Chemical Doping of Graphene Nanoribbon Field-Effect Devices
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Graphene is a single layer of carbon atoms arranged in a honeycomb lattice, and has rapidly attracted growing attention because of its unusual electrical properties associated with the massless carriers.1 In particular, the extraordinary carrier mobility of graphene,2 as high as 200,000 cm2/Vs, provides exciting opportunities for high-speed electronics and rf applications. While there has been much progress in the fabrication and understanding of graphene devices,3 doping in graphene remains one of the key issues to be addressed for technological applications. Unlike doping in CMOS devices, graphene cannot be doped through substitution by ion implantation, which would damage the graphene lattice and the desirable transport characteristics. While doping in graphene can be obtained by exposure to alkali metals4 (e.g. K) or gas (e.g. NH3 and NO2) via charge transfer, these dopants are unstable under ambient conditions. Thus, it is essential to develop a stable and reproducible doping scheme to make graphene technologically viable. Here we report the first air-stable chemical doping in graphene nanoribbon (GNR) devices, demonstrating both n- and p-doping with a controllable doping concentration of more than 1.5x1011 cm−2. In the doped GNR, we find that the mobility of majority carriers is not degraded by the chemical dopants used here. To further extend the versatility of this chemical doping, we have fabricated p-n junction GNR devices, which, in combination of a top-gate structure, exhibit distinct transport characteristics from the unipolar ones.

Graphene nanoribbon devices (see inset of Fig. 1) are fabricated by mechanical exfoliation of graphite, where the channel between the metal contacts is defined by oxygen plasma RIE using HSQ (Hydrogen SilsesQuioxane) as the protective mask. Nanoribbon structures are studied here because they may produce a desirable bandgap for logic applications in graphene, which is a zero-gap semiconductor in the 2D form. As shown in Fig. 1, graphene devices exhibit a pronounced p-channel behavior in the presence of the HSQ layer, which needs to be removed in order to reveal the intrinsic transport properties of GNR. The intrinsic GNR shows ambipolar transport characteristics, where the conductance exhibits a “V” shape as a function of back gate voltage. To realize n-doping, we immerse the GNR device to a solution of polyethyleneimine (PEI) in ethanol (20 wt%) for 3 hours. PEI is an amine-rich electron-donating polymer that has been first reported by Shim et al. to dope carbon nanotubes.5 Here we show that PEI is also an effective n-type dopant for graphene. Fig. 2 shows the measured conductance G as a function of back gate voltage of the GNR before and after the PEI doping. From the shift of the Dirac point (the minimal conductance), we estimate the doping concentration in the as-doped devices to be ~ 1.5x1011 cm−2 for both single and bilayer graphene devices. After annealing the GNR at 120°C for 8 hours, we find that this doping strength can be further enhanced (Fig. 2). This indicates that the control of doping concentration may be achieved by controlling the annealing/rinsing conditions. We also note that the electron mobility, which is proportional to the slope of the n-branch in the G-Vg curve, does not degrade after the doping and the annealing process. This is in contrast to the n-doping in graphene using alkali metals (K),4 where both the electron and the hole mobilities decrease with increasing doping concentration. Air-stable P-doping in graphene is achieved by functionalization with 4-Bromobenzenediazonium Tetrafluoroborate. On carbon nanotubes, diazonium compounds of this type are known to be electron-accepting.6 Fig. 3 shows the transport characteristics of a graphene device before and after the p-doping treatment, showing a positive shift of the Dirac voltage of more than 40V, corresponding to a doping concentration of ~ 3x1011 cm−2. We note that while the electron mobility of the graphene device becomes lower after the p-doping, the hole mobility is not adversely affected by this chemical p-dopant.

In order to demonstrate the doping profile in graphene using chemical dopants, we have fabricated top-gate structures on GNR, as shown in Fig. 4. The top gate stack consists of 10nm Al2O3 grown by ALD (atomic layer deposition), followed by metal deposition of 20nm Pd as the gate electrode. In Fig. 4, only part of the graphene channel of device B is covered by the top-gate stack, so that exposed region can be doped by chemicals. After immersing the GNR devices in the PEI solution, Fig. 5 shows the conductance as a function of top gate voltage Vtg for a fully top-gated GNR (device A in Fig. 4) for various back gate voltages. We note that this top gate stack renders the channel to exhibit p-type behavior, which may be related to the impurity charges in the dielectrics and the large workfunction of metal gate (Pd). As the back gate voltage increases, the G-Vtg curves exhibit steady horizontal shifts towards negative top gate voltages, as expected from the capacitive effects for a channel sandwiched between two gates. In contrast, device B exhibits dramatically different transport behavior due to the p-n junction, as shown in Fig. 6. At Vtg = -4 V, the conductance of device B increases with increasing back gate voltage, revealing the n-channel behavior in the PEI-doped channel region. For a given backgate voltage, the device exhibits p-type behavior as explained above. Therefore, in device B, the channel can be modeled as an n-type and a p-type resistor in series.

In summary, we have demonstrated the first air-stable n-type and p-type chemical doping in graphene via charge transfer, and shown that the doping does not deteriorate the majority carrier mobility. We have further fabricated top-gated graphene structures and demonstrate p-n junction in GNR devices.

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3Z. Chen et al., Physica E 40, 228 (2007)
4J. H. Chen et al., Cond-Mat/0728.2408
Fig. 1: Resistance of a GNR device measured as a function of gate voltage before and after the removal of the HSQ layer. The inset shows the device schematics. 300nm-thick SiO$_2$ is used as the gate dielectrics.

Fig. 2: Conductance measured as a function of $V_g$ for single-layer (left panel) and bilayer (right panel) GNR devices, showing the n-type doping effect of the PEI treatment and the subsequent annealing.

Fig. 3: Conductance of a graphene device measured as a function of $V_g$ before and after the diazonium treatment, illustrating the p-type doping in graphene.

Fig. 4: (top)SEM image of top-gated GNR devices. The region of graphene covered by the top gate stack is sketched by the dashed lines. The left ribbon is only partially covered by the top gate. (bottom) Schematics of the device structure.

Fig. 5: Conductance of the fully-gated GNR device (device A in Fig. 4) measured as a function of top gate voltage for various back gate voltages.

Fig. 6: Conductance of the partially-gated GNR device (device B in Fig. 4) measured as a function of top gate voltage for various back gate voltages. The open region is doped with PEI.