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Induction heating-assisted repeated growth and electrochemical transfer of graphene on millimeter-thick metal substrates

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ABSTRACT

Chemical vapor deposition in a hot wall reactor is the most common technique for the production of large area single layer graphene. However, growth in this type of reactors is time consuming and the results are limited by the surface quality of the widely used catalytic metal foils as growth substrates. In this work we demonstrate the use of millimeter-thick Cu and Pt substrates for graphene growth via inductive magnetic heating, which allows for fast temperature ramps during heat up and cooling. Based on a detailed growth study, a two-step growth process resulting in continuous monolayer graphene films of high crystal quality with grain size of larger than 90 μm is established. An electrochemical transfer process is used to separate the graphene film from the metallic substrate, yielding excellent results in terms of defect density, doping and residual contamination. Back-gated graphene field-effect transistors fabricated on Si/SiO_2 structures exhibit a high reproducibility with a peak mobility higher than 4000 cm^2/Vs. The combination of the highly time efficient graphene growth and electrochemical transfer together with the reusability of the growth substrates and the possibility of applying novel surface pretreatments pave the way for the use of high quality substrates in industrial applications.

1. Introduction

After its first isolation [1] graphene has gathered significant scientific interest due to its exceptional mechanical, optical, and electronic properties [2]. In order to fully exploit such properties, a well-controlled method to synthesize graphene of high quality on large area is required. While mechanical exfoliation of highly oriented pyrolytic graphite (HOPG) yields graphene of almost perfect crystal structure, this method is restricted to small flake sizes and cannot meet the demand to upscale production. Epitaxial growth on silicon carbide delivers high quality graphene but lacks a suitable transfer process for the use of any desired substrate. Therefore, chemical vapor deposition (CVD) on metal substrates such as Ni, Pt or Cu has become the method of choice for large area applications on arbitrary substrates [3,4]. First introduced by Li et al., this method typically employs methane as carbon containing precursor [5]. The growth substrate is heated close to its melting point and exposed to the gas flow under low pressure. Due to the low solubility of carbon, copper is the most promising candidate to achieve single layer graphene [6]. As grain boundaries and bilayer regions can influence the electronic properties [7,8], CVD of graphene on Cu foil substrates has been extensively studied, aiming towards large domain sizes and low bilayer coverage [9–11]. It has been shown that a proper pretreatment, e.g. electropolishing, of the growth substrate can strongly reduce the density of nucleation centers, confirming the influence of surface contamination and surface roughness on the nucleation of graphene [12–15]. Furthermore, growth studies on Cu single crystals revealed a strong dependence of the nucleation density and domain shape on the underlying Cu orientation [16,17]. Attempts using copper enclosures yielded up to millimeter sized domains [9,18]. However, in these experiments the growth rate is very low, leading to non-closed layers or to time-intensive growth processes which is not suitable for industrial applications.

In this work, unlike in standard furnace-based systems, we use an inductive heating unit to heat millimeter thick Cu and Pt substrates (from now on referred to as Cu/Pt blocks) allowing for fast temperature ramps and proper temperature control. Furthermore, the growth substrate was mechanically polished in order to further decrease the density of nucleation centers. The effect of different process parameters is carefully evaluated by means of scanning electron microscopy (SEM) and Raman spectroscopy, comparing Cu and Pt as growth substrates. Based on this study, continuous films with domain sizes of up to 90 μm on Cu and 20 μm on Pt could be achieved. A frame assisted electrochemical transfer method (bubbling transfer) was applied to detach the graphene from the underlying metallic substrate and transfer the as-grown films. This transfer method is found to yield graphene films with very low defect density and residual contamination level. Graphene field-effect transistor (GFET) devices were fabricated exhibiting field-effect mobilities of up to ~4000 cm^2/Vs.

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2. Materials and methods

2.1. Graphene growth

Graphene films were grown via low pressure CVD on millimeter thick Cu/Pt block substrates in a 1″ quartz tube. Mixtures of 4% H_2 and 5% CH_4 in Ar were used to achieve the desired gas composition. An inductive heating unit was used to heat the blocks to the desired temperature at a rate of 200 °C/min, combined with a pyrometer for reliable temperature control. A high hydrogen flow was applied during heat up and for an additional annealing step of 45 min. The subsequent growth process was started by adding the methane mixture to the desired amount for a chosen growth time. Pressure during growth was set by a valve at the inlet of the rotary pump. After growth, the inductive heater was immediately switched off resulting in cooling rates comparable to the heating rates.

2.2. Raman measurements

Raman spectra were recorded using an Ar-ion laser at 514.5 nm in a μ-Raman setup. The system is equipped with a liquid N_2-cooled detector in combination with an 1800/mm grating allowing for a spectral resolution of 0.5 cm^{-1}. A 100× magnification objective lens was used to obtain a laser spot of approx. 0.5 μm. Automatic acquisition of several spots and Raman maps were possible by the use of a piezo stage in combination with an autofocus unit. Typical spectra were integrated for 20 s. Background signal was subtracted from the presented data when necessary. Single Lorentzian peaks were fitted to the data at position of the D, G and 2D modes to extract all necessary information e.g. peak intensities, widths or positions.

2.3. Field-effect measurements

In order to characterize the electronic properties of the grown graphene sheets, field-effect devices were produced. P-doped Si wafers covered with 300 nm of thermal SiO_2 and with thermally evaporated Ti/Au (10 nm/50 nm) electrodes were used as device substrates. After transfer and resist removal, the graphene channel region was defined by optical lithography by etching in an oxygen plasma (300 s at 200 W). A second thermal evaporation step of Au together with optical lithography was used to contact the graphene channel.

3. Results and discussion

3.1. CVD growth setup

Most common CVD systems are based on hot wall reactors. For Cu [19] and Ni [20] substrates a fast cooling rate after growth has been shown to avoid increasing bilayer coverage. Therefore, typically either the growth substrate is pulled out of the furnace or the furnace is opened to accelerate the cooling process. In contrast to such hot wall reactors and similar to Piner et al., we employ an induction heater, operated at radio frequency (RF), to heat the growth substrate [21]. This technique enables precise control of heating and cooling rates with high limits of approx. 200 °C/min, which can further extend the parameter space for CVD graphene growth. Fig. 1A shows a schematic of our RF setup. The block substrate is placed in a quartz tube, which is surrounded by the RF coil. Here, only the growth substrate itself is heated by the inductive coupling leaving the quartz tube unaffected. Unlike in a recently published work [21], the magnetic field lines are oriented parallel to the quartz tube. Cu/Pt blocks with a thickness of 2 mm were used as growth substrates to increase the cross-section in the magnetic field. A pyrometer is focused on the substrate surface to monitor and control the temperature T in a feedback loop. The gas mixture of Ar, H_2 and CH_4 is set by a massflow control unit. The as-grown layers were analyzed with SEM to determine total coverage Θ, bilayer/multilayer coverage, and domain size. An exemplary SEM picture of one single graphene domain can be seen in Fig. 1B. The domain is represented by the darker shaded area in a flower-like shape and is located across a grain boundary in the Cu substrate (diagonal line). Bilayer and trilayer regions show even darker contrast and are marked by red and yellow dashed hexagons as guide to the eye, respectively. Furthermore, the white spot in the center of the domain, probably related to surface contamination, acts as initiation center for growth. Not only contamination but also surface roughness can induce nuclation [22,23]. Here, the thick substrates are of advantage compared to conventional Cu foils enabling for mechanical polishing in order to achieve a very clean and smooth surface. A side by side comparison of the surface morphology of an untreated Cu foil (bottom) and a polished Cu block (top) can be seen in Fig. 1C, as measured by white light interferometry. While both substrates exhibit a variation of several nanometers in height, the length scale for these fluctuations is much larger on the block making it a much smoother substrate and promising for low nucleation density.

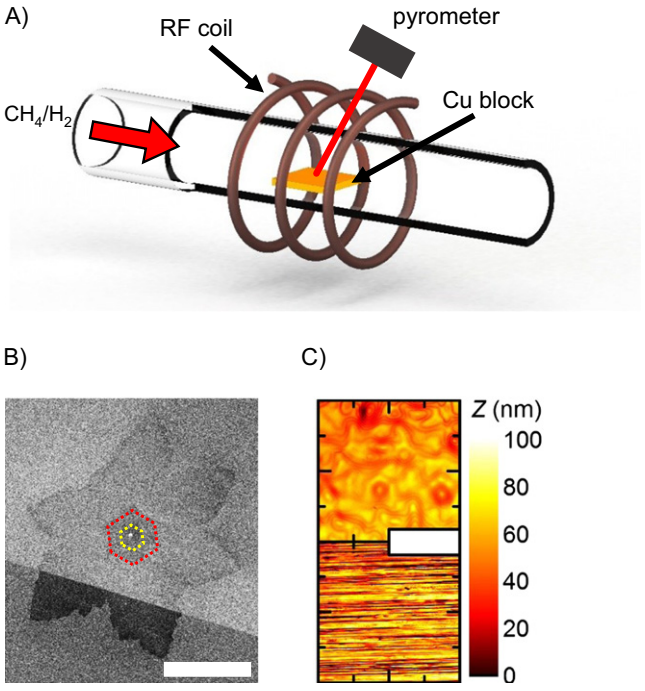

Fig. 1. A) Schematic of the CVD setup including inductive heating unit and pyrometer. B) Exemplary SEM image of one graphene domain on Cu. Bi- and trilayer regions are marked by red and yellow dashed hexagons, respectively. Scale bar is 10 μm. C) Surface morphology of a Cu block (top) and Cu foil (bottom), measured by white light interferometry. Scale bar is 200 μm.

In contrast to the previous work of Piner et al., the use of millimeter-thick substrates in our work enables us to take full advantage of the RF heating technique. [21] In this way, the problem of low heat conductivity and non-uniform heating they observed for foil substrates, which can cause inhomogeneous graphene films, is overcome by using the thick growth substrates. Further, the possibility of reusing the growth substrates (complete parameter study including more than 250 growth runs using only 7 Cu substrates and 1 Pt substrate), enabled by the bubbling transfer described below, opens the way for affordable growth on substrates with high quality surface pre-treatment or single crystalline substrates, which is expected to yield improved growth results [24–26].

3.2. Graphene transfer

After growth, the films were transferred onto p-doped Si wafers covered with 300 nm of thermal SiO_2. Currently, spin coating the graphene/