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Residue reduction and intersurface interaction on single graphene sheets

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ABSTRACT

Large regions of pristine graphene are essential to applications which rely on the ideal graphene properties. Common methods for transferring chemical vapour deposition grown graphene to suitable substrates leaves metal oxide particles and poly(methyl methacrylate) (PMMA) residues on opposing surfaces, which degrade the properties. A common method to reduce the residues include annealing in vacuum or in argon, however, residues remain on the graphene sheet. The present investigation reports on the metal oxide particle ripening and PMMA decomposition on a single graphene sheet during *in-situ* annealing up to 1300 °C in a transmission electron microscope. It is shown that the PMMA residues are increasingly reduced at elevated temperatures although the reduction is strongly correlated to the metal oxide particle coverage on the opposing graphene surface. This is shown to occur as a consequence of an electrostatic interaction between the residues and that this prevents the establishment of large clean areas.

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1. Introduction

Graphene is the first discovered stable two dimensional material [1] and is intensely studied due to its unique properties. A common method for manufacturing the graphene is through chemical vapour deposition (CVD) onto a Cu substrate with subsequent transfer to other, technically more relevant, substrates by applying a poly(methyl methacrylate) (PMMA) support to the graphene surface. The Cu substrate is then removed from the graphene by chemical etching using e.g. $FeCl_3$ [2–4], HNO_3 [4,5], $Fe(NO_3)_3$ [2–4] or $(NH_4)_2SO_8$ [2,4] while the PMMA support is reduced after the transfer process using acetone [2,4–8]. These process steps leave a varying amount of residues, in the form of e.g. hydrocarbons and carboxyl groups from the PMMA support [9] and FeO_x metal oxide particles from the acid if $FeCl_3$ or $Fe(NO_3)_3$ is used [6,7,10]. The residues associated with the transfer process are known to affect the graphene's properties [2–7,11,12]. PMMA residues effectively introduce p-type doping to the graphene sheet [13], decrease carrier mobility and cause wrinkles, tears and cracks [3,4,11]. Additionally, the metal oxide particles limit the thermal conductivity and also cause p-type doping [10]. Together, residues remaining on the surfaces after processing limit the ultimate properties of the graphene. Removal of the residues is thus imperative and several different methods have been reported. The most common method to reduce the amount of PMMA residues from the graphene sheet is through annealing in vacuum or in an Ar/H_2 atmosphere [2–8] as PMMA decomposes during annealing. Annealing graphene with PMMA residues at 160 °C causes a first decomposition of PMMA, while at 300 °C random scissions in the polymer chain occur [9,14]. However, PMMA residues are not completely removed after annealing at 300 °C [15,16] and have been shown to bind covalently to defects in the graphene lattice which may inhibit the decomposition [9,16]. Annealing at 500 °C [17,18] or 700 °C [19] increases the area of clean graphene regions and removes most of the PMMA residues. This is influenced by the healing of graphene at temperatures above 500 °C which is

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reported to remove the defect sites where the PMMA residues may be attached [20,21].

During annealing of graphene with PMMA residues and metal oxide particles at high temperatures, the metal oxide particles may interfere with the decomposition of PMMA residues. This has been observed as metal atoms deposited on graphene sheets attach to the PMMA residues [19,22,23], which indicates a preferential interaction between the metal atoms and the PMMA residues. Annealing at 700 °C [19] or 900 °C [23] removes the PMMA residues and results in agglomeration of the metal atoms to particles. In general, the interaction between the particles and PMMA residues is discussed with respect to in-plane interaction, but not out-of-plane through the graphene sheet. However, any interaction which might occur between the PMMA residues and the particles through the graphene sheet has not been examined.

In this report we investigate suspended Cu CVD grown single graphene sheets by *in-situ* annealing up to 1300 °C in a transmission electron microscope (TEM). In particular, we correlate the decomposition of PMMA residues at high temperatures to the metal oxide particle morphology on the opposite surface of the graphene sheets. As the PMMA residues remain on one side of the graphene sheet, the amount and area of metal oxide particles on the opposing graphene surface is tuned by means of sub-monolayer sputter deposition. Through this, it is concluded that there is a strong correlation between PMMA residues decomposition efficiency at elevated temperatures and metal oxide particle morphology. It is shown that this occurs as a consequence of electronic exchange through the graphene sheet and identifies improved metal oxide particle removal as means to significantly increase the regions of pristine graphene.

2. Experimental procedure

2.1. Sample preparation

Graphene was grown on polished copper using atmospheric pressure CVD with methane (99.999%) as the feedstock. Prior to growth, a 100 μm thick copper foil (from Nilaco, 99.96%) was annealed at 1060 °C with 1000 sccm Ar and 200 sccm H_2 for 2 h, then polished using a chemical mechanical polishing route. The polished copper was then mounted in a 2 inch quartz tube reactor and heated up to 1060 °C for 40 min with constant flows of 1000 sccm Ar and 200 sccm H_2. After reaching 1060 °C, the sample was annealed for 1 h without changing the gas flow. During the atmospheric pressure CVD growth, the H_2 gas was reduced to 50 sccm and 3 sccm of CH_4 (1% diluted in Ar) was injected. After growth, the CH_4 was turned off and the chamber was cooled to room temperature. This method produces large single layer graphene sheets [24].

The graphene sheets were then transferred to DENSsolutions single tilt heater chips. In order to protect the graphene film during Cu etching, a PMMA solution (950 k C4) was spin-coated on the graphene/Cu at 1000 rpm for 60 s. To etch the Cu foil, the sample was floated in copper etchant (CE-100, Transene) for about 30 min. After thoroughly rinsing in deionized water, the PMMA/graphene layer was fished onto TEM heater chip. It was then dried in an oven for 5 min at 120 °C. Finally, the PMMA was removed by exposure to acetone. The success of each transfer was then confirmed by SEM imaging.

2.2. DC magnetron sputtering of Cr

Sub-monolayer Cr was deposited on the PMMA free side of the graphene sheets by dc magnetron sputtering from a 3 inch Cr (99.995% purity) target at room temperature, with 16.4 sccm of Ar introduced up to a partial pressure of 4.7 Pa. A high partial pressure was chosen to limit the kinetic energy of the Cr atoms during deposition. The base pressure of the system was under 7 μPa. The depositions were carried out in a power controlled mode at 6 W at substrate-target distance of ~15 cm for 1, 4, and 8 min. The deposition times were selected based on growth rate calibration on Si substrates and correspond to 0.1, 0.4, and 0.8 monolayers of Cr, respectively. In order to reach stable sputtering conditions, the Cr target was presputtered with source shutters closed for ~5 min prior each deposition with heater chip faced away from the flux, ensuring that absolutely no Cr was deposited during presputtering.

2.3. In-situ annealing

The chips were analysed with the Linköping double corrected and monochromated FEI Titan^3 60–300 operated at 60 kV in both scanning transmission electron microscopy (STEM) and monochromated TEM modes. Low-voltage (60 kV) was applied for imaging and spectroscopy as it reduces knock-on damage [25]. Electron energy-loss spectroscopy (EELS) was performed using a GIF Quantum ERS spectrometer in dual-EELS mode.

An as-prepared, non-deposited sample was heated to 300 °C employing a DENSsolutions single tilt holder [26], and left for 1 h before lowering the temperature to ambient temperature where TEM imaging was performed. The sample was then annealed at 400 °C for 1 h before lowering to room temperature and performing imaging. This was repeated in steps of 50 °C up to 1000 °C, after which the sample was heated to 1100 °C and 1200 °C before imaging. For each temperature, a new region was imaged so any effect of the electron beam was minimized. Prior to and after annealing, the sample was investigated by monochromated TEM and EELS.

The Cr-deposited samples were subsequently investigated by STEM high-angle annular dark field (HAADF) imaging, after which the samples were annealed at 500 °C for 16 min. The temperature was then increased to 1300 °C in steps of 50 °C and for 16 min at each temperature. STEM HAADF images were acquired for each temperature after 1, 2, 4, 8, and 16 min. The region investigated was changed three times to limit any effect of the electron beam on the sample. Before and after heating, EELS spectrum imaging (SI) was performed to investigate the changes in microstructure and chemistry of the graphene and PMMA residues.

2.4. Data analysis

Analysis of the EELS data was performed using Digital Micrograph (DM). Calculation of the chemical shifts in the C–K edge in an EELS spectrum image (SI) was performed by NLLS-fitting of the peaks in the core-loss SI.

The area of the clean regions was determined by using ImageJ[1] with a minimum area of 1 nm^2. The monochromated TEM images were filtered by applying a FFT mask to remove contrast variations from the monochromated beam prior to analysis.

3. Results and discussion

Initially, the as-prepared single layer graphene sheets are almost completely covered by PMMA residues with randomly distributed metal oxide particles. The metal oxide particles are attached to one surface (metal oxide particle side) of the sheet, while the PMMA residues are attached to the other (PMMA residues side), see schematic cross-section in Fig. 1a. The as-prepared sample is

[1] W. Rasband, ImageJ, U.S. National Institutes of Health, Bethesda, Maryland, USA, 1997–2014. URL http://imagej.nih.gov/ij/.

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