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Growth optimisation of high quality graphene from ethene at low temperatures

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A B S T R A C T

Large-area, high-quality graphene was grown via thermal chemical vapour deposition from ethene on Cu substrates at 850 °C. The quality of the graphene was assessed using Raman spectroscopy, SEM and electrical characterisation. The Raman spectroscopy yielded excellent results with an average 2D/G ratio of ~2.75 and 2D FWHM of ~35 cm^{-1} in the flake centres, indicative of single layer growth. Graphene field effect transistors were fabricated from in situ grown graphene lines, displaying mobilities of 1100 $cm^2\,V^{-1}\,s^{-1}$ and 700 $cm^2\,V^{-1}\,s^{-1}$ at room temperature for holes and electrons, respectively, underlining the high quality of the graphene.

1. Introduction

Graphene has the potential to make a significant impact in the field of electronic devices and energy devices, in particular for applications in coatings [1,2], displays [3,4], solar cells [5], sensors [6] and switching devices [7]. The actual fabrication of devices on a large scale remains challenging though, mainly due to difficulties encountered in graphene production. Of the various methods of mechanical cleaving [8], liquid exfoliation [9], chemical reduction of graphene oxide [10], precipitation from SiC [11] and chemical vapour deposition (CVD) [4,12–15] all have their advantages and disadvantages, making their resulting graphene suitable for some and unsuitable for other applications. Graphene produced by CVD is a good candidate for electronic applications because of its high quality even though it does not yet reach the high carrier mobilities reported for mechanically exfoliated graphene [16–19]. Furthermore CVD growth of graphene can be up-scaled cost effectively and gives large-area and reproducible results [4,20].

The CVD growth of graphene generally utilises metal surfaces as catalyst. When using copper as catalytic substrate the graphene has been shown to give full coverage of mostly monolayer with individual flake sizes with lateral dimension of up to mm [12,16]. The monolayer coverage is owed to the very low carbon solubility in Cu, even at elevated temperatures [21]. Currently most high-quality CVD graphene on Cu is grown at 1035 °C at low pressure using methane gas as carbon precursor [17,22]. Such a high temperature, which is close to the melting point of Cu (~1085 °C), causes significant Cu evaporation, especially at the reduced pressure that many processes employ. The effects of the vapourised copper are not fully explored yet, but upon cooling the vapour condenses on the furnace walls as well as the sample, degrading the sample quality as well as reducing the furnace lifetime. Most importantly, the reproducibility of the growth is affected. As vapour pressures follow exponential trends even a small reduction in the growth temperature can have a significant impact on the amount of Cu vapour in the growth atmosphere [23]. Also the process cost is obviously reduced, a factor that will become important once the process is to be used commercially.

Recently there have been several advances towards reducing the growth temperature by varying the carbon precursor and the substrate finish. Generally the copper surface is electropolished [24,25] to smoothen it and prevent multilayer growth. Some reports use liquid carbon precursors, including carbon ring structures like hexane [26,27], benzene [28] or toluene [24] and even alcohols like ethanol or propanol [29]. Continuous graphene films have been grown at temperatures as low as 650 °C from toluene [24] but need impractical liquid precursor handling and showed significantly reduced mobility in comparison to the best values reported for CVD [30]. The lowest observed graphene island growth is at 300 °C from benzene but no continuous film was reported [28].

In this Letter we present the synthesis of graphene from ethene, a cheap and easy to handle gas, at 850 °C on copper substrates. This lowered temperature significantly reduced copper sublimation during growth and allowed for highly reproducible growth. Experimental design [31,32] was used to yield optimised graphene growth in a large scale low-pressure chemical vapour deposition furnace (LPCVD). The process produced high quality graphene as shown by scanning electron microscopy (SEM), Raman spectros-

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copy and electrical characterisation of the transferred graphene films. The reproducible, large-area graphene films of high quality derived from a non-toxic, industrially applicable precursor are a crucial step towards commercial use of graphene. The large-area graphene films are at least 80% monolayer as derived from mapping of the intensity of the 2D peak in the Raman spectrum and confirmed by the contrast in SEM images. Structured films were directly grown on the Cu catalyst and used to make field effect devices which showed hole and electron mobilities of 1100 $cm^2 V^{-1} s^{-1}$ and 700 $cm^2 V^{-1} s^{-1}$, respectively, underlining the suitability of these graphene films for electronic applications.

2. Experimental

Graphene was grown using ethene gas as carbon precursor (BOC gases, 99.999% pure) on 18 μm thick copper foil (Gould Electronics, #JTCHTE).

The foils were cleaned in 10% HCl for 30 s to remove a protective zinc-chromate passivation applied by the supplier and subsequently sonicated mildly in acetone (high-performance liquid chromatography grade (HPLC)) for 5 min to remove any organic impurities from the surface.

Pre-growth patterning of the graphene was done via alumina directed growth. Before growth a pattern was defined on the Cu foil using standard UV lithography (Shipley S1813 positive photoresist). 30 layers of Al_2O_3 (~3.3 nm) were deposited via atomic layer deposition (ALD) in a cold-walled reactor (ATV TP 01 prototype reactor) at 80 °C using water and trimethylaluminium (TMA) as precursors. The photoresist was then removed using acetone (HPLC grade) and mild sonication and the foil was placed in the graphene growth furnace and graphene was grown normally in the pattern originally defined by the photoresist.

Foils (both patterned and unpatterned) were loaded into a quartz furnace (ATV PEO 604), heated to 850 °C under 15 sccm H_2 flow at 1 mbar overall pressure and annealed at 850 °C for 30 min also under 15 sccm H_2. The subsequent growth consisted of a single step exposure to 3 sccm H_2, 1.5 sccm C_2H_4 and 300 sccm N_2 for 10 min at 2 mbar overall pressure. Cooling took place under a small amount of residual H_2 (static, no flow) at 2 mbar and took approximately one hour with three distinctive steps: First cooling with the power switched off to 800 °C in about 10 min followed by automated forced cooling to 200 °C in 30 min and finally natural cooling to 100 °C.

After growth was completed the foils were cleaned by sonication in acetone for 5 min at low power to remove any physisorbed contaminants. Poly (methyl methacrlyate) (PMMA) (950 k, A2) was spin-coated onto the graphene and re-flowed at 130 °C. The Cu substrate was then dissolved in ammonium persulfate solution (~1 M) and repeatedly dipped into deionised (DI) water during the etching process to remove the released graphene flakes from the backside. Once the Cu was fully removed the sample was transferred to a DI water bath using a glass slide and left there to clean for several hours. Finally the graphene was dredged onto the substrate of SiO_2/Si (300 nm dry SiO_2 on Si, 10 mΩ/cm) and left to dry under vacuum at room temperature. Once dry the sample was heated to 130 °C to re-flow the PMMA and improve adhesion. This step could be left out to avoid adhesion of the Al_2O_3 to the SiO_2. This was often preferable as occasionally pyrolytic carbon ended up deposited on the Al_2O_3 which could interfere with the device performance. The PMMA was finally removed using acetone (HPLC grade).

Device contacts for electrical measurements were deposited by thermal evaporation of gold through a shadow mask. These were contacted by a needle prober (Suss) for the actual electrical measurements using a Keithley 2612A source metre. All measurements were taken in the 4-point configuration on devices with a channel length of 200 μm as seen in Figure 4B. The source-drain voltage V_{ds} was kept constant at 20 mV whilst the gate voltage was swept to +60 V and −60 V.

Raman spectroscopy and mapping was performed with a WiTec Alpha 300 R Raman microscope using a 532 nm laser as excitation source. SEM was performed in a Zeiss Ultra using 2 keV acceleration voltage.

3. Results and discussion

Copper substrates were chosen for the inherent ability to catalyse monolayer graphene growth. We demonstrated graphene growth on the same type of foils previously [33]. It is known that ethene decomposes at lower temperature than methane and that it is possible to grow thin pyrolytic carbon films from it at 850 °C [34]. As temperature reduction in graphene CVD was the main objective, the temperature was fixed at 850 °C which was found to sufficiently suppress copper evaporation. Further the overall pressure was held constant at 2 mbar. In order to navigate the entire parameter space offered by the furnace in terms of, gas flows and growth time 'design of experiment' (DoE) was employed [32]. The four parameters varied were the partial pressures of C_2H_4, H_2 and N_2 as well as the growth time. The partial pressure was varied from 0.02 mbar to 1.5 mbar for H_2 and C_2H_4 and from 0 to 1.96 mbar for N_2 whilst the time was varied between 5 and 20 min. These regimes were chosen as they always yielded some kind of carbonaceous deposition as determined by pilot experiments. The output variable defined was the average FWHM of the 2D peak in the Raman spectrum, taken in 10 000 spectra over an area of 20 × 20 μm. This was chosen because the width of a Lorentzian curve fitted to the 2D peak of the graphene Raman spectrum can be directly correlated to the existence and quality of monolayer graphene [35–37].

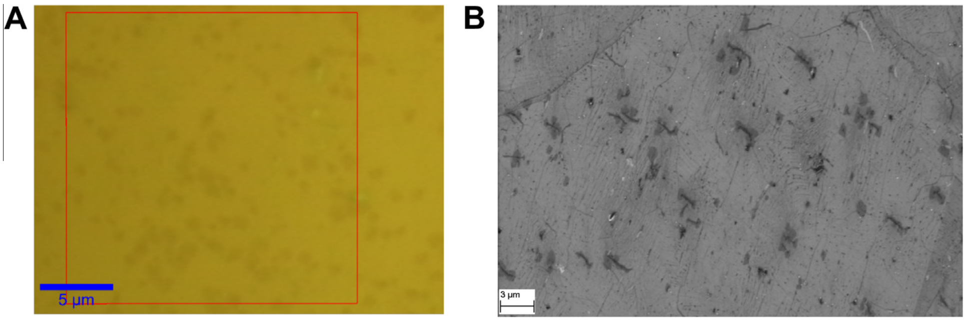

Figure 1. (A) Optical image graphene grown from ethene at 850 °C after transfer to SiO_2. It shows mostly monolayer and some multilayer graphene (darker regions). (B) SEM micrograph of graphene grown from ethene at 850 °C. The image shows homogeneous films of domain diameters of ~1 μm and some onset of multilayer growth (darker regions).