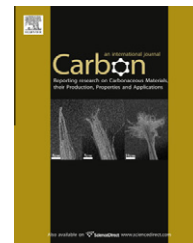


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Tuning Schottky diodes at the many-layer-graphene/semiconductor interface by doping

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ARTICLE INFO

Article history:

Received 5 November 2010

Accepted 14 January 2011

Available online 19 January 2011

ABSTRACT

We report on the use of bromine intercalation of graphite to perform *in situ* tuning of the Schottky barrier height (SBH) formed at many-layer-graphene (MLG) semiconductor interfaces. The intercalation of Br into MLG simultaneously increases interlayer separation between the graphene planes, while at the same time giving rise to an increase (decrease) in the free hole carrier density (Fermi energy) because of the transfer of electrons from carbon to bromine. The associated increase in the graphite work function results in an increase of the SBH, as manifested by lower forward/reverse current densities and higher depletion capacitances. These results are quantitatively understood within the context of the Schottky–Mott model and thermionic emission theory. The presented results have important implications for sensing and high power applications as well as the integration of carbon into semiconductors and carbon/graphene electronics.

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1. Introduction

Schottky barriers formed at metal–semiconductor interfaces are critical components of metal–semiconductor field effect transistors (MESFETs) and high electron mobility transistors (HEMTs) that are widely used in high frequency and high power device applications. External control of the electrical properties of Schottky barriers is an additional degree of freedom that can be crucial for efficient operation of the device. If a higher Schottky barrier height (SBH) is achieved, a larger gate-breakdown voltage, increased power gain, and higher output resistance as well as lower gate leakage and noise can be achieved. To date, the tuning of SBHs on inorganic semiconductors has been achieved by applying pressure [1] on the junction or by controlling the crystal structure and grain size of metal electrodes [2]. However these methods require extreme conditions and processing techniques such as application of ~ 1 GPa of pressure and cryogenic metal deposition, respectively. With respect to organic semiconductors,

electric fields provided by a nearby gate have been found to induce band bending and modulate the SBH of contacts between nanotube films and an organic semiconductor [3].

Schottky barrier formation on various *n*-doped semiconductors such as silicon (Si), gallium arsenide (GaAs) or 4H-silicon carbide (4H-SiC), has been previously demonstrated using highly oriented pyrolytic graphite (HOPG), a semi-metal, as the ‘metal’ electrode [4]. According to bond polarization theory [5] and the Mott–Schottky model [6], graphene substituted for graphite might also be expected to manifest similar behavior since the Schottky barrier characteristics are mainly governed by the first layer of graphite (i.e. a graphene plane) at the interface. Recently, these findings have been confirmed at graphene/SiC interfaces [7]. Here we report that the SBHs of similarly prepared MLG/*n*-Si and MLG/4H-SiC junctions can be tuned over a wide range by bromine intercalation of the MLG. These results not only provide a new technique to externally tune the SBHs of junctions on widely used semiconductors but also offer new

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doi:10.1016/j.carbon.2011.01.029

opportunities to integrate all carbon electronic structures [8,9] with conventional semiconductors.

Prior to bromine intercalation, the Schottky barrier junctions displayed typical rectifying current–voltage (I – V) and linear reciprocal square capacitance versus reverse bias (C^{-2} vs. V_R) characteristics as reported previously [4]. The small coupling between each graphene sheet allows the intercalation of bromine between the planes and increases interplanar separation, pushing graphite toward the graphene limit [10] with smaller γ_1 and γ_2 coupling parameters [11]. The charge transfer between carbon atoms and strongly electronegative bromine intercalants increases (decreases) the total hole carrier density (Fermi energy) of MLG, thus giving rise to an increased graphite work function, ϕ_{graphite} . According to the Schottky–Mott relation, ($\phi_{\text{Schottky}} = \phi_{\text{graphite}} - \chi_{\text{Si/SiC}}$), where χ is the electron affinity of the semiconductor, an increase in ϕ_{graphite} leads to an increased SBH, which is confirmed from current–voltage (I – V) and capacitance–voltage (C – V) measurements.

2. Experimental procedure

Our n -type Si:P (10^{15} – 10^{16} cm^{-3}) and layered 4H-SiC semiconductor wafers, 5 μm epilayer (10^{16} cm^{-3}) on insulating SiC, were supplied by different vendors. Ohmic contacts were made by sequential thermal evaporation and RF sputtering of multi-layer metal stacks at 10^{-7} Torr pressures followed by rapid thermal annealing in N_2 gas [12,13]. The MLG Schottky diodes were formed on these substrates by (a) application of graphite paint: a mixture of residue free 2-butoxyethyl acetate and octyl acetate with graphite powder collected from cutting HOPG by diamond impregnated wire [4], or (b) mechanical exfoliation of MLG from HOPG [14] and (c) transferring MLG from HOPG onto different substrates using thermal release tape. After the mechanical exfoliation, MLG flakes flatten out on the substrate surface due to Van der Waals forces. Fig. 1 shows a schematic of a completed junction.

The MLG contacts were bromine intercalated for various times in a closed container by ‘direct bromine’ gas exposure on (1) MLG/semiconductor and (2) graphite-paint/semiconductor junctions. Prior to bromination, samples were loaded in a glass container (~ 75 cm^3) maintained at atmospheric pressure. After the sample loading process, a quartz capsule was filled with liquid bromine (~ 2 cm^3) and introduced into the glass container. Due to bromine’s low vapor pressure, the liquid bromine vaporizes at room temperature creating a bromine rich gas phase inside the beaker. The glass container was sealed immediately after loading the bromine, thereby preventing the out diffusion of bromine while at the same time maintaining a constant vapor pressure inside. After the intercalation, the glass container was unsealed and slowly exposed to the atmosphere. In addition to these methods, graphite powder was bromine intercalated (as described above) prior to mixing with organic solvents (rather than direct bromination) and ‘brominated graphite paint’ was applied on different semiconducting substrates. The I – V and C – V characteristics were measured by Keithley 182/220 or

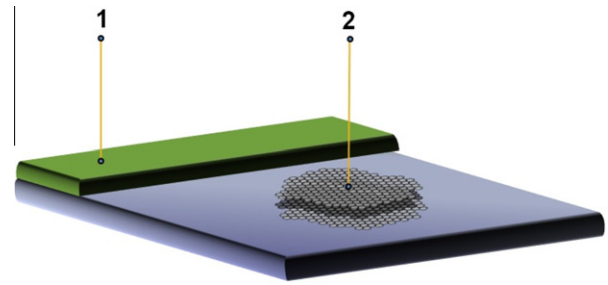


Fig. 1 – Schematics of a many layer graphene (MLG) contacted to an underlying (n -Si 10^{16} cm^{-3}) substrate. Electrode # 1 is a multilayered metal providing good ohmic contact to the semiconductor and the MLG electrode is contacted at the top surface (# 2).

2400 current-source meters and an Agilent 4284A LC capacitance bridge respectively. A total of 15 samples were prepared by ‘direct bromination’ and ‘brominated graphite paint’ methods and all gave similar results/trends, independent of the bromination method and the underlying semiconductor. MLG/GaAs junctions were not studied because of chemical reaction of Br with GaAs.

Bromination induced changes in the MLG properties such as crystal structure, stoichiometry and decreasing E_F were measured by X-ray diffraction (XRD), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS), respectively. MLG samples used in this article displayed typical $\theta - 2\theta$ XRD with 0.5° mosaic spread measured by X-ray omega rocking curve measurements, and no contamination was observed prior to bromination.

3. Results and discussion

Panels (a) and (b) of Fig. 2 display respectively the forward current density (J_{for}) vs. applied voltage ($V \geq 0$) measured across the MLG/ n -Si and MLG/SiC junctions before (red squares)¹ and after (blue triangles) the bromine exposure of 12 min. The I – V characteristics measured on 15 different samples show a good rectification with ideality factors (η) in the 1.12–1.90 range for all junctions. After the bromine doping, the current density typically decreases by an order of magnitude in the forward bias implying that MLG/semiconductor interfaces are sensitive to bromine exposure. Reproducibility of the results has been tested on samples prepared with the different bromine doping techniques described in the preceding discussion of experimental procedure. Moreover, similar trends observed on diodes formed on different semiconductors implies that the sensitivity to bromine is not specific to the type of semiconductor used, but rather originates from bromine induced changes in the physical and electronic properties of MLG.

Panel (c) of Fig. 2 shows the effect of bromine exposure with respect to time as the Schottky diode is exposed during the indicated time intervals to bromine. Before exposure ($t < 6$ min), the diode, which is biased at $V = 1.5$ V, displays a constant J_{for} that upon the onset of doping (leftmost red

¹ For interpretation of color in Figs. 1–5, the reader is referred to the web version of this article.

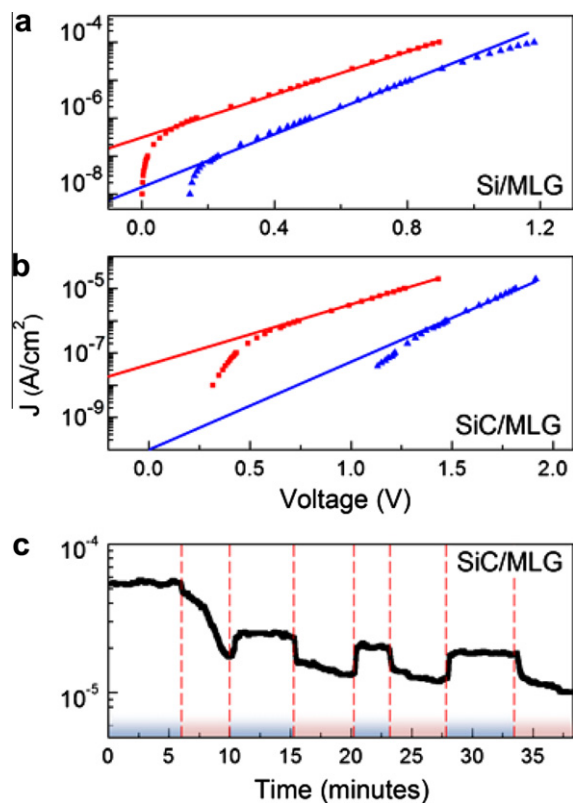


Fig. 2 – (a) Room temperature current density, J , plotted with respect to applied forward bias, V , for MLG on n -Si (b) and 4H-SiC before (red squares) and after (blue triangles) bromination (12 min). (c) The time dependence of J for a MLG/SiC diode biased with 1.5 V in the forward direction with Br exposure being on (red) and off (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

vertical bar on the x-axis) starts to decrease. The decrease in J_{for} is followed by a small increase with the cessation of Br doping and then stabilizes at a lower constant value. With consecutive ~ 5 min. Br exposures, this behavior repeats and J_{for} stabilizes at a value that can be one order of magnitude lower than the original pristine value. The fully brominated MLG thus acts like a ‘residue compound’ [15] which is stable over periods of days with a saturated irreversible concentration of intercalant but which can reversibly accept and then expel additional intercalants during cycles of periodic exposure.

The large intercalation induced change in J_{for} across the diode interface originates from the changes in the SBH. We adopt Richardson’s equation to extract out the SBH and the ideality factor η ,

$$J = J_s(T) [\exp(qV/\eta k_B T) - 1], \quad (1)$$

where $J_s = A^* T^2 \exp(-q\phi_{SBH}/k_B T)$ is the saturation current density, $q\phi_{SBH}$ is the zero bias SBH, A^* is the Richardson constant, T is the absolute temperature, and V is the voltage across the junctions. Before Br exposure the barrier height of the diodes varied between 0.40–0.60 eV and 1.00–1.10 eV on n -Si and 4H-SiC, respectively, with $\eta \sim 1.12$ –1.9 for all junctions. The extracted SBHs are roughly in agreement with the Schottky–

Mott relation, with the values of $\phi_{graphite} = 4.4$ –4.6 eV using $\chi_{Si} = 4.01$ eV and $\chi_{4H-SiC} = 3.20$ –3.30 eV [6,16–20]. On a semilogarithmic scale, J_{for} displays a sufficiently wide linear region (Fig. 2a and b) to assure a robust extrapolation to the ordinate at zero bias, thereby yielding J_s . The observed decrease in J_s and J_{for} imply that the bromination of the diodes effectively increases the SBH, which is consistent with the notion that it is much more difficult to excite electrons over the intercalation induced higher barrier. Using Eq. 1, we find that the SBH increases by 0.1–0.3 eV on MLG/ n -Si and 4H-SiC junctions. According to the Schottky–Mott relation, an increase in the zero bias SBH originates either from an increase in $\phi_{graphite}$ and/or a decrease in χ_{Si} . When bromine atoms with large electronegativity interact with the host material, the graphene planes become hole doped and $\phi_{graphite}$ increases. The absence of an interaction between bromine and Si (or 4H-SiC) determined from XPS also rules out changes in χ , implying that a decrease in E_F and corresponding increase in $\phi_{graphite}$ by hole doping is responsible for the increase of the SBH.

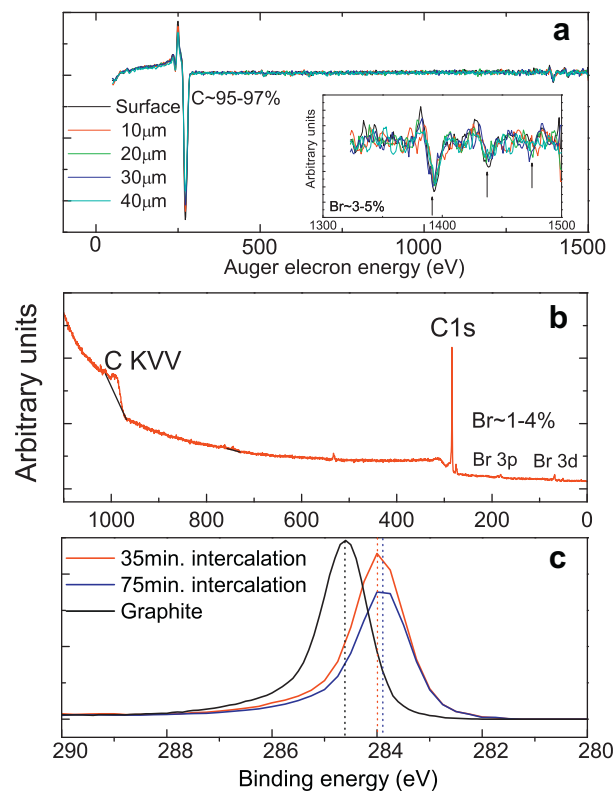


Fig. 3 – (a) Auger electron spectrum (AES) taken on brominated MLG (30 min) from 0 eV up to 1500 eV at the different depths indicated in the legend. Inset: bromine Auger peaks located at 1396 eV, 1442 eV, and 1475 eV corresponding to LMM Auger transitions, (b) X-ray photoelectron spectrum (XPS) of brominated MLG (30 min) measured using a monochromatized Mg X-ray source from 0 eV up to 1100 eV in a UHV chamber and (c) C 1s peaks measured by XPS on pristine (black solid line) and brominated MLG (red and blue solid lines). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Graphite, with a finite overlap between the conduction (E_C) and valence band (E_V), has a low carrier density in the range 10^{18} – 10^{19} cm^{-3} at 300 K corresponding to 10^{-5} – 10^{-4} free electrons per carbon atom. Large interlayer spacing between weakly coupled graphene sheets allows bromine atoms/molecules [15] to easily diffuse between the layers and interact with the host material. Intercalation of Br into graphite/MLG pushes each graphene sheet apart resulting in visual swelling of the graphite associated with the increase in c-axis lattice constant as confirmed by XRD measurements [10]. Due to the low carrier density per carbon, even a small charge transfer between the dopant and adjacent carbon atoms is expected to significantly increase the free carrier density per carbon atom [10]. We detect 1–5% Br doped into the MLG from AES and XPS measurements (Fig. 3a and b) and conclude that each Br atom roughly donates 10^{-2} additional holes per carbon atom. The large change in the carrier density [10] also changes the Fermi level (E_F) of the MLG as confirmed by XPS measurements (Fig. 3c).

We estimate the change in the Fermi energy E_F from the shift in the elemental C 1s peak position caused by the charge transfer between C and Br. Prior to Br intercalation, the C 1s electron binding energy of pristine MLG was measured to be around 284.5 eV, consistent with reported values in the literature [21]. After bromination this peak shifts downward in energy to within the range 283.9–284.1 eV (Fig. 3c). In XPS, the C 1s peak is measured with respect to E_F of the system and any change in E_F manifests itself as a change in the C 1s elemental peak position. The shifts in the C 1s peak positions thus provide a way to estimate the changes in E_F . However, interaction of carbon atoms with highly electronegative bromine create positively charged carbon atoms that possesses a higher binding energy. The experimentally measured decrease in

binding energy, as opposed to an increase as predicted by the electrostatic rule, can be explained by redefining the E_F of the system after the bromination. In brominated MLG, the Fermi level is known to be significantly shifted downward compared to pristine MLG and the C 1s binding energy is thus measured with respect to the lower E_F of the hole-doped system. Accordingly, the increase in the C 1s binding energy is compensated by the decrease in E_F , giving an overall decrease in the C 1s peak position as observed. Similar results and trends have been reported in the literature [22,23] for different graphite intercalation compounds, and this method gives a lower limit of the order of magnitude change of E_F . From Fig. 3c, we estimate this change in E_F for the fully intercalated sample to be in the range 0.4–0.6 eV.

A decrease in E_F , i.e. an increase in ϕ_{graphite} , changes the band structure at the MLG/semiconductor interface as shown in Fig. 4. Before interfacial contact is made, the Fermi level of the semiconductor lies above the Fermi level of the pristine MLG (panel (a)). After the physical contact (panels (c) and (d)), the Fermi energies equilibrate and electrons in the semiconductor flow into the low energy states in the MLG, thereby creating positively charged donor atoms having a density N_D within the depletion width W . The bromine intercalation of MLG increases ϕ_{graphite} , resulting in an increase of SBH as displayed in panel (d). The greater difference between the Fermi level of silicon and brominated MLG requires more electrons to flow from the semiconductor into the MLG, leaving a more positively charged region and an increase in the charge density (capacitance) associated with the depletion width.

While J - V measurements are sensitive to the changes in the zero-bias SBH (Eq. 1), which leads to a decrease in current density for larger barrier heights (Fig. 2), the associated changes in the density of ionized donors N_D across the deple-

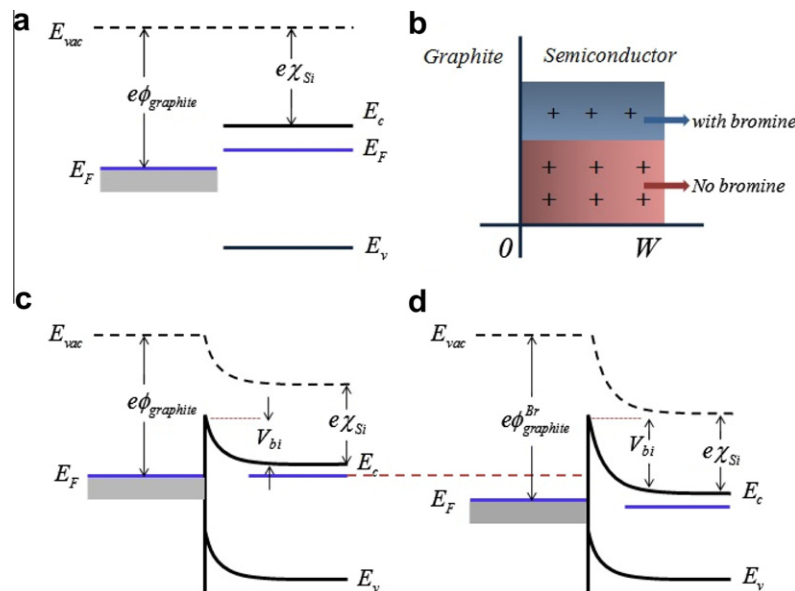


Fig. 4 – (a) Band structure at the metal–semiconductor interface before the physical contact and thermal equilibrium. (b) Change in charge distribution ($\rho(x)$) in the depletion width (W) before (red) and after (blue) the bromination. (c) Charge transfer and associated band bending, i.e. Schottky barrier formation, at the interface after physical contact is made. (d) Change in Fermi level, band structure and Schottky barrier height (SBH) after the physical contact at the brominated MLG/semiconductor interface.

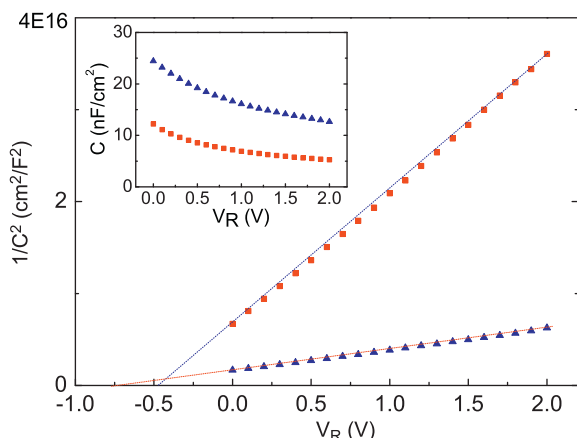


Fig. 5 – C^{-2} vs. V_R plots of MLG/n-Si($1E16 \text{ cm}^{-3}$) substrates at 1 KHz and 300 K before (red squares) and after 12 min of bromination (blue triangles). Inset: C vs. V_R plots.

tion width region W are not reflected in the J - V measurements. On the other hand, the electric field and corresponding potential difference V_{bi} (see Fig. 4b) associated with the separation of charge between an assumed uniform density N_D of ionized impurities and the electrons accumulated at the MLG/semiconductor interface gives rise to a finite depletion capacitance. The potential difference V_{bi} is known as the ‘built in’ potential and is the difference between the potential at the conduction band edge measured at the interface and the potential deep in the semiconductor (see Fig. 4b). Under these conditions, the solution to Poisson’s equation for a specific charge distribution in the depletion region gives the relation,

$$\frac{1}{C^2} = \frac{2(V_{bi} + V_R)}{(eN_D\epsilon_s)}, \quad (2)$$

which predicts a linear dependence between C^{-2} and an applied reverse bias voltage V_R [6]. The parameter ϵ_s describes the dielectric constant of the semiconductor.

Fig. 5 displays C^{-2} vs. V_R plots measured at 1 KHz of a MLG/n-silicon junction at room temperature both before (red squares) and after (blue triangles) bromination for 12 min. The linearity of these plots interpreted within the frame work of Eq. 2 shows that bromination decreases (increases) the slope (N_D) and increases V_{bi} , which is determined by linear extrapolation to the abscissa. The SBH can be expressed as $\phi_{SBH} = V_{bi} + (E_c - E_F)$, where E_c is the conduction band energy. The quantity $E_c - E_F$ is calculated to be 0.14 eV for the unbrominated samples and is therefore a relatively small correction to V_{bi} . Our values for V_{bi} , typically span around 0.40–0.60 eV corresponding to SBHs of 0.54–0.74 eV before the intercalation (Fig. 5 red squares) and increase to 0.60–0.90 eV with SBHs of 0.74–1.04 eV after the intercalation. A 0.2–0.3 eV increase in the SBH roughly agrees with the changes in MLG work function measured by XPS (Fig. 3c). The slopes of the C^{-2} vs. V_R plots for the brominated MLG/silicon junctions were typically smaller by 2–6 times comparing to pristine MLG/silicon junctions. A decrease in the slope, i.e. an increase in charge density in W , can be attributed to a larger difference between $\phi_{graphite}$ and χ_{Si} , hence more electrons flow from Si into the

MLG, creating a more positively charged region as discussed above. The solution to Poisson’s equation at the interface for an increased charge density in W leads to an increase in measured capacitance as illustrated in the inset of Fig. 5.

4. Conclusions

We have demonstrated that Schottky barrier diodes formed at MLG/semiconductor interfaces can be tuned over a wide range by intercalation with bromine. Since bromine is strongly electronegative, the carbon planes are hole doped with a significantly higher carrier density and lower (higher) Fermi energy (work function) than pristine MLG. The sensitivity of the Schottky diodes to bromine intercalation is measured as a decrease in forward-bias current density and an increase in depletion capacitance. XPS measurements confirm the intercalation induced decrease (increase) in the Fermi level (work function). Intercalation thus allows one to tune the barrier of MLG/semiconductor interfaces due to graphite’s low carrier density and open physical structure. Although we have specifically focused on bromine intercalation of MLG, an increase or decrease in the SBH can also be achieved using other intercalants, such as K, Li, Ca, and I_2 [15]. Our results suggest novel sensing applications for MLG/semiconductor junctions, where target atoms and/or molecules are intercalated into the MLG electrode, or graphene/semiconductor junctions, where target atoms and/or molecules are adsorbed onto a single-atom thick graphene layer that is in intimate contact with the underlying semiconductor.

This work is supported by the Office of Naval Research (ONR) under Contract No. 00075094 (BA) and by the National Science Foundation (NSF) under Contract No. 1005301 (AFH).

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