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Rapid chemical vapor deposition of graphene on liquid copper

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ABSTRACT

Molten copper is used to catalyze the graphene synthesis by chemical vapor deposition. The Cu has no grains above melting temperature, which is favorable for graphene growth. Using a vertical cold wall system, the deposition rate is drastically increased as compared with common hot-wall tube furnaces, pushing the method one step forward towards applications. A molybdenum–graphite Joule heater is used to avoid mechanical deformation of the carrier foil for the catalyst to ease the subsequent processes. The rapid deposition makes it possible to observe graphene growth on liquid Cu even at low pressure, where severe Cu evaporation simultaneously occurs.

Since the discovery of electric field effect in graphene in 2004 [1], this material has received a lot of attention, especially in nanoelectronics. It is predicted that the usage of graphene as transparent electrodes in optoelectronic devices could be commercialized within a decade [2]. For the potential large scale application in electronics, the synthesis technology of graphene is obviously the key topic. Earlier graphene production method is mainly based on the mechanical exfoliation of bulk graphite [1]. Soon after, the SiC based epitaxial graphene [3] and the reduced graphene oxide [4] become popular. Nevertheless, these methods in turn have the intrinsic disadvantages of small/irregular size, high cost, and low quality. These techniques seem not to be the best options for high-end consumer electronics. Since 2009, the chemical vapor deposition (CVD) of large area and ~100% monolayer graphene on copper substrate has become the mainstream technique in graphene based nanoelectronic research [5], for its compatibility to existing semiconductor processes, high material quality, and industry acceptable cost. Today, the hole mobility for the CVD graphene transferred to SiO_2/Si can reach 11,000 $cm^2\,V^{-1}\,s^{-1}$ [6]. In just a few years, the size of CVD graphene film evolves from cm in academic labs [5] to 100 m in semiconductor companies [7]. Recently, the metal catalysts are shown to be reusable [8,9]. There is no question that CVD will continue to play a central role in graphene applications.

The solubility of carbon in Cu is extremely low (0.027 at.% at 1000 °C [10]), which constitutes the major reason why Cu replaces Ni (C solubility 1.26 at.% at 1000 °C [10]) as the dominant graphene catalyst. The low solubility helps suppress the segregation effect of carbon in metals, and hence reducing the formation of multilayer graphene. However, the melting point for Cu is merely 1083 °C, very close to the typical graphene growth temperatures at 1000–1050 °C, which poses a stringent requirement on the precise control of temperature. At temperatures so close to the melting point, Cu tends to develop many irregular domains, whose boundaries are the collection sites for structural defects and chemical impurities, although they usually do not affect the continuity of graphene. The Cu grain boundaries are one of the limiting factors that affect the graphene quality. In 2012, graphene grown by CVD on molten Cu was reported [11]. Its advantages include: (1) liquid Cu contains no grain boundaries, and the surface is nominally atomically flat, which reduces the graphene nucleation density and improves the quality; (2) the deposition temperature is higher and the catalytic ability enhanced, favorable for a better graphene lattice; and (3) it relieves the strict requirement on the temperature control. Despite the breakthrough in Ref. [11], there remain several unsolved or unclear issues. First, the growth on liquid Cu is very slow (typical deposition time being several hours). The ultralow throughput dramatically increases the cost and hinders the widespread usage of the technique. Second, molten Cu has a high surface energy and does not wet common sample susceptors and forms round droplets, making many subsequent processes difficult. Although the liquid Cu wets some refractory metal foils such as W and Mo, the foils tend to become corrugated or ruptured due to the aggressive heating. Last, to date, only ambient pressure CVD (APCVD) is used to grow graphene on molten Cu. When low pressure CVD (LPCVD) is used, severe Cu evaporation occurs, and how the graphene grows under such a

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special condition is unknown. In this paper, we use a cold wall CVD system to grow graphene on liquid Cu. Due to the configuration of the machine, the deposition is extremely fast (typically 5 min). The samples are heated using a Joule heater made of graphite. A piece of molybdenum foil is firmly attached to and alloyed (at the interface) with graphite to form a flat and stable heater for the molten Cu. The fast growth speed also allows us to observe the graphene deposition under low pressure, where the nucleation and growth takes place earlier than the Cu vanishes in vacuum. Our results help push the liquid Cu grown high quality graphene towards real applications, and also shed light on the growth under extreme conditions where the Cu severely evaporates during the entire growth.

The graphene is deposited in a vertical cold wall CVD (Black Magic, Aixtron) as schematically shown in Fig. 1(a). An AC current is sent into a Joule heater (500 μm thick) which is capable of temperature ramps as high as 300 °C/min. The heater is made of graphite in order to avoid unnecessary contaminations to the graphene growth. We note that our system is different from the commonly used hot wall quartz tube furnaces (see Fig. 1(b)) and is suitable for rapid CVD [12]. Our typical growth time is 5 min or less, whereas in tube furnaces it usually requires deposition time ranging from 30 min to several hours. Even including the sample loading, heating, cooling and unloading, one CVD run in our system can be done within 40 min, whereas the heating and cooling in hot wall horizontal furnaces typically takes one or more hours. Therefore, the CVD we used here is very suitable for industrial applications where the cost and time of the deposition are essential. The reason of the fast growth mechanism, however, is yet to be clarified. We believe it may be related to the following two reasons. First, in our situation, the gas flow comes from above, rendering a “head-on collision” situation, where most gas molecules have chances to meet the catalyst (see Fig. 1(a)). In horizontal tubes, however, the precursor and the sample are like “large angle scattering” (see Fig. 1(b)). Only a thin layer of gas molecules can interact with the sample whereas the majority is wasted. Therefore, our vertical geometry offers the most efficient use of the precursor. Second, our system is favorable for graphene CVD according to a new growth mechanism. In this year, the new and essential role of the Cu vapor is identified [13]. At high temperature, in the chamber there is copper vapor originated from the Cu catalyst used in the graphene CVD. Massive carburization takes place in the airborne Cu clusters, followed by the dropwise condensations for the clusters to the surface of the bulk Cu catalyst, where the carbon is released and the graphene film grows. Unlike hot wall furnaces where everywhere is isothermal, in our system only the heater and its adjacent places are hot. Therefore, it favors the evaporation and recondensation procedures of the Cu clusters, rendering a fast graphene growth. This effect is especially important for liquid Cu grown graphene, where the Cu evaporation is much more pronounced than the solid Cu case.

At first, 50 μm thick tungsten foil (99.95%) is used as the carrier for the copper (50 μm thick foil, 99.999%). Both the W and Cu are rigorously cleaned in acetone, ethanol, and water in sequence. After sample loading, the chamber is evacuated to <0.1 mbar. Then, in a flow of 1000 sccm Ar and 1000 sccm H_2, at 700 mbar, the Cu on W is rapidly heated to 1090 °C (monitored by an infrared pyrometer) and kept for 10 min. The Cu is fully molten. The atmosphere is adjusted to 960 sccm Ar, 40 sccm H_2 and 5–30 sccm CH_4 (still 700 mbar). The deposition time lasts 5–10 min. The CH_4 is cut off and the system cooled down to room temperature.

After unloading, some Cu samples are placed on a hot plate at 160 °C for 10 min. If the graphene does not cover the whole surface of Cu, it will hinder the Cu oxidation in open air. As a result, the uncovered parts will appear darker in a microscope. Using this facile method, we find that for the graphene sample grown with 5 sccm CH_4 for 5 min, there are just a few graphene monocrystal flakes, whereas for the case with 10 sccm CH_4 for 5 min as shown in Fig. 2(a) and (b), the flakes appear in large quantity. The graphene flakes are of hexagonal shape and distributed relatively uniformly on the Cu surface. Adjacent hexagons are usually having the same rotation orientation. Typical sizes for the flakes are from tens of μm to more than 100 μm. In Fig. 2(b), the origin of the round shaped features is unclear, but they are believed to be related to the surface defects on Cu, which lead to some isotropic processes during the Cu oxidation experiment. If the flow of methane is further enlarged to 20–30 sccm, the flakes will emerge into continuous graphene sheets (not shown).

Instead of the oxidation test, some Cu samples are spin coated with a layer of PMMA polymer and cured at 160 °C for 10 min on a hotplate. Afterwards, they are immersed in a marble solution ($CuSO_4$:HCl:H_2O = 10 g:50 ml:50 ml) to etch away the Cu foil. After 12 h, the samples are picked up and cleaned in water for several times. Then, the graphene films on the PMMA mechanical support are transferred to 300 nm SiO_2 thermal oxides on Si wafers and dried naturally. Finally, they are baked at 160 °C for another 10 min before the PMMA is dissolved in acetone. The as-transferred graphene samples are observed by scanning electron microscopy (SEM) and optical microscopy. Fig. 2(c) and (d) shows the typical SEM images of the graphene grown using 5 sccm CH_4 for 7 and 10 min, respectively. Fig. 2(e) and (f) are optical images of the graphene deposited with 5 sccm CH_4 for 7 and 10 min. Based on these photos, it can be seen that the 7 min growth is incomplete (discrete graphene single crystals), while the 10 min case results in a continuous graphene monolayer. Apparently, liquid copper is suitable for graphene growth of both single crystal flakes and

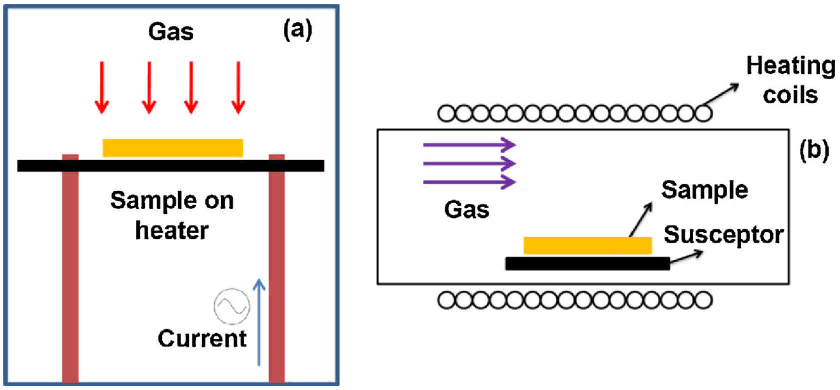

Fig. 1. Schematic diagrams of (a) the cold wall CVD system used in this study and (b) the hot wall tube furnace CVD system.