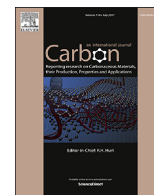
Carbon 118 (2017) 343–347

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon



Effect of stopping-layer-assisted boron-ion implantation on the electrical properties of graphene: Interplay between strain and charge doping

Chan Wook Jang [a], Ju Hwan Kim [a], Dae Hun Lee [a], Dong Hee Shin [a], Sung Kim [a], Suk-Ho Choi [a, *], Euyheon Hwang [b], R.G. Elliman [c]

[a] *Department of Applied Physics and Institute of Natural Sciences, Kyung Hee University, Yongin, 17104, South Korea*
[b] *SKKU Advanced Institute of Nanotechnology, Sungkyunkwan University, Suwon, 440-746, South Korea*
[c] *Department of Electronic Materials Engineering, Research School of Physics and Engineering, The Australian National University, Canberra, ACT, 0200, Australia*

ARTICLE INFO

Article history:
Received 14 December 2016
Received in revised form
15 March 2017
Accepted 17 March 2017
Available online 27 March 2017

ABSTRACT

We report a new method of ion implantation for hole doping of graphene in which a layer of polymethyl methacrylate (PMMA) is used as a stopping layer to control the B-ion distribution in the graphene layer. This method is very useful for graphene doping in many aspects because it employs the ion energy comparable to what is commercially used in the semiconductor processes and strongly enhances the doping effect in contrast to the previous studies, resulting from B-ions-induced gating effect. PMMA/graphene/Cu-foil stacks were implanted with 35 keV B^- ions to nominal fluences (ϕ_B) of 0.5–50 $\times$ 10^{10} cm^{-2} at room temperature. The electron/hole mobilities are sharply reduced by doping at $\phi_B = 0.5 \times 10^{10}$ cm^{-2}, but above this, they increase with increasing ϕ_B, as estimated from the Dirac curves. The Raman data and theoretical considerations suggest that the electrical properties of the B-doped graphene are governed by strain effect at low ϕ_B, but by charge-doping effect at high ϕ_B.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Graphene is recognized as having great potential for wearable, foldable, and transparent electrical/optical appliances thanks to its extremely-high carrier mobility, optical transparency, flexibility, strength, and robustness [1,2]. To enable such applications it is important to be able to tune electrical and optical properties of graphene, which is most readily achieved by doping. Doping of graphene differs from that of conventional semiconductors, and can be classified either: surface transfer doping or substitutional doping [3]. Surface transfer doping (or chemical doping) is simply achieved by electron exchange between graphene and dopants which adsorb on its surface. This shifts the Fermi level of the graphene, thereby controlling its work function as well as reducing its sheet resistance [4–7]. In general, chemical doping does not disrupt the structure of graphene and in most cases is reversible. However, this makes it susceptible to the changes in operating environment and the stability of chemically-doped graphene remains a limitation for many device applications [7,8]. Substitutional doping, which refers to the substitution of carbon atoms in graphene by foreign atoms with different valence, offers an alternative. In principle, this can be achieved by ion implantation [9]. For graphene research the ion implantation offers two other advantages, namely: 1) it is a room temperature process, enabling the doping and annealing processes to be studied independently; and 2) it enables selective doping of device and structures with different species. However, implanted ions have a depth distribution determined by their energy and the extent of this distribution is much larger than the thickness of a graphene layer for typical implant energies. The fraction of ions that stop in the graphene layer is therefore a small fraction of the total. This situation can clearly be improved by reducing the range of the ions but to achieve a significant improvement requires ion-energies well below those available in conventional ion-implanters (i.e. ≤100 eV). As a consequence there have been very few reports on ion implantation doping of graphene [10–13].

In this work, we report a new method for p-type doping of

* Corresponding author.
E-mail address: sukho@khu.ac.kr (S.-H. Choi).

http://dx.doi.org/10.1016/j.carbon.2017.03.058
0008-6223/© 2017 Elsevier Ltd. All rights reserved.

chemical-vapor-deposited graphene by using ion implantation and rapid thermal annealing (RTA). Before B ion implantation, the surface of the graphene/Cu foil was coated with polymethyl methacrylate (PMMA) as a stopping layer for controlling the B distribution. This allowed implants to be performed with 35 keV, compatible with conventional ion-implanters, and strongly enhanced the carrier density in contrast to the previous studies, resulting from B-ions-induced gating effect. Various structural, optical, and electrical tools are employed to evidence the effect of the B implantation, and to demonstrate enhancement of the electrical properties.

2. Experimental

Fig. 1 describes the implantation process used for B doping of graphene. Large-area, high-quality monolayer graphene sheets, as detailed in our previous reports [5–7], were grown on 70-μm-thick Cu foils (Wacopa, 99.8 purity) in a graphite-heater-based chemical vapor deposition (CVD) quartz tube furnace at a growth temperature of 1000 °C with 10-sccm H_2 and 20-sccm CH_4 flowing at a pressure of 3 Torr, and subsequently spin-coated with 200-nm-thick PMMA. The PMMA layer acts as a stopping layer for the implanted ions so that the peak of the implant distribution is centered on the graphene sheet. This method has an advantage in that it employs the ion implantation without greatly reducing the ion energy thanks to the use of the stopping layer, in contrast to previous studies on low-energy (~100 eV) ion-beam doping of graphene [10,11]. The PMMA/graphene/Cu stacks of 2×2 cm^2 area were implanted with 35 keV B^- ions to nominal fluences (ϕ_B) of (0.5, 1, 5, 10, and 50) x 10^{10} B cm^{-2} at room temperature (RT). The peak B concentration for these implants was calculated from SRIM simulation to be in the range of 10^{15}–10^{17} B cm^{-3}. Assuming a thickness of 0.3 nm for the graphene layer this corresponds to a doping concentration of only $3 \times 10^7 - 3 \times 10^9$ cm^{-3} from direct implantation. The Cu foil substrate was subsequently removed by electrochemical etching with aqueous 0.1 M ammonium persulfate solution $(NH4)_2S_2O_8$. The implanted PMMA/graphene stacks were then transferred onto SiO_2/Si substrates, and subsequently heated at 1000 °C for 10 s in a RTA apparatus under vacuum to remove the PMMA and anneal implantation-induced damage. The PMMA residue that remained after annealing was removed by dipping the PMMA/graphene/SiO_2/Si sample in an acetone bath. After a rinse with water, the B-implanted graphene layer was finally obtained on a SiO_2/Si substrate.

The sheet resistance of graphene was measured by the 4-probe van der Pauw method. Atomic force microscopy (AFM) and Kevin probe force microscopy (KPFM) were performed using atomic force microscope systems (XE-100, Park Systems). The bias applied to the KPFM tip was 1.0 V for all devices. To confirm the charge transfer by doping, the doped graphene layers were analyzed by Raman spectroscopy with a laser excitation energy of 532 nm (2.33 eV). Current-voltage measurements were used to characterize the electrical behavior of graphene field effect transistors (GFETs) and were undertaken using an Agilent 4156C parameter analyzer.

3. Results and discussion

Fig. 2a shows an electron energy loss spectroscopy (EELS) spectrum of graphene implanted to a B fluence of 5×10^{10} cm^{-2} after annealing, indicating a clear signature of B atoms in the graphene layer at ~190 eV [11,14,15]. Fig. 2b shows secondary ion mass spectroscopy (SIMS) mass spectra before and after annealing for a graphene film implanted to a B fluence of 5×10^{10} cm^{-2}, clearly showing the presence of ^{11}B. The SIMS intensity is enhanced almost 13 times in the annealed sample, likely due to the aggregation of B from the PMMA on the graphene surface. During annealing, some of this B may additionally interact with radiation-induced defects to increase the doping level.

The surface roughness of graphene was enhanced at larger ϕ_B, as shown by the AFM images (Fig. S1). The KPFM images and the

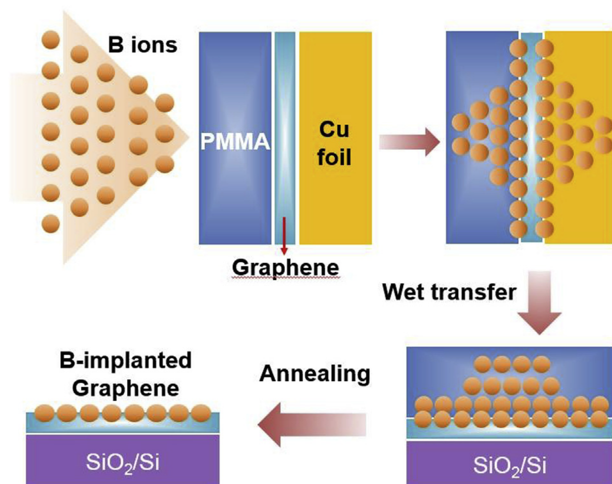


Fig. 1. Schematic diagram of fabrication processes for B-doped graphene on SiO_2/Si wafer: (1) spin coating of PMMA on CVD-grown graphene/Cu foil, (2) B-ion implantation, (3) Etching of Cu foil and wet transfer of implanted PMMA/graphene on SiO_2/Si wafer, and (4) annealing and etching of PMMA. (A colour version of this figure can be viewed online.)

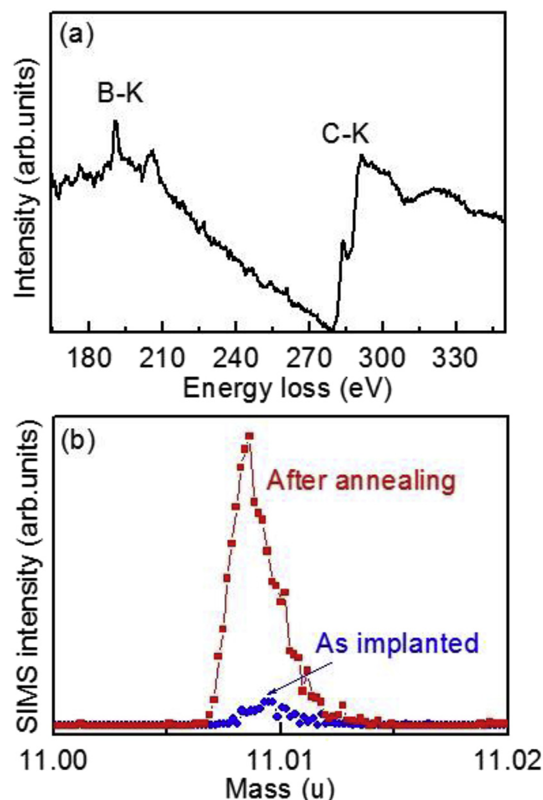


Fig. 2. (a) EELS spectrum after annealing for a grapheme film implanted to a B fluence of 5×10^{10} cm^{-2}. (b) SIMS profiles of ^{11}B ions before and after annealing for a graphene film implanted to a B fluence of 5×10^{10} cm^{-2}. (A colour version of this figure can be viewed online.)

Download English Version:

https://daneshyari.com/en/article/5432029

Download Persian Version:

https://daneshyari.com/article/5432029

Daneshyari.com