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Probing the Mechanical Properties of Vertically-Stacked Ultrathin Graphene/Al₂O₃ Heterostructures

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Abstract

The superior intrinsic mechanical properties of graphene have been widely studied and utilized to enhance the mechanical properties of various composite materials. However, it is still unclear how heterostructures incorporating graphene behave, and to what extent graphene influences their mechanical response. In this work, a series of graphene/Al₂O₃ composite films were fabricated via atomic layer deposition of Al₂O₃ on graphene, and their mechanical behavior was studied using an experimental-computational approach. The inclusion of monolayer chemical vapor deposited (CVD) graphene between ultrathin Al₂O₃ films (1.5 nm – 4.5 nm thickness) was found to enhance the overall stiffness by as much as 70% compared to a pure Al₂O₃ film of similar thickness (~150 GPa to ~250 GPa). Here, for the first time, the combination of graphene and Al₂O₃ in vertically-stacked heterostructures results in advanced hybrid films of unprecedented mechanical stiffness that also possess qualities desirable for graphene-based transistors and flexible electronics.

1. Introduction

The class of materials categorized as two-dimensional (2D) nanomaterials such as molybdenum disulfide (MoS₂), boron nitride (BN), tungsten disulfide (WS₂), and most notably, graphene exhibit
a vast array of fascinating properties such as extreme mechanical strength and stiffness, superior electrical and thermal conductivity, and sensing capabilities. These materials are well suited for applications where flexible, ultrathin films with unique characteristics and comparable mechanical properties are needed. The integration of these materials, specifically graphene, with other 2D materials or quasi-2D materials may also lead to new functional properties for nanocomposite structures. The realm of application of graphene-based nanocomposite structures expands further with the addition of atomic layer deposition (ALD) as it proves to be an effective technique for the fabrication of graphene and oxide heterostructures. Specifically, ALD allows for the accurate deposition of a variety of continuous nanoscale metal oxide films. Examples of the versatility of these heterostructures include the use of graphene/TiO₂ films in supercapacitors, photodetectors, and sensors, and graphene/Al₂O₃ films in DNA detectors, and graphene field-effect transistors. While graphene-based heterostructures boast desirable sensing and electronic characteristics, the measurement and quantification of their mechanical properties and durability are currently lacking. Understanding the mechanical behavior of these materials proves to be important as it can aid in reducing detrimental factors in their potential applications. For example, graphene/metal oxide films are widely used in lithium ion batteries where mechanically-induced electrochemical degradation is known to occur. It has also been illustrated in prior works that there exists a relationship between the Young’s Modulus of battery components and their cycling performance. Additionally, the characterization of the structures synthesized herein offers the ability to predict the mechanical properties of graphene field effect transistors (GFET) encapsulated with Al₂O₃ which can be especially useful where mechanically robust, yet flexible materials are utilized in flexible electronics.
Previously, the mechanical response of MoS$_2$/WS$_2$ heterostructures have been investigated, and it was found that the mechanical properties of the film as a whole were lower than the constituent materials$^{24}$. The reduction in the Young’s modulus was attributed to weak interlayer interactions which led to the mechanical degradation of the films. In addition, in-plane graphene/h-BN heterostructures were also found to exhibit weaker mechanical strength than their respective constituents$^{25}$. Here, failure was observed at the grain boundaries at the interface of the materials, yielding a less mechanically robust film. Only until recently were graphene/metal oxide heterostructures characterized which exhibited an increase in the mechanical performance when compared to the constituent materials. Cao et. al. investigated the role of monolayer graphene in enhancing the stiffness of TiO$_2$ where they were able to show that the addition of graphene offered stiffness enhancement to the TiO$_2$ films$^{26}$.

In this work, the versatility of ALD and the extreme mechanical properties of monolayer graphene was employed to fabricate Al$_2$O$_3$/graphene heterostructures. A series of films were synthesized using oxide thicknesses of 1.5 nm, 2.5 nm, 3.5 nm, and 4.5 nm (using 50, 100, 200, 400 ALD cycles, respectively) to observe the variation of the mechanical response with increased film thickness, and to better understand their complex mechanical characteristics. The heterostructures characterized in this work exhibited higher stiffness than other metal oxide and graphene-based heterostructures$^{26}$, and are desirable for use in transistors as high mobility has been reported in graphene/Al$_2$O$_3$ interfaces$^{27,28}$.
2. Methods

2.1 Experimental Methods

CVD grown single-layer graphene (fabricated by Graphenea SA) was suspended on holey carbon TEM grids (QUANITFOIL®) with holes of 2 μm in diameter, by a wet transfer process where aluminum oxide of varying thickness was deposited onto the graphene monolayer using ALD (Figure 1a, b). Graphene was confirmed to be monolayer via Raman spectroscopy\(^\text{29}\) (see supporting information Section 1). Figure 1c displays the transmission electron microscopy (TEM) micrograph of the graphene monolayer suspended on the TEM grid, from this it can be seen that good graphene coverage exists. A high-resolution TEM (HR-TEM) micrograph of the graphene monolayer with an inset selective area electron diffraction (SAED) pattern can be seen in Figure 1d, verifying the hexagonal structure of graphene. Aluminum oxide (\(\text{Al}_2\text{O}_3\)) at 150°C was deposited using water as the oxygen source and trimethylaluminum (TMA, \(\text{Al}_2(\text{CH}_3)_6\)) precursors with a deposition rate of approximately 0.25 – 0.175 Å/cycle (Figure 1a). The thickness of each film was measured via ellipsometry. The mechanical properties of the free-standing graphene/\(\text{Al}_2\text{O}_3\) heterostructures were investigated through atomic force microscope (NX-10 Park Systems) nanoindentation as accurate control can be had over probe positioning, loading, and indentation rate. A diamond probe (Nanosensors, Inc.) was used to perform the indentations. Before measurements, the AFM was allowed to reach thermal equilibrium to ensure optimum characterization performance. The normal spring constant of the cantilever was determined through the Sader Method\(^\text{30}\) to be 5.03 N/m. An indentation rate of 0.25 µm/s was chosen to avoid dynamic loading effects and eliminate inertial forces, and a fixed piezo displacement of 200 µm was chosen for each indentation. Before and after each indentation, non-contact scans were performed to inspect the film surfaces for potential discontinuities or imperfections introduced.
through the ALD process that could potentially influence the measured mechanical behavior of the heterostructures (see supporting information section 2). Indentations performed with varying rates (0.1 μm/s - 5 μm/s) did not appear to affect the response. Membrane deflection, \( \delta \), was calculated using eqn. 1,

\[
\delta = \Delta z - \delta_{\text{tip}},
\]

where the tip deflection, \( \delta_{\text{tip}} \), is subtracted from the piezo displacement, \( \Delta z \) (Figure 1e) as direct measurement of the film deflection is not possible.

2.2 Numerical Methods

The finite element model was developed using triangular mesh elements for the hemispherical indentation tip and tetragonal mesh elements for the film. Quadratic serendipity shape functions were used. While different thicknesses of Al\(_2\)O\(_3\) films were considered for different ALD cycles, minimum of ten mesh elements per thickness of each layer and graphene is considered to avoid mesh-dependent solutions. The dimensionality of the indentation problem is reduced considering its symmetry about the axis at the indentation point, i.e. symmetry boundary condition is applied at the indentation point, while the film is fixed at the other end. Quasi-static loading was considered, and final deformation was obtained via multiple incremental displacements of the tip to avoid numerical instabilities. The indenter is modeled as a semi-sphere of radius 150 nm, the film is considered to be clamped at the outer edge of the film, and the gravitational forces are neglected. The Al\(_2\)O\(_3\) and diamond were modeled as isotropic materials with a Young’s moduli of \( E_s = 400 \) GPa and \( E_D = 1.05 \) TPa, and Poisson’s ratios of \( \gamma_s = 0.22 \) and \( \gamma_D = 0.1 \), respectively. The system of equations was solved using the Multifrontal Massively Parallel sparse direct Solver.
(MUMPS) in segregated steps of (i) calculating the contact pressure, and (ii) calculating the displacement field.

![Figure 1](image_url)

**Figure 1.** (a) Schematic of the deposition of aluminum oxide on either side of the graphene monolayer with TMA (trimethylaluminum) and water precursors, (b) side-view of Al₂O₃/graphene heterostructure, (c) monolayer graphene suspended on QUANITFOIL® holey carbon TEM grid, (d) high-resolution TEM micrograph of monolayer graphene with inset selective area electron diffraction pattern (SAED), (e) AFM characterization schematic.

### 3. Results and Discussion

#### 3.1 Experimental Characterization

To investigate the condition of the metal oxide films deposited through ALD, HR-TEM imaging was performed on the heterostructures. The TEM micrographs of heterostructures prepared by 50 cycles, 100 cycles, 200 cycles, and 400 cycles can be seen in Figure 2a, b, c, and d, respectively. For each structure, it can be seen that good film continuity exists as no discrete nucleation sites were detected.
Figure 2. HR-TEM micrographs of Al₂O₃-graphene heterostructures prepared by (a) 50 cycles, (b) 100 cycles, (c) 200 cycles, and (d) 400 cycles of atomic layer deposition.

The experimentally-measured and theoretically calculated force-displacement response, $F(\delta)$, for different heterostructures are shown in Figure 3a. The ratio of film thickness to film radius ($t/a$) is very small for the structures investigated herein, (0.15-0.45%) meaning any shearing effects between the interfaces can be neglected\textsuperscript{31,32}. In this case, with a film radius of $a = 1000$ nm, a maximum and minimum film thickness of $t = 4.5$ nm and $1.5$ nm, respectively, the maximum and minimum values for ($t/a$) are 0.45% and 0.15%, respectively. Thus, it is reasonable to assume a purely elastic deformation regime and good interlayer bonding. From Figure 3a, it can be seen that there exists an excellent agreement between the numerical simulation and experimentally-determined results which verifies the validity of the developed model and the assumptions made.
More importantly, from Figure 3a, it is clear that as the number of ALD cycles increase (i.e. increase in film thickness), higher forces were required for the probe to deflect the films to similar depths. This suggests an increase in the mechanical stiffness with increased ALD cycles. The increase in film stiffness – i.e. increase in force per displacement, $F/\delta$ – can be attributed to the increase in the second moment of area of the films, $I$, as $F/\delta$ is proportional to $I$ which itself is directly related to the thickness of the films. The force-displacement response exhibited little difference between loading and unloading (Figure 3b), which excludes the presence of dissipative processes, such as plastic deformation or interlayer sliding during indentation$^{26,32}$.

![Figure 3](image.png)

**Figure 3.** (a) Experimentally-measured (solid lines) and numerical (dashed line) force-displacement response of pristine graphene and heterostructure prepared with varying ALD cycles. (b) Loading-unloading curve of heterostructure prepared with 100 cycles of ALD. Zoomed-in inset shows an approximate 1% difference between loading and unloading. Arrows indicate direction of loading and unloading. It should be noted that each film exhibited similar levels of hysteresis.

Assuming the films are isotropic and elastic, as they have a small thickness to radius ratio$^{1,32}$, the behavior of the films studied in this work can be modeled using the force-displacement response
of a suspended clamped circular sheet made of a linear isotropic elastic material under a centrally-applied load:\(^\text{31}\)

\[
F = \left[ \frac{4\pi E}{3(1-\nu^2)} \left( \frac{t^3}{a^2} \right) \right] \delta + (\pi T) \delta + \left( \frac{q^2 Et}{a^2} \right) \delta^3.
\]  

(2)

Here, \(F\) is the applied force, \(\delta\) is the indentation depth, \(T\) is the pretension of the clamped film, \(\nu\) is the effective Poisson’s ratio, \(E\) is the effective Young’s Modulus, \(a\) is the radius of the film, \(t\) is the thickness of the film, and \(q\) is a dimensionless parameter which is equal to \(1/(1.05 - 0.15\nu - 0.16\nu^2)\). The first term in eqn. 2 relates to the mechanical behavior of a plate with a certain bending rigidity \(^{31,33}\); the second term captures the behavior of a stretched membrane\(^1\), and the final term takes into account the stiffening of a film during the load cycle\(^{31}\). Typically, bending rigidity (first term in eqn. 2) can be ignored in structures exhibiting purely stretch-dominated behavior such as graphene\(^{34}\) or graphene oxide\(^{35}\); however, since it is still unclear whether heterostructures in general exhibit pure stretching, pure bending, or can be considered as ‘transitional,’ the general form of the equation is used for fitting and all three terms are included\(^{26}\) (see supporting information section 3). In this case, it can be assumed that the increase in thickness of the heterostructure, while it increased the stiffness of the film nearly six-fold, does not induce the transition from stretching to bending, even with the bending rigidity taken into consideration, which scales with \((t^2/a^2)\). The unique response of these heterostructures proves to be significant in that by simply varying the thickness of the encapsulating oxide layers, the mechanical behavior of the films can be carefully tuned to fill specific needs.

The statistical histograms of the films’ Young’s Moduli are shown in Figure 4. Here, the modulus for the films prepared with 50, 100, 200, and 400 cycles, as well as the modulus of the pristine graphene is \(255 \pm 23\) GPa, \(246 \pm 18\) GPa, \(224 \pm 25\) GPa, \(209 \pm 21\) GPa, and \(445 \pm 83\) GPa
respectively, which are in the form of mean ± standard deviation. The Young’s Modulus for each film was determined by fitting eqn. 2 to the experimentally-determined force-displacement curves, where $E$ was extracted. These values, including those measured for the single-layer CVD graphene, are significantly less than the modulus of single-layer graphene prepared via mechanical exfoliation (1.0 TPa)$^1$, yet that is to be expected as the load is increasingly transferred into the less-stiff oxide layer instead of the graphene layer as the thickness of the oxide increases$^{26}$. Additionally, the presence of defects as well as various transfer methods offer to reduce the integrity of graphene. A similar phenomenon was observed by Cao et al where a general decrease in stiffness was seen as the thickness of the encapsulating oxide layer increased$^{26}$. This load transfer is why there exists a general decrease in the modulus of the heterostructures prepared with a higher number of ALD cycles. However, for each heterostructure, the modulus is greater than that reported in the literature for ALD alumina films of similar thickness to those prepared in this work (~3.0 nm and ~154 GPa)$^{36}$. This means that for each case of oxide thickness, graphene offered a substantial stiffness enhancement. However, it is expected that for increasingly thicker layers of alumina, the effective modulus of the heterostructures would most likely converge to that of bulk Al$_2$O$_3$, as the load would be entirely supported by the oxide layers.
Figure 4. Histogram displaying the Young’s Modulus for each heterostructure prepared with (a) 50 cycles ALD and 1.5 nm thickness, (b) 100 cycles ALD and 2.5 nm thickness, (c) 200 cycles ALD and 3.5 nm thickness, (d) 400 cycles ALD and 4.5 nm thickness, and (e) pristine graphene.
To investigate the fracture mechanics of the heterostructures, a stiff nanoindentation probe comprising a sapphire cantilever (k = 153N/m) and a diamond tip was employed to load the membranes to failure. Figure 5 displays the results from the fracture analysis where it can be seen that the heterostructures prepared with 50, 100, 200 and 400 cycles, as well as pristine graphene, failed at 730.01 nN, 992.26 nN, 1803 nN, 3200.62 nN, and 491nN respectively. For all cases, the membranes ruptured suddenly which highlights a brittle failure similar to what has been observed previously in graphene oxide films$^{37}$ and similar graphene/metal oxide heterostructures$^{26}$. Additionally, the force-displacement curves illustrated in Figure 4 show no slippage that indicate strong interfacial adhesion between the Al$_2$O$_3$ and the graphene which is in good agreement with the low hysteresis observed in the elastic indentation (Figure 3a). However, it is predicted that with the addition of increasingly thicker encapsulating Al$_2$O$_3$, the intrinsic strength of the heterostructures can be observed to decrease with the inclusion of a higher number of critical defects present in the oxide layer.
Figure 5. Experimentally-measured force-displacement plots of the heterostructures loaded to failure.

3.2 Numerical Analysis

To further understand the effect of number of ALD cycles on the final mechanical properties of the heterogenous films, the nanoindentation process was modeled within the elasticity framework. The governing elasticity equations are,

\[ \nabla \cdot FS = 0, \quad S = C : \varepsilon_{el}; \quad (3) \]

where \( F \) is the deformation gradient tensor, \( S \) is the stress tensor, \( C \) is the elasticity tensor, and \( \varepsilon_{el} \) is the elastic strain tensor. These equations were solved using the finite element (FE) method. Contact pressure is calculated using the augmented Lagrangian method\(^{38} \) where a user-defined
contact stiffness, $p_n$ is augmented with Lagrange multipliers of contact pressure, $T_n$, when the distance between the source and destination nodes in the two contacting bodies becomes negative.

$$T_{pn} = \begin{cases} T_n - p_ng & \text{if } g \leq 0 \\ T_ne^{-p/ng/T_n} & \text{otherwise} \end{cases}$$ \hspace{1cm} (4)

Here, $g$ is the distance between nodes on the source and destination surfaces. Considering the low rate of the loading by the AFM tip during the experiments, quasistatic loading was assumed and inertial forces were neglected.

The stress distribution within indented thin films was analyzed, where the stress distribution for the film synthesized using 400 ALD cycles is shown in Figure 6. The angular stress components are shown in Figure S4 in the supporting information. The shear stress components are maximum close to the encapsulated graphene (Figure 6). The maximum shear stress is radially placed within the contact length of the indenter and the film and slightly away from the centrosymmetric axis.

The stress in the indentation direction, $\sigma_z$, is maximum and compressive at the indentation point on the top Al$_2$O$_3$ film. The radial stress component is plotted for the three material layers in Figure 7. The maximum stress in the encapsulated graphene is an order of magnitude smaller than the maximum stress in the heterostructure film, i.e. 1.5GPa vs 12GPa. The stress in the top layer is maximum close to the indenter tip and goes to zero in the vicinity of its interface with the graphene layer. The maximum stress in heterostructure occurs in the bottom layer where the film is under tension.
Figure 6. FE simulation results; (a) distribution of radial components of the stress tensor, $\sigma_r$; (b) distribution of the normal tensor component, $\sigma_z$; (c) distribution of shear stresses, $\sigma_{rz}$; and (d) distribution of the displacement field around the point of indentation.
Figure 7. FE simulation results for the radial stress component, $\sigma_{rr}$, for the three materials layers in the heterostructure. (a) Top Al$_2$O$_3$ layer, (b) encapsulated graphene where the inset shows the zoomed in view, and (c) bottom Al$_2$O$_3$ layer.

Conclusion

The quantitative analysis of the mechanical characteristics of graphene/Al$_2$O$_2$ heterostructures presented in this work found that the inclusion of monolayer graphene between encapsulating layers of Al$_2$O$_3$ can be seen to enhance the modulus of the oxide films across all thicknesses measured, with stiffness enhancement upwards of 70% realized when compared to pure alumina films of similar thickness. It was also found that increasing the thickness of the encapsulating metal oxide layer improved the capability of the films to withstand load as the thickest heterostructure was able to withstand an applied load of $\sim$3200nN when compared to the thinnest film which failed at $\sim$730nN. Additionally, these findings illustrate the versatility of ALD techniques for use in heterostructure fabrication, and ease of implementation of graphene into thin-film hybrid structures in order to take advantage of its superior mechanical properties. The mechanical properties of the films analyzed show a strong size-dependency as significant variations in the stiffness of the films were observed by manipulating the thickness of the encapsulating oxide layers. The FE simulations further revealed a nonintuitive shear stress distribution which indicates a maximum shear away from the line of symmetry and closer to the point of contact of diamond tip and the film. This is key for reliable performance of the experiments where the shear stress
during the indentation shall not exceed the shear strength of the films to avoid undesirable delamination. These results and the methodology presented prove to be a major step in delineating the complex behavior of nanoscale heterostructures and adds to an increasing body of knowledge pertaining to these materials.

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