Applied Surface Science 328 (2015) 235–240

Contents lists available at ScienceDirect

Applied Surface Science

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

Fabrication of patterned flexible graphene devices via facile direct transfer of as-grown bi-layer graphene

Heun Park[a,1], Kyung Hoon Kim[a,1], Jangyeol Yoon[a], Kuk Ki Kim[b], Seung Min Park[b], Jeong Sook Ha[a,c,*]

[a] Department of Chemical and Biological Engineering, Korea University, Seoul 136-701, Republic of Korea
[b] Department of Chemistry, Kyung Hee University, Seoul 130-701, Republic of Korea
[c] KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul 136-701, Republic of Korea

ARTICLE INFO

Article history:
Received 6 August 2014
Received in revised form
13 November 2014
Accepted 1 December 2014
Available online 8 December 2014

Keywords:
Patterned graphene
Polydimethylsiloxane (PDMS) stamp
Ag nanowire sticker
Direct transfer
Flexible device

ABSTRACT

We report on the fabrication of patterned flexible graphene devices via a facile direct transfer of bi-layer graphene grown on alumina (Al_2O_3) substrate, and the use of Ag nanowire stickers as flexible electrodes. Patterned polydimethylsiloxane (PDMS) stamps coated with vaporized dimethylformamide (DMF) are utilized to transfer as-grown graphene directly onto a flexible polyethylene terephthalate (PET) substrate. The facile direct transfer is attributed to the enhanced adhesion of the bi-layer graphene to PDMS, due to DMF-coating, as well as the weak adhesion between the bi-layer graphene and the Al_2O_3 substrate. In this way, flexible patterned graphene devices have been fabricated with Ag nanowire stickers as electrodes. Stable electrical conduction characteristics were measured over repetitive bending with a bending radius down to 5 mm.

1. Introduction

Graphene, a two-dimensional monolayer carbon sheet, has attracted considerable attention in various fields. It can be used in diverse carbon-based devices due to its excellent mechanical, electronic and chemical properties [1–5]. In order to prepare graphene, many efforts have been made including the use of different techniques, such as mechanical exfoliation of graphite [6], chemical reduction of graphite oxide [7,8], arc discharge [9], and chemical vapor deposition (CVD) [3,10]. Among them, CVD is known to provide high quality graphene in a large scale [10]. In order to widen the application of large-scale growth of graphene to various devices, processing methods for transferring as-grown graphene onto the desired substrates have been developed. In addition, patterning of transferred graphene using different techniques, such as photolithography, mask plasma etching, and soft lithography with a polymer stamp, has been reported [11–13]. Among these techniques, soft lithography has the advantages of simplicity and cost-efficiency [14].

Recently, our group reported that bi-layer nano-graphene could be synthesized on alumina (Al_2O_3) substrate without catalysts by the thermal CVD method. Furthermore, due to its weak adhesion with Al_2O_3, as-grown graphene film could be easily transferred onto the thin film of polymeric materials such as poly(4-vinylphenol) (PVP) and polyimide (PI). However, it is quite complicated to pattern the transferred graphene film where conventional photolithography technique with O_2 reactive ion etching (RIE) process can be used to obtain the graphene channel. Furthermore, it was not transferred onto polydimethylsiloxane (PDMS) surface, which can be easily patterned as a stamp [15]. Even though the successful transfer of as-grown graphene from Cu to target substrates using dimethylsulfoxide-coated PDMS stamp was also recently reported [16], it required an extra step, i.e., transferring the graphene sheet from Cu to SiO_2/Si prior to the final transfer to target substrate. The need for this extra step can be explained by the strong adhesion between graphene and Cu that does not allow the direct detach of the graphene.

We have also demonstrated that flexible graphene devices with Au thin film electrodes showed deterioration of the electric conductivity upon repetitive bending due to the cracking of Au electrodes [15].

In this work, we report on the facile direct transfer of as-grown bi-layer graphene pattern from Al_2O_3 to any target substrate, including SiO_2 and polyethylene terephthalate (PET) film via

---

* Corresponding author at: Department of Chemical and Biological Engineering, Korea University, Seoul 136-701, Republic of Korea.
E-mail address: jeongsha@korea.ac.kr (J.S. Ha).

[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.apsusc.2014.12.003
0169-4332/

simple contact printing with dimethylformamide (DMF)-coated PDMS stamp. With such transferred bi-layer graphene patterns, we could fabricate flexible graphene devices exhibiting mechanical stability over 3000 repetitive bending, with a bending radius down to 5 mm. In particular, the use of Ag nanowires as electrode materials, instead of Au thin film, could improve the flexibility of the graphene device. Here, we provide a facile transfer technique of graphene patterns over large surface area for various applications to flexible and transparent graphene based devices [17–20].

2. Experimental details

2.1. Preparation of PDMS stamp

The PDMS stamp material was prepared by mixing a base (Dow Corning, Sylgard 184 A) and a curing agent (Dow Corning, Sylgard B) with a mixing ratio of 10:1. The mixture was degassed for 30 min under atmospheric conditions to eliminate air bubbles. Then, it was cured in a dry oven (at 70 °C) to make cross links and obtain the final molded PDMS stamp with a pattern.

2.2. Growth of graphene on Al_2O_3 using CVD

Bi-layer graphene sheet used in this work was synthesized by thermal CVD method. 50 nm thick Al_2O_3 employed as a growth substrate was deposited onto SiO_2/Si by atomic layer deposition (ALD) method. The alumina substrate was placed in a quartz tube furnace and the system inside the tube was purged with Ar gas (500 sccm, ultra high purity, 99.9999%). The operating pressure inside the tube was maintained down to 20 Torr by a mechanical pump. Then, the furnace was heated up to 1050 °C in 30 min. After the temperature of the furnace reached 1050 °C, the growth began with adding CH_4 gas (400 sccm, high purity, 99.995%) and H_2 gas (50 sccm) for 180 s. When the growth was over, the system was purged with Ar gas and slowly cooled down to room temperature.

2.3. Transfer of graphene onto a target substrate

The patterned PDMS was gently exposed to DMF (Sigma-Aldrich, 319937) vapor. PDMS was located 5 cm above the boiling liquid-phase of DMF at 200 °C for 30 s. The DMF-coated PDMS was put in contact with the graphene grown on alumina substrate in order to remove the graphene. Then, the graphene transferred to PDMS was put in contact with a target substrate, followed by curing in a dry oven (at 70 °C) for 5 min. Then the PDMS stamp was detached, leaving the graphene on the target substrate.

2.4. Fabrication of an Ag nanowire sticker

A 100 μm-thick PDMS was spin-coated (2000 rpm, 30 s) on a SiO_2 substrate and half-cured at 65 °C for 9 min to produce a sticky film. A few drops of Ag-nanowire solution (1 wt% diluted in water, Ditto Technologies) with an average nanowire diameter of 65 nm and length of 10 μm were coated onto the half-cured PDMS film and dried in air.

2.5. Fabrication of flexible graphene device on a PET substrate

Line-patterned graphene was transferred to a polyethylene terephthalate (PET) film (250 μm). Ag nanowire stickers as electrodes were attached to both sides of the line-patterned graphene channel. Cu wire was inserted between the graphene and the Ag nanowire sticker and connected to the probes for electrical measurements by using an Ag paste.

2.6. Characterizations

Patterned graphene was investigated by taking Scanning electron microscope (Hitachi S-4800) images, atomic force microscope (Park system, XE-100) images, and optical microscope (BX41M, Olympus) images. Raman spectra were taken from the patterned graphene (LabRam Aramis, Horiba Jobin Yvon): The wavelength of the Ar-ion excitation laser and the power were 514.5 nm and 0.5 mW, respectively. Raman mapping image was obtained by a homemade micro Raman spectroscope (PMT detector, SR810 lock-in amplifier, 532 nm wavelength, 50 mW power). FT-IR analysis was performed using a JASCO FT-IR 4100 (Koprti) and measured in ATR mode with a resolution of 4 cm^{-1}.

3. Results and discussion

The fabrication process of patterned graphene based devices via a direct transfer method using PDMS stamp is schematically described in Fig. 1. First, bi-layer graphene was grown on the Al_2O_3 substrate by CVD at 1050 °C with controlled flow of CH_4 and H_2 gases. After soft-contact of the DMF-coated patterned PDMS stamp with as-grown graphene/Al_2O_3 substrate, the PDMS stamp was detached and as-grown graphene was transferred onto the PDMS stamp. Then, contact of graphene/PDMS stamp with a target substrate (SiO_2 or PET) for 1 min, and its subsequent detachment, resulted in the transfer of patterned graphene onto the target substrate. Finally, attachment of Ag nanowire stickers instead of e-beam evaporation of Au thin film was done to form electrodes for fabricating graphene-based flexible devices. The molecular structure of DMF is also illustrated.

The used transfer mechanism exploits the difference in adhesion force at the interfaces. Since the graphene sheet is well dispersed in DMF solution, DMF-coated PDMS is expected to increase the adhesion to graphene compared to bare PDMS. As previously reported [21], DMF, a commonly used polar aprotic solvent similar to dimethylsulfoxide (DMSO) [22], is expected to facilitate the transfer of graphene to PDMS stamp. In addition, the adhesion of graphene to Al_2O_3 substrate is very weak, thus enhancing the transfer of the CVD-grown graphene onto the DMF-coated PDMS.

After contact of graphene/DMF/PDMS with the target substrate for 1 min at room temperature, DMF is released. Therefore, the weakening of the adhesion force, i.e., $E_{\text{GR-SiO2}}$ ($\sim$4.3 meV/Å^2) > $E_{\text{GR-PDMS}}$ ($\sim$2.5 meV/Å^2), results in the transfer of the graphene onto the target substrate [16].

The quality of CVD-grown graphene on Al_2O_3 was investigated by collecting Raman spectra and optical microscope images. Under the growth conditions we used, bi-layer graphene was synthesized with a 2D-peak over G-peak intensity ratio (I_{2D}/I_G) ~ 1 in the Raman spectrum, as shown in Supplementary **Fig. S1.**

DMF was gently coated on a patterned PDMS surface via vaporization of DMF molecules at 200 °C and by keeping the contact with the PDMS surface for 30 s. In order to confirm the coating of DMF, water contact angle and Fourier transform infrared spectroscopy (FT-IR) spectra, shown in Fig. 2, were measured. Fig. 2(a) shows the variation of the contact angle with the increase of the exposure time of the surface to DMF solution. As the exposure time increased, the contact angle decreased until reaching the limit of 91° after 30 s. Thus, the whole PDMS surface is considered to be fully covered with DMF molecules after 30 s. The inset shows the pictures of the contact angles. Since PDMS stamp surface is non-polar (hydrophobic), while DMF is a polar (hydrophilic) solvent, the water contact angle decreased from 124 to 91° after DMF treatment depending on the DMF exposure time. Fig. 2(b) shows the FT-IR spectra collected from the bare PDMS (blue line) and the DMF-coated PDMS