Large-area graphene for sensor applications

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ABSTRACT:

Graphene represents an important new material with potential Department of Defense sensor applications. At the Naval Research Laboratory we have developed three techniques to produce large-area graphene films. We have used this material to construct chemical and radio-frequency electromagnetic sensors. Here we report the initial results of this effort.

Keywords: Graphene, chemical sensor, transistor, RF, nanoelectromechanical

1. INTRODUCTION

Graphene, a single-atomic sheet of graphite, possesses extraordinary structural, electrical and mechanical properties. These extreme properties combined with recent advances in the ability to grow large-area graphene sheets open the possibility of a number of Depart of Defense applications. Consequently, graphene is an important new material that merits substantial research and development.

At the Naval Research Laboratory we have initiated an effort to exploit each of these unique properties for potential Defense applications. We are utilizing graphene's unique structure, in which every atom is a surface atom, for the direct electronic detection of molecular adsorbates[1]. We are exploiting its extreme mechanical stiffness and strength to explore electromechanical devices[2] for mass-based sensing, RF-filters, and mechanical switches. Finally, we are using its high electron mobility and unique band structure to explore high-frequency, low-power radio-frequency (RF) transistors[3].

The viability of each of these applications has been greatly advanced by recent breakthroughs in the ability to synthesize large-area films of graphene[4,5] and chemically modified graphene[1,2]. The initial experimental investigations of graphene were performed on microscopic exfoliated flakes, which provided high-quality material but made device development extremely labor intensive. Recently, however, a number of methods have been developed for forming large-area sheets of graphene. These methods include spin-coating films of chemically modified graphene[1,2], the thermal decomposition of SiC wafers[4], and chemical vapor deposition on catalytic Cu foils[5]. Each of these approaches has advantages and disadvantages for various applications. Thus, we have explored the use of all three types of films for the three application areas mentioned above.

2. LARGE-AREA GRAPHENE

We prepared spin-coated films of chemically modified graphene (CMG) by suspending graphite oxide powder in a solution of methanol and water. The solution was centrifuged to remove large particles and then spin-cast onto a substrate rotating at 4000 rpm. The spin-cast GO films were then annealed in air to remove residual solvent and then annealed in hydrazine vapor to reduce the GO back toward graphene. Details of the process can be found in Refs. 1 and 2. The resulting films range in thickness from 1 nm to 5 nm, are mechanically robust and electrically conducting (~ 10^4 – 10^5 Ohms/square). The low electron mobility of the films (~ 0.01 cm^2/Vs) excludes high-performance electronic device applications. However, we find that these chemically modified films of graphene are well suited for sensor and microelectromechnical applications as described below.

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Graphene films on SiC wafers were prepared by the thermal decomposition of the Si face of 4H- and 6H-SiC wafers[4]. Prior to the film formation the substrates were hydrogen etched at 1600 C to eliminate polishing damage. The substrates were then annealed under moderate vacuum at ~ 1500 C for an hour or more to thermally desorb Si from the SiC. This process produces 1 to 2 monolayer-thick films of graphene on the SiC surface.

Graphene films were also formed using chemical vapor deposition on Cu foils using the procedure described in Ref. 5. These films were transferred to Si substrates by coating the graphene with a film of PMMA resist, etching away the Cu foil, placing the graphene/PMMA film on the substrate and dissolving away the PMMA.

At the present stage of development both the graphene on SiC and the Cu-grown graphene result in a room-temperature Hall mobility of order 1000 cm^2/Vs with background carrier concentrations of order 10^{12} cm^{-2}. This mobility value is well below the interface-phonon-limited value on an SiO_2 substrate (~40,000 cm^2/Vs)[6]. Consequently, research is being conducted to identify and eliminate the scattering mechanisms limiting the mobility in these large-area films. This improvement is critical for the successful application to high-frequency device applications.

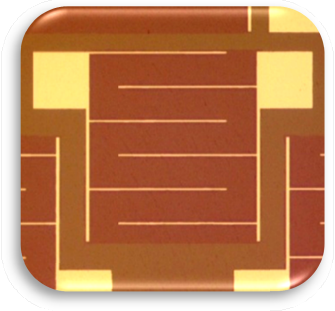
3. SENSOR APPLICATIONS

For the direct electronic detection of molecular adsorbates we have employed a sensor design similar to the design we have used to construct conductance-based sensors composed of carbon nanotube networks. This design optimizes the signal-to-noise ratio by eliminating contact effects and minimizing low-frequency noise[7]. Thus far we have constructed and tested sensors using both graphene on SiC films and spin-deposited films of CMG[1].

For these sensors we monitor the change in conductance of the film in response to timed exposures to dilute vapors of the stimulants of the three main classes of chemical warfare agents. Our preliminary data indicate that the CMG films are more sensitive than the nominally pure graphene films. We attribute this result to the more reactive surface of the chemically modified graphene, which provides more stable adsorption sites than the relatively chemically inert pure graphene surface.

Fig. 1a shows an optical image of a typical sensor. Fig. 1b tabulates minimum detectable dose obtained using the CMG sensors, and these results are compared to the specifications for the Joint Chemical Agent Detector (JCAD) and to our best results obtained using carbon nanotube sensors. (We have compared our minimum detectable dose to that obtained from the capacitance response of carbon nanotube networks, not the conductance response. The capacitance response, because of its low 1/f noise, produces the most sensitive detection using carbon nanotubes[7].) From the table we see that the combination of carbon nanotube and CMG sensors meets or exceeds all of the JCAD specifications. Most importantly we find that the CMG is highly responsive to HCN, which carbon nanotube sensors cannot detect. Thus, the combination of CNT and CMG sensors provides a complete suite of trace-level sensors for the main classes of chemical agents.

a)



b)

Simulant	SWNT: ΔC (ppb)	CMG: ΔG (ppb)	JCAD* specifications $\leq$ 10 s (ppb)
HCN (blood)	>4,000	70	$2x10^6$
CEES (blister)	0.5	0.5	7,500
DMMP (nerve)	0.1	5	170

Figure 1. a) Optical image of a chemically modified graphene sensor. The sensor has dimensions of 0.5 x 0.5 mm^2. b) Table of minimum detectable responses to 10 s doses of simulants for the three main classes of chemical warfare agents. The graphene results are compared to the detection limits of nanotube capacitance sensors and the specifications for live agents of the Joint Chemical Agent Detector.

In addition to chemical agents the DOD and the Department of Homeland Security desire the capability to detect the vapors of explosives. This task is challenging due to the extremely low vapor pressure of solid explosives. Thus, the development of ultrasensitive sensors is required with detection limits in the range of parts per trillion to parts per quadrillion. This level is well below what we have achieved using direct electronic detection.

An alternative approach to achieve ultralow detection limits is to use mass-based detection[8]. In this case, the change in resonant frequency of a high-Q, light-mass resonator is used to detect the increase in mass due to the adsorption of the explosive vapor. In this case the minimum detectable mass per unit area is approximately given by[8]:

$$\frac{\Delta m_{min}}{A} = 2\rho h \sqrt{\frac{\Delta f}{\omega Q}} 10^{-\frac{DR}{20}}$$

where ρ, h, ω and Q are density, thickness, resonant frequency, and Q-value of the resonator, respectively, and Δf and DR are the bandwidth and dynamic range of the measurement, respectively. From this expression it is clear that graphene is a potential interesting sensor material due to its single-atomic thickness and potential for large dynamic range due to the ability of the material to withstand large amounts of strain. Key to the performance of the material will be the ability to form high-Q resonators.

We have explored the use of graphene films for producing high-Q light-mass resonators[2]. Drum resonators, Fig. 2a, were fabricated on top of patterned Si substrates using both Cu-grown graphene and CMG films. The graphene drums were driven thermoelastically with variable frequency laser pulses, and the vibrations were detected optically. A typical resonance spectrum is shown in Fig. 2b. We find that residual strain in the films increases the resonant frequency of the drums to a value much higher than that calculated for a plate-mode resonance with a Young's modulus of 1 TPa. The strain also serves to increase the Q of the resonator. We observe the largest strain (1 to 5 N/m) and correspondingly the highest Q values (up to ~ 10,000 measured in vacuum at room temperature) in the CMG films.

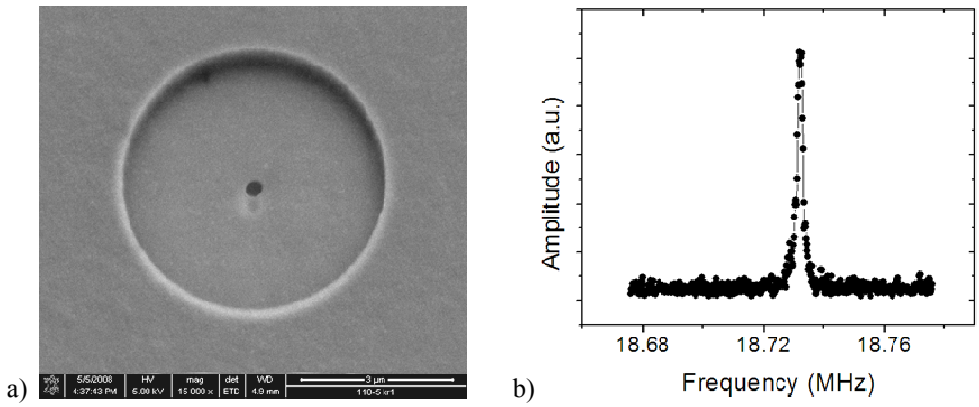


Figure 2. a) Scanning electron microscope image of a chemically modified graphene 5 mm-diameter drum resonator. The hole in the middle of drum was cut to release fluid trapped in the fabrication process. b) Resonance profile of the drum, which has Q = 9300 and a resonant frequency of 18.73 MHz.

These high measured Q values indicate that graphene-based resonators deserve further development for ultrasensitive mass-based sensing. Key to this application will be maximizing the frequency in order to maximize the Q in non-vacuum environments and developing optimal drive and sensing electronics to maximize the dynamic range. Similar analyses indicate that these high-quality, high-frequency graphene-based resonators also have potential to serve as compact tunable filters with low insertion loss and as microelectromechanical switches.

Lastly, we have initiated an effort to explore the use of graphene as the active electronic material for low-noise, RF amplifiers. The high saturation velocity[9] and high electron mobility[6] in pristine graphene should yield ultra-high-frequency amplifiers that operate at low voltage for low-power dissipation. In collaboration with Hughes Research Laboratory, graphene on SiC was fabricated into transistors with a 2 μm-long gate (Figs. 3a and 3b). The devices

achieved an on-to-off ratio of 4 and an $f_T L_g$ product of 10 GHz-μm, which is comparable to state-of-the-art Si transistors. While this initial result is encouraging, significant improvements in material quality need to be achieved before graphene can compete with state-of-the-art InP devices with a $f_T L_g$ product of 22 GHz-μm.

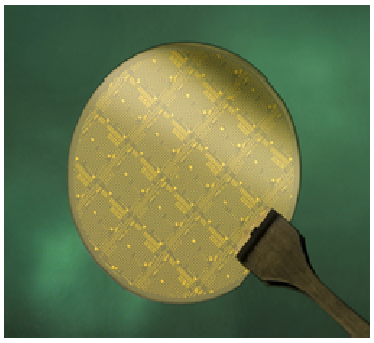
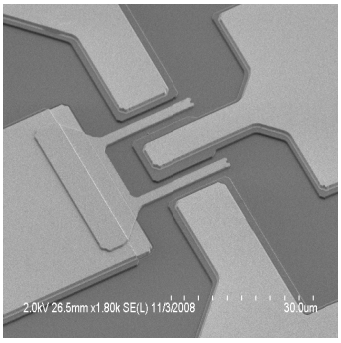
a)  b) 

Figure 3. a) Wafer of graphene transistors fabricated on the Si face of a 2" SiC wafer. b) Scanning electron microscope image of an individual transistor[3]. The transistors exhibited an $L_g f_t$ product of 10 GHz-μm.

4. SUMMARY

In summary, graphene, due to its extreme properties, offers the potential to provide enhanced sensor capabilities for the DOD. At NRL, we have made an initial exploration of the materials growth, device fabrication and testing of several defense-related applications. Our initial survey indicates that using non-optimized material and device design we can achieve performance levels near the state-of-the-art. These initial promising results indicate that graphene merits further development to evaluate its potential for DOD applications.

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REFERENCES

[1] Robinson, J. T., Perkins, F. K., Snow E. S., Wei, Z., and Sheehan, P. E., "Reduced graphene oxide molecular sensors," Nano Lett., 8, 3137-3140 (2008).
[2] Robinson, J. T., Zalalutdinov, M., Baldwin, J. W., Snow, E. S., Wei, Z., and Houston, B. H., "Wafer-scale reduced graphene oxide films for nanomechanical devices," Nano Lett., 8, 3441-3445 (2008).
[3] Moon, J. S., "Development toward wafer-scale RF electronics," ECS Trans. 19, 35-40 (2009).
[4] Gaskill, D. K., et. al., "Epitaxial graphene growth on SiC wafers," ECS Trans. 19, 117-124 (2009).
[5] Li, X. S., et al., "Large-area synthesis of high-quality and uniform graphene films on copper foils," Science 324,1312-1314 (2009).
[6] Chen, J-. H., Jang, C., Xiao, S., Ishigami, M., and Fuhrer, M. S., "Intrinsic and extrinsic performance limits of graphene devices on SiO_2," Nat. Nanotech. 3, 206-209 (2008).
[7] Snow, E. S., Perkins, F. A., Robinson, J. A., "Chemical vapor detection using single-walled carbon nanotubes," Chem. Soc. Rev. 35, 790-798 (2006).
[8] Ekinci, K. L., Yang, Y. T., and Roukes, M. L., "Ultimate limits to inertial mass sensing based upon nanoelctromechanical systems," J. of Appl. Phys. 95, 2682-2689 (2004).

[9] Meric, I., Han, M. Y., Young, A. F., Ozyilmaz, B., Kim, P., Shepard, K. L., "Current saturation in zero-bandgap, top-gated graphene field-effect transistors," Nat. Nanotech. 3, 654-659 (2008).