Hydrazine Doped Graphene and Its Stability

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(Received June 16, 2014, Revised July 30, 2014, Accepted July 30, 2014)

The electronic property of graphene was investigated by hydrazine treatment. Hydrazine (N\textsubscript{2}H\textsubscript{4}) highly increases electron concentrations and up-shifts Fermi level of graphene based on significant shift of Dirac point to the negative gate voltage. We have observed contact resistance and channel length dependent mobility of graphene in the back-gated device after hydrazine monohydrate treatment and continuously monitored electrical characteristics under Nitrogen or air exposure. The contact resistance increases with hydrazine-treated and subsequent Nitrogen-exposed devices and reduces down in successive Air-exposed device to the similar level of pristine one. The channel conductance curve as a function of gate voltage in hole conduction regime keeps analogous value and shape even after Nitrogen/Air exposure specially whereas, in electron conduction regime change rate of conductance along with the level of conductance with gate voltage are decreased. Hydrazine could be utilized as the highly effective donor without degradation of mobility but the stability issue to be solved for future application.

Keywords: Vacuum standard, Ultrasonic interferometer manometer, Static expansion system, Orifice conductance, Dynamic expansion system, Uncertainty

I. Introduction

Graphene doping, which could tune charge carrier concentration along with carrier type, becomes main research topic for applications such as transparent electrode or semiconducting channel node of transistor [1]. The chemical doping has been generally executed by covalent or noncovalent functionalization of molecular materials [2]. The electronic properties of graphene can also be tuned by the chemical modification such as partial or full hydrogenation [3] and fluorination [4]. However the strong covalent bond such as C–H and C–F disturbs sp\textsubscript{2} hybridization of carbon atoms and induces structural defects or chemical impurities, which could highly affect the electronic band structure and transport property of graphene. On the other hand, the doping by the surface charge transfer due to the electron exchange at the interface of graphene and dopants leaves the electronic structure of graphene intact [5]. This is usually achieved by molecular materials absorbed on the surface of graphene. Molecules with electron
withdrawing or donating groups will lead to p-type or n-type doping to graphene by charge transfer, respectively [5]. Accordingly, graphene can be intentionally doped by depositing organic or inorganic materials such as alkali metal atoms or aromatic molecules on its surface [6].

There still exist two main issues regarding graphene doping utilized by charge transfer. First, despite of undisturbed electronic structure of graphene by charge transfer doping, the mobility of graphene has been reported to be degraded by the dopant that could play a role of charged impurity center since it is dominated not by the lattice vibration but the charged impurities at the room temperature [7]. Second, it is significantly difficult to accomplish required stability for device application.

Among the various dopants, highly effective work function changes are obtained using acid or base materials. Hydrazine (N\(_2\)H\(_4\)), strong base, was introduced to reduce graphene oxide into graphene [8]. More recently, diluted hydrazine monohydrate solution was adapted as the n-type dopants using its unpaired electron [9]. Here, we monitor graphene Fermi level shift using highly diluted N\(_2\)H\(_4\) solution and investigate the stability issue along with transport property. N\(_2\)H\(_4\) treatment is very effective to dope graphene with negligible mobility degradation but requires the reliable doping stability as expected.

\section*{II. Experimental Results}

Chemical vapor deposition (CVD) graphene on Cu foil was transferred onto SiO\(_2\)/Si wafer using poly-methyl methacrylate (PMMA) and patterned by photolithography [10]. Device structure is shown Fig. 2. Source and Drain electrodes are formed using thermal evaporation of Au and succeeding lift-off process with 10 \(\mu\)m distance on the graphene bar. Channel width of graphene transistor is 200 \(\mu\)m. After device fabrication, graphene is annealed under vacuum at 250°C for 6 hours to remove PMMA residue, which can generate unintentional hole doping of graphene [10]. Then, device is soaked for 10 second in Hydrazine Monohydrate solution diluted by de-ionized water (1:9) for N\(_2\)H\(_4\) treatment. We took x-ray photoemission of N1s edge and C1s edge and obtained small N1s edge signal with only N\(_2\)H\(_4\) treated devices. Also, C1s showed broadened signal at high binding energy. (Data is not included) Raman spectroscopy is taken using laser of 514 nm wavelength after device fabrication. The channel conductance is measured by 4-point probe method. The device parameters such as mobility or Dirac point are investigated.

Raman data normalized by G peak intensity (I\(_G\)) were taken to monitor graphene during the device fabrication process, which is shown in Fig. 1. Although the slight increase of the normalized D peak intensity (I\(_D\)/I\(_G\)) is found in graphene after vacuum annealing, it appears nearly negligible. I\(_{2D}\)/I\(_G\) ratio is elevated from 1.5 to 2.5 during the graphene transfer, photolithography and vacuum anneal. The initial low I\(_{2D}\)/I\(_G\) value could be originated from hole-doping of graphene judging by the shift of G peak whose positions after transfer, photolithography and vacuum

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure1.png}
\caption{Raman data normalized by I(G) peak. (a) G peak, (b) 2D peak. Inset: G peak shift with process. Black: after graphene transfer (trans), Red: photolithography for device fabrication (photo) Blue: vacuum annealing (va).}
\end{figure}
annealing are 1,596, 1,592 and 1,587 cm\(^{-1}\) respectively. According to the density functional theory (DFT) calculation, G peak stiffening from 1,584 cm\(^{-1}\) and \(I_{2D}/I_G\) ratio decrease around 3 in intrinsic graphene are significant with the increase of charge carrier concentration [11]. Therefore, G peak softening along with 2D intensity boost indicate that the raised charge carrier concentration during the transfer is lowered by following processes such as device fabrication and vacuum anneal. Hole-doping by PMMA residue used as the sacrificial layer during graphene transfer is known to be responsible for the carrier density increase [12]. Vacuum annealing about 200∼250°C helps removing these adsorbed residues.

In order to study electrical property of N\(_2\)H\(_4\)-treated graphene device, channel current (\(I_{ds}\)) with applied Source/Drain voltage (\(V_{ds}\)) at gate floating is measured with the device of 10, 50 and 90 \(\mu\)m channel length as shown in the Fig. 2(a), (b) and (c). \(I_{ds}\) versus \(V_{ds}\) curve is plotted in Fig. 2(d) from the slope of \(I_{ds}−V_{ds}\) curve. We have obtained contact resistances of all the devices from \(y\)-axis interception in curves of Fig. 2(d), using following equation. \(R_{tot}=R_c+R_s(L/W)=V_{ds}/I_{ds}\), where \(R_{tot}, R_c\) and \(R_s\) mean total resistance, contact resistance and channel sheet resistance respectively. \(L\) and \(W\) indicate channel length and width of measured device.

Fig. 2(e) represents the extracted contact resistance of pristine device. The change of contact resistance is unexpected since we soaked graphene in N\(_2\)H\(_4\) solution after the completion of device. It is probably due to the diffusion of N\(_2\)H\(_4\) into the interface of graphene and Au electrode. The charge carrier injection from electrode to graphene could be hindered by diffused N\(_2\)H\(_4\). After 6 hour exposure, it is recovered to the similar level of pristine device.

The electrical transport in graphene transistor is measured by 4 point probe technique using current source. The channel resistance curves of different
channel length of 10, 50 and 90 μm are represented in Fig. 3(a), (b) and (c). Neutral point (V_{NP}), the gate voltage of maximum channel resistance, is located between 60~70 V in pristine device (first measurement) and is displaced below −80 V after N₂H₄ treatment (second measurement), that indicates electron doping by hydrazine treatment. After electrical property measurement, we had preserved all the N₂H₄−treated devices for 2 hours in Nitrogen filled glove box and then re−measured the channel resistance(third measurement), which is green line data of Fig. 3(a), (b) and (c). V_{NP} of those curves already shifts to the gate voltage of −40~−35 V range by N₂ exposure. After third measurement, we left devices exposed to the ambient for hours and measured channel resistance after 2, 4 and 6 hours exposure. V_{NP} continues to shift to the positive side. Unlike N₂ exposure, the maximum resistance at V_{NP} decreases by Air exposure.

From channel resistance curves, we re−plotted the channel conductance data by moving neutral point to origin, which are shown in Fig. 3(d), (e) and (f). The conductance curves of different channel length seem to show common behavior regardless of channel length. The conductance evolution with N₂ or Air exposure looks more stationary in hole−conduction regime than in electron−conduction regime. Hole conduction behavior remains affected during the N₂ or Air exposure without noticeable change. On the other hand, conductance is highest after N₂H₄ treatment in electron conduction regime, Unfortunately, we could not obtain the electron conduction in pristine and hole conduction in N₂H₄−treated devices due to extreme hole and electron doping and thus could not explain the influence on conductance by hydrazine treatment except for the gate voltage close to V_{NP}. N₂H₄ treatment enhance the conductance close to minimum conductivity point judging by the curve shape close to V_{NP} as shown in the inset of Fig. 3(d), (e) and (f). [13]

Fig. 4 (a) shows the minimum conductivity (σ_{min}) change depending on the process at the V_{NP} (Fig. 4(b)), σ_{min} is closely related to the residual impurity and re−

Figure 3. Gate voltage dependent channel resistance with different channel length after N₂H₄ doping (a) 10, (b) 50, (c) 90 μm. Gate voltage dependent channel conductance after moving V_{NP} into the origin (d) 10, (e) 50, (f) 90 μm In (a−f), Black: pristine, Red: N₂H₄ doping, Green: 2 hour N₂ exposure, Blue: 2 hour, Cyan: 4 hour, Purple: 6 hour under ambient. Inset of (d−f) : expanded V_{NP} area.
versely proportional to the carrier mobility which is generally dominated by charged defects in graphene [6,13]. Therefore, process dependent $\sigma_{\text{min}}$ $V_{\text{NP}}$ can illustrate the variation of dopant concentration and inhomogeneous residual charge distribution at the low carrier density. N$_2$H$_4$ treatment shifts $V_{\text{NP}}$ to highly negative voltage side while it lowers $\sigma_{\text{min}}$ and increases mobility. But subsequent N$_2$ exposure reshapes $V_{\text{NP}}$ and mobility to return to the pristine state with keeping similar $\sigma_{\text{min}}$. Then, next exposure under ambient condition recovers $\sigma_{\text{min}}$ and mobility to pristine state and $V_{\text{NP}}$ to the intrinsic Dirac Point.

Also, lowest $\sigma_{\text{min}}$ and mobility are obtained at 10 nm channel length device as shown Fig. 4(a), (c) and (d). The conductance close to neutral point is caused by residual impurity or electron–hole puddle. Therefore, low $\sigma_{\text{min}}$ is expected to show high mobility as previously mentioned. However, in our devices, opposite effects were observed. This phenomenon might be also related with the channel length dependent mobility increase as shown in Fig. 4(c) and (d), which is improbable in diffusive conduction regime. It’s unclear but one of reasons could be in invasive Source/Drain electrode structure we have utilized. The metal electrode on graphene can change work function of graphene and also carrier density. In addition, the electronic band structure change of graphene could be caused by the stress due to upper metal electrode. If we deal with long channel, we have wider region of metal/graphene stack structure in our device structure. Since we soak graphene device with pre-deposited Source/Drain metal electrode during N$_2$H$_4$ treatment, there exists area we cannot control and attach dopants on graphene. Those combined effects by overlapped metal electrodes could be responsible for the unusual behavior of conductivity.

Figure 4. (a) Minimum conductivity ($\sigma_{\text{min}}$), (b) $V_{\text{NP}}$, (c) Electron mobility (d) Hole mobility. In (a–d), Black : 10, Red: 50, Green: 90 $\mu$m, Inset of (c): the ratio of electron to hole mobility.
Highly increased electron mobility with hydrazine treatment becomes reduced by N₂ or Air exposure. Whereas, although hole mobility of N₂H₄ treated device is difficult to measure due to the large V_{NP} shift due to hydrazine treatment, hole mobility does not change with N₂H₄ treatment based on the slope of gate dependent channel conductance curve close to V_{NP} as shown in the inset of Fig. 3(d–f) It is rather reduced by N₂ exposure and then gradually recovered with Air exposure. For the CVD graphene, hole mobility often has been reported to be higher than electron one [14]. Electron and hole conduction asymmetry has been considered by various mechanisms [15–18]. Here, the electron to hole mobility ratio shown in the inset of Fig. 4 indicates the asymmetry is induced by doping [15]. P-type (n-type) doping produces a potential barrier that suppresses electron (hole) conductance and preserves hole (electron) conductance except for initial hydrazine treatment. It was explained that homogeneous potentials created by long range scatters cause conductance suppression of only one carrier type.

Our previous conductance curves are ones obtained from forward gate voltage sweep of −80 V to 80 V. We have attempted to observe hysteresis of forward and reverse voltage sweep for the channel current. The conductance hysteresis on the device of 50μm channel length is plotted in Fig. 5. V_{NP} values of all the curves are higher in reverse sweep direction than in forward sweep. This gap in both sweep direction is smallest in the pristine device and largest in hydrazine treated devices. Specially, R–Vg in the direction of reverse sweep on the hydrazine treated device looks very flattened at hole conduction regime, which exhibits highly asymmetric conductance curve generated by the suppression of hole conduction. With N₂ or Air exposure, conduction curve becomes more symmetric with sweep direction and the gap of V_{NP} is lessened.

The electronegative or electropositive material doping of graphene are expected to lead to a decrease
in carrier mobility arising from Coulomb scattering but without any hysteresis whereas electrochemical doping is effected by redox reactions and shows large hysteresis [19]. This hysteresis could be explained by dipolar adsorbates such as water. The hysteresis is suppressed or vanishes when placing graphene in vacuum and pumping for an extended time. In our devices, loosely bound species are the main culprits for hysteresis [20]. The rapid $V_{NP}$ change and hysteresis reduction after exposure to $N_2$ or Air within several hours might be originated from the weak interaction between adsorbates and graphene.

In order to investigate the stability of hydrazine treated graphene device, gate dependent channel resistance has been measured after exposure for two months. The higher hole doping is observed compared with pristine graphene device judging by $V_{NP}$ shift larger than 80 V (applied maximum positive voltage. It seems that a highly effective electron doping on graphene produced by hydrazine treatment could not be retained under the atmospheric environment. It might be caused by weak binding of graphene and dopant or chemical interaction between dopant and $H_2O$ or $O_2$ gas, which could explain more increased hole doping after hydrazine doping. For the quantitative comparison, channel resistance at zero gate voltage was replotted in Fig. 6(b). No distinctive difference was not detected with channel length.

One interesting point is that channel resistance was measured using four probe method. Therefore, it does not include the contribution of contact resistance. From the Fig. 6(b), we extracted the $y$-axis intercept using line fitting in both devices, which must be zero without contact resistance. They are 44, 52 Ohm for pristine and 2 month Air-exposed device after hydrazine treatment respectively. This channel length independent value could be related to the invasive electrode structure and abnormal relationship between minimum conductivity and mobility.

III. Summary

$N_2H_4$ could play a role of highly productive electron donor for graphene. It does not induce severe degradation of mobility but too unstable to adopt $N_2H_4$ treatment without considering passivation. In the initial stage of $N_2H_4$ treatment, mobility change of electron and hole appears dominated by long range scatters and the contact resistance between graphene and Source/Drain electrode increases. But with exposure under $N_2$ or air, several device parameters such as mobility, channel conductance and contact resistance recover to the level of undoped states by relaxation. In addition $V_{NP}$ exhibits the higher hole doping compared with the pristine graphene device without having hydrazine treatment. For $N_2H_4$ doping, to utilize this method to the real device application, primary issue to settle is how to control and acquire the device stability.

Acknowledgement

This work was supported by the faculty research fund of Sejong University in 2011.
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