Direct Measurement of Dirac Point and Fermi level at Graphene/Oxide interface by Internal Photoemission

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We report the first direct measurement of the Dirac point, the Fermi level, and the work function of single layer gapless graphene by using photoemission threshold spectroscopy. Since the pioneering work of Novoselov *et al* in 2004,[1] graphene has attracted an immense amount of interest from all disciplines.[2] The knowledge of the physics of graphene-based devices has grown dramatically. Along with the recent success of large area chemical vapor deposition(CVD) growth of graphene,[3] it seems the industrial applications such as transparent electrodes,[4] field effect transistors,[5] and quantum well devices[6] are becoming more promising. However, the precise position of the Dirac point and Fermi level at the graphene/oxide interface has yet to be investigated; despite their importance in the design and modeling of graphene-based devices. In this paper, we present the study of a semi-transparent metal/high-*k*/graphene/SiO_2/Si structure, and focus our study on the photoemission phenomena at the graphene/SiO_2 interface. As a result, a complete electronic band alignment of the graphene/SiO_2/Si system is accurately constructed for the first time.

The test structure is shown in Fig. 1. The graphene was grown on Cu using CVD and transferred onto a highly n-doped Si substrate with 300nm-thick SiO_2. A metal layer of 20 nm-Cr/100 nm-Au is used as the contact for graphene. A 2 nm Al seed layer or a 1nm Ti seed layer was deposited and oxidized in atmosphere followed by atomic layer deposition (ALD) of either 8 nm Al_2O_3 or 11.5 nm HfO_2 as the top gate dielectric. A 1 nm-Ti/9 nm-Pt layer was used for the semi-transparent top gate through which incident photons are able to reach the desired interfaces. A physical model of the internal photoemissions (IPE) spectroscopy measurement is shown in Fig. 2. A family of quantum photoelectric current curves is plotted as a function of incident photon energy with -20 to +20 V bias applied to the back gate, as shown in Fig. 3. The photoelectric current plot reveals strong interference produced by the 300 nm thick SiO_2 back gate which enhances the absorption in the graphene. This interference effect enables us to observe threshold transitions (shown in Fig. 4). Yield$^{1/3}$-eV data in Fig. 4 were linearly fitted to obtain the barrier height from the Fermi level of graphene to the conduction band of SiO_2. A cube root relationship is preferred because of the linear density of states (DOS) dispersion of graphene,. We use linear extrapolation to zero field to account for image force lowering of the barrier. From their intercept we extract zero-field barrier heights of 3.25 eV and 3.30 eV for the test structure with Al_2O_3 top gate and HfO_2 top gate, respectively, as shown in Fig. 5. Band alignment of the Si/SiO_2 interface is also measured with the same approach. Φ_e (VB_{Si}-CB_{SiO2}) = 4.3 eV and Φ_e (CB_{Si}-CB_{SiO2}) = 3.23 eV are obtained. To complete the graphene/SiO_2/Si band diagram, the Fermi level position with respect to the Dirac point in graphene is defined by an I_D-V_{GS} measurement (shown in Fig. 6) using the equation relating Fermi level position to the applied voltage (Eq 2, Ref. [7]). In this case V_{GS} is applied to the thin top gate instead of the back gate because of the improved electrostatic control in the channel region of the test structure. Fig. 6 suggests the Fermi level is 0.33 eV (Al_2O_3 top gate) and 0.30 eV (HfO_2 top gate) above the Dirac point.

We show in Fig. 7 the complete band diagram of graphene/SiO_2/Si structure. We obtain the intrinsic position of the undoped graphene Dirac point with respect to the conduction band of SiO_2, 3.58 eV (Al_2O_3 top gate) and 3.60 eV (HfO_2 top gate). Consequently, the intrinsic work function of graphene is found to be 4.50 eV confirming previous reports.[8], [9] Our preliminary study indicated that the intrinsic band offset and work function of graphene is relatively insensitive to the choice of top gate material. This is attributed to the weak Van der Waals forces between the oxide materials and graphene.

[1] K. S. Novoselov, et al., “Electric Field Effect in Atomically Thin Carbon Films,” *Science*, vol. 306, no. 5696, pp. 666–669, Oct. 2004.
[2] A. H. Castro Neto, et al., “The electronic properties of graphene,” *Rev. Mod. Phys.*, vol. 81, no. 1, pp. 109–162, Jan. 2009.
[3] K. S. Kim, et al., “Large-scale pattern growth of graphene films for stretchable transparent electrodes,” *Nature*, vol. 457, no. 7230, pp. 706–710, Jan. 2009.
[4] S. Bae, et al., “Roll-to-roll production of 30-inch graphene films for transparent electrodes,” *Nature Nanotechnology*, vol. 5, no. 8, pp. 574–578, 2010.
[5] J. Kedzierski, et al., “Graphene-on-Insulator Transistors Made Using C on Ni Chemical-Vapor Deposition,” *Electron Device Letters, IEEE*, vol. 30, no. 7, pp. 745 –747, Jul. 2009.
[6] S. Moriyama, et al., “Fabrication of quantum-dot devices in graphene,” *Science and Technology of Advanced Materials*, vol. 11, no. 5, p. 054601, Oct. 2010.
[7] A. Das, et al., "Monitoring dopants by Raman scattering in an electrochemically top-gated graphene transistor," *Nature Nanotechnology*, vol. 3, no. 4, pp. 210 - 215, 2008.
[8] S. S. Datta, et al., “Surface Potentials and Layer Charge Distributions in Few-Layer Graphene Films,” *Nano Lett.*, vol. 9, no. 1, pp. 7–11, 2008.
[9] R. Yan, et al. "Determination of graphene work function and graphene-oxide-semiconductor band alignment by internal photoemission spectroscopy," *Submitted.*

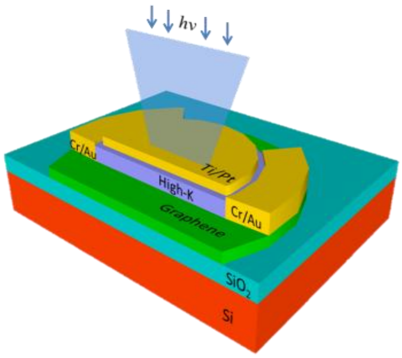

Fig. 1. Schematic of the test structure with High-K/Graphene/SiO_2/Si stack. Al_2O_3 and HfO_2 are used at high-K top gate

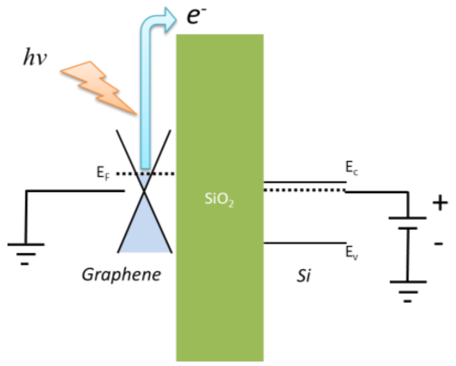

Fig. 2. A physical model of the internal photoemission spectroscopy measurement.

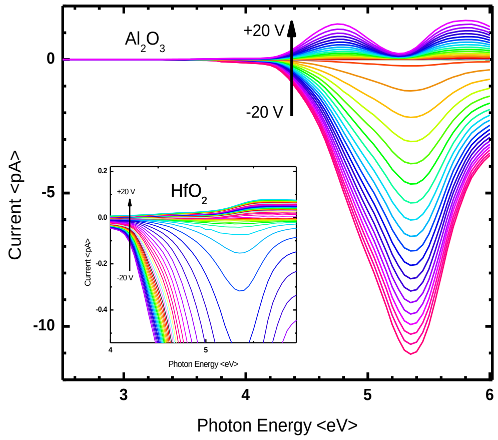

Fig. 3. Photoelectric current from graphene to SiO_2 measured as a function of incident photon energy and with back gate bias as the parameter. Plot shows photoelectric current of the structure with Al_2O_3 top gate and HfO_2 top gate (inset).

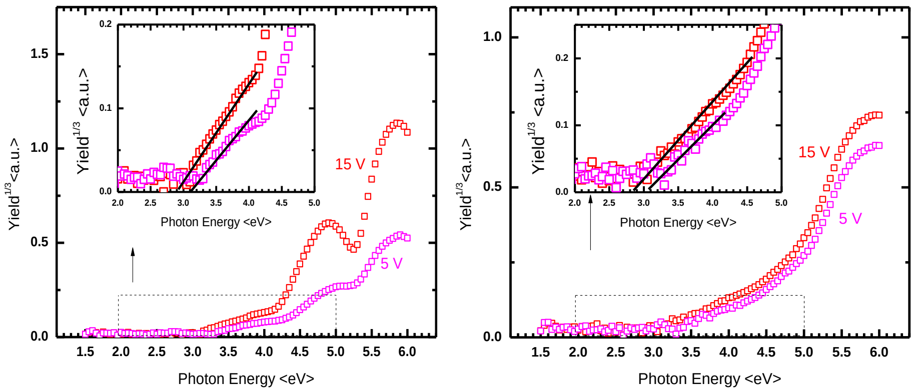

Fig. 4. Yield$^{1/3}$ of emission from graphene to SiO_2 with back gate bias at 5 and 15 V. Plot shows the cubic root of the yield shows good linearity and confirms with the linear dispersion of graphene DOS near the Dirac point. Left figure shows Yield$^{1/3}$-eV of the structure with Al_2O_3 top gate. Right figure shows Yield$^{1/3}$-eV of the structure with HfO_2 top gate.

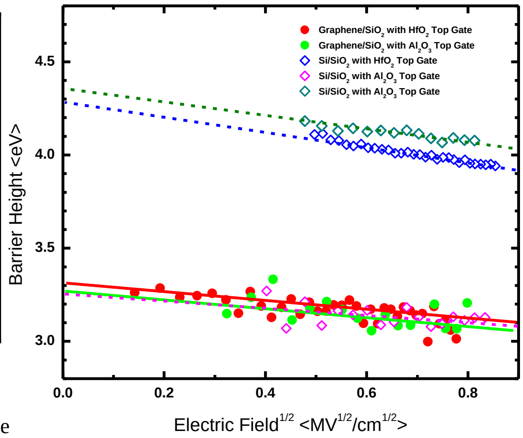

Fig. 5. Schottky plot of the field dependent IPE threshold measured at Graphene/SiO_2 interface for test structures with different top gate high-K. Measured threshold of Si/SiO_2 is also shown in the plot.

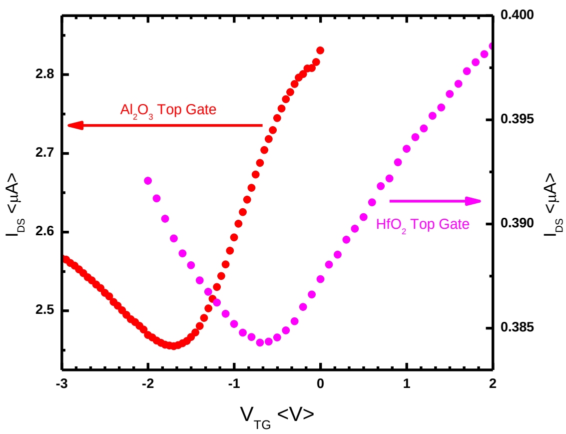

Fig. 6. Transfer characteristics of graphene FET with bias at Al_2O_3 or HfO_2 top gate.

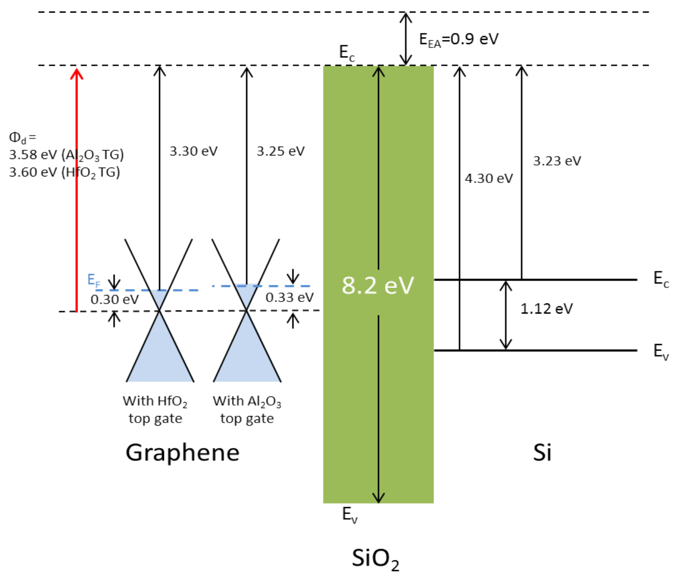

Fig. 7. Complete band diagram of graphene/SiO_2/Si system.