Resistive switching device based on high-mobility graphene and its switching mechanism

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Abstract: Graphene is a promising material for fast memory device, due to its high mobility and potential for ultrasmall linewidth. However, the high mobility are normally obtained with strict limitations, such as Boron nitride substrate and capping layer, or low temperature with mechanical exfoliation. In this paper, we modified the fabrication process of graphene device, and high carrier mobility larger than 10,000 cm²/(Vs) was obtained for graphene grown by chemical vapor deposition. Resistive switching devices based on these high mobility graphene were fabricated, and the conducting mechanism of the switching process were discussed in detail. A model based on a Schottky diode in series connection with a tunneling junction is found to be consistent with the conducting mechanism. Our results are useful for normal research groups with only traditional nanofabrication facility.

1. Introduction
Graphene is a revolutionary two-dimensional material for transistors[1], photodetectors[2] and memory devices[3], due to its high carrier mobility and other special properties. In the original paper of Geim et al. in 2004, the mobility of graphene at room temperature is as high as 15,000 cm²/(Vs)[4], but with exfoliated graphene, which is hard to be used in real application. With chemical vapor deposition (CVD), the original paper of Li et al. in 2009 reported room temperature mobility of 4050 cm²/(Vs)[5]. Recent years, mobility of CVD-grown graphene have been largely improved. Banszerus et al. in 2015 reported high mobility of 50,000 cm²/(Vs) at room temperature for CVD-grown graphene, while mobility as large as 300,000 cm²/(Vs) was observed at ultralow temperature[6]. However, these high mobility device are always fabricated on Boron nitride (BN) substrate and with BN capping layer, so these process are always not available in normal laboratory. Based on CVD-grown graphene and normal silicon/oxide substrate, reported high mobility are usually under 10,000 cm²/(Vs)[7].

Resistive switching is promising for new-generation memory application, due to its nonvolatility, rapid speed and potential for used as memristor[8,9]. Using graphene as resistive switching electrode, resistive device with ultralow switching power of 3 μW have been reported[10], and based on the graphene-oxide heterojunction, resistive devices with self-rectifying effect have been observed[11], which could potentially reduce the circuit area in large scale. However, limited by graphene device process, the high mobility characteristics of graphene have not been adopted in these devices.

In this paper, modified lift-off and patterning process of graphene were used to fabricate resistive switching devices. Based on double-layer lift-off process and solution-assisted patterning process, the mobility of graphene transistor is as high as 18,000 cm²/(Vs), and after resistive switching device fabrication, the mobility is still higher than 10,000 cm²/(Vs). Conducting mechanism of the switching process were discussed in detail. Fowler-Nordheim tunneling and Schottky emission are both in
charge of the high resistance conducting process.

2. Experiments and Results

Single-layer graphene was synthesized by conventional CVD method at 1050°C. The graphene transferring process was a traditional wet process. Firstly, a thin layer PMMA was coated on graphene/Cu and baked at 120°C for 10 min. Then the PMMA/graphene/Cu sample was floated on HCl/H₂O₂/H₂O (volume ratio=2:1:40) solution to etch the copper foil. When the copper foil was completely etched, the PMMA/graphene sample was transferred into deionized (DI) water to rinse for 3 times. Then, PMMA/graphene sample was collected on 300 nm SiO₂/Si substrate and baked at 140°C for 30 min. Finally, the sample was immersed in acetone for 1 hour to clear the PMMA. For electrodes patterning, 5 nm Cr and 40 nm Au were deposited through double-layer photoresist technology with LOR depositing by spin coater as the first layer, and then S1805 as the second layer. Lift-off process based on this double-layer lithography is critical for graphene device with high mobility. To pattern the graphene, we introducing an interlayer in the lithography process to obtain cleaner graphene surface. Firstly, a thin PMMA layer was coated on the graphene, after which a normal photoresist (AZ3100) coating were performed atop the PMMA layer, and baked at 150°C for 10 min. Secondly, photoresists were patterned through photolithography while the PMMA interlayer left unpatterned. Thirdly, the PMMA interlayer and graphene were etched by RIE. Finally, the top photoresists were removed by immersing the sample in NaOH solution (3wt% NaOH in deionized water) for 2 min and rinsing for several times by DI water, and then the interlayer PMMA were removed by acetone solution. For mobility improvement, the process was generally the same as above, except the graphene transfer process. After the copper remove step and before the graphene were transferred onto the silicon substrate, the graphene layer were soaked in the ammonia solution for 30 minutes, and then cleaned by DI water.

As shown in figure 1, the double-layer lift-off process is important for good contact quality between graphene and metal electrode, while the PMMA capping layer and NaOH solution process is of critical importance for the clean surface of graphene device. The mobility calculation were resulted from non-linear fitting based on Kim’s method [12]. From data in figure 1 (d), the hole mobility is 18,530 cm²/(Vs), while the electron mobility is 10,130 cm²/(Vs).

For resistive switching device, we first fabricated normal switching device with both electrodes using metal. After 100 nm Au deposition by thermal evaporation, 10 nm HfO₂ film were deposited by atomic layer deposition, then top electrode were formed also by thermal evaporation with 50 nm thickness, while the electrode pattern were formed by a hard mask.

Figure 1. (a) Fabrication process of graphene transistor. (b) High alignment ability of our lithography equipment. (c) Photo of graphene transistor device. (d) Transfer curve of graphene transistor (Device size is 100 μm*10μm).
As shown in figure 2, metal device fabricated in our lab demonstrated general resistive switching characteristics curves, while special multi-resistance properties were obtained.

Graphene-based resistive device are fabricated on graphene transistors with similar process as normal metal devices. As graphene is a two dimension material without dangling bond on surface, so atomic layer deposition of dielectric film on graphene is not an easy work. To initiate the deposition process, we illuminated the graphene film with UV lamp before atomic layer deposition. The top electrodes were also Ti for oxygen vacancy.

As shown in figure 3, the carrier mobility of graphene remain high after the switching device fabrication process. Based on data from figure 3 (b), the hole mobility is 13,100 cm²/(Vs) and electron mobility is 5425 cm²/(Vs), which is still high for graphene devices on silicon substrate. To facilitate the electrical measurements, we design the top electrode with crossbar structure as shown in figure 3(c). Normal resistive switching curve are obtained, and an initiation process (forming) is needed before the switching cycles.

3. Discussion
The switching mechanism of similar non-symmetrical MIM structure with TiO₂ was proposed to be the shunting of the interface Schottky Barrier by a memristor, with which the low resistance state (LRS) current dominated by the memristor and the high resistance state (HRS) current dominated by
the rectifying Schottky Barrier of top interface\cite{13-15}. While the LRS of our experiments show similar symmetrical I-V curve, the HRS current obviously deviated from rectifying conduction, so the switching mechanism here should be different. As shown in figure 4, the Schottky-emission (SE) plot fit very well with the current under negative (reverse) bias of both planar device and crossbar. Furthermore, from the slope of SE fit, the reflectivity of the switching layer HfO$_2$ are 2.1 and 2.5 respectively, highly consistent with our Spectroscopy Ellipsometry result of 2.1 from film sample on silicon substrate. The difference of the reflectivity of crossbar result should be due to the slight deviation of physical model with the tiny contact area. However, although the negative current can be fit well by SE plot, the current at positive bias cannot be fit appropriately by normal conduction mechanisms, including semi-log, space-charge-limited current (double-log), Schottky emission, Frenkel-Poole emission and Fowler-Nordheim conduction\cite{16}.

As shown in figure 2(c) and 3(d), the LRS current of metal device and graphene device show similar symmetrical conduction with a barrier at low bias. Symmetrical current with a low-bias barrier could be induced by two identical head-to-head Schottky barriers or just one tunneling barrier. The non-symmetrical device structure we adopted formed an ohmic contact at the bottom interface, and the transformation between different low-bias need the two Schottky barriers to change identically when switching, which is obviously hard to achieve, so the model of two identical Schottky barriers cannot be satisfied. However, the tunneling barrier conduction is symmetrical in low bias irrespective of the symmetry of metal work-function of two electrodes, and the resistance of barrier will decreased with increased bias, which is also consistent with our result.

With the considerations above, we propose here that the switching mechanism could be explained by a parallel connection of a Schottky barrier and a tunneling barrier as shown in figure 5(a). The switching between LRS and HRS is obtained by broadening and reduction of barrier width, which is actually the break and recovery of the conduction filament. In LRS, the tunneling barrier width is small so the resistance of Schottky barrier is much larger than the tunneling barrier, and the current dominated by the tunneling barrier. The transformation between different barrier resistances at low bias of several LRS cycles now could be explained by the fluctuation of barrier width when switching from HRS to LRS. The complete ohmic conduction mean the barrier width became zero and the conduction filament is thoroughly getting through. In HRS, the tunneling barrier is widened, and the resistance of the Schottky barrier now is comparable to the tunneling one. Under negative bias, the Schottky barrier is reverse-biased, so the image-force lowering of barrier height made the conductance of Schottky barrier much larger than tunneling barrier, and the current dominated by the former one. However, at positive bias, the rectifying current provided by forward-biased Schottky barrier is much smaller than reverse-biased current dominated by the image-force lowering, so the current at positive bias is then controlled by the tunneling barrier alone or the combination of two barriers. For the symmetrical HRS observed in planar device, the tunneling barrier width is not so wide that still larger than in LRS but much smaller than the non-symmetrical HRS, so the resistance of it is again smaller than the Schottky barrier and current was dominated by the tunneling barrier, and then symmetrical conduction could be obtained. According to our model, the switching behavior should occur at the area under the control of Schottky barrier since the negative current in HRS cannot be dominated by Schottky barrier if the tunneling barrier width exceed the Schottky barrier, so the resistive switching in our experiments here should be interface-dominated not bulk-limited. It should be mentioned here that in this model, the tunneling barrier should not necessary be symmetrical since the tunneling current is independent of polarity in low bias.
Figure 4. Schottky-emission plots of HRS current of metal device (a) and graphene device (b). The electrical field is simply supposed to be linear with the bias voltage.

Figure 5. Models of switching mechanisms. (a) Parallel connection of a Schottky barrier and a tunneling barrier. (b)-(d) Non-symmetrical MIM model at different bias.

4. Conclusion
In conclusion, we modified the microfabrication process of graphene transistor device with double-layer lift-off metal electrodes and solution-assisted graphene patterning. These two modification are of critical importance for the high-quality metal-graphene contact and polymer-free graphene surface. High mobility have been obtained for CVD-grown graphene, and relatively high mobility remained after switching device fabrication. The conducting mechanism of graphene-based resistive switching device are discussed in detail, and the Schottky emission and Fowler-Nordheim tunneling are found to be fitted with experiment data. Our results are of high interests for graphene-based research groups with normal fabrication process ability.

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