CMG:

Expanding Graphene Through Chemistry

Carbon used to be so plain, so ordinary, so common. In its two atomic forms based on chemical bonding, graphite (sp^2) and diamond (sp^3), it certainly has its charms, but it was largely ignored in its unalloyed states for high-tech applications until the discovery of stable, nanoscale structures starting with buckyballs (C_{60}) in 1985. However, how to cheaply mass produce C_{60}, also known as fullerene, remained a mystery. Then, when another even more usable form, nanotubes, was discovered in 1991, interest began to pick up again as the phenomenal properties of these atomic forms of carbon became apparent. Researchers began to speculate that if 1D layers of graphite appeared in balls and tubes, then a flat layer, which they dubbed graphene, must also be attainable. This was achieved in 2004, and since then, the race has been on to produce graphene in quantity at costs that would make it economically feasible for industrial applications. Chemically modified graphene (CMG) has emerged as a new form of graphene that can be manipulated to display some remarkable qualities previously unattainable in pure graphene. NRL researchers have developed a way to cheaply produce large-area, ultra-thin CMG films through which they can test its properties and also produce prototype electrical and mechanical devices. CMG can be fine-tuned to its specific application and has been used to produce sensors of extraordinary sensitivity, illustrating its potential as a key material for tomorrow's commercial and defense-oriented marvels.

Chemically Modified Graphene for Sensing and Nanomechanical Applications

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Chemically modified graphene (CMG) has emerged as a new material whose many attractive properties complement those of pure graphene. Graphene, a single atomic sheet of carbon bonded in a honeycomb lattice, has remarkable physical properties ranging from near-ballistic electron conduction to extremely high mechanical stiffness (more than five times that of steel). Such extreme properties motivate researchers to investigate these materials for use in applications ranging from high-frequency, low-power electronics, to flexible displays, chemical/biological sensors, and high-frequency electromechanical devices. We have developed a process to form large-area, ultra-thin CMG films that enable us to investigate CMG properties and to explore prototype devices. Using these films we have fabricated state-of-the-art chemical sensors and nanomechanical resonators. For chemical sensors, we have increased the sensitivity and reduced the level of noise by tuning the CMG film chemistry. These optimized sensors are capable of real-time detection of explosives and the three main classes of chemical-warfare agents at parts-per-billion concentrations. For nanomechanics, we have utilized chemical modification to produce suspended films under high tension. These high-stiffness, low-mass resonators display quality factors (up to 4000) and figures of merit well exceeding those of pure graphene resonators and are comparable to diamond thin films. Together, these results demonstrate that CMG is an inexpensive, high-performance material that will find application in a wide range of defense and commercial applications.

INTRODUCTION

Atomic carbon forms two primary structures, which are based upon sp^3 (diamond) or sp^2 (graphite) chemical bonding (Fig. 1). Of these, diamond is the less stable form and will transform into graphite when heated (Fig. 1(b)). The sp^2-graphitic structure currently dominates the world of carbon nanomaterials as it forms the full spectrum of low-dimensional geometries. For example, in its most compact stable form, sp^2-carbon arranges into a zero-dimensional (0D) structure known as a buckyball (Fig. 1(e)). By inserting rows of atoms around the equator of this buckyball, a one-dimensional (1D) carbon nanotube emerges (Fig. 1(d)). Finally, if this carbon nanotube is "unzipped" along its length, we have a flat, two-dimensional (2D) sheet known as graphene (Fig. 1(c)).

Interest in these low-dimensional carbon sheets began around 1985 with the discovery of buckyballs, but became mainstream after carbon nanotubes debuted in 1991. The newest member, graphene, created a resurgence of both scientific and technological interest after its discovery in 2004.[1] Electrons in graphene possess a unique "photon-like" dispersion relationship whereby they behave as massless particles. This phenomenon has led to the observation of unique electron transport phenomena, and has enabled researchers to use graphene as a laboratory for exotic quantum physics experiments. In addition, graphene's unique atomic structure, near-perfect electronic conduction, and extreme mechanical stiffness offer promise for a wide range of technological advances in the areas of electronics, electro-optics, sensors, and electromechanical devices.

Graphene Formation

For decades it was theorized that 2D solids were unstable and would melt at any temperature. This notion was disproved in 2004 when the first atomically thin graphene sheet was successfully isolated and studied.[2] In the few short years since then, a modern gold rush has transpired as researchers quest for a low-cost, high-yield production method. The simplest and most ubiquitous technique mechanically exfoliates graphene from bulk graphite, whereby graphite is rubbed across
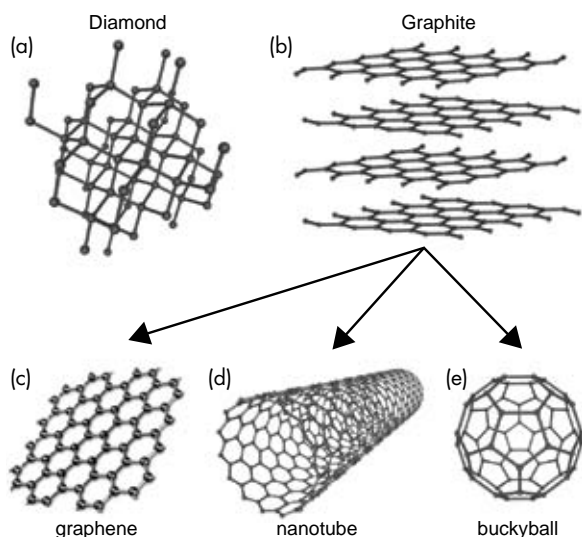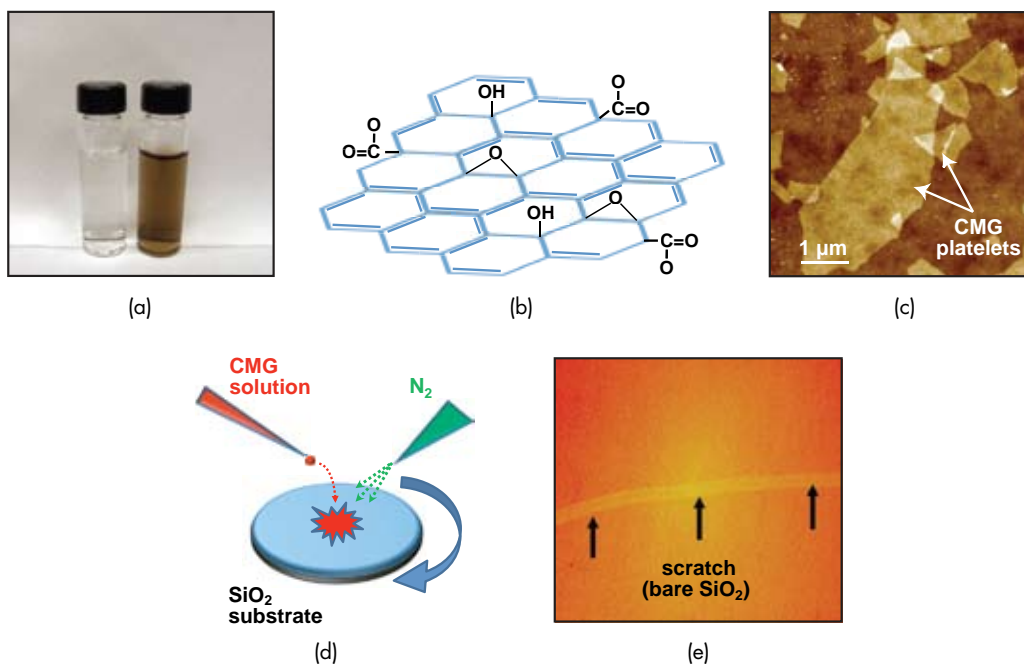
FIGURE 1
The two major allotropes of carbon are (a) sp^3-bonded diamond and (b) sp^2-bonded graphite. The sp^2-bonded allotrope is formable into three low-dimensional structures: (c) 2D sheets known as graphene, (d) 1D nanotubes, or (e) 0D buckyballs.

a flat substrate leaving behind small flakes, some of which are a monolayer thick. This random, low-yield approach precludes its use for large-scale production, though it continues to enable many interesting physics experiments. A second approach forms graphene epitaxially by heating SiC to >1400 °C in vacuum. At elevated temperatures, Si preferentially desorbs from the SiC surface, leaving behind carbon-rich layers that rearrange into thin graphene films. Technologically opposite from mechanical exfoliation, epitaxial

graphene on SiC is large-area but expensive due to the high cost of SiC substrates.

A third approach, and that employed in this work, is chemical exfoliation of graphene from graphite. By attaching oxygen-rich functional groups to graphite's individual atomic planes, the planes become hydrophilic.[3] When immersed in water, H_2O molecules diffuse between these hydrophilic layers and completely exfoliate the graphene sheets (Fig. 2(a) and (b)). These oxidized platelets of graphene can be

FIGURE 2
(a) Photograph showing a vial of pure water (left) and a mixture of exfoliated chemically modified graphene (CMG) platelets and water (right). (b) Cartoon showing oxygen functional groups on a CMG sheet, which include carboxyls, alcohols, and epoxides. (c) Atomic force microscope image of CMG platelets on a glass substrate. The platelets are approximately 1 to 1.5 nm thick. (d) Modified spin-casting technique developed at NRL for the large-area deposition of ultra-thin CMG films. (e) Optical microscope image (20x) of a continuous 2-nm-thick film. A scratch across the center reveals a slight color contrast between the substrate and film.

deposited onto almost any surface using a variety of benchtop techniques. The deposited oxidized graphene can subsequently be chemically reduced back toward graphene using chemical or thermal treatments to form stable films of chemically modified graphene (CMG). We have shown that the chemical modification alters graphene's electronic and mechanical properties in useful ways.[4] Figure 2(c) shows an atomic force microscope (AFM) image of deposited CMG platelets, which typically measure a few microns laterally and ~ 1 nanometer thick. At NRL we have developed a spin-casting technique to form continuous, ultra-thin, large-area CMG films at low cost (Fig. 2(d,e)). We have begun to investigate and develop these films for several DoD-relevant applications.

CARBON – THE ULTIMATE SENSOR MATERIAL

The detection of low-concentration, toxic, and explosive chemical vapors and gases is critical for the DoD and for homeland security. Due to their unique structure, in which every atom is a surface atom, sp^2-bonded carbon nanomaterials represent the ultimate sensor material. We previously developed single-walled carbon nanotube (SWNT) sensors capable of detecting chemical vapors at parts-per-billion concentrations,[5] although these sensors require somewhat sophisticated electronics to realize their full potential. We have found that CMG films can also serve as an extremely sensitive active material while requiring much simpler detection electronics.

Research into the sensing properties of carbon nanomaterials reveals that the transduction mechanisms by which molecular adsorption events are converted into electrical signals are often dominated by interaction with defects in the sp^2-bonded atomic structure. For many classes of molecules, the interaction with defect sites is often much stronger than with the relatively chemically inert sp^2-bonded carbon. Thus, controlling the number and type of defects can greatly enhance both sensitivity and specificity.[6] The optimal defect density will balance the gains in sensitivity against the rapid degradation in conductivity and increase in noise caused by the defects. In this regard, CMG is an ideal material for balancing these effects since it contains a variety of functional sites whose density is controllable.

An Atomically Thin Sensor

Figure 3(a) shows a typical experiment for testing the sensitivity of chemically modified graphene. We start with CMG thin films that consist of 1-nm-thick overlapping platelets. Using standard photolithography, we create interdigitated arrays of Ti/Au electrodes. Importantly, the oxygen functional groups on CMG

are reduced chemically (e.g., with hydrazine, N_2H_4) or thermally (e.g., by annealing in H_2), providing a knob with which to tune the sensor response. These devices are then exposed to pulses of chemical vapors, and the resulting change in material conductance is measured.

Two important parameters are used to consider chemical sensor performance: (1) the level of low-frequency noise (which is generally dominated by $1/f$ noise) and (2) the sensitivity of the conductance response to molecular adsorbates. In general, the $1/f$ noise arises from fluctuations in carrier mobility or carrier density and is ubiquitous in solid-state devices. In the case of SWNTs, such fluctuations can arise from impurity charges in the substrate or the presence of defects within individual tubes. Here, the 2D planar geometry of graphene provides an inherent advantage over SWNTs. When two or more layers are present, the $1/f$ noise in graphene is strongly suppressed due to an effective screening of fluctuating charges in the substrate. Increasing the CMG film thickness to ~ 4 nm lowers the noise below background thermal limits (Fig. 3(b)). Figure 3(c) compares the responses of an SWNT device and a CMG device to doses of 500 parts-per-trillion DNT, a simulant for the explosive TNT. The low-noise response of the CMG device permits lower detection limits than a comparable SWNT device.

Interestingly, the chemical sensitivities of SWNT and CMG devices are complementary. Figure 3(d) compares the minimum detectable levels (MDLs) of SWNT and CMG devices for hydrogen cyanide (HCN) and simulants for mustard gas (CEES), sarin (DMMP), and TNT (DNT). These results highlight how different classes of molecules can distinctly interact with different surface sites — HCN weakly interacts with nominally pristine sp^2-bonded nanotubes while strongly interacting with remnant defects in CMG; the reverse is true for organophosphates (i.e., DMMP), and the responses to aromatics and alkane derivatives are similar (i.e., DNT and CEES, respectively). Enhancement of the specific oxygen functional group that interacts strongly with each simulant should allow even lower MDLs for CMG-based sensors and will enhance chemical selectivity.

CARBON – THE ULTIMATE ELECTROMECHANICAL MATERIAL

Nanoelectromechanical systems (NEMS) extend microelectromechanical systems (MEMS) to nanometer dimensions and are an exciting frontier for next-generation devices in sensing, RF technology, and computing. When NEMS resonators shrink below 100 nm, they achieve high operating frequencies (up to 10^9 Hz) with extreme sensitivities. Importantly, NEMS resonators already display extremely low mass sensitivities and are a viable route to parts-per-quadrillion

(a)

(b)

(c)
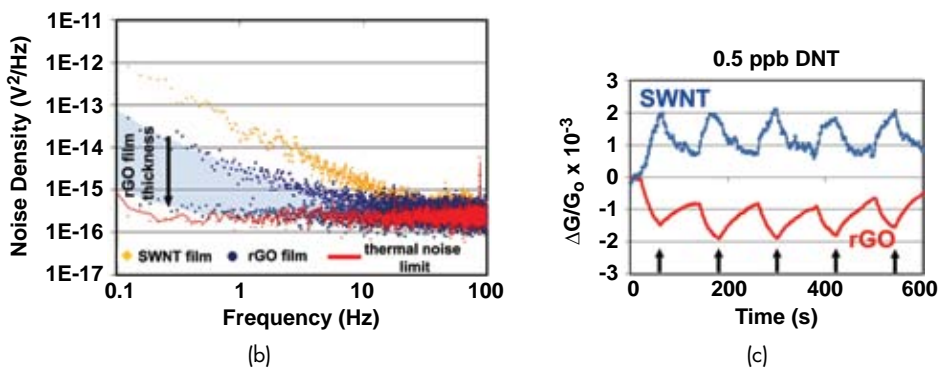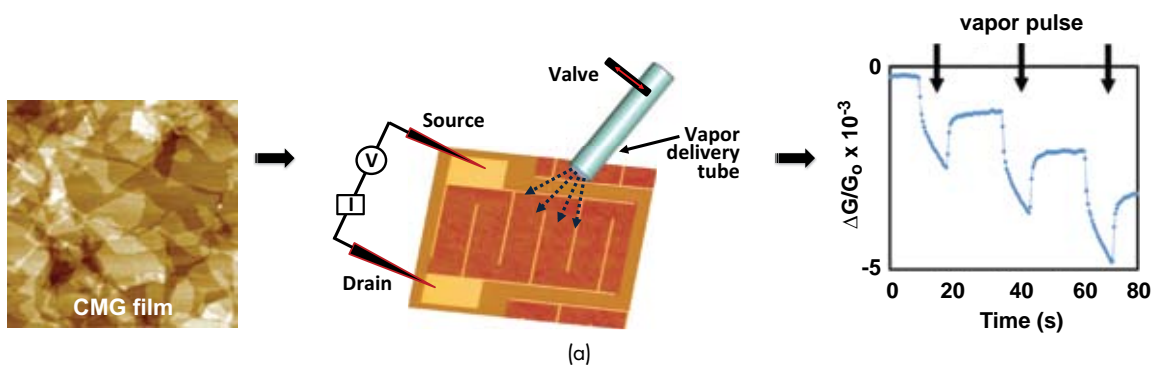
Simulant	SWNT: 10 s (ppb)	CMG: 10 s (ppb)	JCAD specifications 10 s (ppb)	CDC specifications (ppb)
HCN	>4,000	70	2×10^6	5×10^{4} [a]
CEES	0.5	0.5	7,500	0.5 [b]
DMMP	0.1	5	170	17 [a]
DNT	0.1	0.1	———	———

[a] Immediately Dangerous to Life or Health (IDLH): 30 minutes does not cause death
[b] Threshold Limit Value (TLV): lifetime exposure without adverse health risk

(d)

FIGURE 3
(a) Approach for characterizing the sensing properties of CMG thin films. (b) Plot showing the noise density vs frequency spectrum for an SWNT device (orange diamonds) and two CMG (also known as rGO, reduced graphene oxide) devices with different film thicknesses (blue circles). (c) Response curves for an SWNT and a CMG (rGO) device to 0.5 parts per billion DNT. (d) Comparison of the minimum detectable level for an SWNT network sensor and a CMG network sensor to 10-second pulses of HCN, CEES, DMMP, and DNT, as well as the corresponding response to live agents using the target specifications for the Joint Chemical Agent Detector (JCAD) and exposure limits provided by the Centers for Disease Control (CDC).

chemical detection. For any NEMS system, the most important material properties are the Young's modulus, E, and density, ρ, which dictate the speed of sound in the material, c, and fundamental frequency, f_o, of the device, with $f_o \propto c = (E/\rho)^{1/2}$. Critically, of the many materials one might choose, carbon in the form of carbon nanotubes or graphene exhibits the highest E/ρ ratios.

One drawback to nanoscale resonators, however, is the tendency to lose mechanical energy at increasing rates, which results in low quality factors (Q) and diminished performance. For graphene-based systems, a reason behind this increased energy loss is poor adhesion of the resonator to its support structure. The sp^2-bonded carbon is fairly inert and adheres poorly to many substrates. Fortunately, chemically modified graphene offers a route to enhancing the performance of graphene-based NEMS since attached functional groups can better anchor the material to its surroundings.

An Atomically Thin Drumhead

To explore the incorporation of CMG materials into NEMS devices, we developed a process to transfer ultra-thin films (> ~4 nm) onto prepatterned substrates. Subsequent to film deposition as shown in Fig. 2, films are released intact from the substrate using a
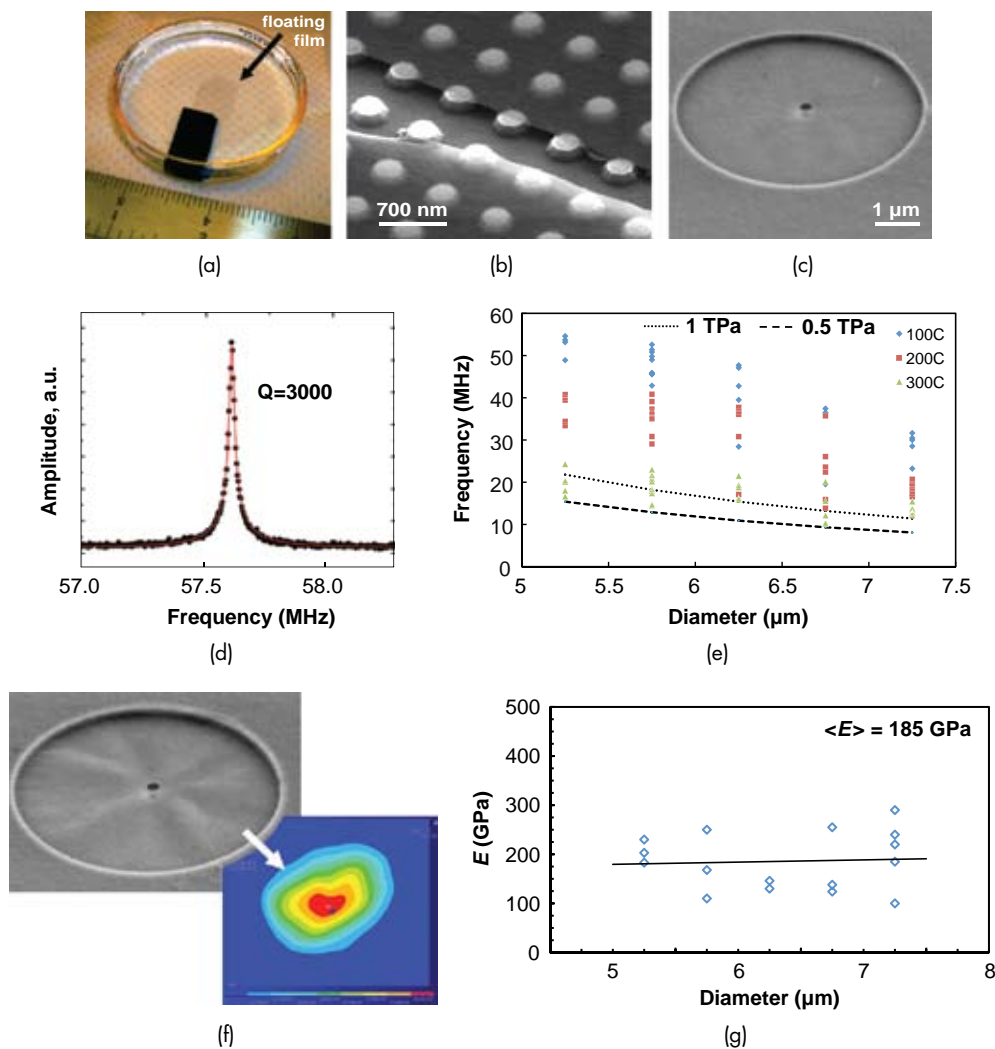

FIGURE 4
(a) Photograph showing an 8-nm-thick CMG film floating in water. The thin film measures approximately 1 × 0.5 inches. (b) Scanning electron microscope (SEM) image of a suspended CMG film after drying on a bed of pillars. (c) SEM image of a suspended CMG drum resonator with a small hole milled in its center. (d) Amplitude vs frequency plot of the fundamental mode, where the Q-value is 3000. (e) Plot of frequency vs drum diameter for a 15-nm-thick film. The resonators are annealed at successively higher temperatures to release tension. (f) Perspective SEM image of a buckled resonator after tension release and the expected frequency response determined from finite element modeling. (g) Plot showing the Young's modulus vs drum diameter for several drum resonators.

basic solution and transferred into water (Fig. 4(a)). These delaminated films are subsequently recaptured and dried on substrates prepatterned with pillars (Fig. 4(b)) or holes (Fig. 4(c)) to form suspended resonators. Importantly, the controlled deposition, delamination, and transfer of CMG films opens the door to numerous mechanical and nanoelectromechanical experiments.

To probe the elastic properties of these films, we use the well-established technique of laser interferometry to measure vibrations of the suspended drum resonators (Fig. 4(c)). A blue (412 nm) diode laser thermoelastically excites the CMG drums into resonance, while a red (633 nm) HeNe laser interferometrically measures the frequency of vibration in a Fabry-Pérot configuration. The fundamental frequency of vibration and overtone spacings depends on the tension (T) in the drums, which can act either as a plate ($T \approx 0$) or as a membrane ($T > 0$). Determination of Young's modulus (E) is straightforward when the drum responds in the plate mode. For a circular plate, the frequency modes are given by

$$f_{mn} = \frac{\pi h}{4 a^2} \sqrt{\frac{E}{3\rho (1 - s^2)}} (\beta_{mn})^2 \qquad (1)$$

where h is the film thickness, a is the drum radius, ρ is the material density, s is Poisson's ratio, and β_{mn} is the nth root of the mth-order Bessel function.

Unexpectedly, the measured f_o for all drum resonators is significantly higher than that expected from Eq. (1), which signifies the resonators are under tension. This built-in tension together with enhanced adhesion to the SiO$_2$ substrate from remnant oxygen groups notably improves the quality factors. Pure graphene resonators typically have Q-values of 10 to 200,[7] whereas our CMG resonators consistently show quality factors over 1500 (Fig. 4(d)), with 4000 the highest value measured to date. These values compare favorably with state-of-the-art diamond resonators, which typically have Q-values of ~3000 at room temperature. Combined with the extreme low mass of these resonators, we estimate their mass sensitivity at 10^{-18} grams.

Though the tension enhances the mechanical response of the resonators, extracting the Young's modulus requires removing the tension, which we accomplished through thermal annealing. Figure 4(e) shows f_o vs drum diameter for a 15-nm-thick film after annealing in argon at different temperatures. After annealing at 300 °C, the release of tension causes the originally flat drums to buckle, meaning the flat-plate approximation of Eq. (1) will not accurately describe the resonance response. To more accurately extract

the Young's modulus, we use finite element modeling (FEM) instead (Fig. 4(f)). Figure 4(g) shows the FEM results after modeling 16 textured drums and reveals that the modulus averages 185 GPa, which is approximately the same as steel.

SUMMARY AND OUTLOOK

Our work with chemically modified graphene demonstrates the versatile nature of this material system. At NRL we have developed a low-cost, large-area deposition technique in which thin films are readily fashioned for both electronic- and mechanical-based devices. Not only do these films show promise as the active area of conductance-based chemical sensors, their large stiffness and low density make them feasible for use in nanomechanical systems also. For sensing applications, the relatively large number of chemically active groups affords the possibility of covalent chemical functionalization for increased chemical or biological selectivity. The nanomechanical experiments point to the exciting opportunities afforded by chemically modifying sp^2-bonded carbon to form hybrid sp^2–sp^3 interbonded materials that exhibit both strength and processability. Indeed, we foresee a bright future for graphene-based technologies.

ACKNOWLEDGMENTS

References
[1] A.K. Geim and K.S. Novoselov, "The Rise of Graphene," *Nature Materials* **6**(3), 183–191 (2007).
[2] K.S. Novoselov et al., "Electric Field Effect in Atomically Thin Carbon Films," *Science* **306**(5696), 666–669 (2004).
[3] S. Stankovich et al., "Synthesis of Graphene-based Nanosheets via Chemical Reduction of Exfoliated Graphite Oxide," *Carbon* **45**(7), 1558–1565 (2007).
[4] J.T. Robinson et al., "Reduced Graphene Oxide Molecular Sensors," *Nano Letters* **8**(10), 3137–3140 (2008); J.T. Robinson et al., "Wafer-scale Reduced Graphene Oxide Films for Nanomechanical Devices," *Nano Letters* **8**(10), 3441–3445 (2008).
[5] E.S. Snow et al., "Chemical Detection with a Single-Walled Carbon Nanotube Capacitor," *Science* **307**(5717), 1942–1945 (2005).
[6] J.A. Robinson et al., "Role of Defects in Single-Walled Carbon Nanotube Chemical Sensors," *Nano Letters* **6**(8), 1747–1751 (2006).
[7] J.S. Bunch et al. "Electromechanical Resonators from Graphene Sheets," *Science* **315**(5811), 490–493 (2007).

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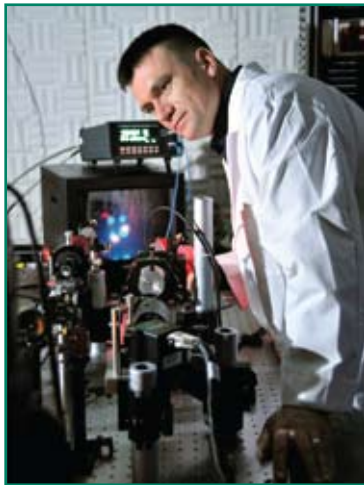
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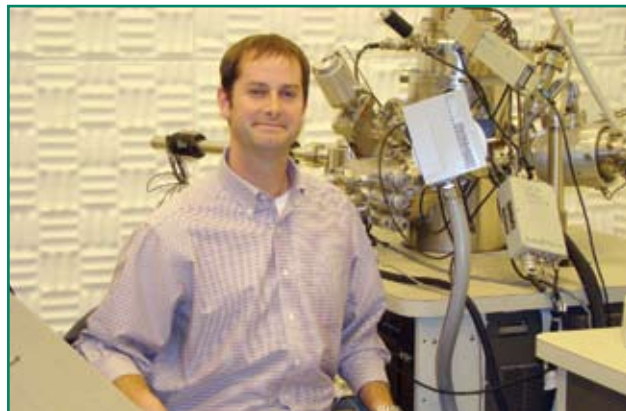

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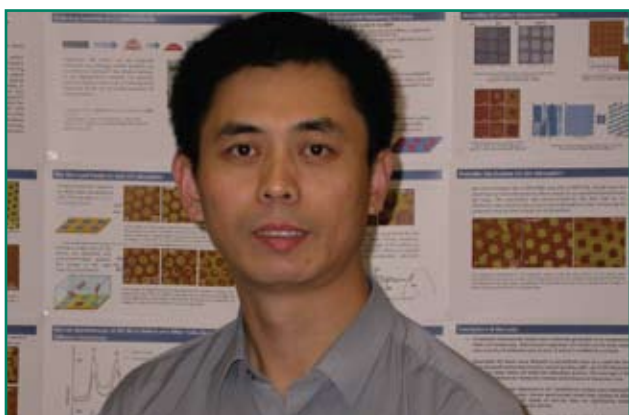
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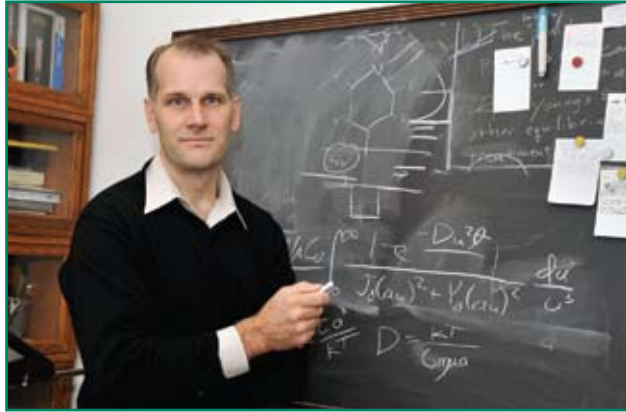
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