CARBON 94 (2015) 378–385

Contents lists available at ScienceDirect

CARBON

journal homepage: www.elsevier.com/locate/carbon

Multilayered graphene films prepared at moderate temperatures using energetic physical vapour deposition

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ARTICLE INFO

Article history:
Received 27 March 2015
Received in revised form 22 June 2015
Accepted 27 June 2015
Available online 29 June 2015

ABSTRACT

Carbon films were energetically deposited onto copper and nickel foil using a filtered cathodic vacuum arc deposition system. Raman spectroscopy, scanning electron microscopy, transmission electron microscopy and UV–visible spectroscopy showed that graphene films of uniform thickness with up to 10 layers can be deposited onto copper foil at moderate temperatures of 750 °C. The resulting films, which can be prepared at high deposition rates, were comparable to graphene films grown at 1050 °C using chemical vapour deposition (CVD). This difference in growth temperature is attributed to dynamic annealing which occurs as the film grows from the energetic carbon flux. In the case of nickel substrates, it was found that graphene films can also be prepared at moderate substrate temperatures. However much higher carbon doses were required, indicating that the growth mode differs between substrates as observed in CVD grown graphene. The films deposited onto nickel were also highly non uniform in thickness, indicating that the grain structure of the nickel substrate influenced the growth of graphene layers.

1. Introduction

Graphene is a single layer of sp^2 bonded carbon atoms which form a hexagonal lattice. It was first practically isolated from graphite in 2004 via mechanical exfoliation and has since attracted much attention due to its remarkable properties [1,2]. For example graphene has a room temperature electron mobility of $1.2 \times 10^5\ cm^2\ V^{-1}\ S^{-1}$ [3], the highest of any semiconductor or conductor. Even higher values for mobility ($2 \times 10^5\ cm^2\ V^{-1}\ S^{-1}$) have been recorded for suspended graphene [4]. Graphene is also transparent, absorbing only 2.3% of incident light per layer over a 400–7000 nm range [5]. Additionally a suspended single layer of graphene has been shown to have a thermal conductivity of 5.3 kW/m K [6]. The unique properties of graphene make it a potential candidate for a range of electronic applications such as organic solar cells, ultra capacitors, biosensors, nano-electronics and batteries.

For a large-scale graphene application to be commercially viable, a fabrication method is needed that is controllable, scalable, cost effective and produces minimal defects. A range of methods are currently being employed to produce graphene, such as the unzipping of nanotubes [7,8], sonication of thermally expanded graphite (as graphene oxide) [9–11], epitaxial growth on silicon carbide [12,13], exfoliation [14,15], chemical vapour deposition (CVD) [16,17] and plasma enhanced CVD [18]. CVD is considered to produce the highest quality large-area sheets of graphene at the lowest cost [19]. However CVD is very sensitive to growth conditions (eg gas concentration, deposition time, temperature and substrate) [20–23] and a transfer process is required post-deposition in order to relocate graphene to a desirable substrate [24,25].

A less studied technique to produce graphene is physical vapour deposition (PVD). Despite it being widely used to produce carbon materials such as 'tetrahedral amorphous carbon' [26,27], 'diamond like carbon' [28] and a range of nanostructured graphitic materials [29], there is relatively little published on graphene synthesis [30–32]. These previous works on graphene only consider nickel substrates and employed a post deposition annealing process in order to obtain graphene. PVD is both controllable and scalable and is already used in industry to create coatings with specific hard wearing, corrosion resistant, optical and biocompatible properties [33]. Here, we investigate the synthesis of graphene using PVD in a filtered cathodic vacuum arc (FCVA) system. The effect of substrate type, temperature and dose are explored, and the properties of the resulting graphene films characterised.

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http://dx.doi.org/10.1016/j.carbon.2015.06.071
0008-6223/

2. Experimental details

2.1. Synthesis

Silicon wafer ⟨1 0 0⟩ (bearing a native oxide layer of ~3 nm), copper (99.99%) and nickel (99.95%) foil were used as substrates. The silicon substrate was used as a control to highlight the influence of substrate type. Carbon films were deposited using a FCVA system (Fig. 1) equipped with a double bend magnetic filter to minimise the deposition of macroparticles [33] which can be ejected from the carbon cathode (99.999% C, Nano Film International, Singapore). A 60 A current was used to generate a carbon plasma and films were deposited after a base pressure of 10^{-6} m Torr was reached. The plasma which consists of ~100% C^+ ions [33] and electrons, was initiated using an earthed graphite tipped striker. To ensure that all depositions were performed onto similar growth surfaces, all substrates were heated in the chamber for 10 min at 750 °C immediately prior to use. Depositions were performed at floating substrate potential with a constant flux of 2.3×10^{15} atoms/cm^2 s at ambient temperature (~25 °C), 400 °C and 750 °C. The amount of carbon deposited on the various substrates was expressed in terms of dose (atoms/cm^2), and was calibrated by the film thickness as measured on silicon. For comparison with the FCVA deposited films, a graphene film was also prepared on the copper foil in a 44 mm id CVD reactor at 1050 °C with a flow rate of 200 sccm of argon, 15 sccm methane and 100 sccm of hydrogen.

2.2. Transfer

Graphene was transferred from the growth substrate to glass slides using a polymer-support method. A poly(methyl methacrylate) solution (PMMA, 40 mg in 1 ml of anisole) was spin coated onto the deposited graphene films and air dried to leave a ~500 nm thick support film. The PMMA/graphene/Cu sample was then floated on a solution of ammonium persulfate ($(NH_4)_2S_2O_8$, 0.1 M) to etch away the copper. After the copper was completely etched away, the remaining PMMA/graphene film was rinsed thoroughly with milli-Q deionized water then collected graphene-side down on an ozone-treated glass slide. Graphene deposited onto nickel was etched and transferred in a similar manner except that a 0.35 M solution of iron chloride ($FeCl_3 \cdot 6H_2O$) was used as the etchant. The PMMA was removed from the graphene sheets by repeatedly dipping in fresh dichloromethane until free of polymer.

2.3. Characterisation

Raman spectroscopy was performed using a Renishaw Raman system 100 with a 514 nm Ar^+ laser and 50 μm spot. Secondary electron images from scanning electron microscopy (SEM) analysis of the surface of the carbon films were collected using a FEI Nova NanoSEM. Cross-sectional transmission electron microscopy (TEM) specimens were prepared using a focused ion beam. These specimens were analysed using JEOL 2100F TEM at 80 kV. The transparency of the graphene films between 400 nm to 700 nm was measured using a Cary UV–vis spectrophotometer. The resistivity of the graphene films was measured using two different techniques. The sheet resistance was measured using a four point probe and a two point probe with silver-paint contacts.

3. Results and discussion

Temperatures in the range of 700–1100 °C and generally around 1000 °C are reported for CVD growth of graphene using volatile organic carbon compounds [16,17]. The effect of temperature during PVD using a carbon plasma was studied by coating substrates held at different temperatures with a set dose of carbon atoms (4.6×10^{16} atoms/cm^2, equivalent to a fully dense layer approximately of 4 nm or 12 atoms thick). The Raman spectrum for a film deposited on silicon at 25 °C (Fig. 2a) shows a broad asymmetric peak at ~1500 cm^{-1}, characteristic of amorphous carbon [34]. This peak is broadened at a deposition temperature of 400 °C, and resolved at 750 °C into two peaks at ~1350 cm^{-1} and ~1580 cm^{-1}. These peaks are often observed in nano and micro crystalline graphitic materials and are referred to as the D and G peaks, and can be attributed to the 'defective' edges and defect-free centre of graphene layers respectively [35]. This indicates that the elevated growth temperature has allowed the carbon atoms to adopt the sp^2 bonding configuration resulting in a nano-crystalline graphitic material. However there is no 2D (G′) peak at ~2700 cm^{-1} in these films which together with the large D peak indicates that the films do not contain significant amounts of single or organised multi-layer graphene [36].

A carbon dose of 4.6×10^{16} atoms/cm^2 deposited on copper at 25 °C or 400 °C gives similar Raman spectra to silicon under the same conditions (Fig. 2b). However at 750 °C a clear difference is observed. The D and G peaks are fully resolved and, most importantly, a 2D peak appears at ~2700 cm^{-1}. This indicates the presence of ordered single or multilayer graphene and confirms

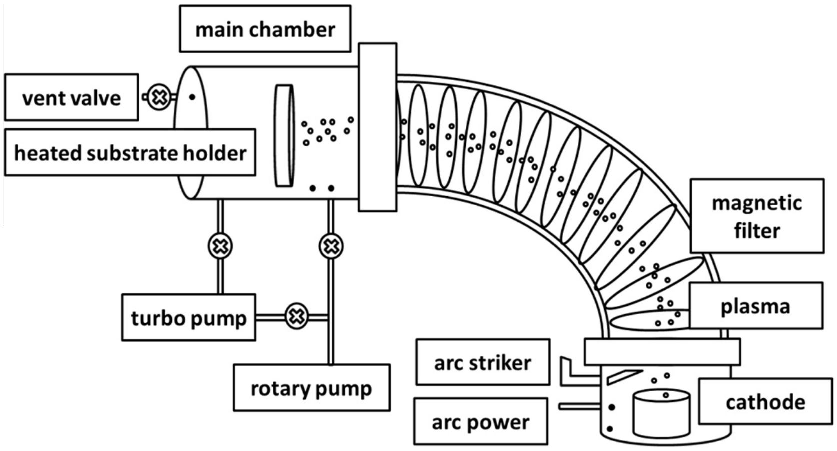

Fig. 1. Schematic diagram (not to scale) of the FCVA system. For more details on FCVA see reference [33].