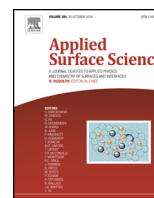




Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

A comparison of various surface charge transfer hole doping of graphene grown by chemical vapour deposition

S. Chandramohan^{a,b,*}, Tae Hoon Seo^c, V. Janardhanam^a, Chang-Hee Hong^a, Eun-Kyung Suh^{a,*}^a Department of Semiconductor Science and Technology, Semiconductor Physics Research Center, Chonbuk National University, Jeonju 54896, Republic of Korea^b Department of Physics & Nanotechnology, SRM University, Kattankulathur 603 203, Tamil Nadu, India^c Soft Innovative Materials Research Center, Korea Institute of Science and Technology, Jeonbuk 55324, Republic of Korea

ARTICLE INFO

Article history:

Received 17 October 2016

Received in revised form 9 January 2017

Accepted 11 January 2017

Available online xxx

Keywords:

Graphene

Charge transfer doping

Molybdenum trioxide

Rapid thermal annealing

ABSTRACT

Charge transfer doping is a renowned route to modify the electrical and electronic properties of graphene. Understanding the stability of potentially important charge-transfer materials for graphene doping is a crucial first step. Here we present a systematic comparison on the doping efficiency and stability of single layer graphene using molybdenum trioxide (MoO_3), gold chloride (AuCl_3), and bis(trifluoromethanesulfonyl)amide (TFSA). Chemical dopants proved to be very effective, but MoO_3 offers better thermal stability and device fabrication compatibility. Single layer graphene films with sheet resistance values between 100 and 200 ohm/square were consistently produced by implementing a two-step growth followed by doping without compromising the optical transmittance.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Since its discovery in 2004, graphene has become the most studied material owing to its two-dimensionality and unique band structure, which is fundamentally responsible for the remarkable electro-optical properties [1]. Especially, the superior carrier transport properties and exceptionally high optical transparency unified in an atomically thin sheet make it promising as a transparent conductive electrode (TCE) in place of brittle TCE of common use such as indium tin oxide for applications in a range of optoelectronic devices and flexible touch screens [2–8]. However, the low intrinsic carrier concentration and defects generated during the growth and transfer processes are known limiting the high conductivity requirement for practical applications [9,10], a key problem averting graphene's progress to budge from the laboratory to industry. While integration of graphene with already established flexible TCE materials like metal nanowires seems to be an appealing solution [11], this approach has limited relevance when it is necessary to

modulate the work function for specific device applications. Alternatively, a renowned *charge transfer doping* [12] has become the universal approach to realize low sheet resistance with a simultaneous work function regulation by exploiting the unprecedented charge-transfer interaction property of graphene i.e., being atomically thin with a vanishing density of states at the Dirac point, the Fermi level is very sensitive to external perturbations such as adsorption of metals, molecules, etc. Indeed, experiments have demonstrated that charge doping of graphene has the potential in achieving low sheet resistance values down to 30 ohm/square [2,4]. Following the pioneering work by Bae et al. [2], interest has arisen in developing doped graphene TCE and in recent years numerous studies have been conducted using different chemicals [5,12–15], strong acids [4,6], and organic molecules [16–18]. Of various p-type chemical dopants explored to date, metal chlorides are known to give the maximum doping efficiency [2,4,13] whereas the bis(trifluoromethanesulfonyl)amide (TFSA) provides better stability under normal ambient conditions [16]. However, majority of the chemical dopants including metal chlorides and TFSA on graphene surface have been found insoluble in water or organic solvents [19], inhibiting their use in device manufacturing that involves lithography and etching processes. Recently, few studies showed that relatively stable doping of graphene with sheet resistances below 20 ohm/square can be achievable through FeCl_3 intercalation [19,20], but it depreciates the optical transmittance drastically.

* Corresponding authors at: Department of Semiconductor Science and Technology, Semiconductor Physics Research Center, Chonbuk National University, Jeonju, 54896, Republic of Korea. Department of Physics and Nanotechnology, SRM University, Kattankulathur 603 203, Tamil Nadu, India.

E-mail addresses: chandramohan.sa@ktr.srmuniv.ac.in (S. Chandramohan), eksuh@jbnu.ac.kr (E.-K. Suh).

On the other hand, high work function transition metal oxides have been recognized as potential candidates for p-type doping of graphene and carbon nanotubes [21–27]. The advantage of using metal oxides is that they can be simply deposited onto graphene as thin film coating to not only dope graphene effectively without compromising the optical transparency [23], but also to provide graphene a conformal protective layer for integration in device technology [25]. Especially, molybdenum trioxide (MoO_3), a wide band gap material with unusually large electron affinity of 6.8 eV, has been broadly studied for graphene doping in organic electronic devices [23–25]. Unlike chemical dopants, the MoO_3 is demonstrated to be stable to environment [24], chemical [21], and high temperatures [22,26]. The doping mechanism is also studied to some extent through spectroscopic investigations for both stoichiometric MoO_3 [23] and substoichiometric MoO_x [28]. Majority of the previous studies considered growth and *in situ* evaluation of doping in high vacuum conditions and a major issue yet to be resolved is the instability of MoO_3 surface potential to air exposure and its impact on the doping efficiency and stability for long time exposure to environment. Despite promising results, disagreement exists between studies reported by different groups on the doping stability against air exposure. Therefore, understanding of the stability of potentially important charge-transfer materials for graphene doping is a crucial first step. Herein we give a systematic comparison on the doping efficiency and stability of single layer graphene doped by MoO_3 , AuCl_3 , and TFSA with respect to various factors such as the surface chemistry of graphene (amount of polymer residues), ambient exposure, and dopant morphology.

2. Materials and methods

Graphene used in this study was synthesized on electrochemically polished copper foil by low pressure CVD. Single layer graphene with reduced defect density aided by a two-step growth process was grown by using methane as a carbon precursor [29]. The transfer of graphene to arbitrary substrates (Al_2O_3 and SiO_2/Si) was performed by etching the Cu in ammonium persulphate after spin coating a thin polymethyl methacrylate (PMMA) layer on the surface of graphene as a protective layer. The detached PMMA-supported graphene was then washed in deionized water several times and transferred to the target substrates. The PMMA was dissolved in acetone followed by annealing at 400 °C for 600 s in a rapid thermal annealing system. In our experiments, the temperature ramp up and cool down times were 30 s and 300–600 s, respectively. The cool down was done under the flow of 10 slm N_2 until the temperature reduces below 50 °C. The MoO_3 (99.98%, Aldrich) deposition was carried out in a thermal evaporator under a base pressure of 10^{-6} Torr. The deposition rate was below 0.5 Å/s in most cases. For comparison, both AuCl_3 and TFSA are employed in our study, because these two materials in solution form have been shown very effective for the hole doping of graphene. Doping of graphene with AuCl_3 and TFSA was performed by dissolving the respective materials in nitromethane and spin-coating the solution on the surface of graphene. The three different doping processes are illustrated in Fig. 1.

The optical transmittance measurements were carried out by using a JASCO V-570 ultraviolet-visible-near-infrared (UV-vis-NIR) spectrophotometer. Raman spectra of graphene were obtained by using a 514 nm line of an argon ion laser. The resistivity measurements were carried out using a Hall Effect measurement system at room temperature with a magnetic field of 0.556 T. The surface topography was probed by atomic force microscopy in tapping mode. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific K-alpha instrument with a monochromized Al K α x-ray source (1486.6 eV). Ultraviolet

photoelectron spectroscopy (UPS) measurements were performed on an AXIS Ultra DLD spectrometer where He I discharge lamp ($h\nu = 21.22$ eV) was used as an excitation source.

3. Results and discussion

The opto-electrical characteristics of graphene films before and after doping with different materials are evaluated. Fig. 2(a) shows the optical transmittance spectra taken on 15 mm² graphene films doped with 10 mM AuCl_3 , 20 mM TFSA, and 5 nm MoO_3 . It can be seen that the optical transmittance of graphene is not deteriorated at moderate solution concentrations (for TFSA and AuCl_3 cases) or MoO_3 film thickness. The dependence of optical transmittance with respect to MoO_3 film thickness is shown in Fig. 2(b). It is observed that the MoO_3 /graphene hybrid possess high transparency exceeding 90% at all the MoO_3 film thickness studied from 1 to 20 nm. In addition, the maximum percentage of reduction in transmittance is estimated to be only 3.7% at 550 nm, corresponding to the MoO_3 film thickness of 20 nm. On the other hand, the optical transmittance of the AuCl_3 doped graphene films is known to have a strong dependence on the dopant concentration such that increasing the AuCl_3 concentration leads to increasing density of Au nanoparticles on the graphene surface [13,30]. In our study, 10 mM AuCl_3 and 20 mM TFSA solutions are considered optimum because the maximum decrease in sheet resistance can be achieved at those optimum concentrations [13,31], which will be shown later.

Fig. 2(c) shows the sheet resistance values of graphene measured before and immediately after the MoO_3 deposition for different film thicknesses. The measurements were performed on graphene transferred to SiO_2/Si substrates with van der Pauw contact geometry under normal ambient conditions. Some of the graphene films employed in this study were subjected to rapid thermal annealing (RTA) at 400 °C in an inert ambient for 10 min in order to eliminate the PMMA residues prior to the deposition of MoO_3 (the respective data are marked with an asterisk symbol in the figure). As can be seen in Fig. 2(c), the deposition of MoO_3 lowers the sheet resistance of graphene to values nearly half to that of its initial values for MoO_3 thickness above 3 nm. The results bring into picture that the effect of film thickness is insignificant beyond this optimal thickness (3 nm) at which a maximum decrease in sheet resistance of 56% is observed. This result is consistent with recent findings that the change in sheet resistance of graphene is approximately 50% and saturation occurs for 3–4 nm MoO_3 [23]. In addition, for majority of annealed samples (sample #4–7), the decrease in sheet resistance after MoO_3 deposition is estimated to vary between 43% and 50%. It is known that air exposure of graphene could result in change in the electronic properties of graphene and therefore the actual doping efficacy can vary from sample to sample if the experimental conditions are not invariant in all the cases. To avoid the inconsistency, we carried out similar experiments in a clean room condition (samples 9 and 10) and prior to MoO_3 deposition the samples were subjected to mild heat treatment at 150 °C. In this case, the doping efficacy is estimated to be 67% and 56%, respectively, for the pristine and annealed graphene. It is apparent that the doping efficacy has increased for graphene subjected to mild heat treatment prior to the deposition of MoO_3 and the doping efficacy of annealed graphene is relatively low compared to pristine graphene. Similar experiments were performed for AuCl_3 and TFSA doping and the results are shown in Fig. 2(d). In this case also annealed films showed relatively low doping efficacy compared to pristine graphene.

Residual polymer is known to impact the electronic properties of graphene and many studies have been reported in the past demonstrating that residual polymer leads to p-type doping and carrier mobility degradation in graphene transferred to foreign

Download English Version:

<https://daneshyari.com/en/article/5350145>

Download Persian Version:

<https://daneshyari.com/article/5350145>

[Daneshyari.com](https://daneshyari.com)