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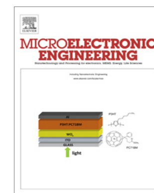

Investigation of the utility of cellulose acetate butyrate in minimal residue graphene transfer, lithography, and plasma treatments

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ABSTRACT

Residues on graphene substrates from polymer-supported transfer and lithography can significantly degrade device performance. Using Fourier transform infrared (FTIR), Raman spectroscopy and Auger electron spectroscopy (AES), cellulose acetate butyrate (CAB) dissolved in ethyl acetate is shown to leave minimal polymer residue on graphene after substrate transfer. The polymer can also be used as a protective under-layer between an electron beam resist and the graphene during electron beam lithography, as well as a protective over-layer during inductively coupled plasma (ICP) etching to slow the etch rate of graphene and remove protruding polymer residues without etching the underlying graphene. CAB is therefore shown to be a useful material for the handling and processing of graphene.

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1. Introduction

The fabrication of exfoliated graphene in 2004 was the beginning of extensive research into the use of the material, in a number of applications such as RF devices, touchscreen displays, sensors, and biosensors [1]. Graphene can be produced in a number of ways, which vary in cost and the quality of the material produced. Chemical vapor deposition is one of the most promising methods of mass-producing graphene. Metals such as copper, nickel, ruthenium, iridium, palladium, cobalt, and rhenium have been reported to be suitable substrates. Of these, copper and nickel are the most widely used. Growth is performed at temperatures of the order of 1000 °C with a hydrocarbon gas as the precursor [2]. The metal substrate catalytically decomposes the hydrocarbon gas, providing a source of carbon, which is adsorbed into the substrate. The carbon then precipitates out of the metal to form graphene [3].

For electronics applications, it is undesirable to have the graphene layer supported on a metal substrate. Strong electron interactions between the π electrons in graphene and d states in the metal layer have been reported, with the strength of the interaction varying with the metal [4]. A strongly interacting metal substrate can open a band gap in the electronic states of graphene, thus reducing carrier mobility. CVD graphene grown on metals must therefore be transferred to an insulating substrate before fabricating an electronic device.

Many uses of graphene, such as sensors or biosensors [5], require surface modification (functionalization) of the surface [6]. Understanding these processes requires the use of sensitive surface analysis techniques, such as X-ray photoelectron spectroscopy (XPS) or Auger electron spectroscopy (AES). Graphene functionalization techniques will necessarily be hindered by the presence of polymer residue on the surface of graphene, both in terms of variation in process conditions, and complication of the analysis, particularly in grafting organic species to graphene surfaces.

Removal of these resist residues is therefore critical for device optimization. This can be done using appropriate solvents, such as acetone, chlorobenzene, or commercial photoresist strippers such as Nano Remover PG (Microchem). Annealing in ultra-high vacuum (UHV) or inert gas (Ar) atmosphere is also a common technique used to remove residues [7]. Passing high currents through graphene devices can remove some residues through a combination of electromigration and Joule heating. Currents on the order of tens of milliwatts have been shown to remove adsorbed contamination through few μm^2 graphene devices [8]. However, care must be taken when doing this not to destroy any device components, for example by destroying the top gate by dielectric breakdown at higher voltages in a gated device. Solution state ozone processing conditions have also been reported for use with epitaxial graphene grown on silicon carbide, however this has not yet been

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demonstrated for use with resist residues, and may degrade the graphene if the process is too aggressive.

Plasma etching (or "ashing") of polymers and resists can be performed on graphene. However, commonly used etch gases for polymer removal (e.g. O_2) will also attack the graphene substrate, creating defects in the lattice, as evidenced by Raman spectra. Inductively coupled plasma etching utilizes separate generators to create the plasma and platen bias and electromagnetic induction provides energy to the plasma. Using this technique, one can achieve high etch rates due to high ion density and high radical densities, as well as a high degree of control over etch selectivity and damage to substrate by using low ion energy plasmas. However, even at very low plasma densities, ICP etching of residues on graphene can cause charging effects, which may change the surface functionality of graphene, or cause damage to other device components [9].

Auger electron spectroscopy (AES) is a chemical analysis technique used to provide semi-quantitative elemental analysis of a sample surface [10]. AES is a very surface sensitive measurement due to the small escape depth (a few nanometers) of Auger electrons and hence is extensively used for measurements of surface contamination. Using an electron beam as an excitation source provides improved resolution over conventional chemical analysis methods such as XPS, which is determined by the spot size of the electron beam. Therefore, AES spectroscopy is an ideal technique for chemical characterization of localized regions of contamination, a common problem associated with lithographic processes [11].

2. Material and methods

2.1. Materials

Graphene substrates grown via chemical vapor deposition (CVD) on 1 cm^2 nickel substrates were purchased from Graphene Supermarket. Raman spectra were obtained from this material transferred onto SiO_2/Si. Poly (methyl methacrylate) (950 PMMA C) was purchased from Micro Chem. Cellulose acetate butyrate powder (Sigma–Aldrich) was dissolved in ethyl acetate (Sigma–Aldrich), producing a 30 mg/mL solution. Both PMMA and CAB were applied by spin coating at 4000 rpm and baking at 180C for 3 min. For negative EBL exposure, a layer of CAB was spin coated at 4000 rpm and baked at 180 °C. AZ 2070 ebeam resist was spun at 3000 rpm and baked at 90 °C for 3 min. After exposure, the resist was post baked at 110 °C for 3 min.

2.2. CVD transfer process

Following the methods seen in the literature [12], transfer of Ni-grown CVD graphene was performed using PMMA and CAB (as above), and the underlying metal was etched using $FeCl_3$ solution. After the polymer-supported graphene had been released from the metal substrate, it was carefully retrieved and transferred to the target substrate. SiO_2/Si substrates were used for recording Raman spectra and lithographic tests. Samples used for AES analysis were transferred to Au substrates to reduce charging and for clearer spectral analysis.

2.3. Processing conditions

Inductively coupled plasma (ICP) etching was performed on an SPTS Technologies ICP Etch tool. An O_2 plasma (40 sccm) with 500 W coil power and 100 W platen power was used. Small substrates were supported on a carrier wafer for etching.

An eLine system from Raith GmbH was used for the electron beam lithography (EBL) in this work. An aperture size of 30 μm, beam current of 1 nA, and area dose of 200 $\mu As/cm^2$ were used for lithography.

2.4. Analysis methods

Raman spectroscopic measurements were acquired at Swansea University using a Renishaw inVia Raman system. The system contains a charge-coupled device (CCD) detector and a Leica DM2500 microscope with a 50× objective lens. An excitation wavelength of 532 nm (green, 100 mW) was used. The inVia system is controlled using Renishaw Windows-based Raman Environment software (WiRE 3.2). The software can control a motorized sample stage, which enables the automatic capture of Raman maps over a sample area.

Fourier transform infrared (FTIR) spectroscopy was performed on a Perkin Elmer Spotlight 400 FTIR microscope. The Spotlight system features a germanium attenuated total reflectance (ATR) imaging for high spatial resolution during the imaging of solid surfaces.

Auger electron spectroscopy (AES) was performed using an Omicron LT Nanoprobe (base pressure 1×10^{-10} mbar) equipped with a NanoSAM electron analyzer. All measurements are performed with beam acceleration voltage of 5 kV and 1 nA beam current, using a 90 μm beam aperture.

3. Results

3.1. Rinsing of CAB and PMMA from graphene

FTIR spectra were obtained from graphene samples before application of CAB (Fig. 1, black curve), after application of CAB (blue curve), and after rinsing away the CAB in ethyl acetate (red curve). Peaks attributed to C–H and C=O bonds were used to identify contributions from the polymer over-layer.

Peaks were seen at 1744 and 1156 cm^{-1} attributed to CAB (C=O stretch, and =C–H respectively) which were absent after rinsing. Correcting for the baseline, the ratios of the peak intensities at 1156 cm^{-1} and 1634 cm^{-1} (C–C stretching mode of sp^2 network, indicative of graphene) was ~0.95 before rinsing, and ~0.01 after rinsing.

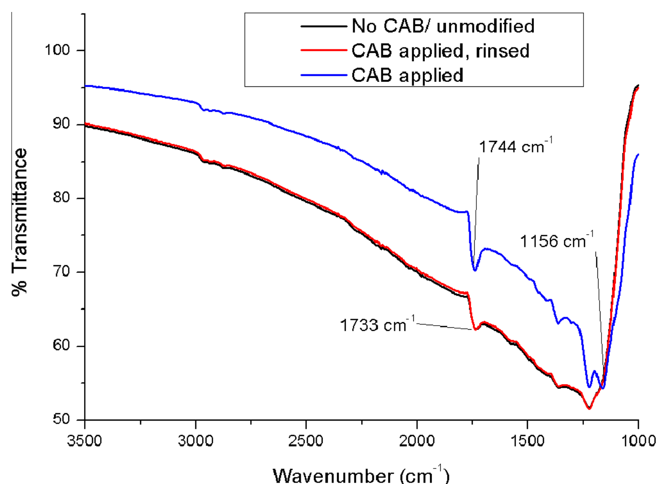

Fig. 1. FTIR spectra from unmodified graphene (black curve), with CAB applied (blue curve) and CAB subsequently rinsed from the surface. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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