CARBON 86 (2015) 288–300

Available at www.sciencedirect.com

ScienceDirect

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

Dry graphene transfer print to polystyrene and ultra-high molecular weight polyethylene – Detailed chemical, structural, morphological and electrical characterization

Evgeniya H. Lock [a,*], Dean M. Delongchamp [c], Scott W. Schmucker [b], Blake Simpkins [d], Matthew Laskoski [d], Shawn P. Mulvaney [d], Daniel R. Hines [e], Mira Baraket [b,1], Sandra C. Hernandez [g], Jeremy T. Robinson [f], Paul E. Sheehan [d], Cherno Jaye [c], Daniel A. Fisher [c], Scott G. Walton [g]

[a] Materials Science and Technology Division, Naval Research Laboratory, Washington, DC 20375, USA
[b] National Research Council Postdoctoral Research Associate, Washington, DC 20375, USA
[c] Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA
[d] Chemistry Division, Naval Research Laboratory, Washington, DC 20375, USA
[e] Laboratory for Physical Sciences, College Park, MD 20740, USA
[f] Electronics Division, Naval Research Laboratory, Washington, DC 20375, USA
[g] Plasma Physics Division, Naval Research Laboratory, Washington, DC 20375, USA

ARTICLE INFO

Article history:
Received 29 September 2014
Accepted 25 January 2015
Available online 31 January 2015

ABSTRACT

Graphene (Gr)–polystyrene (PS) and graphene (Gr)–ultra-high molecular weight polyethylene (UHMW PE) laminates were fabricated using a transfer print approach that relies on differential adhesion to remove graphene from Cu foil without chemical etching. The polymer surfaces were prepared using plasma functionalization followed by N-ethylamino-4-azidotetrafluorobenzoate (TFPA) deposition. Then, the graphene on Cu foil and the TFPA coated polymers were pressed at elevated temperature and mild pressure. Finally, they were separated by mechanical peeling. No additional processing was applied. Detailed chemical, structural, and morphological characterization of PS and UHMW PE before and after graphene transfer print was performed using a suite of complementary surface analysis techniques including X-ray Photoelectron Spectroscopy (XPS), Near Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS), Raman Spectroscopy, and Atomic Force Microscopy (AFM). The charge carrier density and charge carrier mobility of the transferred graphene were determined using Hall effect measurements. We found that graphene's electrical properties were preserved and comparable to those of graphene on SiO_2/Si. Furthermore, modulation of TFPA attachment to PS and UHMW PE led to different TFPA-layer microstructure and therefore to a different amount of functional azide groups available to form carbene bonds with graphene causing changes in graphene's compressive strain, doping and mobility.

Published by Elsevier Ltd.

* Corresponding author.
E-mail address: evgeniya.lock@nrl.navy.mil (E.H. Lock).
[1] Current address: Laboratoire de Chimie Inorganique et Biologique, 38054 Grenoble, France.
http://dx.doi.org/10.1016/j.carbon.2015.01.048
0008-6223/Published by Elsevier Ltd.

1. Introduction

Plastics made from organic polymers are attractive substrates for flexible, transparent, cost effective electronics due to their physical properties [1–5]. The production of flexible wearable electronics, RFID tags, transparent conductors and devices for solar cells, embedded electronics and displays, and transparent conductors for window heating will depend on successful integration of polymers and conducting layers [6–10]. Currently, polymers are coated with conductive oxide films e.g. indium tin oxide (ITO) [7]. However, ITO is rigid and brittle, which causes cracking when it is bent, leading to a dramatic decrease in conductivity. Furthermore, de-bonding between ITO and the polymer substrate can occur under compressive strain if the ITO/polymer adhesion is not strong enough. Thus, the production of alternative transparent conductive electrodes is a critical technology need [11]. Integration of graphene onto polymer substrates could allow for a combination of graphene's electrical and thermal conductivity, remarkable chemical stability and low permeability with the flexibility and mechanical advantages of plastics [12–16].

Production of large area graphene/polymer laminated composite structures is not trivial, generally relying on graphene transfer from growth substrates (e.g. copper (Cu) foil or SiC) onto polymers. To date, there is no direct graphene synthesis route on polymer surfaces [17,18]. Even though different graphene transfer techniques have been developed, stable defect-free graphene attachment to polymeric substrates remains challenging [19,20]. We recently developed a dry etch-free graphene transfer print method based on differential adhesion [21] that is broadly applicable to temperature- and solvent-sensitive organic substrates. We have shown transfer of graphene from Cu foil to PS using different printing tools [22]. We found that the key to successful graphene transfer lies in the preparation of the polymer surfaces and in the uniform application of finite force to the polymer/Cu foil stack [22].

Here, we provide detailed characterization of polystyrene (PS) and ultra-high molecular weight polyethylene (UHMW PE) films before and after graphene transfer to understand the effect of substrate preparation on graphene's electrical properties. We use a suite of complementary surface analysis techniques including X-ray Photoelectron Spectroscopy (XPS), Near Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS), Raman Spectroscopy, and Atomic Force Microscopy (AFM) to characterize the chemistry, structure and morphology of the polymers. In addition, the charge carrier density, charge carrier mobility, and strain of transferred graphene on PS and UHMW PE are determined using Hall effect measurements. We will show that modulating the attachment of TFPA molecules to the polymer surfaces affects the TFPA layer structure and thus affects graphene's structural and electrical properties.

2. Experimental

2.1. Materials

Polystyrene with 250 μm thickness was purchased from Tekra. Ultra high molecular weight polyethylene film with 75 μm thickness was purchased from Goodfellow. 1-Ethyl-3-[3-dimethylaminopropyl]carbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS) were purchased from Thermo Fisher Scientific. 2-[Morpholino]ethanesulfonic acid (MES), NaCl, and sodium phosphate were purchased from Sigma Aldrich. The activation buffer was composed of 0.1 M MES, 500 mM NaCl, and the pH was adjusted to 6.0. The coupling buffer was made from 100 mM sodium phosphate, 150 mM NaCl, with the PH adjusted to 7.2.

2.2. Graphene growth

Graphene was grown on polycrystalline Cu foil using a technique that selectively produces single layer films under appropriate conditions [23]. We further verified that our graphene films were single layer by transferring a portion of each foil pocket to 100 nm SiO_2 on Si, where the layer count can be optically determined [24].

2.3. Plasma treatment of polymers

Electron beam-generated plasma was used for polymer functionalization prior to TFPA molecule deposition as previously discussed [25,26]. The electron beam was produced by applying a -2 kV pulse to a linear hollow cathode for a selected pulse width and duty factor. The emergent beam passed through a slot in a grounded anode and was then terminated at a second grounded anode located further downstream. Beam spreading from collisions with the background gas was suppressed by a co-axial magnetic field (150 G) produced by a set of external coils. The system vacuum was maintained by a 250 L/s turbo pump, with a base pressure of 5×10^{-6} Torr. The operating pressure was achieved by introducing CO_2 (purity >99.995%) through the mass flow controllers and throttling the pumping speed using a manual gate valve. The samples were placed on a 10.2 cm diameter stage located at 2.5 cm from the nominal edge of the electron beam. The stage was held at ground potential and room temperature. Polymers were treated at a pressure of 100 mTorr, for 1 min, at a duty factor of 10%.

2.4. N-ethylamino-4-azidotetrafluorobenzoate (TFPA) linker molecule synthesis

All starting materials were of reagent grade and used without further purification. N-succinimidyl-4-azidotetrafluorobenzoate was synthesized from a previously published procedure [27]. Proton Nuclear magnetic resonance spectroscopy (^{1}H-NMR) was performed on a Brüker ADVANCE 300 spectrometer. **N-ethylamino-4-azidotetrafluorobenzoate (1)**: Ethylenediamine (6.36 g, 105.8 mmol) and 100 mL acetonitrile were added to a 250 mL round bottom flask. The mixture was cooled to 0 °C and (N-succinimidyl-4-azidotetrafluorobenzoate (2.00 g, 6.02 mmol) in 25 mL acetonitrile was added dropwise over 20 min. The reaction was stirred at 0 °C for an additional 1 h and the white precipitate that had formed was filtered using a Buchner funnel. To the filtrate was added 100 mL chloroform and washed with water (3×50 mL) and dried over magnesium sulfate. The solvent was then removed *in vacuo* and