Ternary Graphene Field Effect Transistors using Chemically doped Graphene

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Abstract

Chemically doped graphene is used to demonstrate a ternary graphene field effect transistor. Graphene pn junction formed by polymer doping process could be sustained after a dielectric passivation and a thermal annealing to stabilize the interface. Double peaks in I-V curve originated from two different doping states of graphene channel, three current levels were observed and middle current level was able to control with polymer concentration and the channel length ratio of chemically doped graphene and pristine graphene.

1. Introduction

As the number of devices in integrated circuit increases thanks to high scalability, the power consumption question become critical. Multi-valued logic (MVL) can save energy because it simplifies the circuits and reduces the number of interconnects. MVL devices such as carbon nanotube FETs (CNTFETs), single electron transistors, quantum dot FETs, and resonant tunneling transistors [1-4] are widely studied since more than five decades, but most of these devices are too complex to fabricate or only work in cryogenic temperature. Even in the case of the most actively studied device, CNTFETs, the most researches are based only on theoretical simulation. Therefore, alternative and more realistic devices are needed. Recently, ternary GFET was demonstrated by introducing a metal strip at the middle of the graphene channel. The authors also controlled the position of medium current state by choosing the work function of metal strip [5]. However, the doping seems difficult to control because the interface metal-strip/graphene is too sensitive to this type of doping.

In this work, another concept of ternary GFET is suggested by using chemical doping effect of graphene. This device shows that current level, especially that of the middle state became more easily controllable by different types and different concentrations of dopants.

2. Experiments

CVD grown single-layer graphene was transferred on 90 nm SiO₂/highly p-doped silicon substrate through the PMMA mediated transfer method. Graphene channel was patterned by O₂ plasma and Au (30nm) hard mask was used to prevent graphene damage during the etching process. 100nm Au source and drain electrodes were patterned using photolithography and wet etching process. The graphene channel width and length were defined as 30 μ m and 9 μ m.

Graphene dopants, which are ethanol based solutions, were prepared using poly-acrylic acid (PAA) and poly-ethylenimine (PEI) with concentrations ranging from 0.002 wt% to 0.2 wt%. Simultaneously fabricated GFETs were immersed in the dopant solutions during 3 hours. Residual polymers on graphene were rinsed using ethanol while chemical dopants remained with less than 1 nm in thickness. Fig. 1(a) shows graphene band diagram for different types of dopants. Experimental work functions of chemically doped graphene on Cu foil were measured using ultraviolet photoemission spectroscopy (UPS), Fig. 1(b). Due to its amine group PEI has enough electrons that could be transferred to graphene. In contrast, electrons attraction is expected in PAA due to the carboxyl groups electronegativity. Consequently, increasing the concentration of PEI results in lowering the work function of graphene and upward shifting of its Fermi level. While PAA leads to opposite result.



Fig. 1 (a) Band diagram of doped graphene. (b) Work function of chemically doped graphene were measured using UPS system.

In order to improve the stability of the chemically-doped GFETs, dielectric passivation layer was deposited using atomic layer deposition (ALD) at different temperatures; 50, 100, 130 and 150 °C. Trimethylaluminum (TMA) was used as precursor for the ALD process. H₂O source was used as oxidant. The TMA pulse/N₂ purge/H₂O pulse/N₂ purge cycle was repeated 300 times. Finally, the devices were annealed under vacuum (~ 10⁻⁶ torr) during 1 hour at different temperatures; 100, 150, 200 and 300 °C. Keithley 4200 Parameter analyzer was used for electrical measurements.

3. Results and Discussion

Typically, the electrical performance of polymer doped graphene is easily degraded due to polymer reaction with oxygen and water molecules in air. To improve the device stability and reduce the hole doping effect in air, passivation layer using ALD Al₂O₃ was deposited on GFETs and devices were thermally annealed in vacuum. However, ALD deposition temperature and annealing temperature should be optimized due to glass transition temperature of the polymer (PEI : 217 °C, PAA : 106 °C). Fig. 2 shows the change for the position of Dirac voltage and the value of hysteresis after Al₂O₃ deposition and thermal vacuum annealing process with different temperature.



Fig. 2 Dirac-point voltage (a) and hysteresis window (b) of undoped, PEI 0.2 wt% and PAA 0.002 wt% doped GFETs for different Al₂O₃ deposition temperatures and (c-d) vacuum-annealing temperature performed after Al₂O₃ deposition at 130 °C.

The results shown in Fig.2 show that ambient hole doping, due to oxygen and water molecules available in air, can be minimized by Al₂O₃ deposition at 130 °C and thermally annealed at 300 °C. Note that higher temperatures have showed different tendency. Indeed, when Al₂O₃ is deposited at 150 °C, the Dirac-point shifts to high voltages in undoped and PEI doped GFETs, while it moves toward zero in PAA doped GFET. This means that the performed chemical doping is deteriorated during Al₂O₃ deposition. In conclusion the best results are obtained for the ALD process temperature of 130 °C. After passivation, GFETs were annealed at various temperatures, Fig. 2(c) and (d). When the annealing temperature increases Dirac-point voltage and hysteresis-window of all devices decrease. Let's also add that the Dirac voltage as well as the hysteresis window tend to zero in undoped GFET at 300 °C. This indicates that temperatures, of 130 °C for ALD and 300 °C for annealing, allow to analyze the doping effect excluding any eventual additional contribution.

Air stability was analyzed for chemically doped GFETs with different types and concentrations of polymer. Fig. 3(a) shows the I_d - V_g characteristics of the different devices considered here. Dirac voltage difference between chemically doped and undoped GFETs are maintained for every doping type and concentrations over at least 200 hours as shown in Fig. 3(b).



Fig. 3 (a) I_d-V_g curves of chemically doped GFETs with PEI or PAA. Black line shows the curve of pristine GFET. (b) Dirac voltage difference between undoped and chemically doped GFETs (V_D = 0.1 V, L_{channel}×W_{channel} = 9×30 μ m²). Doping effects were maintained up to 200 hrs.



Fig. 4 (a) 3-D schematic view of the device studied in this work and the corresponding electrical model. (b): Simulated I_d – V_d curves of ternary GFET for different dopants and concentrations, and the ratio of (c) PAA or (d) PEI doped graphene channel length.

As shown in Fig. 4(a), the gradual doping of graphene can lead to three current states. Therefore, this device can be modeled by two GFETs, doped and undoped, in series. Ternary GFETs were simulated based on the experimental results of I_d - V_g characteristics. Fig. 4(b) shows the ternary characteristics (I₀: Off, I₁: Middle, I₂: On) for GFET as a function of the dopant and its concentration when the length of chemically doped-channel and undoped graphene are 3 µm and 6 µm, respectively. In the ternary logic, the current level of the middle state is very important and needed in circuit configuration. Our results show the current level of the middle state, I₁ in Fig.4 (c-d), can be precisely controlled by changing the ratio of doping channel length.

3. Conclusions

A new structure of ternary GFET was demonstrated by using chemical doping of graphene. Passivation and annealing temperatures were optimized. The effect of different types of dopants with different concentrations on graphene Fermi level was investigated. Simulation results, performed considering a series connection of doped and undoped GFETs, are in good agreement with the experimental results.

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