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Hybrid cold and hot-wall reaction chamber for the rapid synthesis of uniform graphene

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ABSTRACT

We introduce a novel modality in the CVD growth of graphene which combines cold-wall and hot-wall reaction chambers. This hybrid mode preserves the advantages of a cold-wall chamber such as fast growth and low power consumption, while boosting the quality of growth, similar now to conventional CVD with in hot-wall chambers. The synthesized graphene forms a uniform monolayer. Electronic transport measurements indicate significant improvement in charge carrier mobility compared to graphene synthesized in a cold-wall reaction chamber. Our results promise the development of a fast and cost-efficient growth of high quality graphene, suitable for scalable industrial applications.

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1. Introduction

Cold-wall chambers (CWC) are advantageous for the growth of graphene as they are fast and cost-efficient. The set-up is constructed in a compact manner and the small size of the reaction chamber allows lower gas consumption. In such chambers, the heating energy selectively heats up the specimen, i.e. a copper foil in contact with the hot stage, optimizing energy efficiency and thus reducing growth costs [1]. On the other hand, knowledge of and experience with the chemical vapor deposition (CVD) of graphene in CWC is relatively sparse. Successful reports on the growth of graphene in CWC are rare in comparison with tube oven systems, i.e. hot-wall chambers (HWCs) [1–4]. The sparsity of reports accounts for a general sense of distrust in the community regarding the utilization of CWCs. This manuscript studies the CVD growth of graphene in a CWC; we identify the origin of imperfections and offer solutions to improve the quality of the synthesized graphene, including improved growth parameters and adoption of the growth principle of the HWC, in other words hybridizing CWC and HWC. The modifications are successful in boosting the uniformity and electronic transport properties of the synthesized graphene, which are now comparable with graphene grown in conventional HWCs.

2. Comparison of the CWC and HWC

Fig. 1 compares typical CWC and HWC setups. In the HWC, the heating elements are placed outside the chamber tube; heat radiation entering the transparent quartz tube heats up the specimen (copper foil) placed inside the tube (inset in Fig. 1-b). Typically, the heating element is embedded in a large block of an insulating material to minimize energy dissipation to the environment. This block, however, acts as a thermal mass which delays both the heating (to start the growth) and the cooling (at the end of the process) of the chamber. In a CWC, on the other hand, the specimen is placed directly on a resistively heated stage inside the chamber (inset in Fig. 1-a). In typical designs, the size of the heating stage can be as small as the size of the specimen with no insulating materials required, which makes fast processing possible. The two chamber designs find their main difference in their heating regime: uniform radiation in a HWC provides a heating zone larger than the specimen with a uniform temperature whereas the CWC provides heating selectively to the specimen, giving rise to a considerable thermal gradient between the hot stage ($T > 1000\ ^\circ C$) and the cold walls ($T \sim$ few tens of $^\circ C$) during the operation of the CWC (inset Fig. 1-a and b). Fig. 2-a and b characterize graphene grown in a CWC. For this growth, we adopted a recipe similar to what has been developed earlier [1,2,5]; we shall refer to this recipe as “conventional recipe”, detailed in Methods. In short, the recipe includes: i) heating the copper foil to 1035 °C, ii) annealing for 10 min and iii)

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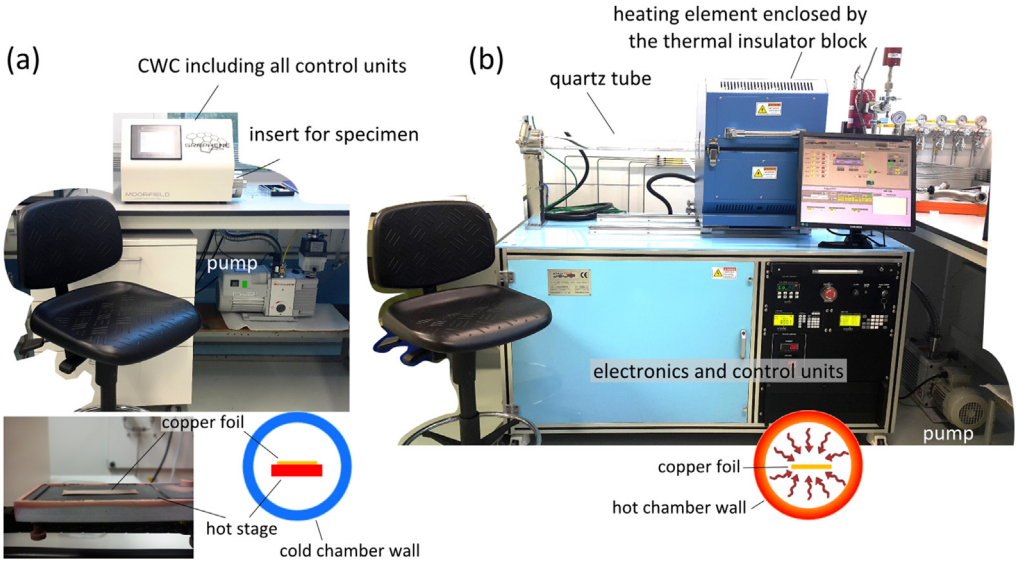

Fig. 1. Cold- versus hot-wall reaction chambers for the growth of graphene. a) Photograph of a commercially available cold-wall chamber (nanoCVD-8G, Moorfield Nanotechnology): The main unit has the dimensions of 40.5 cm × 41.5 cm × 28 cm and weighs 27 kg. The bottom-left inset shows the hot-stage (4.0 cm × 2.5 cm) hosting a copper foil. b) Photograph of a commercially available hot-wall chamber (planarGROW-2B, planarTECH): The unit has the dimensions of 1.75 m × 1.60 m × 0.75 m and weighs ~200 kg.

growth by flow of methane/hydrogen gas mixure in 7:2 ratio for 3 min. The synthesized graphene covers the surface of the copper foil completely, yet suffers from several imperfections, summarized in Table 1:

Table 1
Imperfections of chemically synthesized graphene in a CWC.

Imperfection	Possible origin	Possible solution
multilayer areas	presence of the defect sites on Cu	increasing the annealing duration
	excessive carbon precursor	lowering CH_4/H_2, shortening the growth
pronounced Raman D peak	contaminations in the supplies	using higher quality supplies
	oxidation during transferring	optimizing the transfer process
heterogeneous growth	non-uniform heating	hybridizing the CWC and HWC

The presence of multilayer areas is the first imperfection, evident as rounded or linear patches of different contrasts in Fig. 2-a. Indeed those multilayer islands are nucleated at the defect sites on the copper foil and grow in the presence of excess carbon precursors [6]. Prolonging the annealing step up to 1 h lowers the defect site density by improving the surface quality of the copper. Lowering the CH_4/H_2 ratio diminishes the excess of carbon precursors. We note that a much lower CH_4/H_2 ratio of 2 sccm/1000 sccm achieved a uniform monolayer coverage in a HWC process [6].

Local crystalline defects, revealed by the prominent D peak in the Raman spectrum form the second type of imperfection (Fig. 2b). Impurities in the utilized gases and/or the oxidation during transfer to the wafer are among potential sources of the D peak in CVD graphene. Solutions can be found by improving the purity of gases and optimizing the transfer process.

Heterogeneous growth and crystalline quality is the last imperfection, evident from dissimilar Raman spectra recorded at different spots on the sample. The heterogeneity persisted even after prolonged annealing to improve the uniformity of the copper foil. The long quartz tube used in the HWC ensures steady, laminar flow of gases where they reach the copper foil [7]; the absence of such a "guide" in the short reaction chamber may cause local eddies and non-uniform stream. The huge thermal gradient between the hot stage and the walls of the chamber and non-uniform heating due to the small heating zone are additional potential sources of the inhomogeneity. Indeed this imperfection can be viewed as an intrinsic side effects of the compact and energy-efficient design of the CWCs.

3. Hybridizing the cold and hot wall growth principles

A way to overcome the side effects of the compact design is to cover the stage with a quartz plate, leaving a gap of about 2 mm for the flow of gases over the copper foil (Fig. 2-c). The benefit is twofold: the flow of the gases through the gap is inside the laminar boundary layer associated with the quartz cap; hence is uniform [7,8]. Secondly, in this design, the heat radiating from the hot stage during the growth is reflected back to the copper foil by the reflective surface of the quartz plate; hence, effectively, a small reaction chamber forms that takes the best features from the CWC and HWC designs. Fig. 2-d and e present optical microscopy, SEM and Raman characterization of graphene synthesized with the improved recipe in the hybrid C/HWC. It is clear that the modifications in the growth recipe and the growth mode (detailed in the Supplementary Materials, section 1) improve the uniformity of growth and prevent onset of multilayer formation. Although there is still a D peak in the Raman spectra, the lower I_D/I_G ratio indicates an improved crystalline structure. The inset in Fig. 2-e focuses on a selected spectrum between 1200 cm^{-1} and 1700 cm^{-1}. D, G and D′ peaks are de-convoluted by means of Gaussian fits. We estimated $I_D/I_{D'} = 2.75$, close to the value reported for the grain boundary defects [9] indicating that the synthesized graphene suffers from a high population of grain boundaries, i.e. small grains. The complementary electron diffraction pattern of a suspended graphene sample (Fig. 2-f) shows the presence of regions without any preferred lattice orientation, i.e polycrystalline graphene (visible as the extra diffraction points next to the characteristic diffraction pattern of monolayer graphene). Note that Raman spectra with

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