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Role of Cu foil in-situ annealing in controlling the size and thickness of CVD graphene domains

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ABSTRACT

Producing graphene with minimal crystalline defects and a controllable number of layers is highly desirable for its integration in advanced technological applications. Here we show how the chemical vapor deposition (CVD) protocol can be adjusted in order to control the size, the shape and the thickness of graphene domains. More particularly, this work focuses on the correlation between the conditions employed during the Cu foil *in-situ* thermal treatment and the subsequent graphene growth. The influence of Cu pre-growth treatments has been systematically investigated by considering two different pressure regimes (1 and 800 mbar) and various gas compositions (pure Ar, Ar/H_2 and Ar/O_2 mixtures) while using identical graphene growth conditions. We show that exposing the Cu foil to oxygen, either present as residuals in the Ar feedstock or precisely dosed using the Ar/O_2 gas line, effectively contributes to reduce the catalyst carbon content prior to graphene growth and hence significantly decreases the nucleation site density. It is also found that annealing the Cu catalyst in a hydrogen-free environment favors the formation of defect-free multi-layer graphene branches that extend underneath the millimeter-size single-crystalline graphene top layer. Our results provide clear guidelines to control the formation of graphene nuclei and additional layers.

1. Introduction

Graphene's excellent physical properties offer great prospects for the realization of groundbreaking practical applications, particularly in the field of high-frequency electronics, photonics and sensing [1–3]. Presently, chemical vapor deposition (CVD) on copper is the most technologically advanced graphene manufacturing approach as it yields continuous large-area graphene films with a thickness limited to a few layers [4,5]. Unfortunately, CVD-grown graphene falls short in terms of structural quality compared with its exfoliated counterpart due to defect lines called graphene grain boundaries (GGBs). These defects, originating from the nucleation, growth and coalescence of adjacent graphene domains, are known to be detrimental to graphene's electronic and mechanical properties and must be avoided in order to fully exploit graphene's high potential once integrated in functional devices [6,7].

Because of this limitation, significant research efforts have been directed to produce graphene sheets made of larger graphene domains and thus containing a lower GGBs density. This approach, introduced in 2010 by Li et al. [8], triggered a race among the scientific community towards the development of methods leading to ultra low nucleation site density at the earlier stage of graphene growth so that the domains can expand over large areas before coalescing with each other. A major milestone toward the growth of large graphene domains (GDs) consists in processing the Cu foils in order to remove the Cu surface morphology irregularities that have been shown to be preferential sites for nucleation, get rid of the Cu surface contamination and improve the catalyst purity [9–11]. In this regard, *ex-situ* Cu foil treatments including wet surface cleaning [12–15], mechanical/chemical/electrochemical surface polishing [10,13,16,17], repeated growths [18] and Cu surface oxidation [19,20], have been widely employed to improve the catalyst before loading it into the CVD furnace. *In-situ* treatments, including long-duration high-temperature annealing [16,17,21–24], substrate melting/re-solidifying [25], Cu surface recrystallization [21,24] and Cu foil exposure to oxygen [26–28] taking place during the CVD protocol prior to the graphene growth step, have also been reported to reduce the nucleation site density.

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Unlike the CVD growth pioneering works that used to ban oxygen from the synthesis process by carefully stripping the Cu native oxide layer on top of the catalyst prior to the CVD process and warming up the CVD furnace under a reducing atmosphere [10,29], very recent reports demonstrated that the most simple and effective Cu treatments for reducing the nucleation density consist of using *ex-situ* oxidized Cu foils or directly introducing oxygen *in-situ* inside the CVD furnace prior to graphene growth. However, opinions differ regarding the actual mechanisms whereby oxidizing the Cu foils drastically limits the formation of graphene nuclei [11,19,20,23,26–28,30–39].

Up to now, different research groups demonstrated the production of graphene single-crystals with lateral dimensions exceeding a few millimeters using in-situ Cu foil treatments. Unfortunately, these results were achieved using a wide variety of CVD procedures including the combination of different (i) catalytic substrate treatments, (ii) CVD conditions (pressure regime, H_2-to-CH_4 ratio, temperature, CH_4 partial pressure), (iii) complex Cu substrate geometries (Cu foil rolls, stacks and enclosures) [36,40–44] and, (iv) particular CVD furnace configurations (quartz cuvettes, confined reaction space) [34,45,46]. Such wide diversity of factors makes it challenging to appreciate the actual relative effectiveness of reported Cu foil treatments and understand the mechanisms involved for the nucleation and formation of graphene. Moreover, to our knowledge, the influence of the Cu foil treatments on the formation of additional layer during the subsequent graphene growth step has not been addressed yet.

In this work, we systematically study the influence of Cu foil *in-situ* thermal treatment conditions on the subsequent growth of graphene. Conducting a Cu thermal treatment directly inside the CVD furnace during the warming up and/or just before starting the graphene growth step seems to be a more promising approach compared with *ex-situ* treatments requiring the use of chemicals or additional equipment. Cu foils have been annealed at high temperature (1050 °C) for various durations (from 0 to 60 min) either under low (1 mbar) or near ambient (800 mbar) pressure conditions with various atmosphere compositions including pure Ar, Ar/H_2 and Ar/O_2 gas mixtures. Optimal Cu annealing conditions yield the growth of high-quality compact graphene domains with lateral dimension reaching a few millimeters. It is also found that employing hydrogen-free atmosphere prior to graphene growth triggers the formation of a new kind of defect-free multi-layer that spreads underneath single crystals of graphene and extends over a few millimeters. This work provides a rigorous comparison of the relative effectiveness of Cu thermal annealing processes reported in the literature and offers relevant guidelines for the optimization of graphene synthesis procedure. Finally, this work gives some fundamental insight about the role of oxygen in growing graphene and more particularly how to use it to tune graphene domain density and thickness.

2. Results and discussion

2.1. Nucleation site density

In order to evaluate how graphene growth is affected by the *in-situ* Cu foil treatment conditions, a series of CVD experiments has been carried out with varying Cu annealing conditions while keeping identical graphene growth steps. An identical CVD growth step throughout the various experiments, which is essential to ensure the adequacy and scientific rigorousness of this comparative study, has been achieved using a pressure-controlled CVD setup [38]. Fig. 1 shows the temperature, pressure and gas flow profiles that have been employed for the different steps involved in the CVD protocol, that is, CVD furnace warming up, Cu annealing, graphene growth and furnace cooling down. In order to limit the impact of the conditions used during the 1 h-long CVD warming step and ensure that graphene growth behavior is predominantly dictated by the high-temperature Cu annealing step conditions, it has been decided to warm up the CVD furnace under a low pressure (1 mbar) of an inert gas (pure Ar). Once the furnace reaches the growth/annealing temperature (T_{gr}), the annealing gas (pure Ar, Ar/H_2 or Ar/O_2 mixtures) is injected in the CVD furnace and the metering valves between the CVD furnace and the pumping system are adjusted to achieve the desired global pressure. Two different pressure regimes are considered in this work: a low pressure (LP) and a near-ambient pressure (NAP) regime thereby mimicking low pressure (LPCVD) and ambient pressure (APCVD) growth processes reported in literature. The global pressure of the NAP regime is set to 800 mbar in order to maintain the proper sealing of the LPCVD set-up. Once the Cu annealing step is completed, the CVD furnace is purged (the pressure drops down to 1 mbar) before injecting Ar/CH_4 (26 sccm, 2000 ppm in Ar) and Ar/H_2 (350 sccm, 10% in Ar) gas mixtures to start graphene nucleation and growth. This process step ensures that regardless of the gas composition or global pressure employed during the Cu annealing step, the graphene growth step will be achieved under the exact same conditions, that is with identical global pressure, partial pressure of methane and hydrogen-to-methane ratio profiles. The graphene growth step is performed under a pressure of 800 mbar as it yields graphene domains with a more compact shape and smoother edges and also reduces Cu foil evaporation loss (see Supporting Information Section S1) [47,48]. In order to produce isolated graphene domains that can be individually observed and counted and hence, obtain an estimation of their shape, size and density, the graphene growth step duration (t_{gr}) has been adjusted for each CVD experiment. Details about the CVD experiments are included in Supporting Information Section S2. Fig. 1c and d shows the evolution of the graphene domain density as a function of Cu annealing duration (ranging from 0 to 60 min) for both LP and NAP regimes and different gas atmosphere compositions. Given the strong affinity of copper for oxygen, particular precautions have been taken while annealing the Cu substrate under the Ar/O_2 atmosphere. It appeared essential to maintain a relatively low partial pressure of oxygen in the CVD furnace in order to avoid excessive Cu oxidation during the annealing step that would eventually lead to the degradation of the Cu foil physical integrity upon the reducing treatment caused by the subsequent graphene growth step. In order to maintain a relatively smooth Cu surface and avoid any Cu foil damage, the oxygen gas feedstock dilution has been chosen to be 1% O_2 and 500 ppm O_2 in Ar for the LP and NAP Cu treatments, respectively (see Supporting Information Section S3 for more details). Starting graphene growth directly after the furnace warming step ($t_{ann} = 0$ min) yields a graphene domain density of about 1400 GDs/cm^2. This represents about a 200-fold improvement compared with the graphene density that would have been obtained using 200 sccm of Ar/H_2 instead of Ar in the warming up step, which is consistent with previous works (see Supporting Information Section S4) [30,38]. When performed under a hydrogen-free atmosphere, the high temperature Cu foil annealing step effectively contributes to decrease the nucleation site density as the number of GDs has been reduced by at least one order of magnitude after 1 h. On the other hand, annealing the Cu foil under a reducing atmosphere composed of 10% of hydrogen has a mixed influence on the graphene domain density. The Ar and Ar/O_2 trends suggest that extending the Cu annealing duration beyond 1 h would further reduce the nucleation site density and annealing under near-ambient pressure has a potentially greater beneficial effect than annealing under low pressure.