CrossMark

Phosphorus doped graphene by inductively coupled plasma and triphenylphosphine treatments

Dong-Wook Shin*, Tae Sung Kim, Ji-Beom Yoo*

SKKU Advanced Institute of Nanotechnology (SAINT) and Center for Human Interface Nano Technology (HINT), Sungkyunkwan University (SKKU), 440-746, Republic of Korea

ABSTRACT

Graphene is considered a host material for various applications in next-generation electronic devices. However, despite its excellent properties, one of the most important issues to be solved as an electronic material is the creation of an energy band gap. Substitution doping is a promising method for opening the energy band gap of graphene. Herein, we demonstrate the substitutional doping of graphene with phosphorus using inductively coupled plasma (ICP) and triphenylphosphine (TPP) treatments. The electrical transfer characteristics of the phosphorus doped graphene field effect transistor (GFET) have a V_{dirac} of ~ -54 V. The chemical bonding between P and C was clearly observed in XPS spectra, and uniform distribution of phosphorus within graphene domains was confirmed by EELS mapping. The capability for substitutional doping of graphene with phosphorus can significantly promote the development of graphene based electronic devices.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Intrinsic graphene is a semi-metal or zero-band gap semiconductor with ambipolar charge transport, which hampers the application of the material in various functional devices [1]. The introduction of a band gap to graphene or tailoring its transport properties are stringent prerequisites for practical applications. Substitutional doping is a useful tool to the tailor electronic properties (p or n-type doping) or open energy band gap of intrinsic graphene at the nanoscale [2–4]. In addition to substitutional doping, there are several methods for opening a band gap for graphene: fabricating the nanoribbons [5,6], quantum dots [7], nanomesh [8], using an external electric field [9], and epitaxial growth on SiC substrate [10,11]. Even though these methods can form a band gap for graphene, they are far from practical applications due to their poor controllability and complicated processes.

Theoretical and experimental studies on the doping of graphene with different atoms (e.g. B, N, S, P and Si) have were reported [2,12–16]. Generally, substitutional doping of graphene results in the disruption of the ideal sp^2 hybridization of carbon atoms as well as significant changes in their electronic properties

and chemical reactivity. Substitutional doping of graphene with boron (B) or nitrogen (N) has been mostly investigated because of the similarity in the chemical bond length (C—C: 1.42 Å, B—C: 1.48 Å and N—C: 1.41 Å, c.f. P—C: 1.78 Å, P atom does not exist in-plane of graphene [14]). However, theoretically, the band gaps for phosphorus (P, 0.53 eV) and sulfur (S, 0.45 eV) doped graphene are higher than those of B (0.14 eV) and N (0.14 eV) at the same doping concentration (one atom substituted in 5 × 5 unit cell of graphene) [14,17]. Phosphorus doping of graphene is relatively easier than nitrogen doping because the formation energy of P-doped graphene from gas dopant atoms is about 7.1 eV/atom [14] compared to that of N-doped graphene (8.0 eV/atom) [13], suggesting that P doping is more energetically favorable. Therefore, substitutional doping of graphene with P atom is a promising candidate for obtaining n-type doped graphene.

Recently, several techniques to substitute a foreign adatom in the lattice of graphene have been reported and developed, including methods to directly synthesize graphene substituted with a foreign adatom [18–20] and to modify the electronic properties of graphene with the foreign adatom after growth [2,21,22]. Among them, controllable ion doping using reactive microwave plasma was suggested as an effective method for tunable band gaps of B-doped graphene [2]. Herein, we report a study on the transport properties and chemical composition of P-doped graphene via inductively coupled plasma (ICP) treatment and annealing with triphenylphosphine (TPP). ICP treatment was used to form the defects on chemically reacted sites on the

* Corresponding authors.
E-mail addresses: shindong37@skku.edu (D.-W. Shin), jbyoo@skku.edu (J.-B. Yoo).

graphene. The annealing process with TPP induced the substitutional P-doping of graphene due to the reaction between the phosphorus and the reactive defect site of graphene. We believe the substitutional doping of graphene with predictable transport properties may pave the way for the development of graphene based devices.

2. Experimental

2.1. Graphene growth on Cu foil

Graphene was synthesized by thermal chemical vapor deposition (CVD). Copper foil was prepared at 75 μm thickness and manufactured by Wacopa Co., Ltd. In the first step of synthesis, a roll of copper foil was inserted into a quartz tube and heated to 1000 °C (heating rate: 16 °C/min) with a flow of 10 sccm of H_2. The copper foils were heat-treated to increase the grain size as well as to clean them for 30 min. For the synthesis of graphene, a gas mixture of CH_4 and H_2 was flowed for 30 min (1000 °C) with rates of 20 and 10 sccm, respectively. Finally, the sample was cooled to room temperature for 90 min under flowing H_2. Graphene was transferred to SiO_2/Si substrate (SiO_2:~300 nm) using the Au assisted transfer method.

2.2. Au assisted transfer and photolithography

Au film of 30 nm thickness was deposited on the as-prepared graphene/Cu foil by thermal evaporation (deposition rate: 0.2 Å/s), and then Cu was etched in the plastic bath filled with $FeCl_3$ from Sigma Aldrich. The Au/graphene film was cleaned with deionized water and HCl (10 vol%), and transferred to the SiO_2/Si substrate. Conventional photolithography was used to form electrode patterns on the Au/graphene film. For selective Au etching, the PR pattern on the Au/graphene was used as the etch mask. Selective Au and graphene etching was performed with a gold etchant and O_2 plasma using a reactive ion etcher (RIE, Miniplasma-Cube, Plasmart), respectively.

2.3. Characterization of P-doped graphene

The electrical transport characteristics of raw graphene and those of the ICP and TPP treated graphene were measured at room temperature with a source-drain (S-D) bias voltage of V_{ds} = 0.1 in a vacuum probe station (under 10^{-6} torr) coupled to a semiconductor parameter analyzer (Keithley 4200). The Raman spectra of the graphene on the SiO_2/Si substrate (~300 nm thick) were measured using a confocal Raman system (WiTec) with laser excitation at 532 nm and a 50× objective lens, before and after ICP and TPP treatment. Samples of 1 × 1 cm (graphene transferred on SiO_2/Si) were measured by X-ray photoelectron spectroscopy (XPS, VG microtech ESCA 2000). The phosphorus distribution and crystalline structure of the ICP and TPP treated graphene were studied by electron energy loss spectroscopy (EELS) and selected area electron diffraction (SAED) pattern using transmission electron microscopy (TEM).

3. Result and discussion

Graphene field effect transistors (GFETs) are generally fabricated by the transfer of graphene onto SiO_2/Si substrate using a polymethlymethacrylate (PMMA) layer and the conventional photolithography process. Despite a cleaning process during the fabrication of GFETs, the PMMA and photo resist (PR) layers used in these processes remain as residual contamination on the GFET channel, which affects the electronic structure of the graphene. We introduce a "Au assisted" transfer method with the advantage of

avoiding the exposure of graphene to polymers (PR, PMMA), as shown in the inset of Fig. 1a. Also, the contact resistance between the electrode and the graphene can be minimized [23]. For P-doped graphene, GFETs were treated with inductively coupled plasma (ICP: 10 W in an Ar environment for 45 s) and triphenylphosphine (TPP: H_2/Ar: 100 sccm/100 sccm at 200 °C for 2 h) (the inset of Fig. 1b). Specially, the Au film used for the graphene transfer was used for the electrodes. As the same contact metal was used for all of the devices in this work, variations in the work function of the contact metal that may dope graphene can be excluded [24]. The electrical transfer characteristics of the aforementioned GFETs are shown in Fig. 1. The charge neutral point, V_{dirac}, of raw graphene was not observed (Fig. 1a). This means that graphene was heavily p-type doped by the H_2O/O_2 redox system [24,25]. After ICP and TPP treatments, V_{dirac} was shifted to −57 V, and the average value of V_{dirac} was ∼ −54 V (over 10 devices). The transfer characteristics of the GFETs treated by ICP and TPP clearly show that phosphorus can indeed create more n-type characteristics than the well-known nitrogen atom by easily donating electrons to the graphene network [26].
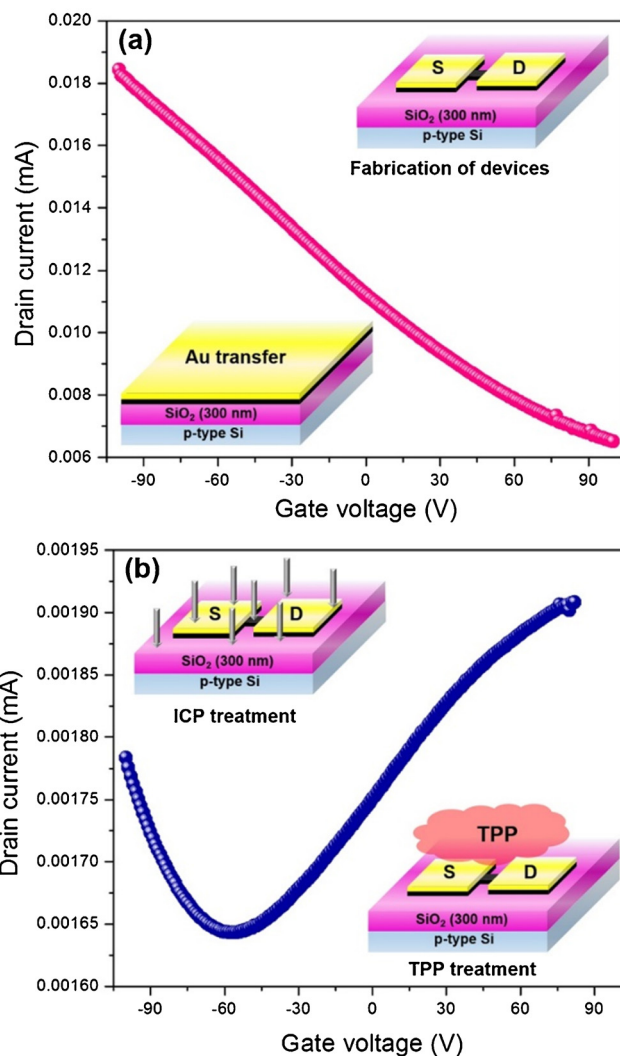

Fig. 1. Transfer characteristics of GFETs. (a) Raw graphene and (b) ICP and TPP treated graphene. The inset in (a) is the schematic for Au assisted transfer of graphene and the device structure of GFET. After GFET was fabricated, it was treated with ICP and TPP (schematic of inset in (b)).