Research Paper

Charge Carrier Density Tuning of Graphene by Water Gating

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ABSTRACT

In this work, the conditions of water-gated carrier density accumulation on graphene were investigated. In particular, either negative or positive electric potential in deionized water could be observed, leading to an increase or decrease in the hole charge carrier density, respectively. Furthermore, it was determined that the critical positive electric potential for water gating of graphene is required to return the accumulated carrier density back to its initial state. Taken together, these results provide valuable insight into the relationship between carrier accumulation and the deionized water gating method.

Keywords: Graphene, Carrier density, Water gating

I. Introduction

Graphene has been favored for atomically thin electrodes for nano-scale devices due to its high electrical conductivity [1–3]. Since the high charge carrier doping condition of graphene is one of the critical requirements for high conductivity electrodes, the accumulation of carrier density on graphene has been extensively studied. The use of electrolytes to potentially produce highly doped graphene by various methods has also been investigated for applications in several fields [4–13]. However, when a critical electric potential is applied to graphene via electrolytes such as ionic liquid or gel [7–9], undesired sp^3 bonds were observed to form on the graphene [4–13]. Thus, in order to maintain distinct sp^2 electric potential structures on graphene during the application of an electric gate voltage, a stable electrolyte is required. Water is a promising electrolyte for this use, and water-gated field effect transistors have previously been reported [5,12]. However, more detailed information regarding the carrier density variation of graphene with water-gating is required.

In this work, the behavior of carrier density accumulation on graphene is investigated. In particular, the ability to tune the carrier density when employing deionized (DI) water gating with electric potential is explored. Finally, detailed information regarding the effect of accumulating charge carriers on graphene when either negative or positive electric potential is supplied through DI-water is presented.

II. Experimental details

In order to identify graphene conductance, graphene was prepared on a 280-nm-thick silicon dioxide (SiO_2)/highly doped silicon (Si) substrate by the mechanical exfoliation method. Subsequently, titanium (Ti) electrodes were placed in contact with graphene by a conventional electron-beam lithography process [Figs. 1(a) and 1(b)]

[8,9,13]. Owing to the natural formation of a thin oxide layer on Ti when exposed to air, this oxide was employed as a barrier for blocking the interaction between the water-gate and Ti electrodes. As shown in Fig. 1(a), the resistance variation of graphene was inspected by two-terminal measurement during the application of either back-gate voltage (V_{BG}) or water-gated voltage (V_{WG}) through a SiO_2 /Si substrate or DI-water (resistivity = 8 ~ 10 M Ω)/platinum (Pt) bar, respectively.

Figures 2(a) and 2(b) show the resistance of graphene as a function of V_{BG} and V_{WG} , respectively. As shown in these figures, the initially accumulated carrier density in graphene was $n = (C_{BG}/e) \cdot V_{CNP-BG} \approx 5 \times 10^{11} \text{ cm}^{-2}$, where $C_{BG} = 12 \text{ nF/cm}^2$ is the capacitance of the 280-nm-thick SiO_2 substrate, e is the charge of an electron, and $V_{CNP-BG} = 8.35 \text{ V}$ is the charge neutral point. When DI-water gating is used instead of the SiO_2 substrate for the same graphene, the charge neutral point $V_{CNP-WG} = 0.15 \text{ V}$. The capacitance of DI-water (C_{WG}) was calculated to be $C_{WG} = 668 \text{ nF/cm}^2$, because the initial accumulation of carrier density under applied V_{BG} corresponded with the

Figure 1. (Color online) (a) Schematic diagram of water gating by a platinum bar for graphene FET with Ti electrodes. (b) Topography image of graphene FET in contact with Ti electrodes on an SiO_2 / Si substrate. Here it was utilized highly doped silicon substrate for applying back-gate voltage, V_{BG} .

Figure 2. Resistance variation of graphene as a function of (a) back-gate voltage, V_{BG} and (b) water-gate voltage, V_{WG} .

accumulated density under applied V_{WG} as follows,

$$n = (C_{BG}/e) \cdot V_{CNP-BG} = (C_{WG}/e) \cdot V_{CNP-WG} \quad [10-12,14] \quad (1)$$

III. Results and discussion

Figure 3 shows the resistance of graphene as a function of time for different values of applied V_{WG} . When the (1) $V_{WG} = -0.6$ V was applied to graphene, a decreased resistance of approximately 4.4 kΩ was observed. Subsequently, the resistance of graphene was measured as 5.4 kΩ for (2) $V_{WG} = 0.6$ V and as 4.3 kΩ for (7) $V_{WG} = 2.0$ V. Furthermore, $V_{WG} = (1) -0.6$ V, (6) 1.5 V, and (7) 2.0 V were gradually applied to graphene again as shown in the second light-green area within **Fig. 3**. Similar resistances of graphene were obtained from the first measurement denoted by the blue area in **Fig. 3**. Although, the variation of resistance as a function of V_{WG} was observed, this result was not enough to clearly understand the effect of V_{WG} on the accumulated carrier density variation on graphene. Thus, V_{CNP-BG} from the resistance curves was represented as a function of V_{BG} [**Fig. 4**] after each V_{WG} at (1) ~ (7) were applied to graphene, as shown in **Fig. 3**.

Figure 4(a) presents the resistance curves of graphene as a function of V_{BG} after the application of $V_{WG} = (0) 0$ V, (1) -0.6 V, and (3) 0.7 V ~ (7) 2.0 V. Compared with the neutral point of $V_{CNP-BG} = 8.35$ V [marked by the black dashed line of the black transport curve in **Fig. 4(a)**] under (0) $V_{WG} = 0$ V, V_{CNP-BG} was increased by approximately 10 V [the red transport curve in **Fig. 4(a)**] for (1) -0.6 V and V_{CNP-BG} remained approximately 10 V during the application of $V_{WG} = (2) 0.7$ ~ (5) 1.2 V [denoted by the dashed transport curves in **Fig. 4(a)**]. When V_{WG} greater than (6) 1.5 V and (7) 2.0 V was applied [the blue and brown transport curves in **Fig. 4(a)**], V_{CNP-BG} decreased by approximately 3 V.

As an estimate of the variation of the accumulated carrier density (n), **Fig. 4(b)** exhibits the relationship between n and V_{WG} . The accumulated carrier density was observed to be $n = 5.09 \times 10^{11}$ and $10.65 \times 10^{11} \text{ cm}^{-2}$ for $V_{WG} = (0) 0$ V and (1) -0.6 V, respectively. As previously mentioned with regard to V_{CNP-WG} in **Fig. 4(a)**, although $V_{WG} = (2) 0.7$ V ~ (5) 1.2 V were applied, the carrier density was maintained between $n = 10 \times 10^{11}$ and $n = 13 \times 10^{11} \text{ cm}^{-2}$, as marked by pink area in **Fig. 4(b)**. Meanwhile, $n \approx 2 \times 10^{11} \text{ cm}^{-2}$ was measured for $V_{WG} = (6) 1.5$ V ~ (7) 2.0 V as marked by blue area in **Fig. 4(b)**. Moreover, similar behavior [red dots in **Fig. 4(b)**] was also observed in the second cycle with the application of $V_{WG} = (1) -0.6$ V, (6) 1.5 V, and (7) 2.0 V after finishing the first cycle in its entirety. This indicates that although water-gating leads to changes in the doping of graphene when negative electric potential ($V_{WG} = -0.6$ V) is applied, a critical

Figure 3. (Color online) Resistance variation of graphene as a function of time for different applied $V_{WG} = (1) -0.6$ V, (2) 0.7 V, (3) 0.9 V, (4) 1.0 V, (5) 1.2 V, (6) 1.5 V and (7) 2.0 V. The water-gating ranges from $V_{WG} = (1) -0.6$ V to (7) 2.0 V were applied twice, with the first and second applications denoted by the blue and green areas, respectively.

Figure 4. (Color online) (a) Resistance curves of graphene as a function of V_{BG} after applied V_{WG} from (1) -0.6 V to (7) 2.0 V. (b) Accumulated carrier density of graphene as a function of V_{WG} for (0) 0.0 V, (1) -0.6 V, (2) 0.7 V ~ (5) 1.2 V, and (6) 1.5 V ~ (7) 2.0 V. Black and red dots indicate the n for the first and second cycles of V_{WG} application.

positive electric potential ($V_{WG} \geq 1.5$ V) can be applied to return accumulated carrier density to its initial condition from the highly p-doped condition generated by negative electric potential.

IV. Conclusions

In this work, carrier density accumulation was observed in response to DI-water gating. When a critical negative electric potential ($V_{WG} = -0.6$ V) was applied via DI-water, the accumulated hole carrier density was observed. Furthermore, once the applied voltage exceeded a critical positive electric potential ($V_{WG} \geq 1.5$ V) through DI-water, this accumulated carrier density could be restored to the initial carrier density condition. This result provides meaningful insight into the relationship between carrier accumulation and the DI-water gating method.

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