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2013 Nanotechnology 24 195202
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Identifying the mechanisms of p-to-n conversion in unipolar graphene field-effect transistors

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Received 8 January 2013, in final form 8 March 2013
Published 12 April 2013
Online at stacks.iop.org/Nano/24/195202

Abstract
The mechanisms of p-to-n conversion and vice versa in unipolar graphene field-effect transistors (GFETs) were systematically studied using Raman spectroscopy. Unipolar p-type GFETs are achieved by decorating the graphene surface with a thin layer of titanium (Ti) film, resulting in a Raman D peak. The D peak is observed to recover by annealing the GFET in nitrogen ambient followed by silicon nitride (Si₃N₄) deposition, suggesting that the Ti adatoms are being partially removed. Furthermore, unipolar n-type GFETs are obtained after the passivation on p-type GFETs. The threshold voltage of the n-type GFET is dependent on the thickness of the Si₃N₄ layer, which increases as the thickness decreases. A comparison between the Si₃N₄ and SiO₂ passivation layers shows that SiO₂ passivation does not convert the GFET into n-type graphene, which identifies the significance of ammonia (NH₃) for the formation of the n-type GFETs. This study provides an insight into the mechanism of controlling the conduction behavior of unipolar GFETs.

Online supplementary data available from stacks.iop.org/Nano/24/195202/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

High carrier mobility and large transconductance in graphene field-effect transistors (GFETs) are the key features of interest for nanoelectronics applications [1, 23]. Being a zero bandgap semiconductor, pristine graphene always shows ambipolar conduction [19, 20], which is not favorable for most digital electronics applications [2]. For instance, the minimum current point (Dirac point) only appears at a single gate voltage (threshold voltage in a transfer curve), below or above which the channel current will increase significantly, resulting in a poor stability of the digital OFF state of the device. Therefore, it is crucial to achieve unipolar conduction where both ON and OFF states are well defined [25].

Electrostatic doping of graphene can be easily implemented using the gate voltage to shift the Fermi level away from the Dirac point and tune the threshold voltage. However, this method is unable to remove the ambipolar traits of GFETs [27]. Graphene can be substitutionally doped during CVD growth with boron or nitrogen to display unipolar p- and n-type conduction respectively [4, 17, 21, 26]. However, in both chemical doping scenarios, the graphene needs to undergo high temperature processing and localized doping of graphene is not possible. Furthermore, the defects in graphene drastically reduce mobility using such a chemical doping approach [21, 24]. A new controllable approach of converting GFET from ambipolar to unipolar is thus required.

More recently, Yan et al successfully suppressed the hole conduction in a GFET to produce n-type conduction using a film of poly(ethylenimine) [28]. It is believed that
the suppression of the hole conduction is due to doping induced by the polyfilm. Romero et al demonstrated that unipolar n-type can be achieved by exposing GFET in NH₃ ambient but the GFET loses the n-type characteristics after a few hours [13]. Recently, we have successfully demonstrated unipolar p- and n-type GFETs at ambient conditions using CMOS compatible approaches. Unipolar p-type conduction can be achieved using titanium (Ti) decoration, where the Ti adatoms on graphene serve as hole dopants. Unipolar n-type conduction can also be realized through an annealing process followed by coating of a silicon nitride (Si₃N₄) dielectric film on unipolar p-type GFETs [14]. Nevertheless, the mechanism of the p-to-n conversion using Si₃N₄ on graphene remains ambiguous.

In this work, the successive modulation of graphene conduction among p-type, ambipolar and n-type is detailed. The function of the Si₃N₄ passivation was deduced using Raman spectroscopy. We proposed that the annealing process in nitrogen desorbed the water molecules and oxygen (p-dopants) from graphene, while the graphene was further n-doped by the NH₃ molecules that are one type of reaction gas for Si₃N₄ formation. Unlike substitutional doping of nitrogen atoms, our doping process does not induce a large D peak in the Raman spectra. The function of the Si₃N₄ passivation was solely to isolate graphene from the surrounding environment. The influence of the Si₃N₄ passivation thickness on the threshold voltage was studied and a comparison between the Si₃N₄ barrier layer and SiO₂ barrier layer was made. Our CMOS compatible fabrication process serves as an alternative method for obtaining unipolar GFETs with a low level of defects.

2. Experimental section

The graphene flake was prepared by mechanically exfoliating graphite and was subsequently transferred onto the SiO₂ substrate (285 nm) [20]. Both optical microscope and Raman microscopy were used to locate and confirm the presence of the monolayer graphene flake on the substrate. Then, 10 nm Ti metal was deposited onto the entire surface to protect the graphene from further process contamination [14]. Subsequently, the contact electrodes were fabricated by standard lithography and lift-off processes. The electrodes were composed of 20 nm Au on top of the 10 nm of Ti. The Ti metal above the graphene channel was etched away using hydrofluoric (HF) solution, as reported in our previous work [14]. Electrical and Raman characteristics of the GFET were extracted at this point, which is referred to as step 1. In step 2, the same GFET was then annealing in nitrogen ambient at 200 °C for one hour, cooled to 100 °C followed by 500 nm-thick Si₃N₄ coating with silane and ammonia as the reaction gases. The gas flow rates of silane and ammonia were 100 sccm and 20 sccm respectively.

This GFET was left in the room ambient for a period of three weeks and the GFET characteristics was measured again (step 3). Lastly in step 4, the GFET was immersed into HF solution to remove the Si₃N₄ layer. At various steps, Raman spectra were acquired using WITec Raman microscopy equipped with a 532 nm laser. The spot size of the laser beam was about 1 μm in diameter using a 100× objective lens. A grating of 1800 line mm⁻¹ was used to provide a spectral resolution of <1 cm⁻¹ [16]. The entire Raman spectra are normalized to a Si peak and the electrical measurements are carried out at room temperature in ambient conditions.

3. Results and discussions

3.1. Conduction modulation of GFETs

The GFETs were characterized at each step of the process (step 1: as-prepared p-type GFET, step 2: GFET after deposition of the Si₃N₄ passivation as shown in figure 1(a), step 3: GFET with the Si₃N₄ passivation after three weeks, step 4: GFET after the removal of the Si₃N₄ passivation) and the transfer characteristics of a typical device are illustrated in figure 1(b). A notable change of the threshold voltage and hole/electron mobility can be observed at various steps in the device fabrication. The threshold voltage of the as-fabricated GFET is positive (+60 V in step 1), and then changes to negative (−76 V in step 2). Subsequently in step 3, the threshold voltage becomes less negative and then positive again when the Si₃N₄ layer is finally removed in step 4. The shapes of the transfer curves in step 1 and step 4 are similar with a shift in threshold voltage, which indicates that the GFET after removal of the Si₃N₄ layer restores the p-type GFET characteristics. The hole and electron mobilities can be extracted using the following formula, $\mu_{\text{GFET}} = (1/V_{\text{DS}}) \times (g_m/C_{\text{BG}}) \times (L/W)$, where $C_{\text{BG}}$ is the unit area back gate capacitance and $W/L$ is the aspect ratio of the GFET [16]. Given $V_{\text{DS}} = 100$ mV, $C_{\text{BG}} = 11.5$ nF cm⁻², the maximum field-effect mobility of the featured GFET is tabulated in figure 1(c).

During step 1, the GFET displayed p-type behavior due to the Ti layer serving as the hole dopant [14], as well as adsorption of oxygen and water molecules from air ambient [13]. The use of Ti is also necessary to prevent possible contaminations from the lithography process while defining the source/drain electrodes. In step 2, the negative threshold voltage as well as the increased electron conduction in the positive gate bias region in step 2 indicate that the unipolar p-type GFET had been successfully converted into a unipolar n-type GFET [28]. The change of GFET to n-type conduction is partially due to the removal of the oxygen/water molecules (p-type dopants) [20]. Romero et al reported that graphene on SiO₂ substrate possesses an n-type behavior GFET due to the surface states of SiO₂ donating electrons to the graphene. However, the GFETs have to undergo an annealing time of more than 20 h to achieve a negative threshold voltage [22]. In contrast, the n-type GFETs demonstrated in this work were achieved in less than 2 h during the Si₃N₄ process. Based on these electrical characteristics, the possibility of electrical doping can be ruled out as electrical doping can only shift the Dirac point of the transfer curves without any significant change in their shape [27]. Another possible explanation of the conduction
change could be attributed to the exposure of NH$_3$ as n-type dopants [13]. It is worth noting that the GFET loses n-type properties slowly over a period of $\sim 3$ weeks (step 3), and that the p-type characteristics can be completely revived after removing the Si$_3$N$_4$ layer (step 4). The cause of a GFET losing its n-type conductivity could also be the re-adsorption of the oxygen/water molecule related p-dopants after being in air for a long period of time. These trends of changing characteristics from p-type to n-type were repeatable across 11 out of 12 GFETs that were fabricated. The remaining one which displayed ambipolar characteristics is likely to be caused by a neighboring piece of graphite flake, resulting in the poor passivation of the GFET. In order to fully understand the mechanism behind the evolution of electrical behavior, a Raman study was systematically conducted on four GFETs.

### 3.2. Raman study of GFETs

The GFETs used in this study were all fabricated from monolayer graphene as verified by Raman spectroscopy (see figure 1(d) for a typical Raman spectrum). The intensive peaks observed at a Raman shift frequency of $\sim 1580$ cm$^{-1}$ and $\sim 2680$ cm$^{-1}$ correspond to the G peak and 2D peak, respectively. The G peak arises from the doubly degenerate zone center $E_{2g}$ mode, while the 2D peak is the second order of zone boundary phonons [9]. The intensity of the 2D peak as compared to the G peak ($I_{2D}/I_G = 1.25$) as well as the full width at half maximum (FWHM) of the 2D peak (32.13 cm$^{-1}$) are indicators of monolayer graphene [9]. In order to eliminate the influence of Si$_3$N$_4$ in the Raman characterization results, the Raman spectrum was taken above the graphene passivated by Si$_3$N$_4$ and compared to another spectrum taken above the Si$_3$N$_4$ surface only (see figure 2(a)). The Si$_3$N$_4$ Raman profile demonstrates a slight hump around 1580 cm$^{-1}$, which coincides with the G peak of the graphene signal. The Si$_3$N$_4$ Raman profile was then subtracted away from the as-measured Raman scan to obtain the normalized Raman profile. These processes were repeated for all Raman spectra obtained in steps 2 and 3 of the experiments to eliminate the background signal generated from the Si$_3$N$_4$. From figure 2(b), it is worth noting that only the width of the D peak had been affected by the noise, due to the significantly low intensity of the D peak. Little shift or no influence to the D, G and 2D peaks were observed.

The pristine graphene had a negligible D peak at $\sim 1350$ cm$^{-1}$ as previously seen in figure 1(d). After the deposition of the Au/Ti electrodes, the defect peak started to surface as seen in figure 3(a), step 1. The D peak arises...
Figure 2. Demonstrates the influence of Si$_3$N$_4$ passivation on the Raman scan results during steps 2 and 3 of the experiment. (a) Raman spectrum of the graphene covered by the Si$_3$N$_4$ layer and the Si$_3$N$_4$ Raman noise profile. The normalized Raman profile was obtained by subtracting the Si$_3$N$_4$ background noise from the as-measured Raman profile. (b) Values of the D, G, 2D peaks and their respective FWHMs. Only the FWHM of the D peak was influenced by the Si$_3$N$_4$ Raman noise profile.

Figure 3. (a) Raman spectra of a typical GFET taken at various steps of the experiment. (b) A decrease in the $I_D/I_G$ ratio was observed after the deposition process of Si$_3$N$_4$. The error bars indicate the standard error of the four GFETs.

from the Ti adatoms that were attached to the graphene surface [14]. A significant decrease of the D peak intensity was seen after the deposition of Si$_3$N$_4$ at step 2 (n-type). Conversely, Geng and co-workers observed an increase in the D peak when the graphene was heated in NH$_3$ ambient at 900°C [10]. The increase in D peak was due to disorder induced within the graphitic plane in their case. We proposed that the differences between these two experiments were due to the different chemical doping mechanisms [18]. The substitution transfer doping usually requires high temperature and/or existing vacancies in the lattice structure to occur [11, 21]. The increase of the D peak intensity is due to the disruption of the lattice structure by the addition of a foreign atom [21]. From our results, we eliminate the influence of the substitution transfer doping mechanism based on two facts: (1) our experiment was carried out at a maximum temperature of 200°C, (2) the decrease of $I_D/I_G$ from 0.5 in step 1 to 0.079 in step 2. We suggest that the doping caused by NH$_3$ below 200°C was only weakly adsorbed onto the graphene surface and resembled that of the surface transfer doping mechanism [15]. Another interesting observation of the D peak is that even after the removal of the Si$_3$N$_4$ passivation (step 4), the $I_D/I_G$ ratio remains below 0.1 as compared to the initial GFET (step 1) (see figure 3(b)). The recovery of the D peak could show that defects to the lattice such as Ti adatoms had been partially removed [12]. This recovery is due to the annealing process at 200°C in nitrogen ambient [11].

For the doping scenario, the shifts of the G and 2D peaks also provide additional information on the type of doping [18]. In order to eliminate the influence of spatially dependent Raman shifts, at least two Raman spots were collected on each investigated sample [12]. In figure 4, a downshift of 3.46 cm$^{-1}$ and 7.4 cm$^{-1}$ from step 1 to 2 was observed on the G and 2D peak respectively. The reason for the downshifting of both the G and 2D peaks could be twofold: (1) reduction of the p-type dopants and/or (2) increase of the n-type dopants [7, 8, 14]. Downshifting of the G and 2D peaks at the same time has been experimental observed when the p-dopants in graphene are reduced [6, 14].
Similarly, this downshifting agrees well with the interaction with n-dopants such as nitrobenzene [6, 7]. From step 2 to step 3, the G and 2D peaks upshift by 3.21 cm$^{-1}$ and 7.84 cm$^{-1}$, respectively. This is consistent with the increase of p-type dopants (oxygen/water molecules) as suggested by the ambipolar behavior in figure 1(b). By comparing step 1 and step 4, both the G and 2D peaks have downshifted, which is in agreement with the reduction of Ti adatoms (p-dopants) [14]. From the trends of the G and 2D peaks, the influence of p-dopants is likely to dominate over the n-dopants, which is of a lower doping level as will be discussed later.

The intensity ratio between the 2D peak and the G peak ($I_{2D}/I_G$) is known to be sensitive to the doping concentration. An increase in the doping concentration for both n- and p-dopants will result in a decrease of $I_{2D}/I_G$ [5, 6, 18]. From figure 5, the ratio of $I_{2D}/I_G$ at step 2 is the highest (lowest doping concentration) and step 3 is the lowest (highest doping concentration). These results reaffirm that the n-dopant concentration was lower than the p-dopant concentration, and that the G and 2D peak shifts were dominated by the p-dopants. From step 2 (n-type) to step 3 (ambipolar), the decreases of the $I_{2D}/I_G$ to 0.80 indicates that the doping concentration increases. As the GFET was left in the atmosphere ambient for this interval, we propose that the increase in doping concentration is largely due to the re-adsorption of the oxygen/water molecules onto the GFET surface because of the diffusion of gaseous species through the Si$_3$N$_4$ film. The transition from step 3 (ambipolar) to step 4 (p-type) also results in a decrease of the doping concentration, which could indicate that most of the NH$_3$ dopants had been removed by the wet etching process of Si$_3$N$_4$ passivation. By comparing the GFET at step 1 and step 4, the doping concentration at step 4 is lower, which is in agreement with our previous observation of the D peak. Now we come to address the mobility variation shown in figure 1(c). One may see that the defect levels in steps 2, 3, and 4 are comparable (see D peaks in figure 3), which
rules out lattice disorder as the reason for varying mobility. As shown in figure 5, the Raman peak intensity ratio $I_{2D}/I_G$ is a minimum at step 3 in comparison with those at steps 2 and 4. Increasing doping concentration level will reduce the field-effect mobility because of dopant-induced scattering [3], leading to the higher electron and hole mobilities with ambipolar conduction (step 3).

In order to further confirm that the increase in threshold voltage was due to re-adsorption of oxygen/water molecules, 750 nm-thick Si$_3$N$_4$ was deposited onto the GFET and the thickness of the Si$_3$N$_4$ was reduced step by step while monitoring the shift in threshold voltage (see figure 6). As discussed previously, the GFETs display p-type characteristics after removing the Si$_3$N$_4$ passivation. These devices undergo the same Si$_3$N$_4$ passivation process, and n-type behavior was restored again when passivated by 750 nm-thick Si$_3$N$_4$: demonstrating that the n-type modulation is repeatable on the same GFET. When the Si$_3$N$_4$ passivation layer is reduced by less than 200 nm, the GFET displayed p-type conduction with positive threshold voltages. This clearly demonstrates that if the passivation Si$_3$N$_4$ is too thin or porous, exposure to atmospheric ambient will results in the re-adsorption of oxygen/water molecules.

In order to verify our hypothesis about the role of ammonia, another set of experiments has been conducted as follows. The Si$_3$N$_4$ passivation was removed and then subsequently replaced by thick SiO$_2$ passivation (see supplementary information available at stacks.iop.org/Nano/24/195202/mmedia). However, in the case of SiO$_2$, no n-type conduction can be observed. The only difference between the two deposition processes (Si$_3$N$_4$ and SiO$_2$) is the distinct reaction gases. That is NH$_3$ was changed to N$_2$O for SiO$_2$ deposition, resulting in the obvious contrast between the conduction behaviors with Si$_3$N$_4$ and SiO$_2$ passivation on the same device. This clearly demonstrates the importance of the NH$_3$ for the modulation of the GFET from p- to n-type conversion.

4. Conclusions

The controllable fabrication of unipolar p- and n-type GFETs has been demonstrated and an ambipolar intermediate state was observed. The mechanisms of the p- to n-type then to ambipolar and finally to p-type conversion have been systematically investigated using Raman spectroscopy. The conversion of p- to n-type conduction is mainly due to the desorption of the oxygen/water molecules. In addition, the exposure of NH$_3$ gases involved in the Si$_3$N$_4$ deposition process further doped electrons to graphene to produce unipolar n-type GFETs. The NH$_3$ dopants are believed to be weakly attached onto the graphene surface by surface transfer instead of a substitutional doping mechanism, as no obvious increase in the D peak is observed in the Raman spectra. The effect of NH$_3$ dopants can be removed by wet etching of the Si$_3$N$_4$ layer. The threshold voltage of the n-type GFET was found to increase as the thickness of the Si$_3$N$_4$ layer decreases. On the other hand, passivation using a SiO$_2$ layer does not result in n-type GFETs. This further enhances the importance of the presence of NH$_3$ for n-type GFET formation. The function of the Si$_3$N$_4$ layer is to isolate the oxygen/water molecules from adsorbing onto the graphene surface and then to obtain air-stable unipolar GFETs.

References


