# Relationship between heating atmosphere and copper foil impurities during graphene growth via low pressure chemical vapor deposition

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## ARTICLE INFO

## ABSTRACT

Low-pressure chemical vapor deposition synthesis of graphene films on two different Cu foils, with different surface oxygen and carbon contents, was performed by controlling $H_2$ and/or Ar flow rates during heating. The influences of heating atmosphere on the final impurity level, quality of the synthesized graphene films and thickness uniformity were investigated depending on Cu foil impurities. Heating of carbon-rich, but oxygen-poor Cu foil in $H_2$ environment resulted in covering the foil surface by residual carbon which then acted as active sites for multilayer graphene growth. Ar-only flow was required during heating to promote high quality graphene growth on this foil. On carbon-poor, but oxygen-rich Cu foil high quality graphene growth was promoted when the heating was carried out under $Ar/H_2$ environment. Almost no carbon residues were observed on this foil even under $H_2$ only flow during heating. The heating atmosphere affected not only graphene growth, but also the type and amount of impurities formed on the surface. $H_2$ and $Ar/H_2$ heating resulted in the formation of spherical nanometer-sized impurities, while irregular-shaped, large (a few μm) $SiO_2$ impurities were observed when Ar alone was used during heating. Quality of the grown films was tested by Quantum Hall Effect measurements.

## 1. Introduction

Graphene is a single atom-thick plane of carbon atoms arranged in a two-dimensional honeycomb lattice. In spite of having an atomic thickness, it is the strongest thermodynamically stable material ever known [1]. It is an excellent electrical conductor, which shows room temperature ballistic transport [2] and has an extremely high intrinsic thermal conductivity at room temperature, which is among the highest of any known materials for sufficiently large, suspended flakes [3]. Due to these unique properties, graphene is a promising material for many applications such as field effect transistors, transparent electrodes, sensors, energy storage systems and nanocomposites. However, production of high quality graphene-based materials at industrial scale is a prerequisite for

making the potential applications of graphene real. Chemical vapor deposition (CVD) is a promising method for large-area graphene production at a large scale with low defects, good uniformity and controlled number of graphene layers. The graphene films made on metal film or foil surfaces can be easily removed and transferred onto dielectric substrates. This enables one to produce large area, planar graphene films with relatively low defect density and is well-suited for flexible transparent electrodes and electronic applications where the growth can be patterned precisely in combination with lithographical methods.

Graphene growth on Cu foils has shown great promise for large-area, single layer graphene [4]; however, there are also some challenges. The quality, thickness and uniformity of CVD-grown graphene films depend on various parameters such as gas flow rates, growth temperature and time, pressure during the entire growth process, cooling rate, etc. The surface morphology and purity (amount of impurities) of the Cu foil both play a critical role in the graphene growth, as well. Disorder, defects and impurities originating from both the metal catalyst itself and/or from the

synthesis process (i.e., from synthesis parameters and transfer process) act as active sites for graphene nucleation, enhancing the catalytic activity of the Cu surface and leading to thickness non-uniformities across the grown film [5]. These surface irregular-ities may also affect the mobility of the CVD-synthesized graphene significantly. It was shown that high quality and uniform CVD-grown graphene films exhibit anomalous Quantum Hall Effect (QHE) at low temperature and high magnetic field [6]. However, the structural characteristics and disorders at the microscopic and macroscopic scales have strong influence on transport properties of graphene. The mobility of CVD-grown graphene is limited by dis-order originating from both growth and transfer processes. In order to improve the thickness uniformity and enhance the transport properties of CVD grown graphene, the amount of disorder, defects or impurities has to be eliminated or at least minimized by con-trolling the process parameters (such as growth temperature, time, pressure and gas flow rates during the entire CVD process), transfer route and Cu foil properties. Pre-cleaning Cu foil surface using chemical etchants (i.e., acid solutions), electropolishing and hydrogen annealing have commonly been applied in order to provide a clean and flat surface by reducing surface irregularities. However, it should be taken into account that the amount and type of Cu foil impurities may show variations from batch to batch or depending on supplier which make it difficult to remove these impurities equally by standard cleaning routes, and this may cause irreproducibility issues [7]. In recent years, several studies have focused on reducing graphene nucleation density by controlling $H_2$ and/or Ar partial pressures during pre-graphene growth steps (heating up to growth temperature and annealing) [8–12]. Gan and Luo [8] observed that heating chemically etched Cu foil in Ar only environment produced a rather rough and uniform surface with copper oxide nanoparticles which were then reduced to copper nanoparticles with size of several to tens of nanometers during annealing in $Ar/H_2$ environment. They suggested that heating in Ar only environment is crucial for introducing selective nucleation centers in the graphene growth step, and consequently enabling the control of graphene sizes. Zhou et al. [9] showed that graphene nucleation density was reduced by nearly two orders of magnitude when the Cu foil was heated/annealed in pure Ar gas compared with that heated/annealed in the $Ar/H_2$ mixture. The authors attributed graphene nucleation reduction to higher nucleation barrier on the copper oxide compared with the fresh copper sur-face. Hao et al. [10] found that graphene nucleation density was reduced by introducing oxygen into the CVD chamber just before introduction of methane. This enabled growth of cm-scale gra-phene domains. The authors attributed the nucleation density reduction to passivation of Cu surface active sites by the oxygen on the Cu surface. Jung et al. [11] performed atmospheric pressure CVD growth of graphene domains on Cu foil using various volume ratios of $H_2$ and Ar during annealing in order to investigate the influence of partial pressure of $H_2$ during annealing on the growth rate and shape of the graphene domains. It was observed that the mean size and density of graphene domains increased with an increase in hydrogen partial pressure during the annealing time. The authors also reported synthesis of snowflake-shaped carbon aggregates when only $H_2$ was used during the annealing process [11]. Shin and Kong [12] investigated the effect of hydrogen introduction in each step of atmospheric pressure CVD process and found that a pristine graphene monolayer was obtained when no hydrogen was used in the process. These studies have revealed the critical role of pre-graphene growth atmosphere on graphene nucleation density and domain size (consequently on graphene quality). However, the reported conditions for obtaining optimum graphene quality show variations which could arise from differences in as-received Cu foil characteristics (surface morphology and purity) used in these

studies. Therefore, it is crucial to understand the relation between Cu foil impurities and heating and/or annealing atmosphere(s), and its effect on graphene growth and quality.

The objective of this study was to perform low-pressure CVD growth experiments of graphene films on two different Cu foils belonging to two different batches of the same commercial source by controlling the $H_2$ and/or Ar flow rates during heating in order to investigate the influence of heating atmosphere on the final im-purity level, quality of the synthesized graphene films and thick-ness uniformity depending on copper foil impurities. The electrical characterization of the graphene films transferred onto $SiO_2/Si$ substrates was performed at low temperature under high magnetic field, in the Quantum Hall regime which constitutes a special hallmark of graphene in order to test the graphene quality.

## 2. Experimental procedure

### 2.1. Graphene synthesis, transfer process and characterization

Graphene synthesis was carried out in a commercial CVD sys-tem with a 4 inch quartz tube inside a horizontal tube furnace (EasyTube 3000 Ext., First Nano, USA) equipped with a screw dry vacuum pump (Busch BA100 A) which allows the control of the pressure in the reaction chamber between 0.1 and 700 Torr. The system also contains a dedicated secondary pump to ensure effective seal in the reaction chamber. Graphene growth was per-formed on Cu foils as a catalytic substrate. 25 μm thick and 99.8% pure Alfa Aesar foils with the same lot number (13382), but sup-plied from two different sources at different times (i.e., from different batches) were used as catalysts. The X-ray photoelectron spectroscopy (XPS) analysis of the as-received foils was performed using a Thermo Scientific Thermoelectron K-Alpha apparatus. The photoelectron emission spectra were recorded using Al-$K_\alpha$ radia-tion (hν = 1486.6 eV) from a monochromatized source. The X-ray spot diameter on the sample surface was 400 μm. The pass energy was fixed at 30 eV. The spectrometer energy calibration was per-formed using the Au $4f^{7/2}$ (83.9 ± 0.1 eV) and Cu $2p^{3/2}$ (932.8 ± 0.1 eV) photoelectron lines. The background signal was removed using the Shirley method [13]. Atomic concentrations were determined from photoelectron peak areas using the atomic sensitivity factors reported by Scofield [14] and taking into account the transmission function of the analyzer. This function was determined at different pass energies from Ag 3d and Ag MNN peaks collected on a silver standard. XPS analysis indicated the presence of C, N, O and Cu elements on the surface of the 'CROP' foil, and P, C, Ca, O and Cu elements on the surface of the 'CPOR' foil (see Supplementary Information, Figs. S1 and S2). The carbon and ox-ygen contents of these foils exhibited significant differences (Insets in Figs. S1 and S2). Accordingly, the relatively carbon-rich, but relatively oxygen-poor foil was denoted as 'CROP' and relatively carbon-poor, but relatively oxygen-rich foil was denoted as 'CPOR'. Table 1 shows the sample naming according to CVD synthesis conditions and pre-cleaning type of the Cu foils.

Prior to loading the Cu foils into the reaction chamber, they were cleaned using acetone, deionized (DI) water, acetic acid (glacial-100%) or nitric acid (5.4 (w/w)), DI water, acetone and isopropyl alcohol, subsequently. After loading the samples into the chamber, the system was purged with Ar gas (purity 99.999%) and a leak test was performed at base pressure with a leak-back rate below 0.05 Torr per minute. Then, the sample was heated from room temperature to 1000 °C at a pressure of 0.5 Torr (unless otherwise stated). Heating was performed under different atmospheres such as Ar, $Ar/H_2$ or $H_2$ (purity 99.999%) to clarify the effect of heating atmosphere on graphene growth and graphene quality. For the annealing step, the system was maintained at 1000 °C for 30 min