

Supporting Information for

Selective-area, Water-Free Atomic Layer Deposition of Metal Oxides on Graphene Defects

Michael F. Mazza,[†] Miguel Cabán-Acevedo[‡], Harold J. Fu[‡], Madeline C. Meier[‡], Annelise C. Thompson[‡], Zachary P. Ifkovitz[‡], Azhar I. Carim[‡], and Nathan S. Lewis^{‡,||}*

[†]127-72, 210 Noyes Laboratory, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

^{||}Beckman Institute, California Institute of Technology, Pasadena, California 91125, United States;

*Corresponding Author: nslewis@caltech.edu

Materials and Methods

Monolayer Graphene

CVD-grown graphene on Si was purchased from Advanced Chemicals Supplier Material (ACS Material) and was used as received. The Si(100) substrate was doped p-type with a resistivity $< 0.01 \Omega \text{ cm}$. Monolayer graphene was grown on Cu foil and transferred with a PMMA (poly methylmethacrylate) protection layer *via* a wet transfer process. The grain size of the as-deposited monolayer CVD-graphene film was $\sim 50 \mu\text{m}$ prior to transfer.

Atomic Layer Deposition

Titanium dioxide (TiO₂), aluminum oxide (Al₂O₃) and titanium aluminum oxide (Ti_xAl_yO_z) were deposited using a Cambridge Nanotech S200 ALD system. All depositions were performed with 20 sccm N₂ carrier gas at a base pressure of ~ 0.6 torr. Titanium (IV) isopropoxide (TTIP, 98% STREM) was heated to 75 °C and used as the titanium source. Trimethyl aluminum (TMA, 98% STREM) at room temperature was used as the aluminum source.

The ALD recipe for the water-free deposition was:

$$\text{TTIP}(0.013\text{s}) - 40\text{s} - \text{TMA}(0.011\text{s}) - 40\text{s} \quad (1)$$

Scanning Electron Microscopy

Scanning electron microscopy (SEM) was performed using a FEI Nova NanoSE 450 at accelerating voltages between 3 and 15 keV with a 5 mm working distance.

X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed using a Surface Science M-probe ESCA/XPS. The system had a chamber base pressure of $<2 \times 10^{-8}$. The sample was illuminated by a 1486.7 eV Al K α monochromatic x-ray source at 35° relative to the surface. Photoelectrons were collected by a hemispherical energy analyzer with a 100 mm radius and a pass energy of 25 eV. The analyzer had a resolution of ~ 0.8 eV. Data were acquired using the ESCA25 Capture (Service Physics, Bend OR; V5.01.04) software and were evaluated using CasaXPS software. The high-resolution peaks were referenced to the graphene carbon 1s peak at 284 eV.

Kelvin Probe Force Microscopy

Atomic-force microscopy (AFM) was performed using a Bruker Dimension Icon. Samples were affixed to a steel disc using Ag paint. The scan was performed with the PeakForce setpoint at 5.0 nN, the scan rate at 0.501 Hz, and a PeakForce amplitude at 150 nm using a SCM-PtSi (Bruker) probe with a nominal tip radius of 15 nm. PeakForce Kelvin Probe Force Microscopy (PF-KPFM) was performed during the scan, in which height, adhesion, and potential maps were collected concurrently. Adhesion maps provided qualitative data comparing relative adhesion of the heterogeneous surface scanned and were not calibrated to a reference sample.

Raman Spectroscopy

Raman spectra were collected with a Renishaw inVia Raman microprobe equipped with a Leica DM 2500 M microscope, a Leica N Plan 50x objective (numerical aperture = 0.75), an 1800 lines mm⁻¹ grating, and a CCD detector configured in a 180° backscatter geometry. A $\lambda = 532$ nm diode-pumped solid-state (DPSS) laser (Renishaw RL532C50) was used as the excitation source and a ~ 100 μ W radiant flux was incident on the surface of the sample. A $\lambda/4$ plate was used to circularly polarize the incident excitation. No polarizing collection optic was used.

Supporting Data

Thermal ALD Controls

ALD was performed on graphene/Si surfaces using water as the counter-reactant to determine how the oxidant-free deposition chemistry differed from conventional ALD. The ALD

recipes were performed at mutually the same temperature, purge times, precursor dose times, and number of cycles. The recipes are shown below:



Figure S1 shows SEM images of the two controls. Aluminum oxide formed a near conformal film after 200 cycles (Figure S1a). Line features assigned to initial defect nucleation were observed through the film. Little deposition was observed with only moderate selectivity for line defects for the titanium oxide control (Figure S1b). This result is consistent with a substantially lower growth rate for TTIP relative to TMA at 110 °C. Water-based ALD recipes supersaturate the basal plane with adsorbed water, resulting in fractional nucleation on the basal plane. The film therefore becomes less selective, with precursors with higher growth rates more quickly becoming conformal. These control experiments indicate that removing water from the recipe directed anisotropic deposition and allowed for robust anisotropic films to form on the surface before creating a conformal film.

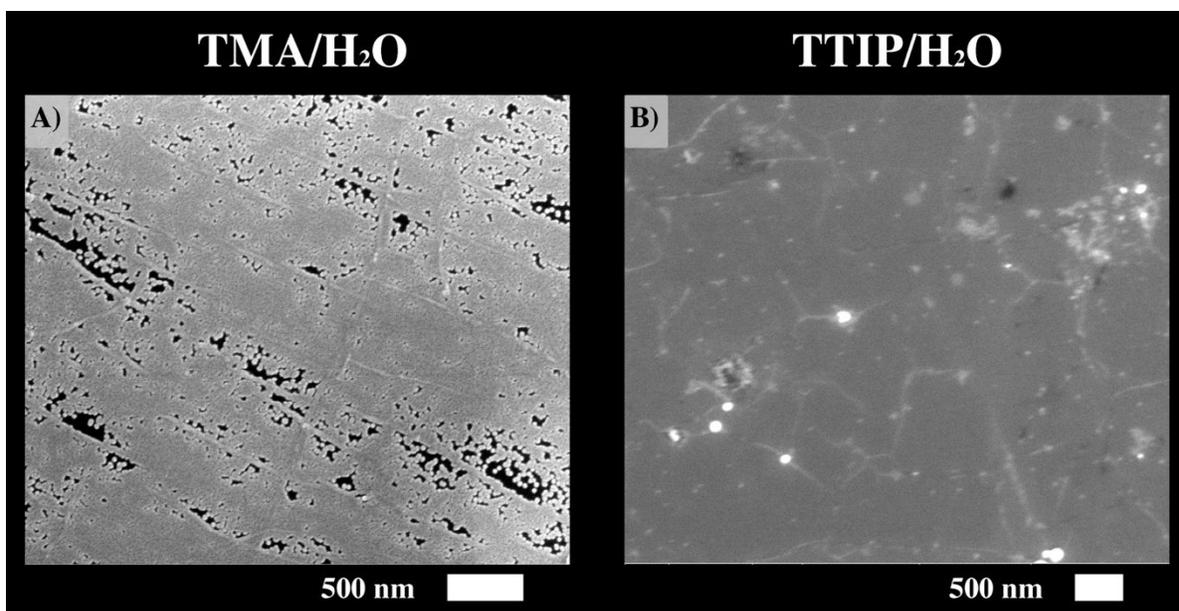


Figure S1. SEM images of monolayer graphene samples after 200 ALD cycles. A) Water-based aluminum oxide deposition and B) Water-based titanium oxide deposition.

KPFM Mapping Data

KPFM mapping data were obtained concurrently with the AFM data shown in the main text. These maps showed clear differences in the contact potential and in the adhesion force between the line defects selectively passivated with $\text{Al}_x\text{Ti}_y\text{O}_z$ and the graphene basal plane. These data were not included in the main text because the surface scanned was not calibrated to a reference sample.

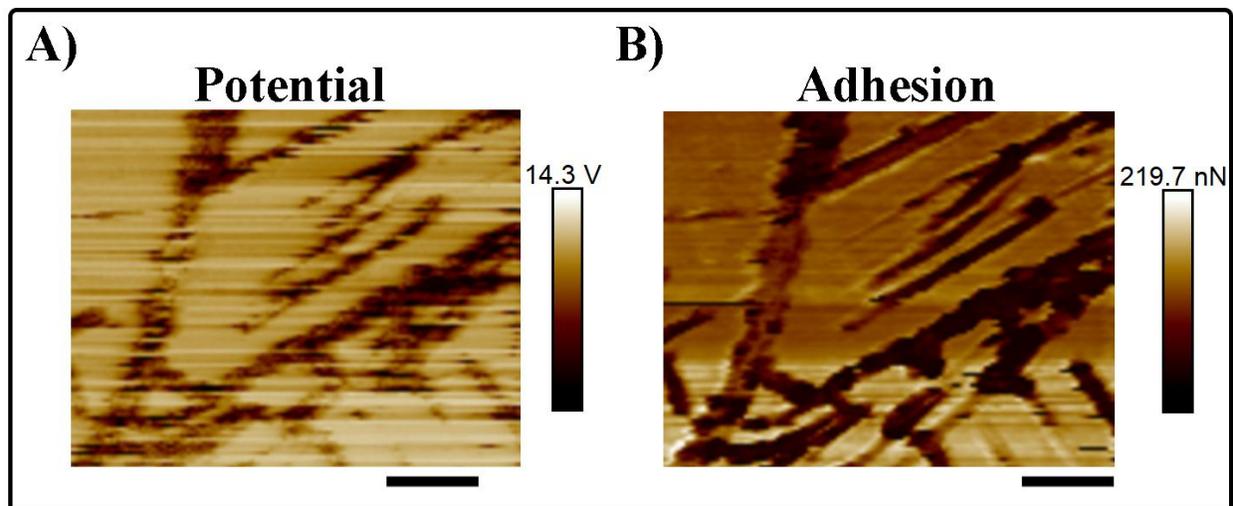


Figure S2. KPFM mapping data showing A) contact potential and B) surface adhesion force differences between the deposited defect regions and the pristine basal plane. Scale bars are 500 nm.

Temperature Dependence of Deposition Selectivity

The combined TTIP/TMA recipe was performed at various temperatures to optimize the anisotropic growth behavior as well as to probe the surface chemistry (Figure S3). Each sample was deposited according to the recipe outlined in the Methods section, and SEM data were collected after 200 cycles. The coverage was strongly dependent on the deposition temperature. At low temperatures, selectivity was lost and the metal oxide deposition resembled a nonconformal film (Figure S3a). The deposition was most anisotropic at 110 °C, with very little deposition observed outside of the line patterns (Figure S3b). This temperature-dependent behavior is observed across similarly patterned regions on the sheet, with a notable increase in selectivity at 110 °C (Figures S4a,b) At higher temperatures, deposition occurred at random nucleation sites as well as at large-scale line networks (Figure S3c).

These results are consistent with a narrow regime in which selective-area ALD occurred. At very low temperatures, precursors condensed on the graphene basal plane. At higher

temperatures, the metal-oxide precursors more readily reacted with the graphene basal plane, leading to more conformal coverage and less deposition concentrated on defects.

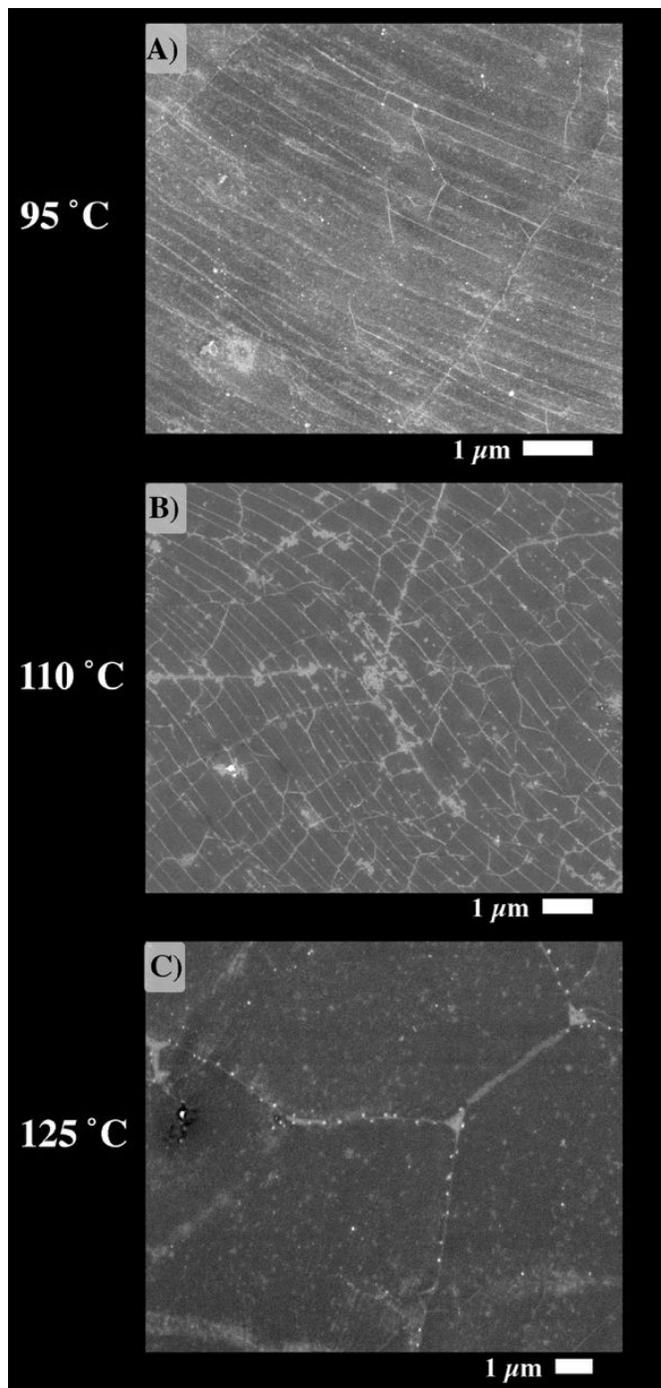


Figure S3. SEM images showing the temperature-dependent selectivity of the water-free ALD recipe. Images show the deposition behavior at A) 95 °C, B) 110 °C, and C) 125 °C.

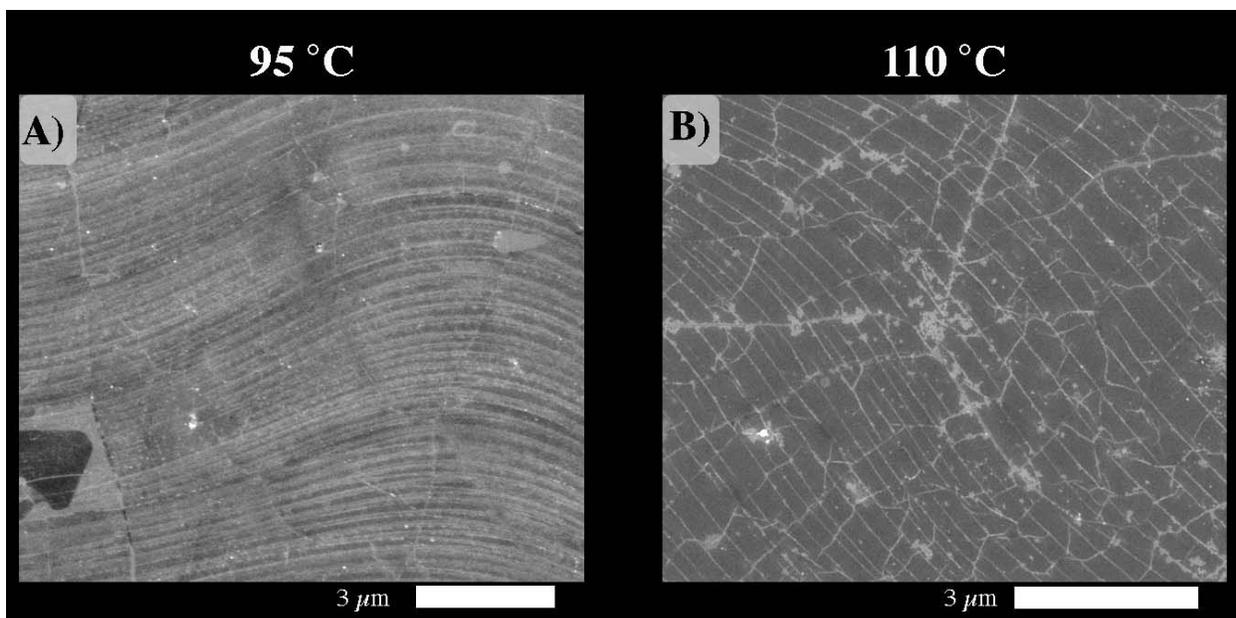


Figure S4. Lower-magnification SEM images showing differences in selectivity with similar deposition patterns at A) 95 °C and B) 110 °C.

Raman Spectroscopy

Raman spectra were taken on two cut regions of the same CVD-graphene on silicon sample. One chip was left pristine and the second chip was exposed to 200 cycles of the water-free ALD recipe at 100 °C as detailed in the methods section above. The spectra show that the ALD recipe does not damage the graphene sheet, as shown by the relative intensities of the D and G peaks.

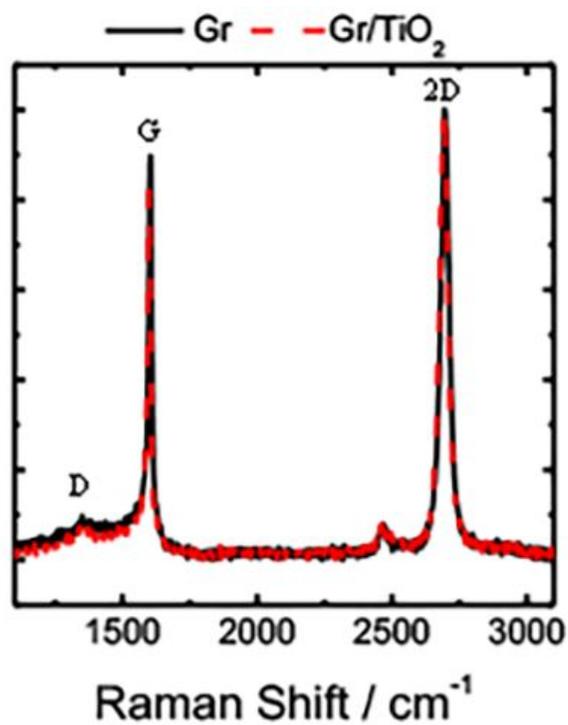


Figure S5. Raman spectrum showing the quality of the graphene layer without deposition (black) and after 200 ALD cycles (red).

Statistical Estimate for Average Film Thickness

To experimentally determine an *average* film thickness, line traces were taken across 10 spots of the AFM map shown in Figure 2. The average thickness was determined to be 8 nm with a standard deviation of 2 nm.

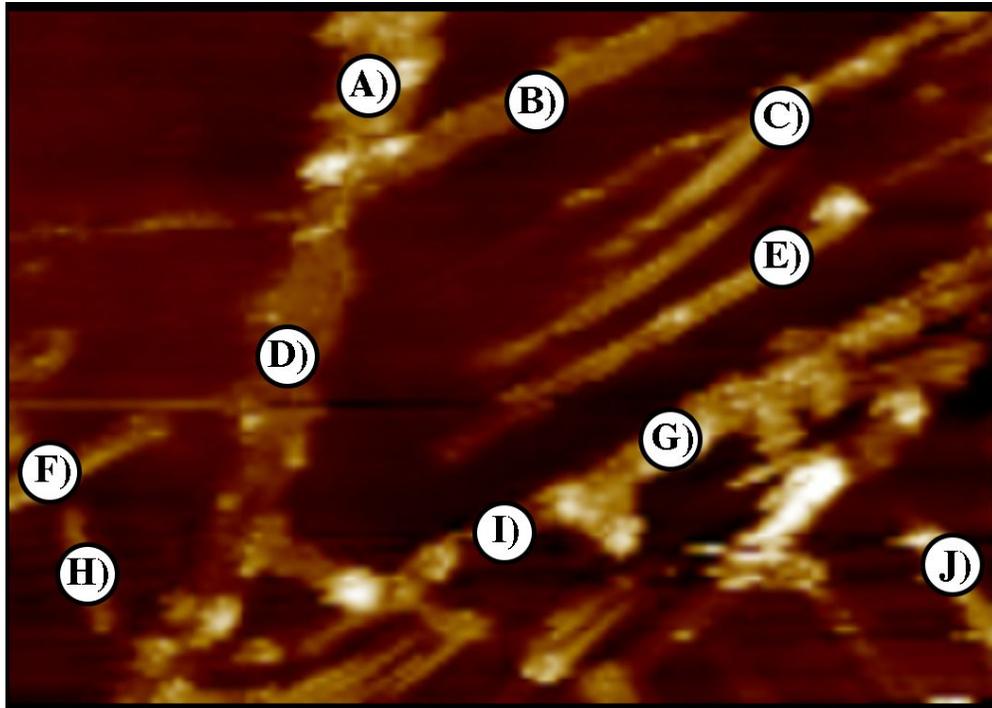


Figure S6. AFM map of the 10 spots used for the statistical determination for average film thickness. The thickness is estimated at 8 ± 2 nm.