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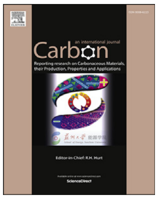

Optimisation of copper catalyst by the addition of chromium for the chemical vapour deposition growth of monolayer graphene

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ABSTRACT

The effect of adding chromium (Cr) to the copper catalyst for chemical vapour deposition growth of graphene is investigated. We observe a suppression of the formation of multilayer islands of graphene in the Cr-rich regions. This is shown with optical microscopy, scanning electron microscopy and scanning Raman spectroscopy. In addition, carbon isotope labelling is employed to elucidate the mechanism by which the formation of multilayer islands is minimised. The use of mixed catalysts is an important step in the optimisation of catalytic growth of graphene.

1. Introduction

Chemical vapour deposition (CVD) is a well-established method for growing large-area graphene for numerous high-performance applications [1–4]. The graphene prepared by this technique is of high quality and can be further processed directly on the catalytic substrate (as-grown) or after transferring to any other desired substrate. However, one of the drawbacks of this technique is that CVD graphene typically contains some bilayer/multilayer areas [5]. This can deteriorate the electronic and optical properties of graphene due to the lack of uniformity introduced by the multilayer islands [6,7]. To avoid these detrimental effects, several modifications of the CVD growth process have been suggested to suppress the growth of bilayer/multilayer islands. Weatherup et al. reported the use of a Ni–Au alloy catalyst for low-temperature graphene growth in which they found that gold lowers the stability of surface carbon and thereby lowers the graphene nucleation density significantly [8]. In this case, the resulting graphene grown by the alloy catalyst was a combination of monolayer and bilayer/multilayer in contrast to copper that generally assures monolayer graphene with sparse secondary graphene islands Other groups have employed other methods for multilayer suppression namely by means of a post-growth H_2 etching step [7], pulsed-CVD as opposed to continuous dosing of carbon feedstock [6] and very recently via a W foil placed inside a copper enclosure [9].

We report on the modification of the copper catalyst for graphene growth by the addition of chromium (Cr). Cr has been used in the steelmaking industry for many years in the mass production of high-strength and corrosion-resistant stainless steel [10,11]; and it is well-known that chromium partakes in strengthening of the materials by forming various carbides at the grain boundaries [12–14]. Chromium was previously shown to have an effect in graphene growth, when Cr- containing ink was printed on Cu foil and used for structured graphene growth for making graphene field effect transistors (GFETs) [15]. We have chosen to investigate this as these characteristics can be translated into the CVD growth of graphene by controlled introduction of chromium. We report on the systematic study of the effect of deposited Cr on the formation of bilayer/multilayer islands studied by optical microscopy, scanning electron microscopy, scanning Raman spectroscopy in combination with carbon isotope labelling [16]. We establish that chromium has a strong effect on suppressing the formation of multilayers and propose a mechanism for the observed effect.

2. Experimental methods

2.1. Substrate preparation

Electroplated copper foil (Gould GmbH, 25 μm) was immersed in 10% HCl solution (Sigma–Aldrich) for 30 s to remove the backside chromate and then rinsed in Millipore water thoroughly. Subsequently, the copper foils were sonicated in HPLC grade acetone for 5 min. The chromium layer was sputter-deposited to a thickness of 2 nm through a shadow mask onto the copper foils,

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enabling site-specific analysis of as-grown and transferred samples (see Fig. 1, step 1–3). A Cr layer thickness of less than 2 nm resulted in the incomplete suppression of multilayers, and thicknesses greater than 2 nm, disrupted the growth completely.

2.2. *CVD growth*

The graphene was grown by CVD in a hot-wall quartz tube furnace (step 4 in Fig. 1). Copper substrates were loaded into the furnace and ramped up to 1035 °C under 50 sccm flow of hydrogen. Then the furnace dwelled at this temperature for 10 min so as increase the grain size of the copper substrate. Graphene was grown by passing a mixture of 10 sccm of methane and 5 sccm of hydrogen for 20 min to achieve complete coverage. In order to investigate the evolution of graphene islands during the growth in the regions containing chromium, the isotope methane labelling method [16] together with various growth times were used. The growth step was performed by introducing a gas mixture 10 sccm of $^{12}CH_4$ or $^{13}CH_4$ and 5 sccm of H_2. Then a dribble flow of 0.5 sccm of $^{12}CH_4$ and 2.5 sccm H_2 was set and the furnace was force-cooled to room temperature via compressed air.

2.3. *Transfer*

The graphene was transferred onto SiO_2/Si substrates using cellulose polymer as the supporting layer which is elaborated elsewhere [17]. In short, nitrocellulose (NC) was spin-coated onto the as-grown graphene on copper and after etching away the copper using Ammonium persulfate (APS), the polymer-graphene stack was dredged onto the wafer. After an initial air-drying, samples were annealed in a vacuum oven to improve the adhesion of graphene to the substrate. Finally, the polymer layer was dissolved in acetone at room temperature (step 5 and 6 in Fig. 1).

2.4. *Characterisation*

Raman spectroscopy was performed with a Witec Alpha 300R system with 532 nm laser as excitation source, operating at maximum power of $P \leq 6$ mW. Scanning electron microscopy was carried out in a Carl Zeiss Ultra Plus field emission gun scanning electron microscope (FEG-SEM) equipped with an Oxford Instruments INCA system for energy dispersive X-ray (EDX) elemental analysis as well as selective backscattered (EsB) detector.

3. Results & discussion

In order to ascertain the effect of chromium on the growth of graphene, two sets of samples were grown with the same experimental conditions: one with a thin layer of chromium on top of the copper substrate and the other with no chromium. Then, the as-grown samples were examined using high-resolution SEM and EDX to determine the resulting growth quality. Fig. 2 shows the thus observed effect of chromium on graphene growth.

Fig. 2(a) shows an SEM image of an area of normal growth that contains no chromium. The dark spots spread over the image are multilayer islands indicated by green arrows. On the bottom of the image the brighter area is another copper grain whose boundary is marked with a red arrow and the black arrows show the wrinkles which are usually observed in CVD-grown graphene and attributed to thermal expansion mismatch between graphene and copper [18–20]. Fig. 2(b) depicts an area of graphene that was influenced by chromium. The most obvious difference is that the dark spots seen in (a) are absent here, suggesting that the formation of multilayers has been suppressed. However, we do see additional white nanowire features (marked with red arrow). These features are shown in more detail in Fig. 2(c). Fig. 2(d) shows the EDX spectra taken from an individual nanowire (point 1) and a reference point (point 2) indicated in Fig. 2(b). The EDX spectrum shows that in addition to carbon and copper the nanowire feature also contains chromium, suggesting that some chromium carbide has formed in these regions. Based on these results, we propose that some carbon reacts with chromium forming a carbide during growth. Both chromium and carbon are largely insoluble in copper, suggesting that they will exist almost completely as surface species. More detailed morphological and compositional analyses of the nanowire feature are presented in the section S.1-1 of the supplementary information. Additionally, XPS measurements on copper foil before and after growth are presented in section S.1-2 indicating there was no Cr detectable on the surface after growth.

In this work graphene has been synthesised at 1030 °C (as this is known to effectively form high-quality graphene monolayers [3,21,22]) and hence the growth is *diffusion-controlled* [23]. In this regime the growth rate is nearly independent of the temperature and is instead governed by the mass transport of reactants at the substrate surface. For diffusion limited growth we know from Fick's laws that coverage is a function of time. So, we have measured the coverage of graphene on copper at different points during growth. Fig. 3 shows SEM images and coverage vs. time plots, highlighting the effect of growth time.

Other factors involved in the CVD process such as partial pressure of methane and hydrogen and total pressure of the CVD reactor were kept unchanged to simplify the interpretation of the results.

Fig. 3(a) and (c) show SEM images of the surface after 30 s growth. Both areas show a dendritic growth morphology which is expected for diffusion-controlled growth [24]. However, graphene domains in the Cr-containing area display a more serrated type of dendrite. Observation of irregular morphologies with a larger number of lobes has been ascribed to the disturbed diffusion path of surface carbon [25].

In addition to the more serrated growth morphology, the surface is covered with white spots (see Fig. 3 c). EDX indicates (Fig. S2) that

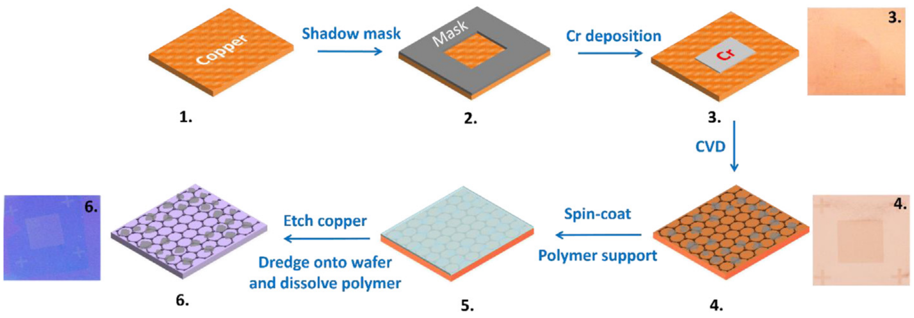

Fig. 1. Schematic representation of the sample preparation process flow (A colour version of this figure can be viewed online.).