Doping effect on shift of threshold voltage of graphene-based field-effect transistors

B. Guo, L. Fang, B. Zhang and J.R. Gong

A method of controllable doping by ion irradiation in reduced graphene oxide (RGO) is presented, and the threshold voltage of the RGO-based field-effect transistor can be finely tuned in the range from more than 30 V to about −20 V using this approach. Evidence of doping was also provided by Raman spectroscopy and Fourier transform infrared spectroscopy.

Introduction: Graphene, a two-dimensional (2D) network of sp^2-hybridised carbon atoms, has many extraordinary properties owing to the long-range π-conjugation and a linear energy-momentum dispersion relation near the Dirac point. In particular, it has aroused tremendous interest in the electronic device community because of the unique electronic properties, such as the highest carrier mobility. Therefore, graphene is considered as a candidate material for applications in post-silicon electronics. However, most electronics applications are handicapped by the absence of a bandgap in graphene. Much effort has been aimed at tuning or opening the energy gap in graphene, for example, cutting graphene into nanoribbons [1], doping during the chemical vapour deposition [2] and tuning the electrostatic field [3]. A good reduced graphene oxide (RGO)-based field-effect transistor (GFET) should display a rapid transition between the on and off state at the threshold voltage, which is defined as the gate voltage where the carrier type changed, and the threshold voltage should locate in the range of the electrocircuit works. For example, if the operation range of the device is from −20 to 0 V, while the threshold voltage is 30 V, then the electrocircuit does not work. Therefore, a controllable threshold voltage is very important for the GFET.

In this Letter, we report a method of controllable doping by ion irradiation in RGO and the effect of doping on the shift of the threshold voltage of the GFET. Our method is simple, scalable and compatible with current CMOS processing.

Experiment: The graphene used in our experiment was made by reducing graphene oxide (GO). The GO sheets were synthesised using a modified Hummer's method from natural graphite flakes (around 100 meshes, purchased from Alfa Aesar). Then, an aqueous solution of the GO sheets was dipped onto the 300 nm SiO_2/Si substrate. The graphene was obtained after the reducing process according to [4]. The graphene sheets on the substrate were put into the vacuum chamber for the N^+ ion irradiation. The energy of an N^+ ion is 30 keV, and the flux of N^+ ion irradiation was 1×10^{14} cm^{-2}. After irradiation, the sample was annealed in N_2 at 1100°C for 30 s for doping. The above parameters were optimised based on our previous work [5]. The Raman spectroscopy (Renishaw's inVia plus laser Raman spectrometer) and FTIR (PerkinElmer's Spectrum One Fourier transform infrared spectrophotometer) measurement were performed before and after doping, and all the representative spectra can be repeated from the different samples under the same experimental conditions, showing good reproducibility.

For the fabrication of the FET device, the source and drain electrodes were defined by photolithography and thermal metal deposition of Cr/Au (5 nm/100 nm), and RGO was used as the channel material between the source and drain electrodes. The electronic property was measured by a Keithley 4200 semiconductor characterisation system in air.

Results: After N^+ ion irradiation, the sample was measured by Raman spectroscopy, together with that without irradiation as a control. Curves (i) and (ii) in Fig. 1 show the Raman spectra of the representative graphene samples of RGO and doped RGO, respectively. The D and G bands of the Raman spectra of RGO and doped RGO are broad, and the spectra exhibit weak 2D peaks owing to the existence of many defects and oxygen functional groups on the surface of the sample. The D peak of the doped RGO shows an upshift of 15 cm^{-1} relative to that of RGO, which is consistent with the upshift of the D band observed in nitrogen-doped carbon nanotubes synthesised by the CVD method [6]. The ratios of intensities of the D and G band show an obvious difference between RGO ($I_D/I_G > 1$) and the doped RGO ($I_D/I_G < 1$). The D band intensity of the doped RGO is more prominent than that of RGO, in agreement with the result induced by doping [7]. For futher understanding of the effects of N^+ ion irradiation on the RGO, we performed the FTIR measurement, and curves (i) and (ii) represent the spectra of RGO and doped RGO, as shown in Fig. 2. As can be seen, the peaks located at 1380 and 1085 cm^{-1} are more prominent after doping. Also, curve (ii) has an additional peak located at around 810 cm^{-1} compared to that of curve (i), owing to the existence of the N-H bend (oop). This difference is attributed to the breaking of the bonds of functional groups of GO, for example, H-O-H, C-OH, C-H, and the formation of a new functional group, such as N-H, on the surface of the RGO after ion irradiation [8].

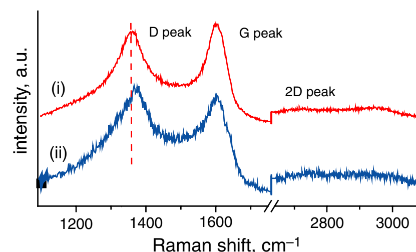

Fig. 1 *Raman spectra of RGO and doped RGO*
(i) RGO
(ii) Doped RGO

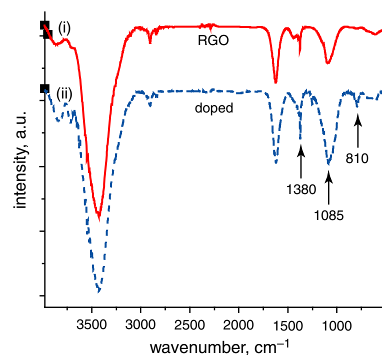

Fig. 2 *FTIR of RGO and doped RGO*
(i) RGO
(ii) Doped RGO

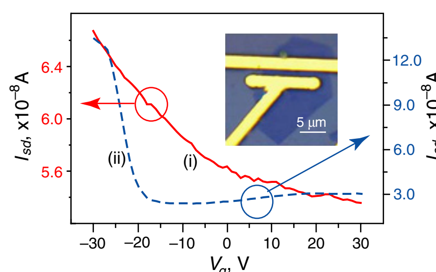

Fig. 3 *$I_{sd} - V_g$ curves of GFET and doped GFET at 1×10^{14} cm^{-2} flux of irradiation*
(i) GFET
(ii) Doped GFET
Inset: Representational optical image of FET

To investigate the effect of doping on the electronic properties, we fabricated FET devices, and the optical image of the devices is shown in the inset of Fig. 3. The source-drain current and back-gate voltage ($I_{sd} - V_g$) curve of the GFET is labelled as curve (i) in Fig. 3. As shown by this curve, the carrier type is hole, and the ambipolar property does not appear. The threshold voltage of the GFET is more than 30 V owing to the existence of oxygen functional groups and the physisorbed molecular oxygen. The threshold voltage of the FET locates at around −20 V (curve (ii), dashed) after doping at the 1×10^{14} cm^{-2} flux of irradiation. The downshift of the threshold voltage indicates the electron doping effect of the channel [2], consistent with the above Raman spectroscopy and FTIR results. And the $I_{sd} - V_g$ curve also shows a unipolar property of the FET, similar to that of conventional CMOS. It should be noted that the current was enhanced after N^+ ion irradiation, and the

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electronic properties of the device were not degraded. All the measurements of the electronic properties were performed at a source-drain voltage of 0.03 V.

Conclusion: We have demonstrated a method of controllable doping by ion irradiation in RGO, which can finely tune the threshold voltage of the GFET from more than 30 V to about −20 V. The simple and scalable method is compatible with the current CMOS technique.

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