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Large-scale cellulose-assisted transfer of graphene toward industrial applications

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ABSTRACT

CVD graphene has attracted a great deal of interest from both academia and industry. The strong motivation to commercialize high quality CVD graphene films and related devices has been restricted by the lack of a cheap, efficient, clean and reliable graphene transfer process. In this article, we report a novel graphene transfer technique which provides a route to high-throughput, reliable and economical transfer of graphene without introducing large cracks and residue contamination from polymers, such as PMMA or magnetic impurities. The transferred graphene was thoroughly characterized with Raman spectroscopy, Atomic Force Microscopy, and X-ray photoelectron spectroscopy. Fabricated large area graphene-based field effect transistors exhibited high mobilities, which were about 2 times higher than those for devices prepared with graphene transferred by the conventional wet transfer method. This new graphene transfer technique has the potential to expedite the large scale industrial utilization of CVD graphene in electronics, spintronics, catalysis and energy storage.

1. Introduction

Graphene is a one atom thick two dimensional carbon material, whose valence and conduction bands touch each other at the Dirac point [1,2]. The fascinating properties, which originate from the unique electronic structure of graphene, motivate the wide interest in its potential application in many fields, such as electronics [3–8], spintronics [9], optics [5], environmental engineering [10,11], and aerospace [12]. Chemical vapor deposition (CVD) is among the most promising methods for production of macro-size, continuous, high-quality graphene films for industrial applications [13–16].

The first step in the fabrication of devices based on CVD graphene is transfer of the as-grown graphene from copper or nickel to a targeted substrate, usually SiO_2/Si, boron nitride, or quartz. Although several transfer methods have been developed so far, few can be used for industrial applications due to their time-consuming, costly, or challenging scalability [17,18]. A conventional graphene wet transfer method [13,14] widely employed in academia utilizes poly(methyl methacrylate) (PMMA) as the supporting layer and etching of the Cu or Ni substrate with iron chloride or iron nitrate [19–22]. However, researchers have been struggling with the degradation of graphene's intrinsic properties by contaminations from residues of PMMA and paramagnetic Fe^{3+} [23–25]. Few advances have been made towards a high-throughput economic transfer of graphene for commercialization needs. Although the roll-to-roll (R2R) method can transfer large scale graphene onto targeted substrates [16,26], the thermal release tape is known to leave contamination on the graphene layer [14,27] and R2R method is not applicable to SiO_2/Si substrates, limiting its application in the semiconductor industry. The face-to-face graphene transfer method offers large-area, continuous graphene films with reduced density of transfer defects, however, the process is designed for "stiff" substrates [17]. The clean lifting transfer (CLT) method solved the issue of PMMA residue by making use of an

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electrostatic attraction force to protect graphene during the transfer process. However, this method uses high voltage and it has a strict requirement for the surface flatness of the as-grown graphene on Cu or Ni, which restrict its potential industrial application. Additionally, the contamination with paramagnetic Fe^{3+} remains an unresolved issue. For transfer methods that employed ammonium persulfate as the etching solution in order to avoid contamination from paramagnetic materials [28–30], the cost and time increased dramatically.

In this article, we discuss the development of a novel technique for the transfer of graphene on various substrates. The method utilizes cellulose acetate as the coating layer, which protects graphene from unfavourable forces and contaminations during the transfer process by forming a soft flexible thin film on top of graphene. The etching of Cu foil, used in the CVD graphene growth, is accomplished with a hydrogen peroxide – hydrogen chloride solution, which decreases the possibility for magnetic contamination of the graphene. This cellulose assisted transfer (CAT) method largely reduces the cost, time and contaminations of the obtained graphene layer and can be expanded to industrial scale applications. The main advantages of the CAT method in comparison with other graphene transfer techniques are summarized in Table 1. The transferred grapene films were characterized with Raman spectroscopy, atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) to evaluate the quality of the obtained films. The fabricated field effect transistor (FET) devices showed high mobility and high on-off ratio.

2. Experimental

2.1. CAT graphene transfer

As-grown monolayer CVD graphene (Graphene Supermarket) was first spin coated with a cellulose acetate solution (Average Mn ~ 50,000 by GPC, Sigma Aldrich, 4.5 mg/mL dissolved in acetone) at 2000 rpm. The spin-coated thin film dries immediately as the acetone evaporates. The graphene on the uncoated side was etched away by oxygen plasma (Oxford Plasmalab 100/180 model; forward power 30 W; ICP power 300 W, etching time 30 s). An aqueous solution of H_2O_2 and HCl was prepared by mixing equal volumes of 2 M HCl and 1 M H_2O_2; the solution etches away the Cu substrate (25 μm) underneath the CVD graphene within 10 min. The graphene sample was thoroughly cleaned by replacing the etching solution with distilled water. The substrate with the transferred graphene was placed on a hot plate and kept at 35 °C for 10 min, followed by baking at 200 °C for 20 min. After the substrate with the graphene was cooled down to ~60 °C, it was exposed to acetone vapors for 5 minutes and then submerged into a hot acetone bath for ~15 minutes to remove the cellulose acetate.

2.2. PMMA graphene transfer

As-grown monolayer CVD graphene was first spin coated with a PMMA solution (950 PMMA A4, MicroChem, 10% by volume dissolved in chlorobenzene) at 2000 rpm. The spin-coated thin film was kept at room temperature overnight inside a clean petri dish. The graphene on the uncoated side was etched away by oxygen plasma as described in section 2.1. Then the PMMA/Graphene/Cu sample was placed on the surface of $FeCl_3$ solution (0.5 M) to etch away the Cu substrate (thickness 25 μm; typical etching time 60 min). After the Cu was removed, the etching solution was replaced with clean water by repeatedly flowing out the waste solution and flowing in clean water until neutral pH was reached. The substrate with the graphene was transferred to a hot plate and kept at 35 °C for 10 min. After this step the temperature was increased and maintained at 200 °C for 20 min. The substrate with the graphene was cooled down to ~60 °C and kept in a hot acetone bath overnight to remove the PMMA.

2.3. Raman spectroscopy and mapping

Raman spectra and mapping of CVD graphene were recorded with a Nicolet Almega XR Dispersive Raman microscope using laser excitation of 532 nm at 25% power. The laser spot size is around 1 μm with a 50 x objective lens. The Raman mapping area for all samples is 20 μm × 18 μm, with a step size of 1 μm in both x and y directions.

2.4. Atomic force microscopy (AFM)

AFM images were collected in a tapping mode with Digital Instruments, Nanoscope IIIA.

2.5. X-ray photoelectron spectroscopy (XPS)

XPS of transferred CVD graphene on 300 nm SiO_2/Si substrates was carried out with a Kratos AXIS ULTRADLD XPS system equipped with Al Kα monochromated X-ray source and a 165 mm mean radius electron energy hemispherical analyzer. Vacuum pressure was kept below 3×10^{-9} torr during the acquisition. The high-resolution scans were run using a power of 300 W, 20 pass energy and a step size of 0.05 eV. A low-energy electron flood from a filament was used for charge neutralization. The size slot for the XPS is 300 μm × 700 μm. The peak fits consist of Lorentzian and Gaussian distributions.

2.6. Fabrication of field effect transistors (FETs)

Drain and source electrodes (10 nm Cr/100 nm Au) were evaporated by an E-beam evaporator onto 300 nm SiO_2/Si substrates with a shadow mask. After that, the as-grown monolayer CVD graphene was transferred onto the pre-patterned substrates by the conventional PMMA transfer and CAT methods, respectively. The channel dimensions of all graphene devices are 0.25 mm (length) × 1 mm (width). No photolithography was employed to exclude the effect of photoresist residues on the electronic

Table 1
Comparison of several parameters of different graphene transfer methods.

Graphene transfer method	Approximate time for one transfer	Cost	On/off ratio FET ($V_G = 30$ V)	Contamination	Comment	Ref.
Conventional wet transfer (PMMA/Fe^{3+})	1–2 days	High	2.2	Magnetic, PMMA	Light sensitive	[14]
Clean lifting transfer (Static charge/$Fe3^{+}$)	2 h	High	2.4	Magnetic	High voltage	[15]
Polymer-free transfer (IPA/$(NH_4)_2S_2O_8$)	4 h	Medium	N/A	No	Low yield	[30]
Cellulose acetate transfer (Cellulose/H_2O_2/HCl)	1 h	Low	3.5	No	High throughput	Present study