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Influence on graphene doping characteristic by developer

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In this paper, one contrast experiment is reported. Two identical back-gate graphene transistors samples are fabricated. One is washed by developer for 3 minutes and washed by deionized water for 10 seconds. The other is washed only by water for 10 seconds. For the first sample, the Dirac point voltage of a graphene transistor decrease 35 V, while that of a graphene transistor in the second sample increase more than 17 V. This phenomenon indicates that developer can decrease P-doping of graphene, and reasons have been analyzed. While the first sample is exposed in atmosphere for a week, Dirac point voltages are still less than those before washed. This result shows that the influence of developer has not disappeared.

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Keywords: Graphene, Doping, Developer

1. Introduction

Graphene, a single atom thick hexagonal lattice carbon material, has attracted much attention in recent years due to its excellent physical and electrical characteristics, such as high hardness, high transmittance, high thermal conductivity, high carrier mobility, etc. [1-5]. However, two-dimensional structure makes it sensitive to environment. The relation between graphene and external condition has been researched [6-9]. Many researchers reported that graphene could become P-doping as it absorbed oxygen and water when it exposed in atmosphere [10-12]. So, it is easy for graphene to become P-doping, and many researchers devoted themselves to decrease P-doping and increase N-doping.

The remarkable feature of P-doping and N-doping is that Dirac point voltage of transfer characteristics of graphene field-effect transistors (GFETs) is greater and less than zero voltage respectively. Tingting Feng et al changed Dirac point voltage from greater than zero to closed to zero by depositing Al film on graphene [7]. Beidou Guo et al obtained N-doped graphene by NH_3 annealing after N+-ion irradiation of graphene samples [13]. Byung Hoon Kim et al reported N-type graphene induced by dissociative H_2 adsorption at room temperature [14]. Yung-Chang Lin et al showed that Controllable graphene N-doping by means of NH_3 plasma exposure [15]. In this paper, we find that developer could make Dirac point voltages of GFETs decrease, and this trend could maintain for one week.

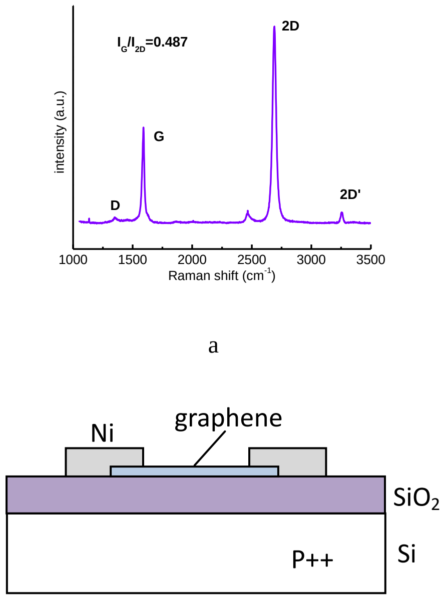
2. Experimental details

Graphene was grown on Cu foil by chemical vapor deposition, and transferred on the SiO_2(300 nm)/Si substrate. This process was same as Ref. [16]. Raman spectrum of the graphene is in Fig. 1a. The Si substrate was heavy P-doping, and its resistivity was less than 0.05 Ωcm. After transferring on the substrate, graphene became to channel shape by oxygen plasma etch. Then 40 nm metal Ni was deposited by electron beam evaporation and lifted off, and source and drain electrodes are fabricated. Schematic diagram of a GFET is in Fig. 1b. Two samples were fabricated by the above process. After fabricating, the samples were tested by Agilent Semiconductor parameter analyzer under atmosphere conditions. The temperature is 21 ℃, and the humidity is 40%. After testing, the first sample was washed by RZX-3038 developer for 3 minutes, and washed by deionized water for 10 seconds. Thetetramethylammonium hydroxide (TMAOH) concentration of the RZX-3038 developer was 2.38％. As to the second sample, it was only washed by deionized water for 10 seconds. After washing, the two samples were baked in 120 ℃ for 5 minutes and also tested in room temperature and atmosphere. The test condition was that the drain voltage was 1 V, and gate voltage was swept from 0 V to 40 V.

3. Results and discussion

Fig. 1a shows Raman spectrum of the graphene.

From the spectrum, Raman shift of D, G and 2D peak are 1347cm^{-1}, 1591cm^{-1}, and 2690cm^{-1} respectively. D peak is very weak. Full width of maximum height(FWMH) of G and 2D are 22.2cm^{-1} and 35.8cm^{-1} respectively. The intensity ratio of G to 2D peak (I_G/I_{2D}) is 0.487. These situations indicate that graphene is single atomic thick and with high quality. Fig. 1b shows schematic diagram of a GFET. From the Fig. 1b, we could see that the GFET is global back gate structure.



a

b

Fig. 1. The raman spectrogram of graphene and schematic diagram of a GFET. a. The raman spectrogram of graphene b. schematic diagram of a GFET

Fig. 2a and b show the transfer characteristics of a GFET in the first sample before and after developer/water washed respectively. The length and width of its channel are 8μm and 30μm respectively, and they are same to the GFET in Fig. 2c and d. It can be seen that Dirac point voltage changes from 71 V to 36 V after washing by developer and deionized water. Fig. 2c and d show the transfer characteristics of a GFET in the second sample before and after water washed. Dirac point voltage changes from 83 V to greater than 100 V. In short, Dirac point voltage decreases 35 V in the first sample, but increases large than 17 V in the second sample. This phenomenon indicates that the P type impurities of graphene are decrease in the first sample and increased in the second sample. The fabrication process of the two samples is identical. In washing process, the difference in the two samples is that the first sample was washed for 3 minutes by developer and the second one was not. Therefore, the decrease of P-doping is depended on developer. In Fig. 2c and d, water increases P-doping of the second sample, and this phenomenon is similar to some reports [11, 17, 18]. The first sample was also washed by water, but the test result shows that P-doping decreased. From this reason, P-doping decrease from developer is more than the test result.

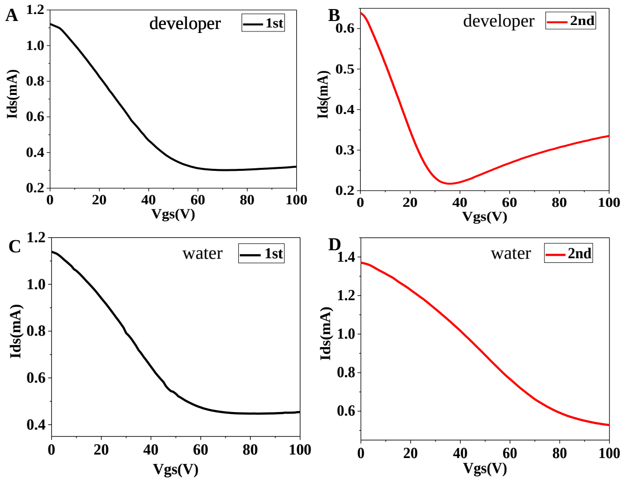
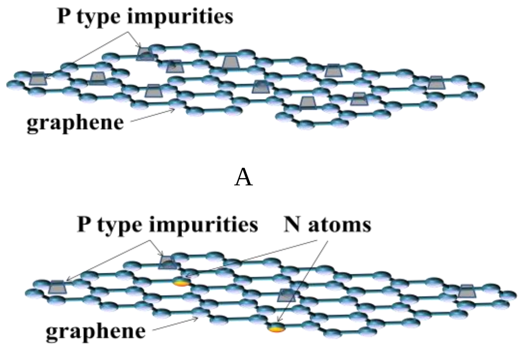


Fig. 2. The transfer characteristics of a GFET in the first and second sample. Fig. 2a and b, the transfer characteristics of a GFET in the first sample before and after washed. Fig2.c and d, the transfer characteristics of aGFET in the second sample before and after washed

As to the reason of the reduced P type impurities, the developer contains TMAOH. The molecular formula of TMAOH is C4H13NO, and it is weakly alkaline. The C4H13NO is easy to release electrons, and it includes nitrogen. We think that two factors decrease P doping in graphene. One is that some holes are filled by electrons that are from C4H13NO. The other is the formation of carbon-nitrogen bonds at the margins and defects of graphene. The schematic diagram is shown in Fig. 3.



A

B

Fig. 3. Graphene before and after washing by developer and deionized water. A. Before washing. B. After washing

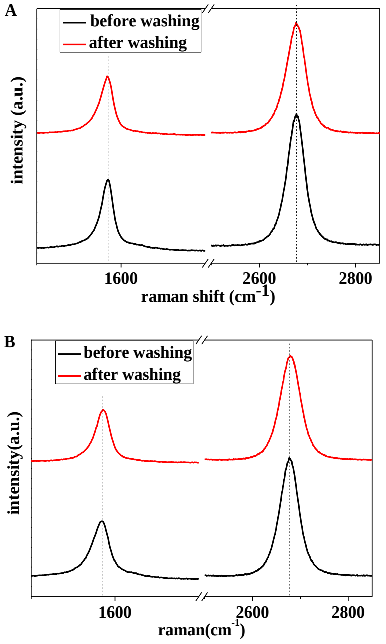


Fig. 4. The Raman spectra before and after washing. A. The Raman spectra before and after developer and deionized water washing. B. The Raman spectra before and after deionized water washing

Besides, the Raman spectra have been performed before and after washing by developer and deionized water, and only deionized water. The results are shown in Fig. 4A and 4B respectively. We can see that the G and 2D peaks left shift, the I_G/I_{2D} decreases slightly, and FWHM of the G peak increases in Fig. 4A. According to Ref. [18], these illustrate that P type impurities in graphene are reduced. The tendency in Fig. 4B is in contrast with the above, and the P type impurities increase.

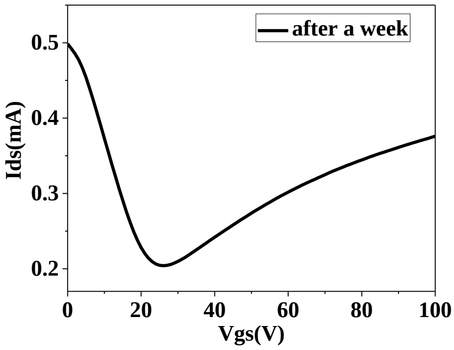


Fig. 5. The transfer characteristics of the GFET in the first sample one week after washed

After washing and testing, the first sample was exposed in atmosphere for one week. Then another electrical test was performed. The transfer characteristic of the GFET is shown in Fig. 5. We could see that the Dirac point voltage is 26 V. It is less than both 71 V before washed and 36 V after washed. The results indicated P-doping has not increased while the sample was exposed in atmosphere. The influence of developer has not disappeared. Five transistors in the first sample have been tested for the three times. The results are shown in Table 1. Channel widths of GFETs are all 30 μm, and lengths are 6 μm, 8 μm and 30 μm. The results show that both the second and third Dirac point voltages are less than the first ones for all GFETs. But for the third ones and the second ones, some results show that the former is greater than the latter, others show opposites. These results showed in Table 1 indicate that it is not occasional for developer to decrease P-doping of graphene. After a week, the P-doping of graphene is less than those before developer washed. In the week while the first sample were exposed in atmosphere, more holes are filled or more C-N bonds were formed in graphene, and some oxygen and water were absorbed on surface of graphene. If the former plays a major role, the Dirac point voltage decrease; if the latter does, the contrary is the case.

Table 1. The Dirac point voltages of five GFETs in the first sample for the three tests

developer and water washed	No.1	No.2	No.3	No.4	No.5
Channel length(μm)	30	30	8	6	6
The 1st Dirac point voltage(V)	>100	83	71	90	>100
The 2nd Dirac point voltage(V)	53	35	36	37	45
The 3rd Dirac point voltage(V)	57	41	26	25	35

Table 2. The Dirac point voltages of five GFETs in the second sample for the two tests

Water washed	No.1	No.2	No.3	No.4	No.5
Channel length(μm)	30	30	10	10	8
The 1st Dirac point voltage(V)	>100	92	93	75	78
The 2nd Dirac point voltage(V)	>100	>100	>100	87	>100

Table 2 shows transfer characteristics of five GFETs in the second sample for the two tests. Channel widths are all 30 µm, and lengths are 8 µm, 10 µm and 30 µm. The results indicate that four Dirac point voltages increase, and the other Dirac point voltage has been not manifested. As for the Dirac point voltage which could not show, from the transfer characteristic trend, we could see those Dirac point voltage is slightly larger than 100V before water wash, and much larger than 100 V after water wash. Water could increase graphene P-doping, and this result agrees with Ref. [11, 17, 18].

4. Conclusion

In summary, Dirac point voltages of GFETs have decreased while GFETs was washed by RZX-3038 developer for 3 minutes and washed by deionized water for 10 seconds. However, Dirac point voltages have increased while GFETs was washed only by deionized water for 10 seconds. The above phenomenon indicates that developer can decrease P-doping of graphene. Two factors have been analyzed. Electrons are transported from TMAOH to graphene. The other is that some C-N bonds are formed in some defects and edges of graphene. In addition, after one week, Dirac point voltages of GFETs are less than those before developer and water washed. This phenomenon indicates that influence of developer has not disappeared. The above results offer a potential method for graphene doping, graphene washing, and graphene circuits fabricating.

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