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Controllable and fast synthesis of bilayer graphene by chemical vapor deposition on copper foil using a cold wall reactor

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HIGHLIGHTS

- Large areas of bilayer graphene were synthesized in a cold wall CVD reactor.
- The coverage of bilayer graphene is up to 90% after 15 min growth time.
- H_2/CH_4 ratio can effectively influence the properties of the synthesized bilayer graphene.
- A nucleation activity model was proposed as an explanation of the growth.

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ABSTRACT

Bilayer graphene is attractive for digital device applications due to the appearance of a bandgap under application of an electrical displacement field. Controllable and fast synthesis of bilayer graphene on copper by chemical vapor deposition is considered a crucial process from the perspective of industrial applications. Here, a systematic investigation of the influence of process parameters on the growth of bilayer graphene by chemical vapor deposition in a low pressure cold wall reactor is presented. In this study, the initial process stages have been of particular interest. We have found that the influence of the hydrogen partial pressure on synthesis is completely the opposite from that found for traditional tubular quartz CVD. H_2/CH_4 ratio was also found to effectively influence the properties of the synthesized bilayer graphene in terms of its atomic structure, whether it be AB-stacked or mis-oriented. Different pretreatments of the copper foil, in combination with different annealing processes, were used to investigate the nucleation process with the aim of improving the controllability of the synthesis process. Based on an analysis of the nucleation activity, adsorption-diffusion and gas-phase penetration were employed to illustrate the synthesis mechanism of bilayer graphene on copper foil. After optimization of the synthesis process, large areas, up to 90% of a copper foil, were covered by bilayer graphene within 15 min. The total process time is only 45 min, including temperature ramp-up and cool-down by using a low pressure cold wall CVD reactor.

1. Introduction

Graphene is regarded as one of the most promising candidates for future post-silicon microelectronics due to its outstanding electrical and physical properties such as extremely high electrical mobility [1], high thermal conductivity [2], ballistic transport [3], and high optical transparency [4,5]. However, the lack of a bandgap severely hinders the application of monolayer graphene in the field of digital electronic devices [1,6]. Recently, the synthesis of bilayer graphene has attracted massive attention for electronic device applications because a band gap can be induced under an electrical displacement field [7,8]. Potentially, this is a property which could be used for developing different electronic devices such as field-effect transistor-based switches and pseudo-spintronics [9].

Chemical vapor deposition (CVD) is considered the most competitive approach for large-scale industrial growth of bilayer graphene as it is capable of producing a high-volume of graphene material and compatible with silicon processing [4,10]. In most studies, the CVD synthesis of bilayer graphene was conducted in

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tubular quartz reactors [11–16]. Such reactors are also called hot wall reactors since the heating source, usually a resistive or inductive coil, surrounds the outside of the quartz tube. However, due to the large heat capacity of a hot wall CVD reactor, the temperature ramp-up and cool-down procedures are time consuming, as is the synthesis process itself [14,15]. From this perspective, industrial scale synthesis of bilayer graphene by hot wall CVD might be limited in terms of throughput and efficiency. In contrast to the hot wall reactor, the cold wall reactor has a very low heat capacity using only a local heater adjacent to the sample [17]. The effective reaction is conducted in a limited space, which not only shortens the heating, cooling and growth periods, but also prevents the contamination of the chamber. Therefore the synthesis of graphene by cold wall CVD can efficiently improve the throughput and reduce the cost of production [18].

CVD synthesized graphene can be deposited on either metal substrate or insulating substrate. In compared to the growth on the metal substrate, direct growth on insulating substrate can omit the transfer step. Usually, the transfer step deteriorates the performance of graphene and complicates the whole process. Even though graphene growth directly on the insulating substrate without transfer process is attractive, its further application is hindered so far due to either high cost of substrate [19,20] or non-uniformity and low quality [21]. For the CVD of graphene on metal substrate, copper is one of the best catalyst options due to its low carbon solubility (typically 1.3 atoms % at 1000 °C). The synthesis of graphene on a copper foil by CVD is believed to be a self-limiting process [6,22]. Once the copper foil is covered by a monolayer of graphene, this layer will block the growth of more layers, indicating that this method is not suitable for synthesizing multilayer graphene. Different strategies have been employed to overcome the self-limiting effect, such as non-isothermal synthesis [12], plasma treatment [23], tailored cooling phases [24] or additional metallic elements to form catalyst alloys [16].

The theoretical [25] and experimental work [11] have both shown that hydrogen plays an important role in the growth of bilayer graphene. By and large, a higher partial pressure or a higher H_2/CH_4 aspect ratio both favor the deposition of bilayer graphene on copper in hot wall reactors [11,25]. However, only very few studies have been reported when it comes to cold wall reactor deposition of bilayer graphene on copper foils. Liu et al. specified that the purity of the copper foil is of crucial importance for bilayer graphene deposition on a copper [26]. Kidambi et al. explored parts of the process parameter space for depositing graphene on copper foil [27]. However, there is still a lack of comprehensive understanding of the growth mechanisms and guidelines for optimizing the deposition process are missing for the cold wall deposition of bilayer graphene.

In this work, a systematic study of the influence of process parameters on the growth results by using of cold wall CVD is presented and compared with the influence of process parameters in hot wall CVD. We found that graphene growth on copper in cold wall CVD is not an inherently self-limiting process independent of the ratio of H_2/CH_4, which means that adlayers appear as long as there is sufficient growth time. Furthermore, it was discovered that the H_2/CH_4 ratio can effectively influence the properties of the synthesized bilayer graphene in terms of its atomic structure, whether it be AB-stacked or mis-oriented. The lower the H_2/CH_4 ratio, the more likely is the deposition of a graphene adlayer. A high hydrogen partial pressure will suppress the nucleation of any adlayer during the initial phase, as well as decreasing the growth rate of both the monolayer and bilayer graphene throughout the full deposition process. This finding is completely opposite to previous findings concerning the role of the hydrogen partial pressure during deposition of graphene in a hot wall reactor. We also confirmed that cold wall CVD process is a bottom growth process.

Different pre-treatments of the copper foil in combination with different annealing processes were used to investigate the nucleation process with the aim of increasing the controllability of the synthesis process, in particular during the early stages. Based on an analysis of the nucleation activity, adsorption-diffusion [28,29] and gas phase penetration [22,30] were employed to illustrate, analyze and understand the synthesis mechanism of bilayer graphene on copper. After having optimized the synthesis process, this process was used to cover large areas, typically up to 90% of the sample copper foil, with bilayer graphene within 15 min of growth time. The total processing time was only 45 min, including temperature ramp-up and cool-down when using a low pressure cold wall CVD reactor. Our findings not only shines new light on the mechanisms of the CVD of bilayer graphene by using low pressure cold wall reactors, but also facilitates the fast and simple growth of bilayer graphene on copper foils.

2. Experimental methods

2.1. Synthesis of graphene in a cold wall CVD reactor

This section outlines the experimental procedure for synthesizing bilayer graphene on copper foil. In these experiments, 50 μm thick copper foils with a purity >99.995% (from Advent research materials Ltd) were used as the catalyst substrates for the chemical vapor deposition of graphene. Prior to loading the copper foil into the CVD chamber, the trimmed copper foil was cleaned by acetone and isopropanol to remove any organic contamination, where after the thin oxide surface layer was removed by acetic acid for 5 min.

After the copper foil was suspended above the graphite heater held by an alumina frame, the bell jar was immediately pumped down to 0.1 mbar. The temperature of the graphite heater was ramped up to 800 °C at a rate of 300 °C/min in an argon or argon/hydrogen atmosphere. Hereafter, the automatic heating was stopped, and the temperature was slowly raised manually until hotspots, which indicated that the copper foil was very close to its melting point of 1060 °C. Once the hotspot was visible on the surface of the copper foil, the heating power was decreased and the temperature held at around 1000 °C. When the temperature was found stable, the copper foil was annealed for 5 min in hydrogen to completely remove any native oxide. Finally, the carbon feedstock, 5% of methane in argon, was introduced into the chamber for initiating the growth. After the growth was completed, the chamber temperature was decreased to below 100 °C before the graphene film synthesized on the copper foil was taken out. A typical growth procedure with the two-step temperature ramp-up, a five minute anneal, a fifteen-minute growth, and the final chamber cool-down is shown in Fig. 1. After growth, while still on the copper foil, the graphene layer was characterized by scanning electron microscopy (SEM).

2.2. Transfer process and characterization

After SEM characterization, the graphene film was transferred to a Si/SiO_2 substrate by use of a standard procedure [31] involving polymethylmethacrylate (PMMA) and a polyethylene glycol terephthalate (PET) plastic frame to support the thin PMMA/graphene film, after the copper foil was etched away, during 12 h in an ammonium persulfate solution (0.2 mol/L). Then the PMMA/graphene film was rinsed in deionized water for five minutes, before being placed on the target Si/SiO_2 substrate where it was left for a couple of hours to dry naturally in air. After a final five-minute bake at 180 °C the PMMA was removed in acetone at 50 °C.

After being transferred to the SiO_2/Si substrate, the graphene film was characterized by optical microscopy, scanning electron