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Synthesis of multi-layer graphene films on silica using physical vapour deposition

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ABSTRACT

Carbon films and underlying copper template-layers have been deposited energetically in the same filtered cathodic vacuum arc system at 750 °C. The high quality <111> copper template-layers were supported on either silicon or silica and were subsequently sacrificially etched. On silicon, copper silicide formed during the copper deposition process, inhibiting ordered growth in the carbon film. On silica, large areas of multi-layer graphene (up to ~10 layers) oriented parallel to the substrate were synthesised and these remained intact after the sacrificial etching process. The ability to produce both copper and multilayer graphene layers in one system enables simplified fabrication of this material.

1. Introduction

The synthesis of graphene device layers on CMOS compatible substrates is advantageous for an increasing number of applications, including dye-sensitized solar cells [1], super capacitors [2], biosensors [3], nano-electronics [4] and batteries [5]. Large areas of graphene (up to 1 cm^2) have been grown on metallic templating surfaces such as copper [6]. Whilst it has been demonstrated that large area graphene can be grown on SiO_2 directly without the need for a catalyst [7] and in atmospheric pressure CVD systems [8], the growth rates achieved are so low that the growth processes take many hours to complete. A motivation for this work was to deposit graphene at moderate temperatures in short periods (minutes or less) using a scalable method. With regard to the latter, FCVA is a proven method for large scale deposition of high quality carbonaceous films [9]. Furthermore, this method would enable transfer to a wide range of substrates, requires no toxic gases and is achieved with low system cost.

Several authors have reported methods for the transfer of graphene from metallic template layers to other substrates such as silica [10,11]. An alternative approach is to grow graphene on copper films deposited onto silicon or silica [12,13]. Subsequent sacrificial etching of the copper film then enables transfer of the graphene directly onto the underlying substrate. This method of transfer reduces the probability of damage to the graphene when compared with transfer from a separate metallic foil substrate [12]. Transfer of chemical vapour deposition (CVD) grown graphene to an underlying substrate has been demonstrated using evaporated and/or sputtered copper under-layers [12,13]. However, further simplification of the process would be achieved if the graphene and copper films could be deposited in a single vacuum system.

Previously, we reported the growth of graphene films on copper and nickel foils using the carbon plasma generated by a filtered cathodic vacuum arc (FCVA) [14]. Our results showed that the energetic carbon flux enabled graphene to grow at higher rates and lower temperatures (~750 °C) than typical for CVD. The FCVA technique can also produce other high quality films, including a range of metals, nitrides and oxides [15,16]. In particular, it is possible to prepare low roughness copper films with the preferred crystallographic orientation suitable for graphene growth [17]. Here, FCVA is used to prepare both copper under-layers and carbon over-layers with varying microstructures including that of

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graphene.

2. Experimental detail

The schematic in Fig. 1 shows the steps involved in synthesis of the carbon films. Silicon <100> and silica (thermal oxide 1000 nm thickness on Si) substrates were placed in the FCVA system (see Ref. [14] for details) and copper under-layers ~200 nm thick were deposited with a range of substrate biases at room temperature using a 99.99% pure copper cathode. Carbon films were then deposited on the copper under-layers at floating substrate potential (20 V) and at a temperature of 750 °C. The carbon flux was generated from a 99.99% purity 68 mm diameter carbon cathode. Relocation to the underlying silica substrate was achieved by etching the copper with ammonium persulfate ($(NH_4)_2S_2O_8$), 0.1 M).

The copper and carbon films were examined using atomic force microscopy (D3100 AFM), x-ray diffraction (XRD) and scanning electron microscopy (Nova NanoSEM). Raman spectroscopy was performed on the carbon films using a Renishaw Raman system 100 with a 514 nm Ar^+ laser and 50 μm diameter spot. Cross-sectioned samples were obtained from samples prepared using a FEI Scios focused ion beam (FIB) system and imaged using a JEOL 2100F transmission electron microscope (TEM) operating at 200 kV. The sheet resistance of the transferred graphene was measured using a four point probe.

Room temperature X-ray absorption spectra (XAS) were collected from the carbon films after transfer at the soft X-ray beamline of the Australian Synchrotron. A horizontally polarized X-ray beam was incident at angles of 20°, 55° and 90° from the surface. The signal used for the spectra was the total electron yield. The X-ray absorption near edge structure (XANES) on the carbon K-edge from graphene and graphenic carbon films includes peaks caused by 1s - π^* and 1s - σ^* transitions. All spectra were normalized to the intensity of the 1s - π^* peak. The angular dependence of these peaks is a measure of the structural order within the material [18].

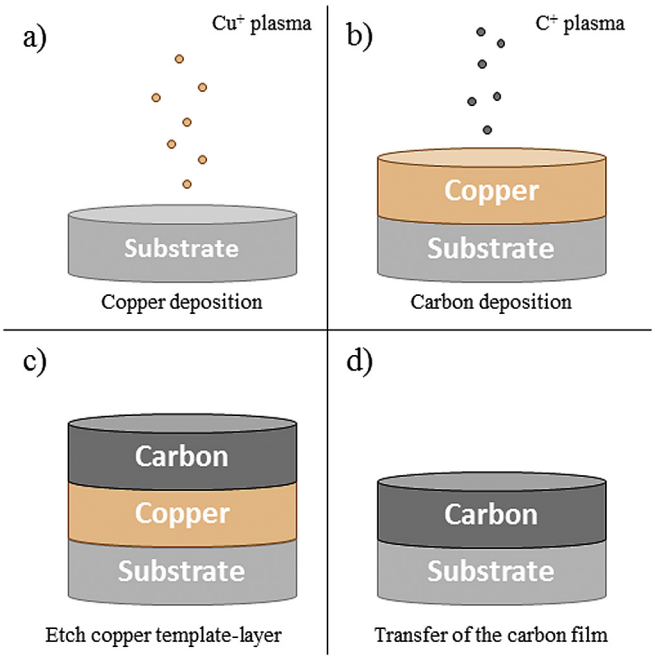

Fig. 1. Schematic showing the growth sequence and transfer process employed to fabricate carbon films on silicon/silica substrates. (A colour version of this figure can be viewed online.)

3. Results and discussion

3.1. Deposition of copper

The relationship between the substrate bias (determining the average incident ion energy [19]) and the roughness of the deposited copper films was investigated using AFM. Fig. 2 compares the surface morphology of copper films grown on silicon and silica with an earthed substrate holder (Fig. 2a and (c)) with films grown with a substrate bias of −50 V. The copper films deposited on silicon at 0 V (earthed) have an RMS roughness of 99 nm. An earthed substrate holder attracts electrons from the plasma leading to increasing temperature during deposition. The increase in deposition temperature resulted in the formation of larger agglomerates, as observed in Fig. 2a. The copper film deposited on silicon with a bias of 25 V applied had a lower roughness. As bias was applied to the substrate holder, electrons were repelled and ions were accelerated towards the growing film. The increase in the kinetic energy of the incoming ions promoted densification and reduced agglomeration, leading to smoother films. As the bias was increased to 50 V, a further reduction in the roughness was observed (Fig. 2c).

Fig. 3 shows the relationship between substrate bias and RMS roughness, measured by AFM. The roughness of films deposited onto silica wafers followed a similar trend to that observed in the films deposited on silicon. The film deposited with an earthed substrate holder was again the roughest and contained the largest copper agglomerates (Fig. 2a). As the substrate bias was increased, a reduction in the roughness of the deposited copper films was observed. In general, films deposited on silica were smoother than those deposited on silicon. Before depositing graphene, the copper films were annealed in vacuum at 750 °C as this temperature was found to be required for the growth of graphene by FCVA [14]. The insets in Fig. 2 show the morphologies of the copper films after annealing at 750 °C with enlarged agglomerates caused by Ostwald ripening during annealing.

The microstructure of the FCVA deposited copper films was measured before and after annealing using XRD and was compared against commercial copper foil (Fig. 4). Before annealing, the intensity of the (200) peak produced by the copper foil was much greater than that of the (111) peak (Fig. 4a). After annealing at 750 °C, the (111) peak produced by the copper foil was more intense

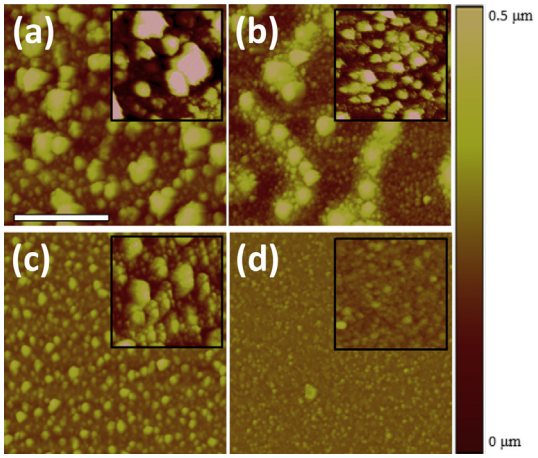

Fig. 2. Atomic force micrographs of copper template layers energetically deposited onto silicon (top row) and silica (bottom row) with the substrate holder earthed ((a) and(c)) and biased at −50 V ((b) and (d)). Insets show the morphology of the films after annealing at 750 °C for 10 min. The scale bar is 3 μm in length. (A colour version of this figure can be viewed online.)