Highly Air-Stable Phosphorus-Doped n-Type Graphene Field-Effect Transistors

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As silicon integrated circuits approach their theoretical limits, many groups have focused on non-silicon-based organic materials in the hope of discovering new materials upon which the next generation of electronic devices will be based.[1] Carbon nanomaterials are promising alternative candidates to replace silicon in device technologies. Recently, graphene has attracted great attention not only because this perfect two dimensional carbon crystalline structure enables unprecedented exploration of fundamental physics, but also because of its exciting potential in post-silicon nanoelectronics.[2–4] Graphene is a monolayer of graphite in which a carbon backbone forms a two-dimensional (2D) hexagonal structure as a zero-gap semiconductor. The extremely high mobility in graphene nanosheet has made it a promising candidate for high frequency transistors.[5,6] On the other hand, field-effect transistors (FETs) using graphene nanosheet as a semiconducting channel between the source and drain suffer from the absence of a bandgap.[2,9] In this regard, many research groups modified the electronic structure of graphene to obtain a semiconducting channel and to achieve electronic transport dominated by the preferred major carrier.[10–13] Chemical doping is one subject that draws attention; however, it can introduce defects into the lattice, potentially reducing the carrier mobility.[14,15] As conventional doping usually moves the Fermi level relative to the Dirac point (DP), many reported n- or p-type doping methods have largely demonstrated a shift in the neutrality point while maintaining the ambipolar behavior.[10–13] Several chemical species were reported to produce doping effects during chemical vapor deposition (CVD) graphene.[12] The category and concentration of electron or hole carriers on graphene can be controlled by the introduction of metals or molecules onto the graphene surface. Development of n-type semiconducting graphene is imperative for the complementary circuit since a p-type graphene channel can be easily prepared under air and oxygen atmospheres. There are numerous reports of ways to prepare n-type semiconducting graphene channel by nitrogen atom doping.[16–18] Nitrogen has been known as an effective atom for producing n-type semiconducting graphene channels by donating its lone pair of electrons to the graphene system network. As recognized in many reported results, the lone pair of electrons in nitrogen plays the most important role in generating high electron mobility in the graphene system to produce n-type behavior. Now a day’s air stability is one of the biggest issues. It remains a challenge to investigate the air-stable n-type semiconducting properties of graphene. On the basis of reported results, we can establish a hypothesis that the high donating ability of the electron lone pairs of the hetero atoms are responsible for strong n-type performance as well as it should solve the air stability problem. To investigate this hypothesis, we have conducted electrical measurements to compare nitrogen and phosphorus atoms on graphene nanosheets and also the air stability. The phosphorus atom also has a pair of electrons and its donor ability is much higher than that of nitrogen. Therefore, it is expected that the phosphorus doping effect on the graphene can produce much stronger n-type behavior than that of nitrogen doping. In addition, it is expected that phosphorus doping on the graphene channel is very stable even under oxygen or air atmospheres for the real device applications, due to the high nucleophilicity of phosphorus the resultant n-type effect will overcome the high p-type effect of oxygen and air atmosphere. Until now, however, there is no report on the air-stable n-type semiconducting graphene device produced by phosphorus doped materials. This is the first report demonstrating air-stable n-type behavior of phosphorus on graphene nanosheets. The n-type behavior produced by the phosphorus atom was very strong compared with previously reported hetero atoms such as nitrogen. In this report, we have developed air-stable n-type behavior of graphene nanosheets by doping of phosphorus atoms. Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDX) were employed to evaluate the doping degree and bonding configurations on doped graphene nanosheets. The electrical transport measurements were expected to show that our resultant phosphorus-doped graphene device exhibited much higher air-stable n-type semiconducting behavior than the nitrogen-doped graphene device. In the surface analysis, X-ray photoelectron spectroscopy (XPS) not only detected elements but also distinguished various bonds between the atoms and the surface. We measured XPS after RTA at 250 °C for both samples. The XPS
analysis revealed that phosphorus atoms were incorporated in the as-prepared phosphorus doped double layered graphene sample. The bonding configurations of phosphorus atoms in the phosphorus-doped double layered graphene sheets were determined based on high-resolution P2p XPS spectra. As can be seen in Figure 1a, the peak of P2p at 130.5 eV can be assigned to P-C bonding based on references related to phosphorus-containing carbon materials.\cite{19-21} The N1s spectra of nitrogen-doped double layered graphene also revealed that the peak at 400.1 eV can be assigned to C-N bonding, similar with the previously reported values (Figure 1b).\cite{22} The doping level of nitrogen and phosphorus obtained from XPS was 5.05% and 4.96%, respectively. To confirm the doping level, energy dispersive X-ray spectroscopy (EDX) was also measured, yielding values of 5.14% for nitrogen and 5.01% for phosphorus, respectively, which corroborated the XPS results (see Supporting Information, Table 1). To understand the surface morphology and thickness, scanning electron microscopy (SEM) measurements were performed at different stages (see Supporting Information, Figure S5, S6 and S7).

As we know, n-type semiconducting behavior can be obtained not only by replacing carbon atoms with these atoms in graphene frameworks, but also by the donating ability of their lone pair electrons to the system network. To investigate the electronic properties of our double layered-graphene nanosheets, back-gated graphene field effect transistors (g-FET) with Pt source-drain (S-D) electrodes were fabricated. Then, phosphorus and nitrogen materials were coated on the 1st layered graphene channel, followed by placing the 2nd graphene layer to make a double-layered graphene structure (Figure 1c). The 2nd layered graphene was used as a protection layer for preventing scattering of the doping materials during thermal heating. The resulting double-layered graphene FET was heated to make a chemical bond between the doping material and graphene backbone by rapid thermal annealing (RTA) at different temperatures. Double layered graphene FET fabrication, wherein the single layered CVD graphene was prepared and transferred to a FET device one by one, was conducted according to a previously reported method.\cite{23} In this study, typical electronic properties of the double layered graphene FET were observed after phosphorus and nitrogen material coating in between double layers of graphene, followed by RTA at different temperatures (100–250 °C). The electronic properties of these as-prepared devices were measured. The only single layered graphene device showed p-type behavior in air, which was due to residual PMMA on the graphene surface, moisture,
oxygen, or defects introduced on the single layer graphene during the device fabrication process.[24] To avoid the complication from physisorbed oxygen, the devices were measured in a vacuum (∼4 × 10⁻⁴ Torr). The gate voltage ranging from −200 V to 100 V was swept with a constant drain–source bias at 0.5 V. The DP of the as-prepared single layer graphene FET was found at a positive gate voltage (Vgs) at 48 V in vacuum, which was an indication of p-type graphene FET (Figure 1f). In the case of the double layer graphene FET, the DP was located at 80 V, which showed more p-type behavior, compared with the single layer graphene FET (Figure 1g). In addition, the presence of PMMA over the 2nd graphene layer of double layered FETs made this control device more p-type than those of the single layer.[24] Since it is hard to remove the PMMA by washing with acetone from the double layered graphene FETs coated with phosphorus or nitrogen material, we did not remove the PMMA from the 2nd layer of the double layered graphene used as control device. The DP of the as-prepared phosphorus FET before RTA was −77 V (Figure 1e), while that of the as-prepared nitrogen FET before RTA was 25 V (Figure 1d). In both FETs we observed n-type behaviors with left-shifting of their DPs with respect to the control double layered graphene FET (Figure 1g, DP at 80 V). It is known that pristine graphene and PMMA on the graphene leads to p-type effects[24] with the DP shifting to positive gate voltages, while phosphorus and nitrogen leads to an n-type effect with the DP shifting to negative gate voltage. The high p-type effect competes with the high n-type effect in both cases before RTA, as shown in Figures 1d, 1e and 1g. Therefore, it is hard to see the largest negative DP shifting. As expected, the doped molecular effect would be more clearly observed after RTA at different temperatures. The DP of the as-prepared phosphorus devices prepared by RTA at temperatures ranging from 100 to 250 °C were at negative gate voltages, Vgs, in the range of −110 to −170 V in vacuum, indicating the n-type electron doping behavior due to phosphorus-dopants in between double layer graphene (Figure 2a–d). The DP of the phosphorus coated double layered graphene FET increased gradually from −77 V to −170 V as the RTA temperature increased from 100 to 250 °C. The DP of the as-prepared nitrogen devices prepared by RTA at temperatures ranging from 100 to 250 °C were at negative gate voltages, Vgs, in the range of 0 to −45 V in vacuum, indicating n-type electron doping behavior due to nitrogen-dopants in between double layered graphenes (Figure 2e–h). The DP of the nitrogen coated double layered graphene FET increased gradually from 25 V to −45 V as the RTA temperature increased from 100 to 250 °C. As the RTA temperature increased, the DPs of both phosphorus and nitrogen doped graphene FETs were shifted from a weaker n-type character to a stronger n-type character. In both cases, the greatest DP shift was observed after RTA at 250 °C. These combined results support that, with increasing RTA temperatures, the opposite p-type effect was reduced by possible removal of PMMA and/or chemical bonding effect of the electron donating nitrogen and phosphorus atoms to graphene. The higher RTA temperatures also increased the contact of phosphorus and nitrogen materials by decreasing steric-crowding of those molecules between graphene layers to form a perfectly phosphorus and nitrogen doped graphene sandwich.

To investigate the origin of the exact molecular effects on the double layered graphene, only one layered graphene coated with phosphorus and nitrogen materials without an upper graphene layer was also prepared. In addition, the stability of the graphene FET under oxygen and moisture atmospheres is a very important factor for the possible applications. The electronic properties of the graphene FETs were measured under an air atmosphere (see Supporting Information, Figure S1). The DP of the phosphorus coated single layered graphene FET was −70 V in air, which is comparable to the DP of a previous double layered phosphorus FET (−77 V in vacuum). Further, the DP of the nitrogen coated single layered FET was 22 V in air, which is also comparable to the DP of previous double layered nitrogen FETs (25 V in vacuum). Observation of the very strong

Figure 2. Device structure: Si back gate, SiO₂ dielectric, Pt (S-D). Current-gate voltage (I_D−V_G) curves (recorded at V_D = 0.5 V) of an as-prepared device treated after RTA with phosphorus material at (a) 100 °C, (b) 150 °C, (c) 200 °C, and (d) 250 °C and as-prepared device treated after RTA with nitrogen material at (e) 100 °C, (f) 150 °C, (g) 200 °C, and (h) 250 °C. All devices measured in vacuum.
n-type behavior even in the presence of the high p-doping effect of oxygen and moisture from open air condition is very surprising. This experimental result suggests that the phosphorus material has a much stronger electron donating ability to the graphene channel than that of the nitrogen, showing strong air-stable n-type character even in the presence of high p-doping effects of moisture and oxygen. The air compatibility of double layered graphenes with phosphorus material was also examined by measuring the electrical properties after exposure of the FET device under open air for one month. The DPs were found to be −68 V and −77 V at air and vacuum conditions, respectively, indicating there is not much difference in the air atmosphere. As such, the phosphorus doped double layered graphene FET (PDGFET) had a high air-stability that is important for the realization of devices (see Supporting Information, Figure S2).

According to previous reports, the lone pair of electrons in the nitrogen atoms can play an important role to produce a delocalized conjugated system with the sp²-hybridized carbon frameworks, which can enhance the reactivity and electrocatalytic properties of graphene. As mentioned, the nitrogen containing double layered graphene FET (NDGFET) was also examined and confirmed as an n-type. However, the phosphorus is larger than nitrogen and can donate its lone pair of electrons to the conjugate system of sp²-hybridized carbon frameworks of graphene more easily than nitrogen. As such, phosphorus is a better nucleophile than nitrogen. The summarized electronic measurement data clearly show that the phosphorus can indeed create a much more air-stable n-type character than the well-known nitrogen atom by donating their easily donatable electron lone pairs to the graphene channel network. These experimental results supported our hypothesis that the phosphorus atom, with higher nucleophilicity in comparison to nitrogen, can create a more air-stable n-type character than the previously reported nitrogen atom. We observed almost 100% yields for phosphorus doped graphene FET devices due to this simple and effective procedure. This is the first experimental study that proves the phosphorus atom creates a very high n-type character and shows high stability in air.

Raman spectroscopy is the most direct and non-destructive technique to characterize the structure and quality of carbon materials, particularly to determine the defects and ordered and disordered structures of graphene. Therefore, spectra were collected for the as-prepared samples using micro-Raman spectroscopy at an excitation wavelength of 514 nm under ambient conditions. Two pronounced peaks (G band at 1590 cm⁻¹ and 2D band at 2684 cm⁻¹) were observed for double layered graphene films that were similar to the previously reported values. The samples were made from double layered graphene, as determined by Raman spectroscopy (Figure 3a and 3b). The different results for the G- and 2D-band frequencies of the doubled...
layered graphene films doped with phosphorus molecules before and after RTA are shown in Figure 3a. The D band (1351 cm⁻¹) also appeared after the introduction of molecules in between the graphene layers, most likely because those molecules increased the disorder of the graphene basal plane (see Supporting Information, Figure S4). Raman spectra showed the typical shifts of G (left) and 2D (right) peaks of the double layered graphene films with and without doping molecules (Figure 3a). It was noted that with increasing RTA temperatures, G (left) and 2D (right) bands were shifted more than those before RTA (Figure 3a). The G peak of the resultant material has gradually shifted to 1580 cm⁻¹ with increased RTA temperatures in comparison to the double layered graphene films (1590 cm⁻¹) (Figure 3a). The 2D frequency was upshifted by doping with phosphorus and nitrogen molecules. Further, the 2D peak gradually shifted to 2714 cm⁻¹ with increased RTA temperatures in comparison to the double layered graphene films (2684 cm⁻¹) (Figure 3a). By contrast, the Raman G-band of the phosphorus doped double layered graphene films shifted downwards with the n-type effect from our molecular doping. This chemical doping is distinct from the doping effects introduced by electrical or electrochemical gating, in which the G band shifted downward for n-type doping due to the dynamic effect of carrier population, that is, the departure of the carrier population from the adiabatic ground state. We also observed that the G band of the phosphorus doped double layered graphene (1586 cm⁻¹) was shifted more downwards than that of the nitrogen doped graphene (1589 cm⁻¹) before RTA (Figure 3b). It is expected that the molecular doping imposes defects in the double layered graphene films, and these defects efficiently scattered the electrons to nonadiabatic states. As a result, the dynamic effect becomes less effective. As previously reported, the G band downshift caused by the n-type doping was also observed in SWNTs and single layer graphene films, and it is attributed to electronic effects. It was also observed that the intensity ratio of I₂D/I_G was significantly decreased after molecular doping, which indicates the occurrence of molecular doping in between the graphene layers. These phosphorus and nitrogen molecules with either electron-donating lone pairs caused an apparent decrease in the ratio of I₂D/I_G because of their molecular doping effects. Thus, the molecular doping in between the double layered graphene films is confirmed by the dynamic downfield shift of G and the upfield shift of the 2D band. Based on this result, we can speculate that phosphorus can create more n-type doping behavior than nitrogen with increasing RTA temperatures. We observed the relationships between Raman shifts (the G and 2D peak position shifting in Raman spectra in comparison to only double layered graphene films) and DP shifts of PDGFET (Figure 3c), and Raman shifts with DP shifts of PDGFET and NDGFET (Figure 3d). The Raman spectra of the G and 2D peaks showed downfield shift up to -4 to 10 cm⁻¹, and upfield up to -22 to 30 cm⁻¹, respectively, with respect to double layered graphene before and after RTA, while the DP shifts of PDGFET were about 157 to 250 V, respectively, with respect to double layered graphene (Figure 3c). Raman shifts of the G peaks were downfield by about 4 cm⁻¹ for phosphorus and 1 cm⁻¹ for nitrogen. The Raman shifts of the 2D peaks were upfield by about 22 cm⁻¹ for phosphorus and about 20 cm⁻¹ for nitrogen with respect to only double layered graphene before RTA. DP shifts were about 157 V for phosphorus and 55 V for nitrogen with respect to only double layered graphene (Figure 3d). Thus, phosphorus doping on the graphene channel turned out to be a remarkably strong n-type FET. We also observed an apparent change in the mobility of phosphorus doped graphene FET device in comparison to other devices. The field-effect mobilities were extracted from the drain–source current (I DS)/back-gate potential (V G) curves using the following formula: μ = (ΔI DS/ΔV G)/(L/W)/C ox ΔV G. Here, L and W are the length and the width of the graphene channel, respectively. And C ox is calculated by ε s r A/d, where d is the thickness of SiO2, A is unit area, ε s is permittivity of free space, and ε r is the permittivity of free space. The calculated electron mobility for the phosphorus doped double layered graphene FET is ~5 times than that of the double layered graphene FET device, which is also much higher than that of nitrogen doped double layered graphene FET due to high electron-donating ability of phosphorus (see supporting information Table 2).

In summary, we have demonstrated the relationship between the lone pair electron donating ability of the phosphorus atom, which is much stronger than nitrogen due its higher nucleophilicity, and air-stable n-type performance in molecularly doped FETs. The doping effects were evaluated by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDX), and the results corroborated the electrical transport measurements. The main inspiration of this study was to prove that the PDGFET could create much stronger air-stable n-type behavior than NDGFET. PDGFET showed more n-type behavior than nitrogen samples before and after RTA treatment, and, with increasing RTA temperatures, the n-type behavior of the graphene FET increased in both doped cases. Amazingly, the phosphorus doped n-type showed high air-stability even under an oxygen atmosphere. It is assumed that the strong electron donating ability of the electron lone pairs can protect against a reduction in n-type properties even under an oxygen atmosphere, leading to real device applications. This is the first successful observation of the strong air-stable n-type semiconducting behavior with the phosphorus doped graphene FET, which should lead to its use in applications for air-stable, organic semiconductor n-type channels.

Experimental Section

Materials: Triphenylphosphine, triphenylamine and toluene were obtained from commercial sources and used as received.

Characterization: Raman spectroscopy measurements were taken using a micro-Raman system (Renishaw, RM1000-In Via) with an excitation energy of 2.41 eV (514 nm). All X-ray photoemission spectroscopy (XPS) measurements were made by a SIGMA PROBE (ThermoVG, U.K.) with a monochromatic Al-Kα X-ray source at 100 W. All Raman were done by Sam Han Vacuum development 2404. All the electrical transport measurements were made by Keithley 4200 semiconductor characterization system unit. The microstructure was observed by field emission scanning electron microscopy (SEM; JSM-6701F, INCA Energy, JEOL).

Preparation of Graphene: Graphene was prepared growing graphene films using chemical vapour deposition (CVD) and successfully transferring the films to arbitrary substrates without intense mechanical and chemical treatments.
Preparation of Phosphorus and Nitrogen-Doped bi-layer Graphene Device: First, we transferred one layer graphene on FET device as reported procedure then coated that device with our material with 50 μL (10 mg/mL in anhydrous Toluene) solution. Devices air dried and then transferred another layer of graphene on that. Then the samples were placed in RTA instrument and vacuum for 1.5 h. After flowing 10% H₂ in Ar for 5 min then RTA was done at 100 to 230 °C temperatures for 20 sec.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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