



Clean and efficient transfer of CVD-grown graphene by electrochemical etching of metal substrate

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ABSTRACT

An electrochemical etching technique was developed to achieve a clean and efficient transfer of large-area graphene films grown on copper foils by chemical vapor deposition without degrading the quality of graphene. Clean transfer for continuous graphene films with fewer impurities and unintentional *p*-type doping in comparison with conventional wet-etching in oxidant solutions was confirmed by optical microscopy, scanning electron microscopy, atomic force microscopy, ultraviolet–visible spectroscopy, and Raman spectroscopy. This electrochemical transfer technique can be scaled up for industrial use and generalized to various substrates by selecting suitable oxidation voltage and electrolytes, which opens the door for the fabrication of large-scale graphene devices with enhanced performance.

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1. Introduction

Graphene, a two-dimensional (2D) sp^2 -bonded carbon network, has attracted extensive interest owing to its unique band structure and extraordinary electronic, mechanical and chemical properties [1–5]. Since its first mechanical exfoliation from graphite [6] in 2004, many methods have been developed to prepare graphene including chemical exfoliation [7], epitaxial growth on SiC surfaces [8], chemical vapor deposition (CVD) growth [9,10] and segregation growth [11] on various transition metal substrates. In particular, the low cost, high efficiency CVD growth of graphene shows promise for the production of large-area single-crystal graphene films with high carrier mobility. Moreover, CVD growth of graphene on Cu foils is compatible with large scale manufacturing and integration processes, thus is a leading approach to the fabrication of graphene-based electronic and optoelectronic devices.

Most device applications require an efficient and reliable transfer of CVD-grown graphene from the metal growth substrate onto a target device-compatible substrate without degrading the quality of graphene. Commonly used method to transfer graphene is so-called “poly(methyl methacrylate) (PMMA)-assisted wet etching approach” [14]. The transfer is typically done by spin-coating PMMA film onto graphene and then etching away the underlying metal in oxidant solutions, such as iron (III) nitrate [14], iron (III) chloride [15], ammonium persulphate [16] and nitric acid [17]. After rinsing in DI water, PMMA-assisted graphene is transferred onto the target substrate. PMMA is then removed by acetone. Most

recently, Loh et al. [12] and Cheng et al. [13] have employed an electrochemical cathodic reduction to exfoliate graphene from the metallic growth substrates, which provides a new recyclable transfer approach. Among these popular transfer processes, acidic etchants could lead to bubbles and might damage the graphene film [17]. Iron ion adsorption from the Fe^{3+} based etchants could contaminate graphene [18]. The ammonium persulphate etchant might cause heavy *p*-doping in graphene due to the strong oxidizability of the etchant [16]. Here we present an efficient and reliable method to achieve the clean transfer of continuous CVD-grown graphene films from the growth metal onto arbitrary substrates by an electrochemical etching process. Continuous graphene films with few metal contaminations and little *p*-type doping were electrochemically transferred onto SiO_2/Si substrates.

2. Experimental

2.1. Reagents and materials

All the reagents were analytical reagents. 5% solution of 996 K PMMA (Sigma Aldrich, #182265) in ethyl lactate was spin-coated onto graphene as a carrier layer. 0.5 M H_2SO_4 buffer solution was used as supporting electrolyte during the electrochemical etching process. Traditional 2.0 M $FeCl_3$ etchant was used to dissolve copper for comparison. Ultrapure water (18.2 M Ω cm) was prepared by a purification system (Milli-Q A10) for all experiments.

2.2. Apparatus

Optical microscope (Olympus DX51), scanning electron microscope (SEM, Hitachi S-4800) and atomic force microscope (AFM,

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Veeco Nanoscope IIIa) in tapping mode were used for the morphology characterization of transferred graphene. Ultraviolet–visible (UV–vis) spectrum of transferred CVD–graphene on a quartz plate was taken with Perkin Elmer Lambda 950 UV–vis spectrometer. Raman spectroscopy (Renishaw RM1000) with laser excitation at 632.8 nm was conducted to evaluate the quality of transferred graphene. Air plasma (Femto, Diener Electronics) was used to etch graphene grown on the backside of the copper foil. Electrochemical measurements were performed on a CHI-760C electrochemical workstation in air at room temperature. A conventional three-electrode cell system was used, which consists of a platinum wire as a counter electrode, an SCE electrode as a reference electrode, and a PMMA/graphene/Cu stack as the working electrode.

2.3. Graphene transfer procedures

The graphene samples were grown on a 25 μm thick copper foil by CVD at the temperature of 1050 $^{\circ}\text{C}$ using methane as carbon source according to the previously reported method [13]. The transfer process includes the following steps: (1) As-grown graphene film on the front side of Cu foil was spin-coated with PMMA layer at a rotation rate of 2000 r/min and cured at 175 $^{\circ}\text{C}$ for 5 min, forming a Cu/graphene/PMMA stack. Unwanted graphene grown on the back side of the Cu foil was etched by air plasma for 2 min. (2) The PMMA/graphene/Cu stack was immersed into H_2SO_4 (0.5 M) electrolyte as the working electrode. The copper was electrochemically etched for about 10 min under the potential of 0.5 V (vs. SCE) in H_2SO_4 electrolyte at room temperature. (3) The obtained PMMA/graphene stack was washed repeatedly with deionized (DI) water and transferred onto the substrate (300 nm thick SiO_2 on Si), and dried under infrared lamp before the PMMA was removed by acetone.

3. Results and discussion

3.1. Electrochemical etching process

Differing from conventional graphene transfer methods using a time-consuming wet etching process in oxidant solution, we performed a high-efficiency well-controlled electrochemical oxidation, instead of traditional chemical etchants, to etch away the metal substrate. During the electrochemical etching, the Cu/Graphene/PMMA stack was used as the working electrode. In acidic environments (pH = 0), Cu can be easily oxidized according to the electrochemical reaction, $\text{Cu} - 2\text{e} = \text{Cu}^{2+}$. The electrochemically-generated Cu^{2+} ions readily diffuse into solution from the working electrode (Fig. 1A). The electrochemical oxidation of the bulk Cu electrode was investigated by cyclic voltammetry (CV) in the 0.5 M H_2SO_4 electrolyte. Fig. 1B shows the cyclic voltammetric behaviors of the Cu/graphene/PMMA stack and the Cu foil. Little difference occurs between bulk Cu foil and Cu/graphene/PMMA stack. At a potential of 0.5 V (vs. SCE), a current of about 0.03 A is enough to rapidly etch away the Cu foil. Note that the potential of 0.5 V is much smaller than the oxidation voltage of graphene, avoiding the degradation of graphene quality. Fig. 1C shows the time evolution of current in the electrochemical oxidation process of the Cu/graphene/PMMA stack. During stage I shown in Fig. 1C, the current decreased slowly. Correspondingly, copper was efficiently oxidized and copper ions diffused out of the substrate, thus the copper foil on the graphene became thinner and thinner (Fig. 1D). When the copper foil is further etched into a discontinuous thin film or islands and the underlying graphene is exposed to the electrolyte (Fig. 1E), the current dropped rapidly (stage II of Fig. 1C) due to the inert electrochemistry of exposed graphene. The highly conductive and continuous CVD-grown graphene film

can serve as the robust electrode to facilitate the electrochemical etching of Cu islands. Once the current is close to zero (stage III of Fig. 1C), Cu residues on the graphene surface were completely removed and the electrochemical etching process completed (as shown in Fig. 1F). The whole process ended within several minutes, much faster than the time-consuming chemical etchant-based soaking procedure in conventional etching approaches. Furthermore, Fe contamination, which is difficult to remove completely in conventional transfer methods, is completely avoided in our electrochemical etching process.

3.2. Characterization of electrochemically transferred graphene

The morphology of electrochemically transferred graphene film was characterized by optical microscopy (OM), scanning electron microscopy (SEM) and atomic force microscopy (AFM). Fig. 2A shows a typical OM image of a few-layer graphene film electrochemically transferred onto a Si/ SiO_2 substrate. The thickness-dependent color contrast in optical images of graphene caused by light interference effects on the SiO_2 substrate can be used to identify the layer number of graphene films. Aside from the predominant monolayer regions, some small bilayer islands marked by arrows were also clearly visible. The entire film is clean, continuous, with almost no residual metal particles observed. SEM and AFM provide better spatial resolutions than optical microscopy, which were conducted to determine if nanometer-sized metal residuals remain on the transferred graphene. As shown in Fig. 2B, SEM image demonstrates that the continuous graphene film is mainly smooth monolayer with small ripples and bilayer islands, consistent with the optical image. The AFM image also verified that the graphene film is flat and crackless (Fig. 2C). The metal residues, except some amount of residual PMMA, are rarely observed. X-ray photoelectron spectroscopy (XPS) measurements indicate that electrochemically transferred graphene films have few metal contaminations (especially Fe ion). Note that the electrochemical oxidation transfer technique can be easily scaled up for some practical applications, such as transparent conductive films. As a proof of concept, we demonstrated that centimeter-sized CVD-graphene film was electrochemically transferred onto a quartz substrate (inset of Fig. 2D). The UV–vis spectroscopy was carried out to evaluate the optical uniformity and transparency of as-transferred graphene film. As shown in Fig. 2D, the UV–vis spectrum exhibits the excellent transmittance, comparable to that of samples transferred by the traditional method [14].

Raman spectroscopy is a very powerful tool to probe the quality, stacking order, thickness, and doping concentration of graphene [12]. Fig. 2E shows the typical 632.8 nm laser excited Raman spectra on the monolayer and bilayer regions of the electrochemically transferred CVD-graphene with typical D, G, and 2D bands marked. The D bands ($\sim 1350\text{ cm}^{-1}$), which correspond to defect and disorder level in graphene, are negligible in both monolayer and bilayer regions, indicating the high quality of our CVD graphene film which was not degraded by the electrochemical etching process.

3.3. Comparison of transferred graphene with and without electrochemical etching

To further identify and characterize the quality of electrochemically transferred graphene, we made a systematic comparison of electrochemically transferred monolayer graphene (EO-G) and traditional FeCl_3 etching transferred graphene (Fe-G) [15]. As shown in Fig. 3, extensive Raman spectroscopy was conducted to evaluate the cleanness, doping level, and uniformity for these two types of transferred graphene [12,19]. Thanks to the electron–phonon coupling in graphene, positions of Raman G and 2D bands are very

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