostructure was restrained with 200 kcal/mol; then, while maintaining the same restraint, the system was gradually heated up to 300 K followed by 200 ps NPT MD run. Another 10,000 step minimization was carried out with a 25 kcal/mol restraint on the heterostructure. Then, a second short MD run was performed for 200 ps with the same 25 kcal/mol restraint. Five additional 1,000 step minimizations with decreasing constraint energy (20 kcal/mol, 15 kcal/mol, 10 kcal/mol, 5 kcal/mol, and finally no constraint) were performed, followed by final
equilibration while gradually heating the entire system up to 300 K. Production simulations were executed for 100 ns under NPT condition with a 2 fs time step. The Particle Mesh Ewald (PME) summation method[199] was used to calculate the electrostatic potential under periodic boundary conditions in all directions. We have successfully used similar protocols for MD simulations of various bio-molecules including ligand functionalized gold nano-particles[200], DNA – graphene based surfaces[201], solvent-solute complexes[202], and ionic materials[203].

To refine the structure and dynamics of the three different systems in vacuum, we also employed MD simulations using AMBER 14[198]. For these simulations, we first performed system minimization for 10,000 steps; then the system was gradually heated up to 300 K followed by short MD simulations (2.4 ns) under NVT condition. Production runs were carried out for at least 20 ns at 300 K with a 2 fs time step.

5.2.6. Steered MD Simulations of Graphene-SAMs Heterostructures

Steered molecular dynamics (SMD) simulations were performed to obtain stress-strain curves as well as the elastic modulus values for four different conditions (i.e., two different head groups (-CH3 and -NH2) and two environment conditions (ambient and vacuum)). Coordinates and simulation box information of the last equilibrium MD frame were used as initial input topology files for SMD. For SMD simulations of graphene-SAM interfaces in ambient conditions, interfacial water molecules between the surface and head
groups were included. Moreover, in agreement with the experimental results that showed the presence of water molecules in the vicinity of the interfacial region in ambient conditions, the initial coordinates of FLG-SAM interfaces for the SMD simulations also include all surrounding water molecules that are i) within 4.5 Å of the head group of the SAM and ii) within 2.5 Å of the bottom layer of the FLG. The SMD simulations were performed through the NAMD 2.10 software[204] and the forces were specified to compress in the direction normal to the FLG surface. The simulations (300 K, periodic boundary conditions) were run for 1x10⁷ to 2x10⁷ steps, depending on the indentation speed. During the SMD simulations, the gold surface was fixed and harmonic constraints were applied to the FLG to prevent any lateral displacement of the surface and to maintain the FLG centered over the SAM. This “artificial” bonding is needed in simulation and is reasonable, because in experiment the FLG will remain on top of the SAM and has negligible lateral motion relative to the substrate. To determine any dependence of the elastic modulus on the indentation rate, we performed SMD simulations at three different indentation speeds, i.e., 0.05 pN/time step, 0.001 pN/time step, and 0.00001 pN/time step, with a 2 fs time step and a 5 kcal/mol/Å² spring constant. This range of indentation speeds has been used in previous computational studies of nano-indentation processes[205, 206]. As illustrated in Appendix C, Figs. C2 a) and b), the elastic moduli, calculated from the slopes of the linear regime of the stress-strain curves, were largely independent of
indentation rate. Since the fits at the highest indentation speed yielded the best $R^2$ values (Appendix C, Fig. C2 b)), we chose this condition to report the elastic moduli.

5.2.7. Analysis of MD Simulations

Non-bonded interactions were calculated with the CPTRAJ 15 module in the AMBER 14 package[198]. For the non-bonded interactions, a 12 Å cutoff was used. For interactions with interfacial water, we only captured water molecules within i) 2.5 Å of the SAM head groups, and ii) 2.5 Å of the bottom layer of FLG. For interactions with surrounding water, we captured water molecules within i) 4.5 Å of the SAM head groups, and ii) 2.5 Å of the bottom FLG (excluding the interfacial water). Furthermore, SMD simulation trajectories, captured before the onset of yield in the FLG-SAM heterostructure (colored bars in Appendix C, Fig. C3), were used to calculate the average non-bonded interactions presented in Section 5.3 Results and Discussion. Moreover, the last 10 ns of the MD simulations were taken for the analysis of water-related, non-bonded interactions. The water dynamics in the vicinity of the interfacial region (e.g., the number of interfacial water molecules) was determined by an in-house TCL script and VMD 1.9.1[189] where we used the same distance criteria for interfacial water and surrounding water molecules.

For analysis of the SMD simulations, the engineering stress was calculated by dividing the indentation force at each time step by the original dimension of the FLG surface (2,500 Å$^2$), and the engineering strain was calculated by the change in distance
between the FLG and gold substrate, divided by the initial distance between the top layer of FLG and gold substrate. For the initial stage of the compression, when the pressure is very small, fluctuations in the graphene-SAM interactions can cause a dynamic displacement of the graphene layer, which leads to small, negative strain in the beginning of the stress-strain curves, and is most prominent at low indentation rates. The elastic modulus of the graphene-SAM heterostructures was obtained from the slope of the linear part of the resulting stress-strain curves, where we used a cut-off strain of 0.013 and 0.017 for UDT and AUT, respectively, due to the different yield strain of the heterostructures.

5.3. Results and Discussion

5.3.1. Surface Characterization of SAMs on Au

Table 5.1 summarizes the results from contact angle and XPS measurements of the SAMs used in this study. The measured contact angle values agree well with values reported for these SAMs in the literature[207-209]. As expected, the AUT SAM is much more hydrophilic than the UDT SAM. Similarly, the atomic percentages for different elemental species on both sample surfaces agree closely with reported values[209-212]. Oxygen occurs in the AUT sample due to tightly bound H₂O on the hydrophilic AUT surface[210]. Furthermore, high resolution N 1s XPS spectra (Appendix C, Figure C4) reveal free amine –NH₂ (~399.5 eV) and protonated amine species –NH₃⁺ (~401.4 eV) on
the surface[210, 212, 213]. The –NH$_3^+$ functionality accounts for 33.9 ± 2.8 % of the N 1s peak, which agrees well with the reported value[214]. The apparent protonation of the amine groups likely arises from the presence of tightly bound water molecules[210, 213].

Table 5.1. Surface Characterization of SAMs on Au.

<table>
<thead>
<tr>
<th>SAM</th>
<th>Head Group</th>
<th>Contact Angle (std. dev.) (°)</th>
<th>XPS Atomic Percentage (std. dev.) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AUT</td>
<td>-NH$_2$</td>
<td>42.8 (4.6)</td>
<td>C 55.6 (0.5)  O 4.3 (0.5)  S 1.8 (0.2)  N 3.7 (0.3)  Au 34.6 (0.6)</td>
</tr>
<tr>
<td>UDT</td>
<td>-CH$_3$</td>
<td>97.8 (3.2)</td>
<td>C 48.6 (1.1)  O -  S 2.2 (0.1)  N -  Au 49.2 (1.1)</td>
</tr>
</tbody>
</table>

5.3.2. Graphene on SAMs

Graphene flakes on SAMs can be identified by optical microscopy due to graphene’s light absorption[215]. Figures 5.2a) and b) show a typical example of graphene deposited on UDT. In these images, thin graphene flakes appear purple on the SAM/Au substrate (Fig. 5.2a)), and the contrast among these flakes indicates regions with different graphene layer numbers. The few layer graphene (FLG) region, which looks almost transparent (red arrow in Fig. 5.2a)), is the region of interest in this study. The Raman
spectra on these transparent FLG regions (Fig. 5.2c) show 2D peaks that are distinctly different from those observed on HOPG (Figure 2.8), which suggest that these regions have less than 5 graphene layers[101]. Furthermore, the 2D FWHM is a good indicator of graphene thickness[103]. Given the relatively small 2D peak and the large 2D FWHM, the FLG regions likely have more than 2 graphene layers[101, 103]. Thus, the FLG investigated here is sufficiently thick to shield a SAM’s surface energy and to temper the van der Waals forces interacting between the AFM tip and the FLG surface[216, 217]. The FLG regions on AUT and UDT SAMs have almost the same 2D FWHM (Fig. 5.2d), which suggests that these regions have the same number of graphene layers[103]. Furthermore, the FLG 2D peak is slightly blue shifted on the CH₃-SAM, when compared to that on the NH₂-SAM (Fig. 5.2c inset). This blue shift suggests a pronounced influence of the SAM-modified substrate on the electronic properties of graphene (see below)[15, 105, 175]. Considering that the only difference in the two sets of samples is the SAM head group chemistry, the observed difference in the 2D peak position is due to the interaction between graphene and the SAM through the head groups at the graphene-SAM interface.
Figure 5.2. (a) Optical microscopy and (b) AFM topographic images of a typical few layer graphene on UDT. The red arrows indicate the region where point measurements were made. (c) Raman spectra of graphene on CH$_3$-(black, UDT) and NH$_2$-SAMs (blue, AUT). (d) 2D FWHM comparison of graphene on CH$_3$- and NH$_2$-SAMs for both as-prepared samples and samples after vacuum annealing.

5.3.3. Interfacial Mechanical Properties of Graphene on SAMs

CR-AFM point measurements, conducted on FLG supported on UDT and AUT SAMs are summarized in Figure 5.3. As shown in Fig. 5.3a), the as-prepared FLG-NH$_2$-SAM heterostructure has smaller contact resonance frequencies than the FLG-CH$_3$-SAM
heterostructure over a wide range of forces, which indicates that the FLG-NH$_2$-SAM sample is “softer” than the FLG-CH$_3$-SAM sample. The reduced modulus of the FLG-NH$_2$-SAM sample is about $19.9 \pm 3.2$ GPa while that of the FLG-CH$_3$-SAM sample is $34.8 \pm 3.1$ GPa. The overall out-of-plane elastic modulus of the samples depends on the Au substrate, the SAM layer, the graphene layer and the interface between the SAM and graphene. Since both samples have the same number of graphene layers and have SAMs with the same carbon chain length, the measured, reduced modulus difference likely arise from differences in the interactions at the graphene-SAM interface. However, the layered nature of the samples, and the anisotropy of the materials involved, make the conversion from reduced moduli to Young’s moduli difficult. Assuming that all the materials involved in the layered sample are isotropic and have the same Poisson ratio ($i.e.$, $\sim 0.3$, which is the averaged value of the Poisson ratios reported for graphene ($\sim 0.16$)[5, 218] and alkanethiols on Au ($\sim 0.44$)[219]), the Young’s moduli are $20.5 \pm 2.9$ GPa and $39.6 \pm 2.6$ GPa for the FLG-NH$_2$-SAM and FLG-CH$_3$-SAM heterostructures, respectively. These moduli values are within the range of values reported for the individual materials involved (graphene $\sim 40$ GPa[220]; alkanethiol SAMs on Au: $1$–$75$ GPa[221, 222]). Importantly, after vacuum annealing, both samples showed lower contact resonance frequencies (Fig. 5.3b)) compared to the as-prepared samples (Fig. 5.3a)). Furthermore, the resonance frequencies from the two vacuum-annealed samples were comparable over the applied force range. The reduced moduli of the FLG-NH$_2$-SAM and FLG-CH$_3$-SAM samples are $13.9 \pm 0.8$ GPa.
and 14.5 ± 1.6 GPa, respectively. The Raman spectra obtained from the two samples after vacuum annealing also became more comparable. For the as-prepared samples, the 2D peak from FLG on the NH$_2$-SAM is at 2660.7 ± 2.3 cm$^{-1}$ while that from FLG on the CH$_3$-SAM is blue shifted to 2670.3 ± 3.0 cm$^{-1}$ (Fig. 5.3c)). After vacuum annealing, the 2D peaks from FLG on the NH$_2$-SAM and on the CH$_3$-SAM are closer together and located at 2668.1 ± 4.0 cm$^{-1}$ and 2662.5 ± 3.0 cm$^{-1}$, respectively (Fig. 5.3d)).

Figure 5.3. Contact resonance frequencies of FLG-CH$_3$-SAM (black) and FLG-NH$_2$-SAM (blue) heterostructures: (a) for as-prepared samples and (b) for samples after vacuum
annealing. (c) and (d) are the corresponding Raman 2D peak position for both samples before and after vacuum annealing, respectively.

The Raman 2D peak position is very sensitive to the Fermi level of graphene and thus the observed shift of the 2D peak positions after vacuum annealing provides some physical insights into the observed out-of-plane modulus changes of the samples. In ambient conditions, the Fermi level of graphene depends on the dopant from both the substrate and the air. For example, the O₂/H₂O redox couple from the air is known to p-dope graphene[41, 173, 186]. Furthermore, CH₃-SAMs will slightly dope graphene with electrons through the molecularly built-in electric dipole moment of the SAM and the charge transfer between SAM and graphene[186]. Finally, the amine groups in the NH₂-SAM can donate their lone electron pairs to graphene via a complex charge transfer mechanism, resulting in electron-doped graphene with a doping density that is much higher than that of CH₃-SAM supported graphene[45, 186]. However, graphene on CH₃-SAMSs in ambient environment is usually p-doped[46, 173, 174]. This arises from the small level of electron doping from CH₃-SAMs compared to the level of hole doping arising from adsorbed H₂O from the air at the graphene-SAM interface. On the other hand, although some p-type dopants (O₂ and H₂O from air and partially protonated -NH₃+) can lower graphene’s electron doping density, the electron doping contribution from NH₂-SAMs is sufficiently high so that graphene on NH₂-SAMs is still n-doped[45, 175, 176]. Therefore, FLG on NH₂-SAMs have a red-shifted 2D peak compared to FLG on CH₃-
SAMs[104, 105]. Vacuum annealing will remove the H₂O molecules intercalated in the FLG-SAM interfaces[41, 186], and thus FLG on CH₃-SAMs will become less p-doped while FLG on NH₂-SAMs will become more n-doped. The doping density arising from SAMs is typically on the order of 10¹² cm⁻²[45, 46, 175, 176]. Therefore, the 2D peak position in Raman spectra of CH₃-SAM samples will decrease while that from the NH₂-SAM samples will increase[105].

5.3.4. Molecular Dynamics Interpretation

Our MD simulations showed that water molecules do migrate into the interfacial region between FLG and NH₂-SAMs at equilibrium, as about 1.6 water molecules per nm² were found in this interface (Figs. 5.4a) and b)). In the case of NH₂-SAM, the strong attraction between water and the hydrophilic NH₂-head groups is the key factor driving water migration into the interface (Appendix C, Fig. C5). Moreover, as seen from the time course of the MD simulations (Appendix C, Fig. C5), the interactions between NH₂-terminated chains and water molecules become stronger over time, whereas graphene-water interactions become weaker. This suggests that attractions by NH₂ head groups are sufficiently strong to offset the unfavorable graphene-interfacial water interactions (Appendix C, Fig. C5). In contrast, for the FLG-CH₃-SAM heterostructure, water molecules surround the heterostructure and do not migrated into the interfacial region during the entire simulation. However, there are interactions between the surrounding
water molecules and the CH₃-SAM (Appendix C, Fig. C5). This result agrees well with the fact that NH₂-SAMs are much more hydrophilic than CH₃-SAMs. For protonated amine head groups, –NH₃⁺, the separation distance between graphene and the SAM is the largest among the three cases. This is seen in a thick water layer between graphene and the NH₃⁺-SAM (Appendix C, Fig. C6), in agreement with the notion that protonated amine SAMs are very hydrophilic[186]. As illustrated in Fig. 5.4c), time evolution profiles of the non-bonded interaction energy between FLG and alkanethiol SAMs showed identical trends with those of interfacial water (Fig. 5.4b)). In the case of FLG on a CH₃-SAM, the –CH₃ head groups engage in strong, non-bonded interactions with FLG and no water ingress to the interfacial region is seen. In contrast, for FLG on a NH₂-SAM, the strong non-bonded interactions observed initially (~ 15 ns) in the interfacial region become weaker as water molecules gradually migrate into the SAM-FLG interface. For the NH₃⁺-SAMs, the non-bonded interactions between FLG and SAMs are negligible (Appendix C, Fig. C6). These results show that SAM headgroup identity and the protonation state of the amine groups, are directly related to the presence of interfacial water molecules.
Figure 5.4. (a) Representative MD snapshots of FLG on SAM with –NH₂ (top) and –CH₃ (bottom) head groups (water molecules are colored in dark blue). (b) Number of water molecules and (c) temporal profile of the non-bonded interaction energy between FLG and SAM with –NH₂ (blue) and –CH₃ (black) head groups. Average values over the last 10 ns of the simulations are inserted as bar graphs.

To interpret the experimental observations of changes in the mechanical properties and specifically, to obtain an estimate of the out-of-plane elastic modulus of FLG-SAM heterostructures, we simulate the nano-indentation by SMD. Due to the extremely weak interfacial interaction and the large separation distance between graphene and the –NH₃⁺
head groups, it is not possible to obtain reliable stress-strain curves (Appendix C, Fig. C6) for the FLG-NH$_3^+$ SAM heterostructure. For the CH$_3$- and NH$_2$-SAMs, the simulated stress-strain curves of the FLG-SAM heterostructures show three distinct regimes (Fig. 5.5 a) and c)): (I) At low strains (below 2%), the curve is linear; (II) at intermediate strains (2% ~ 14%), the FLG-SAM layers begin to yield under the mechanical stress and the stress-strain curve gradually levels off, which indicates an elastic to plastic transition; and (III) at high strains (above 14%), the stress-strain curves rise sharply. While the first two regimes are quite typical for materials under mechanical deformation[223], the last regime reflects the constraints of the stiff gold substrate to the overall modulus in the current MD model. We estimate the Young’s moduli of FLG-SAM heterostuctures from the linear slope in Regime I (Fig. 5.5 b)).

In ambient environment, where interfacial water molecules are present, the estimated Young’s modulus of the FLG-CH$_3$-SAM heterostructure (~41.3 GPa) is larger than that of the FLG-NH$_2$-SAM heterostructure (~30.8 GPa) (Fig. 5.5b)). Qualitatively, this modulus difference agrees with our CR-AFM results. Quantitatively, the Young’s modulus of the FLG-CH$_3$-SAM heterostructure predicted by simulation is close to that experimentally measured by CR-AFM (see above), while that for the FLG-NH$_2$-SAM heterostructure is larger than the value obtained by experiments. This discrepancy likely arises because in experiments a significant number (~ 34 %) of amine groups are protonated and interact only weakly with graphene. In addition, the protonation will
increase the amount of interfacial water, which in turn will further decrease the out-of-plane modulus of the system.

Figure 5.5. (a) Simulated stress – strain curves for FLG-NH$_2$-SAM and FLG-CH$_3$-SAM heterostructures in ambient (top) and vacuum conditions (bottom). (b) Estimated Young’s modulus for each case. (c) Representative snapshots of steered MD simulations. The images from top to bottom correspond to regimes I, II and III of a FLG-CH$_3$-SAMs heterostructure in vacuum.

In vacuum, the Young’s moduli values decrease compared to the values in ambient conditions for both the FLG-CH$_3$-SAM and FLG-NH$_2$-SAM heterostructures. This trend also matches the experimentally observed differences in modulus values before and
after vacuum annealing. While the experimentally measured elastic modulus values for the FLG-NH$_2$-SAM and the FLG-CH$_3$-SAM samples are close, the Young’s modulus predicted for the FLG-NH$_2$-SAM is larger than that for the FLG-CH$_3$-SAM sample (Fig. 5.5b), bottom frame), due to differences in the strength of the interfacial interactions (Appendix C, Fig. C7, and Figs. 5.6b) and c)). This discrepancy between experiment and simulation arises because the MD simulations assume a uniform –NH$_2$ termination of the SAM, while in experiments protonated –NH$_3^+$ groups are present at the interface. As shown in Figs. C6 and C7 (Appendix C), the interfacial interaction between FLG and a NH$_3^-$-SAM is significantly lower than that between FLG and a NH$_2$-SAM, which suggests that protonation can significantly decrease the Young’s modulus of the FLG-NH$_2$-SAM heterostructure. In contrast, for the FLG-CH$_3$-SAM heterostructure, the simulation-derived Young’s modulus agrees well with the experimentally determined value. This is reasonable because CH$_3$-thiols are essentially hydrophobic, and thus not susceptible to partial protonation, which also closely reflects the situation modeled in the MD simulations[209, 210].

Water migration at the interface not only changes the electronic properties of SAM-supported graphene but also directly affects the out-of-plane elastic modulus of graphene-SAM heterostructures. The water molecules at the graphene-SAM interface can have two effects on the out-of-plane elastic modulus: First, as shown by MD simulations the presence of water molecules increases the graphene-SAM separation distance and
weakens the graphene-SAM interaction at the interface (Figs. 5.4, 5.6 and C5). Since the NH$_2$-SAM is more hydrophilic than the CH$_3$-SAM, more water molecules are present in ambient conditions at the FLG-NH$_2$-SAM interface (Fig. 5.4b)). This results in weaker interactions between FLG and NH$_2$-SAM than those between FLG and CH$_3$-SAM (Figs. 5.6 and C5). Therefore, the FLG-NH$_2$-SAM heterostructure is softer than the FLG-CH$_3$-SAM. Annealing in vacuum removes the water molecules from the graphene-SAM interface, and the two graphene-SAM heterostructures now have comparable out-of-plane moduli. Second, the elastic modulus of a SAM strongly depends on inter-chain interactions and the order of chain packing. As illustrated in Figures 5.7a) and b), CH$_3$-SAMs under light compression (Regime I) and in ambient conditions (i.e., in presence of surrounding water) show more ordered packing compared to that in vacuum. Since CH$_3$-thiol chains are hydrophobic, water molecules interact slightly with the hydrophobic alkyl-chains (Figs. 5.6b)) and restrict their conformational freedom at defect sites of the SAM (e.g., domain boundaries or substrate roughness induced steps in the actual system, see Appendix C, Fig. C8) (Fig. 5.7a)). In vacuum, water molecules are absent, and the CH$_3$-thiol chains at defect sites (edges in the simulations) are no longer conformationally restricted. This results in an overall decrease in the strength of inter-chain interactions (Fig. 5.6b)) and thus a decrease in the packing order of the alkyl chains (Fig. 5.7b)). This decrease in chain packing also decreases the elastic modulus of the SAM, and thus entails a decrease in the elastic modulus of the FLG-SAM heterostructure[224, 225]. In contrast,
the presence of water molecules increases the CH₃-thiol inter-chain interactions (Fig. 5.6b)) and consequently increases the local order of chain packing (Fig. 5.7b)), which leads to an overall increase in the modulus of the FLG-SAM heterostructure (Fig. 5.5b)).

Figure 5.6. (a) Schematic showing the components of non-bonded interactions that are present in the SAM-FLG system: Interfacial non-bonded interactions between FLG and SAMs (green), inter-chain interactions among SAMs (blue), inter-chain interactions with only the alkyl chains (i.e., without head groups, orange), graphene (bottom layer
only) – water interactions (gray), and interactions between water and the SAM (red). Deconvolution of the non-bonded interaction energy determined for (b) the FLG - CH₃ SAMs and for (c) the FLG - NH₂ SAMs in compression regime I.

Furthermore, as illustrated in Figures 5.7c) and d), NH₂-SAMs under light compression (Regime I) and in ambient conditions (i.e., in presence of interfacial water) also show more ordered packing compared to that in vacuum. For the FLG-NH₂-SAM heterostructure in vacuum, the NH₂ head groups can interact strongly with each other due to hydrogen bond formation (Fig. 5.6c)). However, these strong attractions among the head groups can draw the alkyl chains too close together, which engenders strong repulsion between them (Fig. 5.6c)). The combined effect of these interactions causes the NH₂ head groups to dynamically “bounce” against each other (Fig. 5.7d)). This situation leads to temporary disruptions in the local packing order which again entails a decrease in the modulus of the FLG-NH₂-SAM heterostructure. In contrast, under ambient conditions, interfacial water molecules, which interact strongly with the NH₂-SAM, can reduce head-head attractions and chain-chain repulsions (Fig. 5.6c)), which leads to higher packing order in the NH₂-SAM (Figs. 5.7c) and d)) and results in a FLG-NH₂-SAM heterostructure with higher elastic modulus. In summary, losing the packing order of thiol-chains in SAMs due to lack of the mitigating effect of surrounding or interfacial water on the SAM inter-chain interactions, likely is the major contributor to the
experimentally observed, lower Young’s moduli of graphene-SAM heterostructures in vacuum compared with those found in ambient conditions (Fig. 5.5b)).

Figure 5.7. Histogram of the nearest neighbor distances (head group to head group) in compression Regime I, for a CH$_3$-SAM in (a) ambient conditions, and (b) in vacuum, and for a NH$_2$-SAM in (c) ambient conditions, and (d) in vacuum. The red-dashed lines illustrate average values of the nearest neighbor distances between the well-aligned SAM head groups used as an initial structure in the simulations. The red dotted circles
in the representative snapshots represent regions with lower molecular order, in (b) disruption at the edge and in (d) local aggregations.

5.4. Conclusions

The electronic properties of graphene can be tuned through supporting self-assembled monolayers with promise to realize a wide range of devices for technical applications. Here, we showed the identity of the head group chemistry of a SAM also has a significant effect on the interfacial mechanical properties of SAM-supported few layer graphene. CR-AFM experiments revealed that the heterostructure of FLG supported on hydrophilic NH₂-terminated SAMs was softer than that of FLG supported on hydrophobic CH₃-terminated SAMs. Raman spectroscopy suggested that these differences might be due to a different amount of water molecules associated with the different SAM head groups present at the FLG-SAM interface. The experimentally observed stiffness differences were successfully captured via steered and all-atom MD simulations. The simulation results clearly showed that water molecules located at the FLG-SAM interfaces mediate the interaction between graphene and the SAM and were the key factor for the observed stiffness difference between graphene on hydrophobic and hydrophilic SAMs. The protonation of the amine head groups renders NH₂-SAMs even more hydrophilic, and consequently further weakens the graphene-SAM interactions due to the interfacial water layer. Vacuum annealing of the sample removed water molecules from the interfaces and caused an overall decrease in the out-of-plane stiffness because of
the loss in the packing order of thiol-chains in the SAM, arising from the absence of surrounding or interfacial water molecules. These observations suggest that hydrophobic surfaces are preferable over hydrophilic surfaces in order to achieve better mechanical and electronic stability. Our results provide an important, and often overlooked aspect for the fabrication of substrate-supported graphene electronics.
6. Conclusions and Future Directions

6.1. Conclusions

In this thesis, I applied advanced scanning probe microscopy techniques, including CR-AFM and PFM, to investigate the interfacial mechanical and piezoelectric properties of graphene and 2D materials and heterostructures. I also developed a new method, combining CR-AFM experiments and computations, to provide a quantitative, subsurface nanomechanical fingerprint of the atomic layer structure in 2D materials heterostructures. Furthermore, I observed and interpreted new, interface-induced piezoelectricity in graphene, epitaxially-grown on SiC, by PFM. Finally, I characterized the interfacial mechanical properties of graphene-SAM heterostructures by CR-AFM. This study provided deeper insights into graphene-SAM interactions in different environments, an area that is critical for SAM-engineered, graphene-based devices.

In the first study (Chapter 3), we showed that CR-AFM—which is exquisitely sensitive to stiffness changes that arise from even a single atomic layer of a van der Waals-adhered material– is a powerful experimental tool to nondestructively and quantitatively characterize the structure of atomically thin, layered materials with high lateral resolution. A combined density functional theory and continuum modeling approach is introduced that yields subsurface-sensitive, nanomechanical fingerprints associated with specific, well-defined structure models of individual surface domains. Where such
models are known, this information can be correlated with experimentally obtained contact-resonance frequency maps to reveal the (sub)surface structure of different domains. This method is successfully exemplified for epitaxial graphene grown on SiC (0001) and demonstrated to be applicable to other 2D materials and heterostructures.

In the second study (Chapter 4), we report a piezoelectric contrast between regions with different graphene layers on 6H-SiC (0001) measured by PFM, which reflects the presence of piezoelectricity in these graphene layers. Further experiments on oxygen-intercalated-freestanding graphene and Tetrafluoro-tetracyanoquinodimethane (F4-TCNQ) doped graphene on SiC indicates that the piezoelectric contrast arises from the interfacial dipole moment across van-der-Waals-bonded graphene and partially σ-bonded zerolayer graphene due to the spontaneous polarization of the bulk SiC substrate, which breaks the crystal symmetry in the out-of-plane direction. This finding demonstrates a new way to turn intrinsically nonpiezoelectric graphene into a piezoelectric material by controlling the graphene-substrate interface, which opens new potentials of graphene in piezoelectric material-related applications.

In the third study (Chapter 5) we combine CR-AFM experiments with Molecular Dynamics simulations and show that the head group chemistry of a SAM, which affects the interfacial interactions between graphene and the SAM, can have a significant effect on the out-of-plane elastic modulus of the graphene-SAM heterostructure. Graphene supported on hydrophobic SAMs leads to stiffer heterostructures than graphene
supported on hydrophilic SAMs, which is largely due to fewer water molecules present at the graphene-SAM interface. Our results provide an important, and often overlooked, insight into the mechanical properties of substrate-supported graphene electronics.

6.2. Future Directions

In this section, I provide possible directions for further investigation on interesting interfacial problems of 2D materials and heterostructures by scanning probe microscopy (SPM). In the first subsection, I will motivate the study on the structure and mechanical properties of water molecules confined by 2D materials and some preliminary SPM characterization results. In the second and third subsections, I will introduce some preliminary work on the mechanical and piezoelectrical properties of 2D layered hybrid organic-inorganic perovskite (HOIP) by the techniques used in this thesis.

6.2.1. Structure and Mechanical Property of Water Molecules Confined by 2D Materials

One possible direction is to apply CR-AFM to investigate the elastic and viscoelastic property of water molecules confined by 2D materials and correlate to the structure of these molecules under confinement.

Water confined in nanoscale environments has very different dynamics and structures from that of the bulk water[226-229], which depend on the confinement dimensions, temperature and pressure[226, 227, 230-233]. Understanding the structure
and dynamics of water in confined environments in ambient conditions is fundamentally important because of its relevance to daily life and to the development of advanced technologies[234-236]. However, currently most experimental characterizations of the structure and properties of nano-confined water are performed under cryogenic temperature and under high vacuum, which might not resemble those found in the confined water under ambient conditions[234]. More recently, graphene has been used as a perfect coating material to visualize the first water adlayer on mica in an ambient environment. This is enabled due to graphene’s high flexibility allowing conformal contact with the underlying material and due to its chemical inertness which does not disturb the adsorbate structure[39]. Since the first paper, many studies have been reported about the dynamic pattern evolution of monolayer water molecules under different environmental conditions (e.g., humidity[40], temperature[237]), the phase separation from ethanol[41], and the diffusion properties[40, 41], and how the surface energy of the interfaces, i.e., hydrophobic-hydrophobic (e.g., graphene-graphite[196, 229]), hydrophobic-hydrophilic (e.g., graphene-mica[39, 40, 237-239]), and hydrophilic-hydrophilic (e.g., MoS2-mica[237, 240]), will affect the morphological structure of the confined water. To date structural studies of confined water molecules mainly relies on the AFM topographic images[39, 40, 234, 237] (Fig. 6.1). However, little is known about the mechanical and structural properties (e.g., elasticity and/or viscoelasticity, packing) of these confined water layers. With the sensitivity to changes in local elastic properties[158],
CR-AFM can provide detailed elastic and viscoelastic property maps of these confined water layers.

![Diagram](image)

**Figure 6.1.** Schematics of water adlayer formed on mica surface when it is exposed to ambient environment (A). The adlayers are in dynamic equilibrium with the water vapor in the environment. (B) The graphene transferred to mica surface under ambient condition will thus forms a coating layer on the water adlayer, which enables subsequent AFM characterization. Figures are modified from Ref. [241].

Here, I take water at the graphene-mica interface as an example. When a freshly cleaved mica surface is exposed to an ambient environment, due to the hydrophilic surface and presence of humidity in the environment, the small water molecules will form a water adlayer on the mica surface[39, 242-244], which is in dynamic equilibrium with the water vapor in the environment (Fig. 6.1.A)[242, 243]. When a graphene layer is transferred to the surface, the water molecules will be trapped[39]. Although the water adlayer is still in dynamic equilibrium with the environment[40, 237], the coating of graphene will largely slow down the process, and the structure of the water adlayer will be protected when it is probed by the AFM tip (Fig. 6.1.B)[39]. The first water adlayer was initially believed to be ice-like (IL) water as the thickness (~3.7 ± 0.2 Å) matches to the
interlayer distance in a single puckered bilayer of ice-Iₜ[39]. However, a study on this first water layer in response to the humidity change suggests it can be a monolayer liquid film[40]. Typically, with relative humidity (RH) < 60%, only the first water adlayer will be observed, though small liquid-like nanodrops of water can always be found[234]. A second water adlayer can be formed on top of the first layer and starts to appear only after completion of the first layer. Subsequent water layers adopt a liquid-like form[234].

Figure 6.2. AFM characterization of water confined at graphene-mica interface. (A) Topographic image and (B) corresponding Peakforce QNM DMT modulus mapping.
The tip radius is not calibrated; thus the absolute modulus value is not shown and only modulus contrast is presented. The red arrow indicates some small nanodrops of water formed on top of the first water adlayer. (C) and (D) topographic images of the same regions taken at different times (~ 40 mins).

Figure 6.2 shows a typical example of water confined at graphene-mica interfaces (See Appendix D for sample preparation). The edges of the graphene fold and steps show very straight boundaries while that from the water adlayer is zig-zag shaped (Fig. 6.2.A). A graphene-1layer_water-mica (G-1LW-mica) and graphene-mica (G-mica) regions can be identified. Small nanodrops of water (red arrows in Fig. 6.2.A) can also be found on top of the first water adlayer, consistent with other reports[39, 239]. Due to the sensitivity limits of Peakforce QNM, no mechanical contrast is observed between G-1LW-mica and G-mica regions (Fig. 6.2.B). The nanodrops of water are much softer than the G-1LW-mica and G-mica regions (Fig. 6.2.B), in qualitative agreement with literature[239]. The water adlayer boundary changes over time (Figs. 6.2.C-D), which indicates this water layer is still interacting with the environment.
Figure 6.3. CR-AFM characterization of the water adlayer confined at graphene-mica interfaces. (A) Large area topographic images and (B) zoom-in topographic image of the region marked by the red box in (A). (C) CR-AFM second flexural mode frequency mapping and (D) corresponding Q factor mapping.

Figure 6.3 shows another example of a water adlayer confined at graphene-mica interfaces characterized by CR-AFM. Unlike Peakforce QNM, the G-1LW-mica region clearly gives lower contact resonance frequencies G-mica region, which suggests with the water adlayer significantly decreases the overall elastic modulus of the heterostructure. With the continuum model of layered material and first principles information on the stiffness matrix of mica, water-mica interface, water-graphene interface, and graphene
itself, the elastic property of this water adlayer can be deconvoluted. A preliminary deconvolution, assuming isotropic layer properties (HOPG: $E = 36$ GPa, $\nu = 0.165$, mica: $E = 48$ GPa, $\nu = 0.25$, and water adlayer: $\nu = 0.33$), the Young’s modulus of this monolayer water is about 22 to 23 GPa. Furthermore, the Q factor of the contact resonance peak (Fig. 6.3.D) can be directly related to the viscoelastic damping of the underlying materials[74, 245]. G-1LW-mica has almost the same G-mica region, indicating a solid-like (low viscoelastic) nature of the adlayer of water. Meanwhile, the nanodrops of water (red arrows in Fig. 6.3.D) has much lower contact resonance frequencies and Q factor than other regions. The frequency shift and Q-factor values has some drop-size dependency, which might be related to the size-dependent pressure inside van der Waals nanobubbles[246, 247]. Further study on the water adlayers and these nanodrops can probably unveil some of the physical properties of the recently reported square ice confined inside graphene nanobubbles[229].

6.2.2. Mechanical Properties of 2D HOIPs

Hybrid organic-inorganic perovskites (HOIP), especially three-dimensional (3D) AMX$_3$ (A = small organic cation, M = divalent group 14 element, X = halogen) materials, have attracted great research interest of the photovoltaic research community, due to readily-achievable high power conversion efficiency (22.1%) and low-cost preparation approaches[248-250]. 2D HOIPs are considered as new members of the 2D materials[51],
which have an alternating organic cation and inorganic layer structure[251], as shown in Fig. 6.4.A. The organic layers between the two neighboring inorganic layers form a vdW interface (Fig. 6.4.A). Compared to 3D HOIPs, 2D HOIPs show improved stability when subjected to environmental conditions such as moisture, oxygen and/or UV light[252, 253]. Furthermore, in 2D HOIPs, the organic cations do not need to fit into the cage defined by a 3D inorganic framework[254, 255], which provides more choices for the organic cations to tune the materials’ properties[256-258].

Figure 6.4. (A) Schematic of the 2D layered HOIP structure (modified after Ref.[251]). A is an organic ammonium cation, M is a divalent metal cation, and X is a halogen anion. The dashed line indicates the vdW interface. (B) schematic of AFM
nanoindention on suspended 2D HOIP layer to extract in-plane modulus and strength of the material (modified after Ref.[5]). (C) Optical image of a mechanically exfoliated 2D (PEA)$_2$PbI$_4$ flakes on Au substrate, where PEA = 2-phenylethylamine. The transparency of the flakes indicates the thickness. (D) AFM topographic image of mechanical exfoliated 2D HOIP flakes on Au.

The mechanical properties of HOIPs, including Young’s modulus, viscoelasticity and strength, are not only of great interest to fundamental science, but also critical for mechanical stability of HOIP device applications like flexible solar cells[259, 260]. However, despite the ubiquitous studies of the optical and electronic properties of HOIPs, only a few reports on the mechanical properties of HOIPs can be found. Feng first calculated the mechanical properties of hybrid organic-inorganic CH$_3$NH$_3$BX$_3$ (B = Sn, Pb; X = Br, I) perovskites by first principles[261]. Experimentally, Young’s modulus values of single crystal HOIPs were obtained by nanoindentation, which are in good agreement with the theoretical prediction[259, 260]. Little is known about the mechanical properties of 2D HOIPs and how organic cations will affect their elastic and viscoelastic properties.

The first potential study is to use AFM-based nanoindentation to obtain the in-plane Young’s modulus and strength of the 2D layered HOIPs (Fig. 6.4.B), similar to the experimental investigation on the in-plane mechanical properties of graphene[5]. Due to the weak vdW bonding between the 2D organic layers, the 2D layered HOIPs crystals can be mechanically exfoliated into thin flakes [262](preliminary data are shown in Figs. 6.4. C and D), and transferred to a substrate with small holes to create a suspended 2D layer
of HOIPs. AFM indentation measurements can be performed in the suspended area of the 2D HOIPs and force-distance curves can be recorded. By fitting the force-distance curves with appropriate nanoindentation continuum models, one can obtain the in-plane modulus of the 2D HOIPs. By varying the thickness of the flakes and the organic cations, modulus-thickness and modulus-organic-cation relations can thus be obtained.

![AFM image](image)

**Figure 6.5.** CR-AFM characterization of a 3D CH₃NH₃PbI₃ single crystal in ambient environment. (A) Topographic image and (B) the first flexural mode CR frequency map.

Furthermore, CR-AFM on HOIPs can measure the out-of-plane elastic modulus and viscoelasticity as a function of chemical composition. Figure 6.5 is a preliminary example of CR-AFM on a 3D CH₃NH₃PbI₃ single crystal. Despite the scan lines, due to the rough surface of the single crystal, CR-AFM gives an overall uniform frequency on the crystal. Some low frequency dots can be found on the surface, which likely indicates a chemically degraded region. Further experiments on 3D single crystals will require the preparation of smooth surfaces and environmental control to avoid any surface
degradation because of the known environmental instability of the 3D single crystals. For 2D HOIPs, the experimental requirements on the environmental control can be less strict and a fresh, flat surface can always be prepared by mechanical exfoliation.

6.2.3. Piezoelectricity in 2D HOIPs

The third potential research direction is to apply PFM to investigate the piezoelectricity and/or ferroelectricity in 2D layered HOIPs. The chemical composition of the HOIPs (e.g., Organic cations, halogen) can affect the crystal structure of the HOIPs and lead to piezoelectricity and/or ferroelectricity in the materials. Some 2D layered HOIPs, including (PMA)$_2$PbCl$_4$ (PMA = phenylmethylamine), are reported to be ferroelectric[257, 258]. This piezoelectric and/or ferroelectric effect can extend the application of HOIPs from normal solar-to-electricity energy conversion to other forms of energy harvesting, such as actuators[154] and nanogenerators[155]. For complex and new 2D layered HOIPs, the crystal structure determined by other standard characterization techniques (e.g., single crystal XRD), can be ambiguous. Whether the HOIPs is piezoelectric can be determined by PFM and provide some insights into the symmetry of the crystal structure, since piezoelectricity can only exist in materials with non-centrosymmetric structures[52, 60]. Figure 6.6 shows some representative PFM characterizations of 2D layered HOIPs. The 2D HOIPs are spin coated and crystallized on a Fluorine-doped Tin Oxide (FTO) substrate. PFM measurement with an Pt/Ir coated AFM tip can clearly distinguish piezoelectric (Fig. 6.6.B, (PMA)$_2$PbCl$_4$) and nonpiezoelectric 2D HOIPs (Fig. 6.6. D,
(NMA)$_2$PbCl$_4$, where NMA = 1-(2-Naphthyl)methanamine). By PFM, one can quickly screen out 2D HOIPs with piezoelectricity for further study on ferroelectricity and piezoelectric-related applications.

**Figure 6.6.** PFM characterization of (PMA)$_2$PbCl$_4$ (A and B) and (NMA)$_2$PbCl$_4$ (C and D). (A) and (C) are topographic AFM images. (C) and (D) are PFM point measurements. The linear relationship between piezoresponse and applied AC voltage indicates the presence of piezoelectricity.
Appendix

Appendix A. Additional Information for Chapter 3

Section A.I. CR-AFM Procedures

The spring constant calibration is listed in Chapter 3 Methods section. The cantilever dynamics to convert the CR frequencies to contact stiffness is presented in Section 2.4.1. We determine the tip position on the cantilever using equations (2.5-2.7), and applying mode equivalence technique for the first and the second mode. In this technique, the resonance frequencies of these modes are measured for the free cantilever and the cantilever in-contact with a stiff, solid substrate. The radius of curvature of the cantilever tip was estimated from the contact resonance frequencies on a clean silicon wafer, using the reported bulk material properties for silicon\cite{132} and a Hertzian contact model. The mode equivalence technique is expected to have around 10% error for the $\frac{k^*}{k_c}$ range used in the calibration and the first two modes\cite{82}. The error results in approximately 30% uncertainty in the tip radius, which was accounted in the continuum modeling. The properties of the cantilevers used in Chapter 3 are tabulated in Table S4.
The detailed procedure of converting the measured contact resonance frequencies on the samples to contact stiffness values is as follows:

1. Use the free resonance frequencies of the cantilever to obtain the cantilever specific constant $\sqrt{\frac{EJ}{\rho A}}$ (See Equation (2.5) in Section 2.4.1).

2. Use Equation (2.5) to calculate $\alpha_n L$ from the measured resonance frequencies $f$.

3. Use Equation (2.7) and the calibrated tip position $\frac{L_1}{L}$ and $k_c$ to convert calculated $\alpha_n L$ to $k^*$.

Because of the large uncertainty of $R_t$, the absolute values of the experimentally obtained reduced moduli can vary a lot depending on the $R_t$ number used (See Tables A2-A4 below), which makes the comparison to theoretical values from different structure models difficult. As shown by Hertzian contact model (Equation (3.2) and (3.3)), the ratios of reduced moduli of two different surface regions would be independent of the effective tip radius.
Section A.II. Supplementary SiC Sample Surface Characterization by AFM and Raman Spectroscopy

Figure A1. Frequency histogram (blue) and Gaussian distribution fit (red line) for Fig. 3.3e (ZLG sample) in Chapter 3. (a) ZLG region and (b) MLG region. The frequencies are taken from the entire labeled region and the Gaussian distribution fitting parameters are specified in Table A2.

Table A1. Cantilever parameters calibrated in each experiment. Cantilevers of type MPP-33220-10 from Bruker were used for CR-AFM. $f_{i,\text{air}}$ denotes the cantilever’s free resonance frequency of the $i$th flexural mode in air. $k_c$ is the spring constant of the cantilever. $f_{i,\text{Si}}$ is the contact resonance frequency of the $i$th flexural mode when the cantilever is in contact with Si. $F_{\text{Si}}$ is the total force applied on Si. $L_1/L$ is the relative tip position of the cantilever. $R_t$ is the tip radius. For tip radius calibration, we used a silicon wafer, assuming it is isotropic with Young’s modulus $E_{\text{Si}} = 165$ GPa and Poisson’s ratio $\nu = 0.22$. The uncertainty of the calibrated tip radius by this methodology is about 30% (Section A.I. above)

<table>
<thead>
<tr>
<th>Cantilever</th>
<th>Sample used</th>
<th>$f_{1,\text{air}}$ (kHz)</th>
<th>$f_{2,\text{air}}$ (kHz)</th>
<th>$k_c$ (N/m)</th>
<th>$f_{1,\text{Si}}$ (kHz)</th>
<th>$f_{2,\text{Si}}$ (kHz)</th>
<th>$F_{\text{Si}}$ (nN)</th>
<th>$L_1/L$</th>
<th>$R_t$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>ZLG sample</td>
<td>46.00</td>
<td>284.83</td>
<td>8.14</td>
<td>203.0</td>
<td>563.1</td>
<td>255.1</td>
<td>0.9</td>
<td>67±2</td>
</tr>
</tbody>
</table>
Figure A2. Characterization of terraces on the “ZLG sample” and the “MLG sample” by topographic and tapping mode AFM. Tapping mode AFM is operated in the repulsive
regime \(i.e.,\) driving frequency \(f < \) free resonance frequency \(f_0,\) phase lag \(< 90^\circ\) [263, 264]. (a) Height, (b) the corresponding phase lag image of the ZLG sample, globally offset by \(80^\circ\). On the SiC terrace edges, some MLG is formed. (c) Height, (d) the corresponding phase lag image of the MLG sample region shown in Fig. 3.3h in Chapter 3, globally offset by \(82^\circ\).

Table A2. Measured contact resonance frequencies and total forces for Fig. 3.3e (ZLG sample) in Chapter 3. The experimental contact stiffness \(k^*\) is derived following the methods in Section A.I (above) and the experimental reduced elastic moduli range is derived via the Hertzian contact model with contact stiffness values and calibrated tip radius (See Table A1 above). The large uncertainty in tip radius results in a wide range of reduced moduli. As explained in Chapter 3, this uncertainty essentially cancels when elastic modulus ratios are formed.

<table>
<thead>
<tr>
<th>Region</th>
<th>Force (nN)</th>
<th>CR Frequency (kHz)</th>
<th>(k^*) (N/m)</th>
<th>(E^*) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZLG</td>
<td>287.95 ± 5.05</td>
<td>205.629 ± 0.036</td>
<td>1263.0 ± 6.8</td>
<td>110 – 150</td>
</tr>
<tr>
<td>MLG</td>
<td>287.86 ± 1.65</td>
<td>205.261 ± 0.091</td>
<td>1197.9 ± 15.1</td>
<td>100 - 140</td>
</tr>
</tbody>
</table>

Table A3. Measured contact resonance frequencies and total forces for Fig. 3.3h (MLG sample) in Chapter 3. See caption of Table A2 for further explanation.

<table>
<thead>
<tr>
<th>Region</th>
<th>Force (nN)</th>
<th>CR Frequency (kHz)</th>
<th>(k^*) (N/m)</th>
<th>(E^*) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>220.64 ± 2.65</td>
<td>202.580 ± 0.125</td>
<td>1042 ± 15</td>
<td>91 – 131</td>
</tr>
<tr>
<td>MLG</td>
<td>213.80 ± 4.10</td>
<td>201.720 ± 0.032</td>
<td>945 ± 3</td>
<td>82 - 114</td>
</tr>
<tr>
<td>BLG</td>
<td>209.62 ± 2.63</td>
<td>201.175 ± 0.036</td>
<td>893 ± 3</td>
<td>75 - 105</td>
</tr>
</tbody>
</table>
Table A4. Measured contact resonance frequencies and total forces for Fig. 3.4d (O-intercalated sample) in Chapter 3. See caption of Table A2 for further explanation.

<table>
<thead>
<tr>
<th>Region</th>
<th>Force (nN)</th>
<th>CR Frequency (kHz)</th>
<th>$k^*$ (N/m)</th>
<th>$E^*$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>196.61 ± 3.15</td>
<td>200.450 ± 0.113</td>
<td>869.2 ± 15.3</td>
<td>107 – 156</td>
</tr>
<tr>
<td>II</td>
<td>187.61 ± 2.76</td>
<td>198.210 ± 0.120</td>
<td>648.1 ± 8.9</td>
<td>71 - 102</td>
</tr>
<tr>
<td>III</td>
<td>188.65 ± 2.37</td>
<td>197.970 ± 0.113</td>
<td>630.8 ± 8.0</td>
<td>68 - 98</td>
</tr>
</tbody>
</table>

Figure A3. Time-dependent change of height of the region O (“finger”) features on the MLG sample discussed in Chapter 3 (See Fig. 3.3h). For two different preparations of “MLG samples” (“Batch 1” and “Batch 2”), topographic AFM images at different positions were taken within 1.5 months of preparation (samples stored in air), and again within 4-12 months after preparation. Average step heights are shown either between BLG and region O (“finger”) or between BLG and MLG domains. Each column is averaged by over 20 data points measured on 10 different locations on the samples. The step height difference between BLG and MLG remains unchanged, consistent with the chemical inertness of graphene. In contrast, the relative height of the region O “fingers” changes significantly within this time period, indicating that a slow adhesive or corrosive process affects the “region O” domains.
Figure A4. Raman spectrum of the oxygen intercalated MLG sample. No apparent D peak is found, indicating the absence of the “buffer layer” feature in the investigated region.

Table A5. Entries of the stiffness tensor for 3C-SiC in GPa as calculated by DFT-PBE+TS and employed in this work. $C_{66}^* = (C_{11} - C_{12}) / 2$.

<table>
<thead>
<tr>
<th>Component</th>
<th>This work (orthogonal cell)</th>
<th>Experiment[265]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}$</td>
<td>493</td>
<td>502</td>
</tr>
<tr>
<td>$C_{22}$</td>
<td>493</td>
<td>502</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>89</td>
<td>95</td>
</tr>
<tr>
<td>$C_{13}$</td>
<td>57</td>
<td>n/a</td>
</tr>
<tr>
<td>$C_{14}$</td>
<td>-53</td>
<td>0</td>
</tr>
</tbody>
</table>
Table A6. Entries of the stiffness tensor for graphite in GPa as calculated by DFT-PBE+TS and employed in this work. $C_{66}^* = (C_{11} - C_{12}) / 2$.

<table>
<thead>
<tr>
<th>Component</th>
<th>This work</th>
<th>Experiment[266, 267]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{33}$</td>
<td>530</td>
<td>565</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>166</td>
<td>169</td>
</tr>
<tr>
<td>$C_{55}$</td>
<td>165</td>
<td>169</td>
</tr>
<tr>
<td>$C_{66}$</td>
<td>202</td>
<td>191</td>
</tr>
<tr>
<td>$C_{66}^*$</td>
<td>202</td>
<td>204</td>
</tr>
<tr>
<td>$C_{11}$</td>
<td>1094</td>
<td>1060</td>
</tr>
<tr>
<td>$C_{22}$</td>
<td>1097</td>
<td>1060</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>169</td>
<td>180</td>
</tr>
<tr>
<td>$C_{13}$</td>
<td>-9</td>
<td>15</td>
</tr>
<tr>
<td>$C_{33}$</td>
<td>65</td>
<td>37</td>
</tr>
<tr>
<td>$C_{44}$</td>
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<td>4</td>
</tr>
<tr>
<td>$C_{55}$</td>
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<td>4</td>
</tr>
<tr>
<td>$C_{66}$</td>
<td>460</td>
<td>440</td>
</tr>
<tr>
<td>$C_{66}^*$</td>
<td>463</td>
<td>440</td>
</tr>
</tbody>
</table>
Table A7. 2D elastic stiffness elements for freestanding layers of graphene, hexagonal boron nitride, molybdenum disulfide, and molybdenum oxide as obtained by DFT-PBE+TS in this work in GPa·nm.

<table>
<thead>
<tr>
<th>2D Materials</th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{22}$</th>
<th>$C_{66}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>graphene</td>
<td>357</td>
<td>61</td>
<td>357</td>
<td>148</td>
</tr>
<tr>
<td>h-BN</td>
<td>290</td>
<td>66</td>
<td>290</td>
<td>112</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>135</td>
<td>29</td>
<td>135</td>
<td>53</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>132</td>
<td>21</td>
<td>109</td>
<td>43</td>
</tr>
</tbody>
</table>

Table A8. Calculated reduced moduli values for Fig. 3.3e (ZLG sample) in Chapter 3.

<table>
<thead>
<tr>
<th>Region</th>
<th>$E^*$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZLG</td>
<td>124.065 ± 0.012</td>
</tr>
<tr>
<td>MLG</td>
<td>114.009 ± 1.146</td>
</tr>
</tbody>
</table>

Table A9. Calculated reduced moduli values for Fig. 3.3h (MLG sample) in Chapter 3.

<table>
<thead>
<tr>
<th>Region</th>
<th>$E^*$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O (ZLG)</td>
<td>124.058 ± 0.020</td>
</tr>
<tr>
<td>MLG</td>
<td>113.367 ± 1.389</td>
</tr>
<tr>
<td>BLG</td>
<td>106.206 ± 2.043</td>
</tr>
</tbody>
</table>
Appendix B. Additional Information for Chapter 4

Section B.I. PFM setup

Figure B1. Schematic of piezoresponse force microscopy setup. The sample is glued to a back electrode by silver paste. The back electrode is grounded and the AC voltage is sent to the conductive AFM probe.

Figure B2. XPS F 1s of epitaxial graphene on SiC after the sample has been immersed in F4-TCNQ solution overnight, showing that the molecules has been adsorbed to the graphene surface.
Appendix C. Additional Information for Chapter 5

Section C.I. MD setup

Figure C1. Partial charge information on (a) 1-undecanethiol (-CH₃), (b) 11-amino-1-undecanethiol (-NH₂), and (c) protonated 11-amino-1-undecanethiol (-NH₃⁺) used in this study.
Figure C2. Elastic modulus as a function of indentation speed \( (v) \), 0.05, 0.001, and 0.00001 pN/time step. (a) Stress – strain curve in compression regime I. For each indentation rate, the left figure is in ambient environment and right figure is in vacuum. Black and grey are FLG-CH\(_3\) heterostructures; blue and light blue are FLG-NH\(_2\) heterostructures. The negative strain in the beginning part of some of the curves is due to FLG-SAM force fluctuations when the applied stress is low. (b) Elastic modulus values with corresponding R\(^2\) values (number inside the bar graphs) obtained from the slopes in the linear compression regime for three different indentation speeds, and (c) comparison between reduced modulus values from the experiment and averaged modulus values from SMD simulations.
Figure C3. Temporal profiles of the overall interfacial interaction energy between (a) FLG and CH$_3$ terminated SAMs and (b) FLG and NH$_2$ terminated SAMs in compression regime I. Dark colored and light colored bars with step value (\(t\)) illustrate the approximate yield point. Temporal profiles of inter-chain interactions among (c) CH$_3$ and (d) NH$_2$ terminated SAMs. The dotted lines represent the profiles of inter-chain interactions of alkyl chains without head groups.
Section C.II. SAM Characterization

Figure C4. High resolution N 1s XPS shows the protonation of amine groups in the NH₂-SAM.
Section C.III. MD Simulations

Figure C5. Time evolution of the non-bonded interaction energy between SAMs and interfacial water (red), SAMs and surrounding water (water molecules within 4.5 Å of head groups excluding interfacial water, blue), the bottom layer of FLG and water (gray), and the entire SAM and water molecules (black).

Figure C6. (a) Representative simulation snapshot of FLG on NH$_3^+$-SAMs in water. In this snapshot, water molecules are omitted. (b) Average number of water molecules and (c) average non-bonded interaction energy between FLG and –NH$_3^+$ head groups.
Figure C7. Non-bonded interaction energy between FLG and –CH$_3$ head groups, –NH$_2$ head groups, and –NH$_3^+$ head groups in vacuum condition.
Figure C8. Schematic showing the presence of water in the vicinity of the FLG-CH\(_3\)-SAM interfaces in real systems: (A) The SAM is a polycrystalline structure, with grain boundaries and defects (The image is modified from a STM image of a CH\(_3\)-terminated alkanethiol SAM on Au (111))\(^{[268]}\). The MD simulations simplify this complex scenario into a patch of the FLG-SAM heterostructure with periodic boundary conditions. (B) Due to defects of the SAM and the roughness of the underlying substrate, small water clusters (blue) can present between graphene and the CH\(_3\)-terminated SAM when graphene is transferred to the SAM surface in ambient conditions. (C) Top view, showing that water (blue) can be present at the grain boundaries and defects, which is represented by the surrounding water in MD simulation.
Appendix D. Additional Information for Chapter 6

Graphene Coated Water Adlayer on Mica.

Graphene is mechanically exfoliated and transferred to Mica. Water adlayer will be found as long as the transfer is completed in ambient environment (RH > 25%). If the environment is very dry, the transfer can be done in an open glass dish with some wet tissue nearby. Because mica substrate also consists of weakly bonded layers, the normal scotch tape-based mechanical exfoliation method will not work in this case, during which the mica layers will adhere to the tape and delaminate from the substrate. Instead, a modified mechanical exfoliation method (similar to the method in Ref. [40]) is used, which is described as follows:

1. Exfoliate a piece of HOPG by scotch tape to expose fresh surface.

2. Use tweezer to carefully pick up a piece of graphite from the tape and place it on freshly cleaved mica. The fresh graphite surface need to be placed facing the mica surface.

3. Use a piece of PDMS to gently push the graphite piece to the mica surface.

4. Remove the PDMS stamp and use dry N₂ to blow away the thick graphite debris.

5. Search under optical microscope to identify thin areas of graphene
References


Biography

Qing Tu was born in Jiangxi, China, on Jan. 26th, 1990. He attended Nanchang No.2 Middle School, where he became interested in physics and mathematics through national physics Olympics competition. In 2007, he got admitted to Peking University (PKU) in Beijing, where he received a Bachelor of Science in Theoretical and Applied Mechanics. At PKU, he gained his first training on scientific research under the instruction of Prof. Huiling Duan, and developed a strong interest in mechanics in materials science and nanotechnology. After college, he got admitted as a PhD student to the Department of Mechanical Engineering and Materials Science at Duke University to continue his research on nanomechanics and materials characterization. During his PhD, he focused on applying advanced scanning probe microscopy techniques to investigate the interfaces in 2D materials and heterostructures. He received the fellowship from the NSF Research Triangle Materials Research Science and Engineering Center, and got the special opportunity to work in close collaboration with talented researchers with various backgrounds. In the highly collaborative and interdisciplinary environment, he co-authored one book chapter in the Handbook of Nanomaterials Properties, and four peer reviewed journal articles including Nature Materials, ACS Nano, ACS Applied Materials & Interfaces, and Nanotechnology. He has also presented his research work at national and international conferences, including a Gordon Research Conference, MRS Fall and
Spring Meetings, American Physical Society and American Vacuum Society Annual Meetings.