

Graphene-based FET Structure: Modeling FET Characteristics for an Aptamer-based Analyte Sensor

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Abstract—Graphene is a very promising electronic material that has attracted vast research interests due to its unique electronic properties [1]. In this paper, a graphene-based FET-like aptamer sensor is modelled for the case of an aptamer that binds to a cocaine surrogate. Methylene-blue (MB) is a nanoscale molecule that functions as an electron donor. The graphene in these structures exhibits p-type semiconductor behavior with holes as carriers. The voltage shift caused by electron trapping on the graphene surface is observed and explained by a charge sheet capacitance model. In this work, the graphene-based FET characteristics are modelled to understand the use of this device as a sensor of molecular analytes.

I. INTRODUCTION

Graphene have been the subjects of research ever since the fabrication of monolayer graphene in 2004 [2]. Its unique electrical and mechanical properties have resulted in efforts underlying a wide range of applications such as graphene-based nanocomposites and graphene-based FET structures [3], [4]. In addition to its electronic properties, graphene exhibits ballistic transport of electrons and holes on the sub-micron scale [5], which makes it a promising candidate for next-generation nanoelectronic devices [3].

Aptamers are artificial short DNA or RNA molecules, which perform as receptors for binding to targets of interest such as proteins, cells, DNA, inorganic ions, and small molecules with high specificity [6]. Aptamers are usually selected from combinatorial libraries of synthetic nucleic acids by a process of adsorption, recovery and amplification coined SELEX for systematic evolution of ligands by exponential enrichment [7]. An aptamer-based analyte sensor is a device converting a biological or chemical response into an electric signal.

In this paper, a graphene-based FET-like aptamer sensor is modelled. The aptamer modified with methylene-blue (MB) is used as a conformational change reporter. 1-pyrenebutanoic acid, succinimidyl ester is used as a linker molecule to noncovalently bind the aptamer to the graphene surface by the pyrene group. The graphene in these structures exhibits p-type semiconductor behavior due to residual hydroxyl groups. Electron trapping on the graphene surface is studied and a sheet charge capacitance model is established to explain the observed voltage shift in the I-V characteristics of the FET structure.

II. THEORY AND MODEL

A. Electron trapping on graphene surface

It is known that electrical contacts to a graphene surface typically exhibit high resistance [8], [9], [10]. This is possibly due to the weak electron conduction on the interface. The electronic structure and the weak van der Waals binding cause relatively small matrix elements for electrons to cross the interface [8]. Fig. 1 shows the Brillouin zone and Fermi-level points of graphene. A simple tight-binding computation yields a spectrum \vec{m} with two Fermi points located at $\vec{k}_1 = -2\vec{g}_1/3 - \vec{g}_2/3$ and $\vec{k}_2 = -\vec{k}_1$, which are just the corners of the two dimensional Brillouin zone [11]. In order to have good conduction there must be states near the Fermi level that extend through both sides of the interface. If the Fermi level states do not overlap at the interface, there can be no extended states and thus no transfer of electrons. Another possible factor is that the conduction on the interface may be forbidden by the wave vector conservation or the Bloch symmetry of electrons. A perfect graphene sheet has one electron per carbon in the π orbital. In methylene blue molecules, π -electronic structure with C_{2v} symmetry is also the major contributor to the nonlinear polarizability [12]. When the target molecule is present, MB undergoes a conformational change and could bend in all directions. If the wavevectors do not overlap in the same direction, it is very likely that the electrons contributed by MB will be trapped on the graphene surface.

B. Charge sheet capacitance model of graphene-based FET analyte sensor

1) *Graphene-based p-type MOSFET model:* Graphene has a unique electronic structure with a zero gap and quasiparticles behaving like massless Dirac fermions. A graphene sheet has one electron per carbon in the π -levels and the Fermi level is between the two symmetrical bands. However, band-structure calculations reveals that the electronic structure of a single graphene plane is not strictly symmetrical in energy. This asymmetry of electron-hole can shift the energy of the states localized near impurities above or below the Fermi level [1].

Graphene synthesized by different processing method could lead to different electronic behavior in the graphene-based FET structure. Researchers have reported the observation of p-type

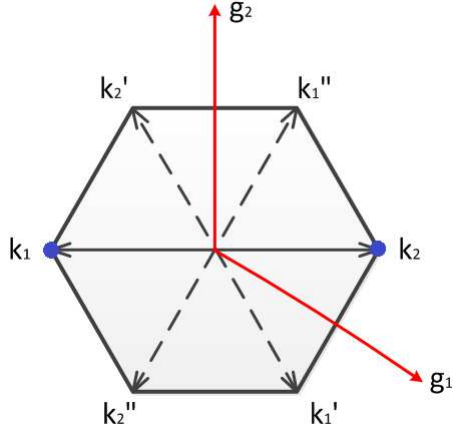


Fig. 1. Two-dimensional Brillouin zone of graphene and Fermi-level points.

behavior of graphene in the FET structure [13], [14], [15]. This may be due to the residual hydroxyl groups inhibiting the n-type behavior of electrons. It has been well documented that hydroxyl groups can inhibit the electrons from functioning as free carriers in silicon FETs [13], [16]. Other researchers have also reported that the electronic structure of graphene on SiO₂ strongly depends on the surface polarity and interface geometry. In the case of an interface geometry where graphene is weakly bonded to an O-polar surface, graphene behaves as a p-doped material [17]. Based on the above analysis, we conduct the device characteristic calculations for a p-type MOSFET model.

2) *Charge sheet capacitance model*: When the cocaine molecule is present, cocaine aptamers with methylene blue at the end will fold to form a three-way junction. The methylene blue could provide excess electron charges to the graphene surface and in turn modify the I-V characteristics of the P-MOS model.

After the inversion layer is formed, the net charge carrier density will reduce due to the external excess charge. We can assume,

$$Q(N_{et}) = Q_p - Q_{ext}, \quad (1)$$

where Q_p is the inversion charge and Q_{ext} is the extra electron charge provided by methylene blue. At equilibrium, the inversion layer charge in MOS-C will balance the charge added to the gate when V_G exceeds V_T . Therefore,

$$Q_p = -Q_{gate} \cong -C_o \Delta V_G = -C_o(V_G - V_T). \quad (2)$$

The external charge Q_{ext} depends on the concentration of cocaine. More cocaine molecules near the structure will cause more aptamers to make the conformational change, leading to additional electron charge at the surface.

To analyze the current-voltage behavior, we begin with

$$J_p = q\mu_p p \mathcal{E} - qD_p \nabla p. \quad (3)$$

Since the current flow in the conducting channel is almost exclusively in one direction (taken to be the y direction), and since the diffusion current is usually negligible compared with more numerous carriers at a certain point, we could simplify the equation to

$$J_p = q\mu_p p \mathcal{E} = -q\mu_p p \frac{d\phi}{dy}, \quad (4)$$

where μ_p is the mobility of holes. Thus the current flow in the conduction channel may be expressed as

$$\begin{aligned} I_D &= \int \int J_p dx dz \\ &= - \int \int q\mu_p \frac{d\phi}{dy} dx dz = (-Z \frac{d\phi}{dy}) \int_0^{x_c(y)} \mu_p(x, y) p(x, y) dx. \end{aligned} \quad (5)$$

The effective mobility $\overline{\mu_p}$ may be defined as

$$\overline{\mu_p} = -\frac{q}{Q_{N(y)}} \int_0^{x_c(y)} \mu_p(x, y) p(x, y) dx. \quad (7)$$

Equation 6 may be further simplified as

$$I_D = -Z \overline{\mu_p} Q_p \frac{d\phi}{dy}, \quad (8)$$

where Q_p is the positive charge/cm² in the channel. Integrating I_D over the length of channel gives

$$\int_0^L I_D dy = I_D L = -Z \int_0^{-V_D} \overline{\mu_p} Q_p d\phi \quad (9)$$

$$I_D = -\frac{Z \overline{\mu_p}}{L} \int_0^{-V_D} Q_p d\phi. \quad (10)$$

In our model, due to the existence of excess electron charges provided by methylene blue,

$$Q_p(N_{et}) = -C_o(V_G - V_T - \phi) - Q_{ext}, \quad (11)$$

where Q_{ext} is the trapped external charge from MB. From the two equations above, we obtain the I_D - V_D relation

$$I_D = \frac{Z \overline{\mu_p} C_o}{L} [(V_G - V_T)V_D - \frac{V_D^2}{2}] - \frac{Z \overline{\mu_p} V_D}{L} Q_{ext}. \quad (12)$$

III. RESULTS AND DISCUSSION

A. Graphene-based FET Structure

We use cocaine as a target to test our graphene-FET aptamer sensor as shown in Fig. 2. The aptamer modified with methylene-blue (MB) as engineered by Baker et al. [18] is used as a conformational change reporter. MB is an electron donor, while chemical oxidation-reduction synthesized graphene usually shows p-type semiconductor behavior with holes as carriers. 1-pyrenebutanoic acid, succinimidyl ester (merchandise name: P130) as the red dot in Fig. 2, is used as a linker molecule to noncovalently bind the aptamer to the

graphene surface by the pyrene group as in the protocol used for Carbon Nanotube [19]. The pyrene group, being highly aromatic in nature, is known to interact strongly with the basal plane of graphite via π -stacking, due to the overlapping of π bonds between aromatic side chains. The cocaine aptamer is about 2-nm in length with 30 bases, which is less the Debye length [20] that defined as the typical distance required for screening the surplus charge by the mobile carrier present in a material. When the target molecule, cocaine, is present, the aptamer will undergo a conformation change and thus change the distance between the MB and the graphene surface. When the MB approaches the surface, it can provide excess electrons that changed the I-V characteristics of the graphene-FET as described previously.

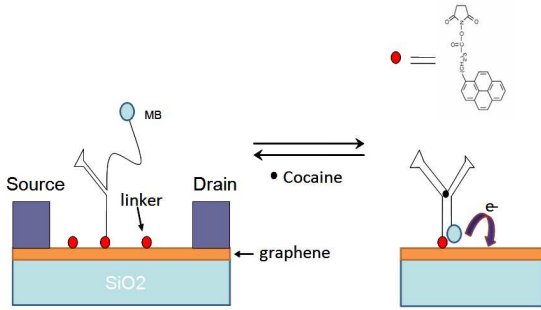


Fig. 2. Scheme of graphene-based FET structure for detecting charges from MB close to the graphene surface.

B. Comparison of the model with the measured data

After device fabrication, cocaine initially dispersed in water is sensed. Fig. 3 shows the current-voltage relationship in the FET structure. The original I_{SD} curve shows typical p-type graphene behavior and agrees well with previous results [15], [21], where the current decreases with increasing V_{BG} from -60 V to 60 V. After the cocaine aptamer is immobilized on the graphene surface, the I_{SD} current experiences a current decrease from 20.5 μ A to 15.8 μ A at -60 V and from 19.7 μ A to 15 μ A at 60 V. Further, when cocaine is present, the I_{SD} continues to reduce with increasing concentration of cocaine. At -60 V, the current drops from 15.8 μ A to 10.5 μ A, 9.7 μ A, and 9.4 μ A for cocaine solution of 0, 1 μ M, 10 μ M, and 100 μ M, respectively; while at 60 V, the corresponding currents are 15.0 μ A, 10.0 μ A, 9.2 μ A, and 9.0 μ A, respectively. The current decrease or conductance reduction is very stable in the variable V_{BG} , as it is expected from the charge sheet capacitance model. The device appears to be saturated up to 100 μ M with a nonlinear current drop to about 45% of original value.

These phenomena can be well explained by the charge sheet capacitance model. As can be seen from the device scheme in Fig. 2, when the graphene surface is exposed to cocaine and causes the conformation change of the aptamers, MB

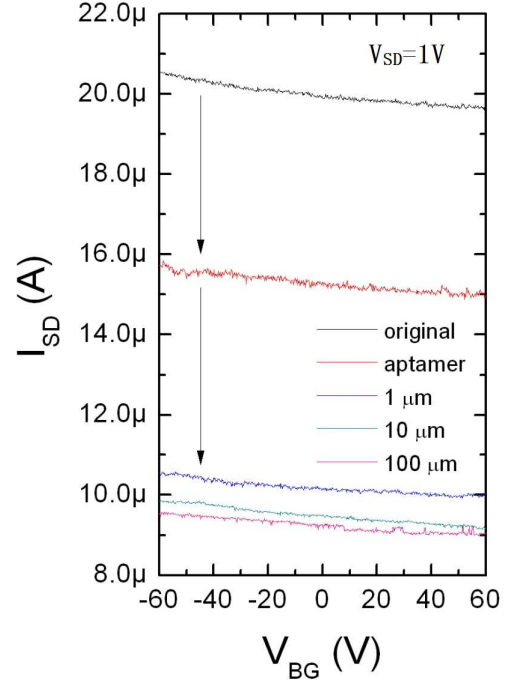


Fig. 3. I_{SD} versus V_{BG} curves of different conditions: original device, aptamer-immobilized, 1 M, 10 M, and 100 M cocaine-in-water-tested with the arrow indication.

will approach the graphene surface and contribute electrons. While ox-re graphene is a p-type semiconductor with hole as carriers, the electrons from MB will lower the carrier concentration of graphene, and thus lower the conductance. Increasing the cocaine concentration will cause more aptamers to make the configurational change, and lead to more electrons being trapped on the surface. The current or conductance exhibits a stable decrease in the variable V_{BG} . This is because the structure will act like a capacitor as explained in the model. The charges trapped at the interface will be compensated in the graphene which acts as p-type semiconductor. If charges have been trapped on the surface the threshold voltage will be shifted. The change in threshold voltage depends on the amount of electron charge trapped at the interface. The relationship between trapped electron charges and shift of voltage may be written as: $\Delta V_{TH} C_0 = Q_{ext}$. Thus, electrons contributed by MB will directly lead to a shift of voltage.

Similar results had been reported for unfunctionalized graphene [15], [21], where a larger current decrease was observed. It is to be noted that the slope of I_{SD} - V_{BG} curve is related to the dimensions of the FET device (Z/L) in the triode regime. Taking the derivative of Equation 12,

$$\frac{dI_D}{dV_G} = \frac{Z\mu_p C_0}{L}, \quad (13)$$

In our structure the length of the channel (15 μ m) is twice the length (7 μ m) in Dr. Yang's device, and the width may also

be relatively smaller due to rough (non-parallel) electrodes. Thus the conductance decreasing rate in our device is relatively lower.

IV. CONCLUSION

In this study, the characteristics of a graphene-based FET aptamer sensor have been modelled and compared with experiment. The device performs as a signal-off sensor and detects cocaine in the micromole concentration regime. The graphene-based FET structures exhibits typical p-type semiconductor behavior due to residual hydroxyl groups. Methylene blue can serve as electron donor to the graphene FET structure. Electron trapping on graphene surface is studied as well as the I-V characteristics of the FET structure. A shift in voltage is clearly observed as expected in the sheet charge capacitance model. These results demonstrate the effectiveness of the model to understand the use of this device as a sensor of molecular analytes.

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REFERENCES

- [1] A. Castro Neto, F. Guinea, N. Peres, K. Novoselov, and A. Geim, *Reviews of Modern Physics*, vol. 81, p. 109, 2009.
- [2] K. Novoselov, A. Geim, S. Morozov, D. Jiang, Y. Zhang, S. Dubonos, I. Grigorieva, and A. Firsov, *Science*, vol. 306, p. 666, 2004.
- [3] N. Staley, H. Wang, C. Puls, J. Forster, T. Jackson, K. McCarthy, B. Clouser, and Y. Liu, *Applied Physics Letters*, vol. 90, p. 143518, 2007.
- [4] K. Xu, D. Erricolo, M. Dutta, and M. Stroschio, *Superlattices and Microstructures*, vol. 51, p. 606, 2012.
- [5] J. S. Bunch, A. M. van der Zande, S. S. Verbridge, I. W. Frank, D. M. Tanenbaum, J. M. Parpia, H. G. Craighead, and P. L. McEuen, *Science*, vol. 315, p. 490, 2007.
- [6] Y. Xiao, X. Qu, K. Plaxco, and A. Heeger, *Journal of the American Chemical Society*, vol. 129, p. 11896, 2007.
- [7] C. Tuerk and L. Gold, *Science*, vol. 249, p. 505, 1990.
- [8] J. Tersoff, *Applied Physics Letters*, vol. 74, p. 2122, 1999.
- [9] J. A. Robinson, M. LaBella, M. Zhu, M. Hollander, R. Kasarda, Z. Hughes, K. Trumbull, R. Cavalero, and D. Snyder, *Applied Physics Letters*, vol. 98, p. 053103, 2011.
- [10] A. Bachtold, M. Henny, C. Terrier, C. Strunk, J.-P. S. C. Schönenberger, J.-M. Bonard, and L. Forró, *Science*, vol. 249, p. 505, 1990.
- [11] P. Wallace, *Physical Review*, vol. 71, p. 622, 1947.
- [12] D. J. Campbell, D. A. Higgins, , and R. M. Corn, *Journal of Physical Chemistry*, vol. 94, p. 3681, 1990.
- [13] S. Gilje, S. Han, M. Wang, K. Wang, and R. Kaner, *Nano letters*, vol. 7, p. 3394, 2007.
- [14] Z. Chen, Y.-M. Lin, M. J. Rooks, and P. Avouris, *Physica E*, vol. 40, p. 228, 2007.
- [15] V. Tung, M. Allen, Y. Yang, , and R. Kaner, *Nature Nanotechnology*, vol. 4, p. 25, 2009.
- [16] T. Ohta, A. Bostwick, T. Seyller, K. Horn, and E. Rotenberg, *Science*, vol. 313, p. 951, 2006.
- [17] Y.-J. Kang, J. Kang, , and K. J. Chang, *Physical Review B*, vol. 78, p. 115404, 2008.
- [18] B. Baker, R. Lai, M. Wood, E. Doctor, A. Heeger, and K. Plaxco, *Journal of the American Chemical Society*, vol. 128, p. 3138, 2006.
- [19] R. Chen, Y. Zhang, D. Wang, , and H. Dai, *Journal of the American Chemical Society*, vol. 123, p. 3838, 2001.
- [20] K. Maehashi, T. Katsura, K. Kerman, Y. Takamura, K. Matsumoto, and E. Tamiya, *Analytical Chemistry*, vol. 79, p. 782, 2006.
- [21] M. Allen, V. Tung, L. Gomez, Z. Xu, L. Chen, K. Nelson, C. Zhou, R. Kaner, , and Y. Yang, *Advanced Materials*, vol. 21, p. 2098, 2009.