Supplementary Information

Ultrathin Oxide Films by Atomic Layer Deposition on Graphene

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Experimental Methods

Graphene is deposited using mechanical exfoliation over pre-defined etched wells similar to previously described methods (see Fig. 1a) [1–3]. A series of wells with ~5-8 μm diameters are defined by photolithography on a silicon wafer with 90 nm of thermally grown silicon oxide. Dry plasma etching (CF_4 + O_2, followed by SF_6) is used to etch wells that are 500 nm – 3 μm and the "scotch tape" method is used to deposit graphene[1].

Atomic layer deposition on the graphene is performed in a homebuilt reactor following a recipe similar to one previously reported for ALD alumina growth on carbon nanotubes [4,5]. The samples are placed inside the ALD reactor, pumped down to ~30 mTorr, and held at 180°C for 30 min - 1 hour before beginning the reaction. The reactor is purged with 20 sequences of argon purging before performing the NO_2/TMA

nucleation treatment. Each argon purge involved dosing argon to 1 Torr for 60 seconds and then pumping for 60 seconds.

The nucleation treatment involves a dose of NO_2 to 1 Torr for 60 sec followed by pumping for 60 seconds. Subsequently, a dose of TMA to 1 Torr for 60 sec is applied, followed by pumping for 60 seconds. This process is repeated 10 times. After forming this adhesion layer, ALD of alumina is performed by cycling TMA/H_20 doses as follows: dose TMA to 1 Torr for 60 sec, pump for 60 sec, then dose Argon at 20 Torr for 60 sec and pump for 60 seconds 5 times, dose H_2O to 1 Torr for 60 sec, pump for 60 sec, then dose Argon at 20 Torr for 60 sec and pump for 60 seconds 5 times. This represents 1 cycle of ALD. After the TMA/H_2O cycles are complete, the reactor is purged again with argon and then the samples are removed. All reactions were performed at 180 (± 0.5) °C.

TEM Imaging of a Graphene/ALD Composite

Cross-sections of alumina/graphene devices on SiO_2 substrates were prepared using a focused ion beam lift-out. Before cross-sectioning, the samples were coated with ~20 nm of amorphous carbon followed by a thick platinum layer to protect the sample surfaces. The samples were imaged using a 200 kV electron beam in a FEI Technai-F-20 TEM/STEM. The composition of each layer was verified with electron energy-loss spectroscopy. TEM/STEM was used to image the alumina that was formed on graphene after 10 cycles of TMA/NO_2 nucleation treatment followed by 5 cycles of TMA/H_20 ALD deposition. From these images, the observed alumina layer was amorphous and 2.8 ± 0.3 nm thick.

Raman Spectrum Verifying the Etching of Graphene

Raman spectroscopy was used to confirm the removal of graphene after etching[1]. Figure S2a shows Raman spectroscopy of a graphene/ALD composite film before etching of graphene. The Raman spectrum shows the G and 2D peaks that are characteristic of a bilayer graphene membrane. After etching, the G, D, and 2D peaks are not detectable in the Raman spectrum confirming that all the graphene was etched away leaving only the suspended pure alumina ALD film (Fig. S2b). Note that the vertical scales in Fig. S2a and S2b are different. Figure S3 shows a comparison of the Raman spectrum on the same vertical scale before and after etching. This wave number range includes the peaks arising from the oxidized silicon substrate and a comparison of these peak sizes serves as a calibration of laser intensity between the 2 measurements. The lack of a visible D, G, and 2D peak in Fig. S3b confirms the successful oxidative etching and removal of graphene.

Elastic Constants of Pure ALD Films

A method identical to one previously used to determine the elastic constants of pressurized graphene membranes was used to determine the elastic constants of the pure ALD films[2]. Figure S4 shows additional blister test data for the other pure ALD films fabricated and tested in this study. All of the films shown in one plot are from the same ALD coating on multiple graphene membrane supports. The *Et* values extracted from the slopes were plotted in Fig. 1b of the main text.

Initial Tension in Graphene and Graphene/ALD Composite Films

Even with no applied pressure difference across the films, the frequency of these nanomechanical resonators still behave as stretched membranes[3]. This is illustrated by the high resonant frequencies exhibited by the membranes even when no pressure difference

exists across the membranes or $p_{int} = p_{ext}$. Neglecting the bending rigidity, the fundamental frequency of a clamped circular membrane under uniform tension, S_0, is given by:

$$f_0 = \frac{2.404}{2\text{À}} \cdot \sqrt{\frac{S_0}{ma^2}} \tag{S1}$$

The initial surface tension in the membranes can be deduced by measuring the resonant frequency of the membranes when no pressure difference exists across the membrane. For the graphene membrane resonator before ALD deposition, this corresponds to a uniform tension of S_0 = 0.073 ± 0.041 N/m (Fig. S5a). After ALD film deposition, the uniform tension is S_0 = 0.21 ± 0.13 N/m (Fig. S5b). This increase in uniform tension indicates that there is a significant increase in the intrinsic stress in the membranes. Future work will seek to understand the origin of this increased tension in the composite membranes to determine whether this intrinsic stress is a result of stress in the pure ALD films or arises from the composite nature of the films.

Pure ALD Films from the Nucleation Treatment

The thinnest suspended pure alumina ALD film fabricated is shown in Figure S6. This film had only 4 cycles of the NO_2/TMA nucleation treatment applied to the graphene. Subsequent etching of the graphene support leaves a continuous and smooth film. The film has a few small voids visible by AFM. Figure S7 shows optical and AFM images for a film made from only 5 cycles of the NO_2/TMA nucleation treatment. This film is also continuous and smooth and there are no pinholes or small voids visible by AFM.

Supplementary References

(1) Novoselov, K. S.; Jiang, D.; Schedin, F.; Booth, T. J.; Khotkevich, V. V.; Morozov, S. V.; Geim, A. K. *Proceedings of the National Academy of Sciences of the United States of America* **2005**, *102*, 10451-10453.

(2) Bunch, J. S.; Verbridge, S. S.; Alden, J. S.; Zande, A. M. V. D.; Parpia, J. M.; Craighead, H. G.; McEuen, P. L. *Nano Letters* **2008**, *8*, 2458-2462.

(3) Koenig, S. P.; Boddeti, N. G.; Dunn, M. L.; Bunch, J. S. *Nat Nano* **2011**, *6*, 543-546.

(4) Cavanagh, A. S.; Wilson, C. a; Weimer, A. W.; George, S. M. *Nanotechnology* **2009**, *20*, 255602.

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Supplementary Figure Captions

Figure S1

Bright-field TEM image of a cross-section of supported alumina ALD film on 5-layer graphene supported on silicon oxide. The amorphous alumina layer is 2.8 ± 0.3 nm thick.

Figure S2

(a) Raman spectrum for one of the graphene/ALD composite films in Fig. 1b. **(b)** A representative Raman spectrum on one of the pure alumina ALD films in Fig. 1C. Note that the vertical scales are different.

Figure S3

(a) Raman spectrum showing the full spectrum of the data in Fig, S2a **(b)** Raman spectrum showing the full spectrum of the data in Fig, S2b.

Figure S4

K(½)´3/a^4 versus • p for (a) 5 pure ALD films with 8 cycles of alumina ALD. The average and standard deviation of all the slopes corresponds to *Et* = 213 ± 12 GPa-nm. (b) 1 pure ALD films with 5 cycles of alumina ALD. The slope is a best fit line and corresponds to *Et* = 179 ± 6 GPa-nm. (c) 8 pure ALD films with 5 cycles of alumina ALD. The average and standard deviation of all the slopes corresponds to *Et* = 219 ± 21 GPa-nm. (d) 5 pure ALD films with 8 cycles of alumina ALD. The average and standard deviation of all the slopes corresponds to *Et* = 280 ± 12 GPa-nm. (e) 3 pure ALD films with 10 cycles of alumina ALD. The average and standard deviation of all the slopes corresponds to *Et* = 355 ± 71 GPa-nm. (f) 9 pure ALD films with 15 cycles of alumina ALD. The average and standard deviation of all the slopes corresponds to *Et* = 375 ± 38 GPa-nm.

Figure S5

Histogram of initial tension in **(a)** pristine graphene membranes and **(b)** graphene/ALD composite membranes

Figure S6

(a) Optical image of a graphene flake with 4 cycles of NO_2/TMA. **(b)** Optical image after etching away the graphene **(c)** Atomic force microscope image corresponding to the red box in **(b)** of the pure alumina ALD film (scale bar = 2.5 μm)

Figure S7

(a) Optical image of a graphene flake with 5 cycles of NO_2/TMA. **(b)** Optical image after etching away the graphene **(c)** Atomic force microscope image corresponding to the red box in **(b)** of the pure alumina ALD film (scale bar = 2.5 μm)

Figures

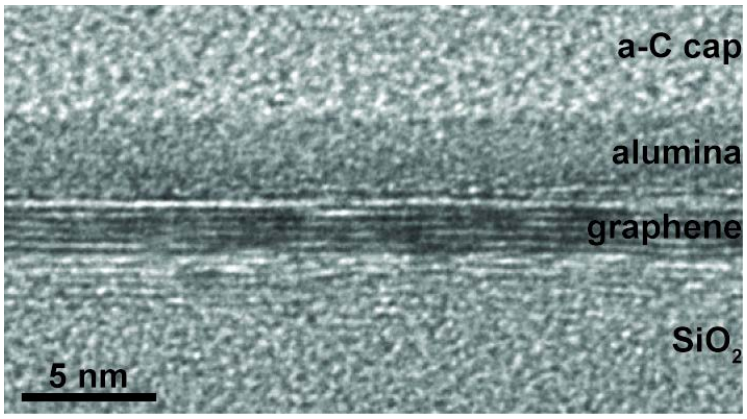

Figure S1

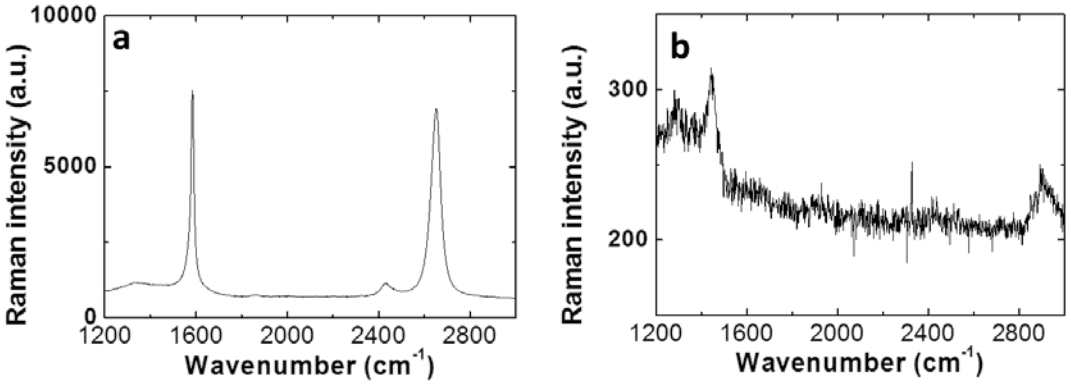

Figure S2

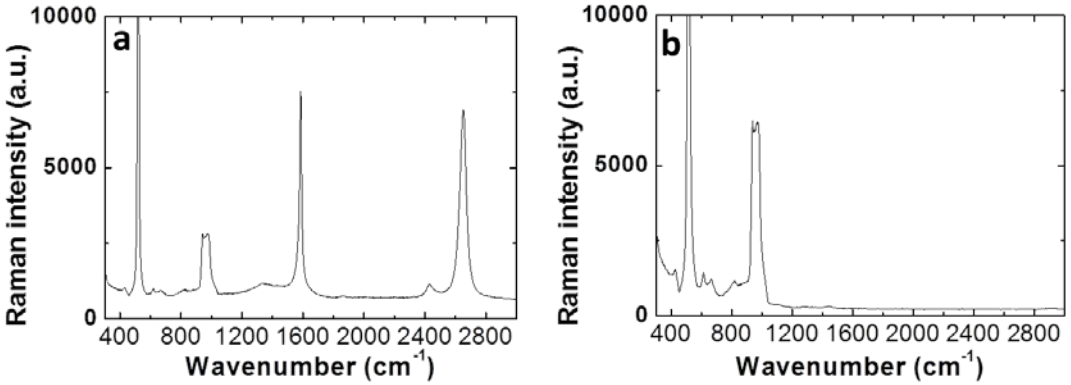

Figure S3

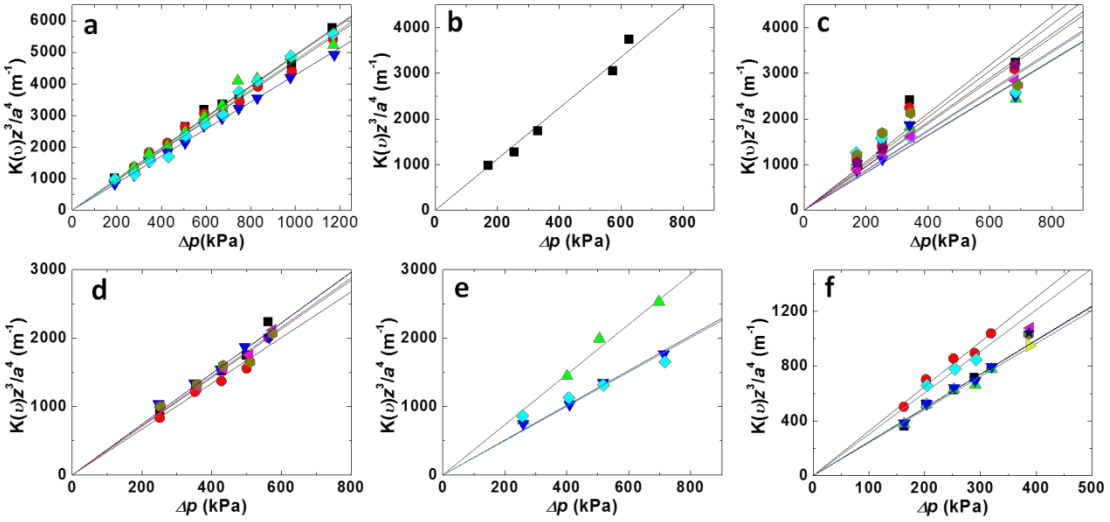

Figure S4

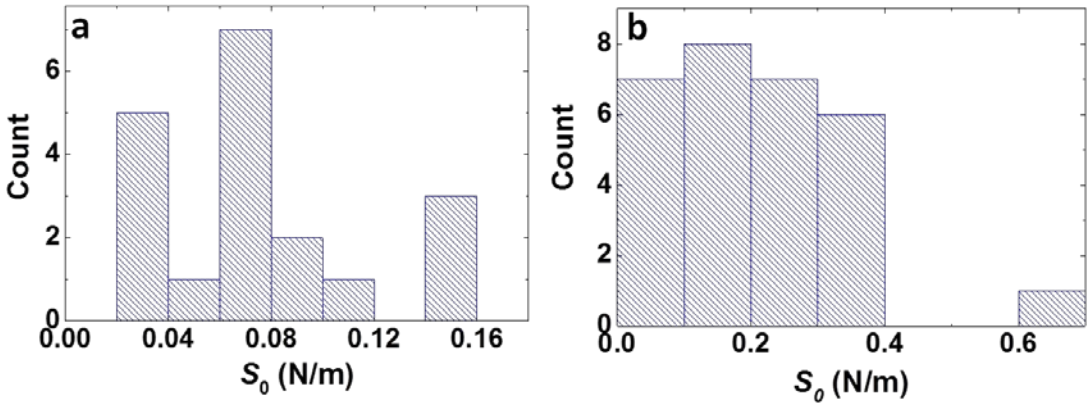

Figure S5

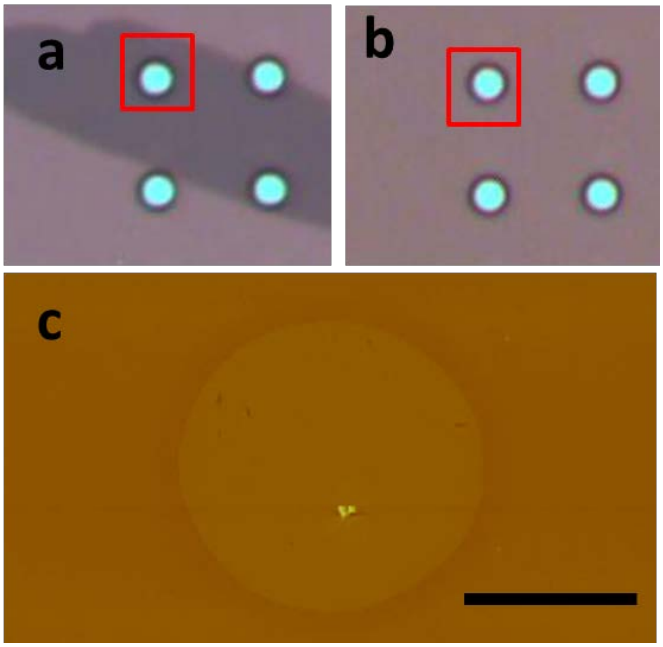

Figure S6

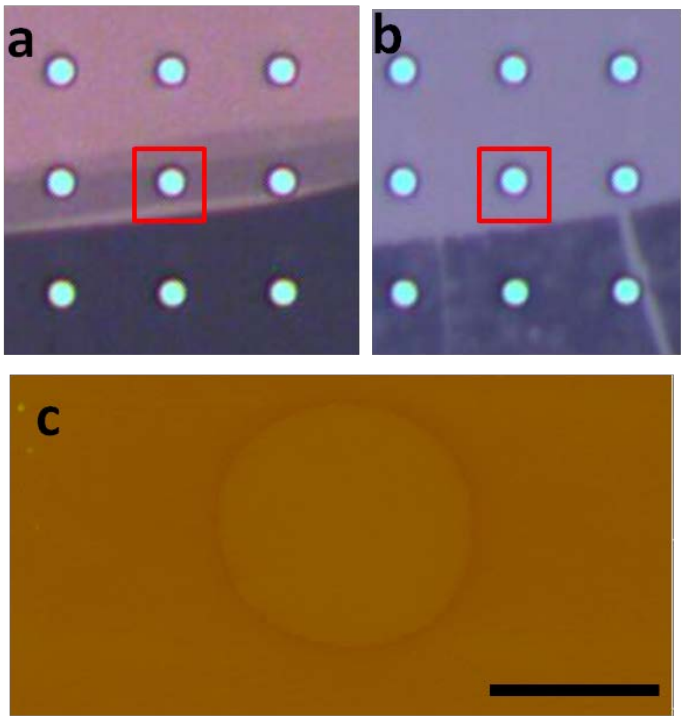

Figure S7