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Graphene transfer with self-doping by amorphous thermoplastic resins

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ABSTRACT

The wet transfer of graphene requires sacrificial layer, which can support graphene during the removal of metallic substrate and prevent mechanical damage of thin graphene. However, the used polymer layer leaves an amounts of debris or residue on the graphene surface. The typical amorphous thermoplastic resins that consist of macromolecular chains with no crosslinks between the chains have been investigated as sacrificial layers for transferring graphene grown on metallic substrate. We have observed that the strong interaction of graphene and polymer provides clean surface without a chuck of residues and largely diminishes wrinkles and folds of transferred graphene. In addition, due to the increased substrate coupling as well as uniform plausible covalent bonding, we have achieved significant amount of electron transfer from graphene. Thus, polymer-self-doped-graphene during the transfer process has no need for the additional doping process or annealing process in order to obtain clean and flat surface with reduced sheet resistance. No thermal budget makes graphene available towards flexible transparent device application.

1. Introduction

Recently, the global scientific and industrial community have paid tremendous attention to graphene as a promising candidate for flexible transparent conductive electrode due to the superior electronic mobility and high optical transmittance [1,2]. The graphene growth using chemical vapor deposition (CVD) has made possible the mass production of uniform large area graphene sheets [2,3]. Since future display devices of large pixels require both low sheet resistance and optical transmittance, graphene requires additional doping process to satisfy both parameters despite of giant electronic mobility. Therefore, various chemical doping via covalent or noncovalent molecular interactions onto graphene surface have been attempted to increase charge carrier density.

Since CVD growth is basically dependent on the catalytic activity of metallic substrate such as Cu or Ni, it is essential to develop reliable graphene-transfer methods from growth substrate onto insulating ones to integrate electronic devices. The most common method is the wet transfer utilizing sacrificial polymer such as Poly(methyl methacrylate) (PMMA) [4]. However, graphene wet transfer generated severe drawbacks by leaving PMMA on the graphene surface. It degrades charge carrier mobility and makes it difficult to obtain the clean graphene surface for molecular adsorption [5,6]. The removal of PMMA has been marginally successful by annealing graphene at high temperature under Ar/H_2 or O_2 gas environments [7,8]. However, high temperature processes creates unexpected defects [8] and high thermal budget prevents the graphene applications for flexible electronics.

Here, we investigate graphene transfer using optically transparent and brittle thermoplastic resins as sacrificial layer. The used polymers are PMMA, polycarbonate (PC) and Polystyrene (PS) with the order of high glass transition temperature (T_g). PC and PS of aromatic structures can be easily removed by the solvents such as chlorobenzene or chloroform and have similar decomposition temperature. The decomposition temperature (T_d) of PMMA is 226–256 °C while ones of PC and PS are ~327 and 318–348 °C [9]. PC has phenyl functional group which can covalently bind with graphene. The stronger adhesion between graphite/PC than graphite/PS has been reported [10]. Our study demonstrates that through comparison of those polymers we could obtain uniform

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flat surface without thermal treatment and simultaneously low sheet resistance by self-doping.

2. Experimental

Single-layer graphene was grown by rapid thermal chemical vapor deposition (RTCVD) using a halogen lamp heater on Cu foil. To transfer graphene onto the intended target substrate, Poly(methyl methacrylate) (PMMA), Polystyrene (PS) and polycarbonate (PC) were spin-coated on to graphene. We used respective average molecular weight of 996 k, 10 k and 45 k for PMMA, PS and PC. In case of low molecular weight PMMA, graphene is too easily torn apart so we utilized most common molecular weight. Cu foil was etched away in ammonium persulfate (APS) solution and graphene/polymer stacks are transferred onto SiO_2/Si(n++) substrate after cleaning in de-ionized water (DI). Then, we removed each polymer by acetone, chlorobenzene and chloroform, respectively. A graphene channel was defined by photolithography and fabricated by etching the regions outside the channels with O_2 plasma at a power of 20 W for 2 min. The source/drain electrodes of Au (100 nm) were deposited using thermal evaporator. The channel length/width (L/W) of measured devices are 35/190 μm, respectively. To investigate the electrical property of graphene transferred by different polymer support, we averaged channel transport curves with the measurement on 20 cells of each polymer type transistor. Raman spectroscopy (Renishaw inVia Raman Microscope) was conducted using a 514-nm laser on the channel area of graphene transistors. The topological images of graphene were obtained using non-contact mode of Atomic force microscope (AFM, NX10, Park systems) using heavily n-doped silicon tip. The Carbon 1s (C1s) signal of graphene samples was measured by X-ray photoelectron spectroscopy (XPS, SIGMA PROBE, ThermoVG) under high vacuum.

3. Results and discussion

Fig. 1(a) shows the sheet resistance (R_{sh}) of graphene as measured by 4-probe measurement. PMMA-G, PS-G and PC-G represent graphene samples transferred by PMMA, PS and PC. The obtained R_{sh}s of PMMA-G, PS-G and PC-G are 1000–2500, 700–1000 and 300–450 Ω/sq, respectively. PC-G exhibited the lowest R_{sh} with better uniformity than the other graphene samples. To measure the optical transmittance at 300–800 nm wavelength, the transfer onto glass substrate was handled exactly the same and simultaneous process onto SiO_2 substrate for three different transfer polymers using same batch graphene. The observed transmittance shown in Fig. 1(b) exhibits no difference in three graphene layers. The inset in Fig. 1(b) enlarges transmittance around 550 nm wavelength. Its value is around 97.3 (±0.2) % which almost corresponds to 97.6% of ideal monolayer [4,11].

We performed Raman spectroscopy using a 514-nm laser after the completion of transistor. For sp^2 hybridized graphene, Raman spectrum of intrinsic graphene shows three distinctive features: D, G and 2D peaks located around 1350, 1580, and 2700 cm^{-1}. Fig. 2(a) displays the normalized Raman spectrum by the G peak intensity (I(G)). We designated characteristic graphene modes with the dotted vertical lines in Fig. 2(a). Raman inactive D peak becomes Raman active with the existence of structural defects, so it is often utilized for the characterization of defects such as graphene edge [12,13]. The normalized the D peak intensity (I(D)/I(G)) is 0.03–0.06 so that it appears to be negligible.

The G and 2D peaks are the most prominent features in graphene and are useful to monitor electronic structure variation such as doping or work function. The G peak corresponds to the E_{2g} phonon at the Brillouin zone center while 2D peak is the second order overtone of the D peak. The G peak blue-shifts with increasing the carrier concentration regardless of the type of carriers [12]. On the other hand, although 2D peak shows blue- or red-shift depending on charge carrier, its intensity analysis is often of use due to the sensitive response to the carrier concentration. Thus, the 2D intensity (I(2D)) along with the G peak shift are generally exploited for the doping analysis [12]. The G peak centers are at 1582 (±2.0), 1584 (±2.0) and 1594 (±2.0) cm^{-1} whereas, I(2D)/I(G) ratios are 3.5 (±0.45), 2.3 (±0.35) and 1.3 (±0.15) for PMMA-G, PS-G and PC-G respectively. Fig. 2(b) shows I(2D)/I(G) ratio as a function of G peak position.

The channel current with applied source/drain voltage (I_{ds}-V_{ds}) at gate-floating exhibits ohmic behavior as shown in Fig. 3(a). The channel resistance value (R_{ch}) calculated from the curve slope of I_{ds}-V_{ds} is around 350 (±20), 280 (±10), 120 (±10) Ω for PMMA-G, PS-G and PC-G. R_{ch} is composed of contact resistance (R_c) and graphene channel resistance (R_g). From the R_{sh} values obtained by 4-probe method, calculated $R_g = R_{sh}*L/W$ for 35/190 μm is approximately 175–437, 122–175, and 52–88 Ω for PMMA-G, PS-G and PC-G. Lower R_g than R_{ch} is reasonable considering the positive contact resistance. However, for PMMA-G, we often obtain larger R_g than R_{ch} in the resistance range of 355–437 Ω. This might be caused by the large fluctuation of graphene sheet resistance for PMMA-G. For 2-terminal I_{ds}-V_{ds} measurement, we use large contact area of source and drain electrodes defined by photolithography. Thus, the obtained data are averaged by all the involved moving paths of charge carriers. But for 4-probe measurement, these contact areas are narrow, determined by the tip. This implies that the electronic states of graphene transferred by PMMA show strong local disorder unlike the ones by PS or PC. This disorder is blamed for large R_{sh} fluctuation of PMMA-G.

Fig. 3(b) exhibits gate voltage (V_g) dependent channel current at

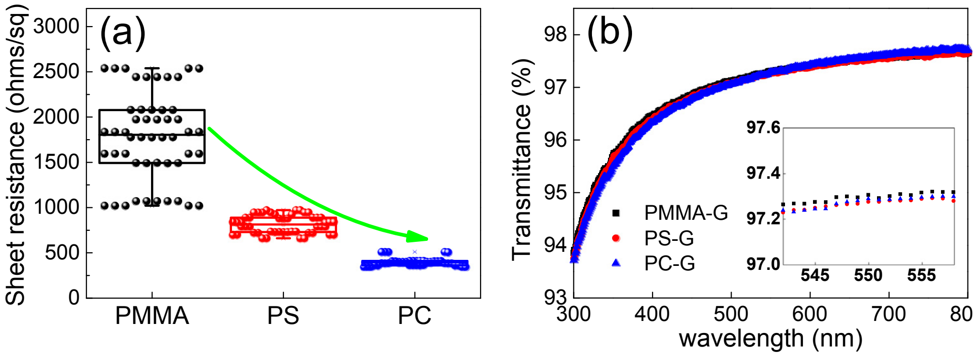

Fig. 1. (a) Sheet resistance and (b) Transmittance of PMMA-G, PS-G and PC-G. The inset of figure (b): the enlarged plot of transmittance near 550 nm. (A colour version of this figure can be viewed online.)