The effects of growth time on the quality of graphene synthesized by LPCVD

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Abstract. The graphene has several unique characteristics and many applications in all fields. Some of these characteristics are the quantum Hall effect at room temperature, the ambipolar field effect, the optical properties, the high electron mobility and the best electronic properties. The ability of fabricating large-area monolayer graphene is hindering its application. In this paper the effects of growth time on the quality of graphene synthesized by low-pressure chemical vapour deposition (LPCVD) has been investigated. Large-area monolayer graphene is synthesized on polycrystalline Cu foil ($\sim$1 cm^2) by controlled experiment LPCVD at different growth times (30, 60, 120 and 150 s). The synthesized graphene was characterized using Raman spectroscopy and scanning electron microscopy (SEM). The Raman spectrum showed a $I_G/I_{2D} \sim$0.2 ratio which indicates that all samples are single-layer graphene and the SEM images demonstrate that the domain size increases when the growth time increases. The growth mechanism of LPCVD of graphene on Cu and the mechanisms governing the Raman scattering process in the films are also discussed. The control over the grain size of synthesized graphene by adjusting the growth time (achieved in this work), provides useful insights for understanding the growth mechanism of LPCVD of graphene and for optimization of the growth process to further improve the quality of graphene. Finally, with analyses of all investigations we found that the quality and the large-area of monolayer graphene improved by increasing the growth time and it is very important consequence for all those who do research on graphene.

**Keywords.** Graphene; LPCVD; polycrystalline Cu; thin film.

1. Introduction

Graphene is a two-dimensional material composed of carbon atoms arranged in a hexagonal atomic structure.[1,2] Recent investigations have revealed that graphene has several unique properties including the quantum Hall effect at room temperature, ambipolar field effect, optical properties, high electron mobility and detection of single molecule adsorption events.[3,4] The exceptional properties of graphene also favour its implementation in a myriad of devices. The ability of fabricating large-area monolayer graphene is hindering its application. So far the graphene of the best electronic properties is synthesized by mechanical exfoliation from highly ordered pyrolytic graphite (HOPG), which is of tens of micrometres in size.[5] Graphene can also be produced by chemical reduction of graphite oxide, high temperature annealing of single-crystal SiC.[6] The most promising, inexpensive and readily accessible approach for deposition of reasonably high-quality graphene is chemical vapour deposition (CVD) onto transition metal substrates such Ni, Pd, Ru, Ir or Cu.[7–11] In particular, recent developments on uniform single layer deposition of graphene on copper foils over large areas have allowed access to high-quality material.[11] Copper has been shown to catalyse the growth of several carbon allotropes such as graphite,[12] diamond,[13] carbon nanotubes[14] and most

recently graphene.[11] In the first stage of graphene growth, the interaction between the carbon atoms and the Cu substrate becomes quite important. Experimental works have shown a preferred growth front for carbon species on the Cu (100) surface. These results were shown indirectly by scanning tunneling microscopy (STM) studies through an *in situ* CH$_4$ decomposition process on both single crystal and polycrystalline Cu. In this work, we investigated the effects of growth time on the quality of graphene synthesized by low-pressure chemical vapour deposition (LPCVD).

2. Experimental

Synthesis was carried out using a chemical vapour deposition set-up. A 1 cm × 1 cm Cu foil sample was introduced into the CVD chamber inside a quartz tube. The Cu foil was heated up to 1000°C and maintained for 30 min in the H$_2$ atmosphere without changing the flowing rate or pressure (total pressure 1.5 Torr) to activate grain growth and improve the crystallinity of Cu. Subsequently, the substrate was heated up to the desired temperature and the growth was started in a mixture of gases (99:0.01:0.99 for Ar:H$_2$:CH$_4$) introduced into the quartz tube. After reaction time, the furnace was cooled to room temperature, under Ar flow for carbon segregation and graphene formation. Four series of samples were prepared in this work at four different growth times (30, 60, 120 and 150 s).

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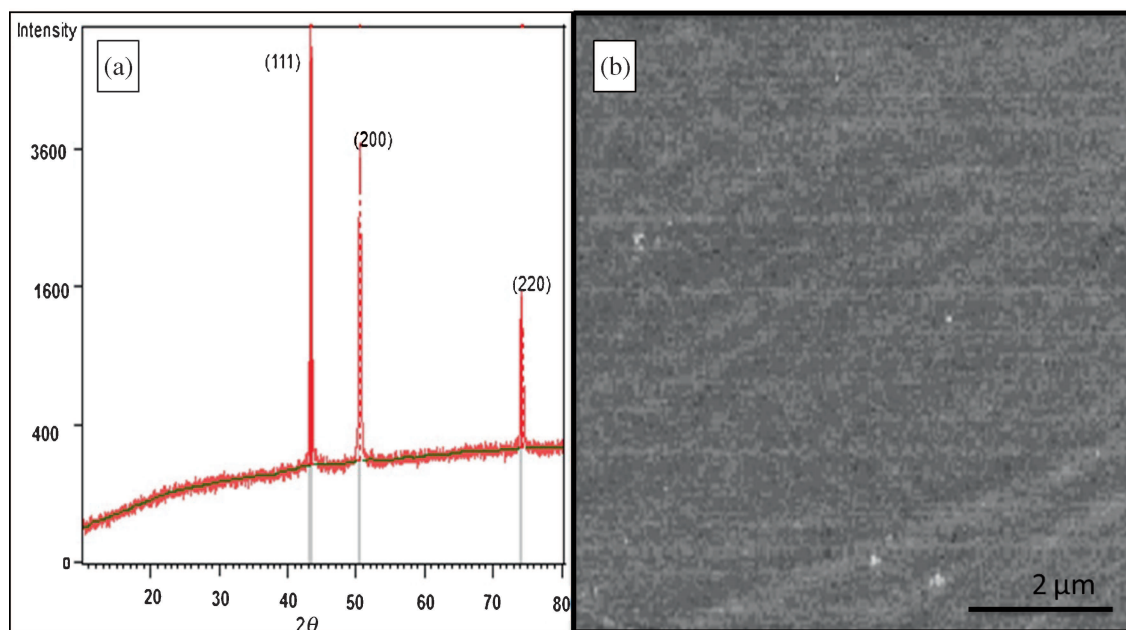
Figure 1. (**a**) XRD pattern and (**b**) SEM image of Cu foil.

This complete set of information allowed us to monitor the full growth process dependent on time. In a thermal CVD process, initial heating of the substrate is required to allow the formation of Cu grains on which graphene domains can nucleate and grow.

3. Results and discussion

Copper has been extensively used as growth substrate owing to its very low carbon solubility (less than 0.001 at%) that is thought to be responsible for the self-limiting precipitation growth and surface decomposition of carbon-containing molecules.[15]

The crystal structures of the Cu foil were evaluated by X-ray diffraction (XRD) (STOE SIADI MP Diffractometer) with Cu Kα radiation (1.5405 Å). The XRD pattern is given in figure 1a. Three diffraction peaks of Cu (111), Cu (200) and Cu (220) can be seen in figure 1a, signifying polycrystallinity of the Cu foil. Crystallographic orientation of the catalyst foil affects several core processes involved in graphene growth, including the carbon precursor dehydrogenation,[15] adsorption,[16] generation of hydrogen atoms[17] and surface diffusion.[18] SEM image of Cu foil before growth is shown in figure 1b. Further studies elaborating on the activation energy of copper-catalysed graphene will be presented elsewhere. Considering the very low energies for hydrocarbon adsorption and carbon diffusion on copper, the rate-limiting step for copper-catalysed graphene growth is deemed to include either CH_4 surface dehydrogenation or carbon lattice integration. Indeed, the estimated effective activation energy shows good agreement with the calculated dehydrogenation energy of CH_4 on copper and carbon lattice-integration estimates.[19,20] Figure 2 shows the
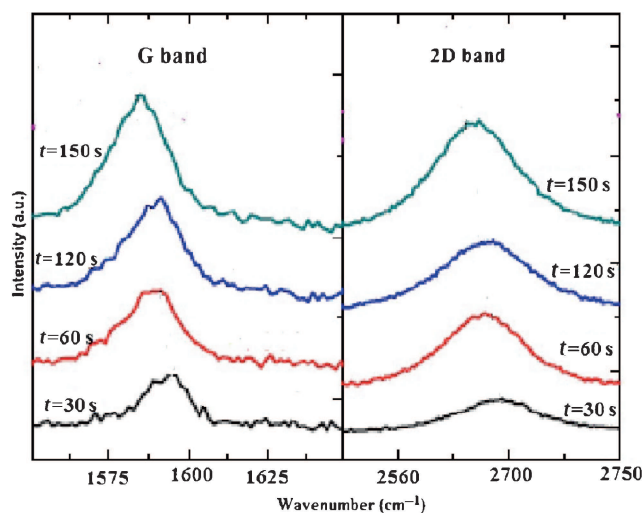
Figure 2. Raman spectra G and 2D peaks of the graphenes films grown under various growth times.

Raman spectra of the graphene grown under various growth times. One can observe two peaks, $\sim$1584 cm^{-1} (G peak) and $\sim$2699 cm^{-1} (2D peak). The G peak known to be associated with the doubly degenerate phonon mode at the Brillouin zone centre, indicating sp^2 carbon networks in the sample. The 2D band is the second order of zone-boundary phonons originates from a second-order Raman process and it is widely used in determining the thickness of graphene. The Raman fingerprint for single-layer graphene, is related directly to the position and 2D-peak width. As the Raman spectra show, the G and 2D peaks shift to low wavenumbers by increasing the growth time, which is due to the strain

effect caused by the substrate. Also this reduction corresponds to the double resonance mechanism and the dispersion curves for electrons and phonons in graphene and graphene-like materials.[21,22] In addition, we can see from Raman spectra that the G and 2D bands intensity increase with growth time due to the influence of a conductive substrate on the electron subsystem in the graphene film. The elimination of the interaction with substrate leads to increase of number of photo-exited electrons taking part.[23,24] We find that the I_G/I_{2D} measurements do not increase with growth time. The values of I_G/I_{2D} are always lower than 0.5 (see table 1), which indicates that all samples are single-layer graphene. It means that the increase in growth time cannot cause multilayer growth. In figure 2, a systematic peak shift towards low wave number is seen for the G band whereas this is not the case for the 2D band, there is an anomaly for 120 s. This could be for many reasons. The following we have discussed one of these. As mentioned, the 2D band is the second order of zone-boundary phonons originating from a second-order Raman process and it is widely used to determine the thickness of graphene. We know that a systematic peak must shift towards low wave number by increasing growth time but

if the thickness of graphene increased by increasing growth time[25,26] a systematic peak must shift towards high wave number by increasing growth time. We can assume that in first step graphene begins to form (after 30 s). In the second step graphene is formed in a separate area (after 60 s). In the third step this separated graphene would be connected to each other to create an integrated graphene that in some regions can increase the thickness of the graphene (after 120 s). Finally, by increasing time, an integrated graphene formed and the multilayers graphene return to monolayer graphene (after 150 s).

Figure 3 shows SEM images of the grown graphene on Cu foils for different growth times. The graphene domains (darker islands) show irregular shapes. The graphene domains grow laterally much like islands grow of epitaxial films. Nucleation of graphene domains with an average domain size of ∼2 μm is observed and at higher growth time the domain size increases. The mechanism of this formation pattern is not certain but it is likely to proceed along the stress-induced ripples on the graphene domain.[27] As the growth time increases, these domains continue to grow and coalesce into larger uniform ones, resulting in a fully covering monolayer of graphene on the Cu surface when the growth time is longer than 150 min. We can see the growth process by increasing the growth time.

The graphene nucleation depends on several core processes happening on the copper surface including the obvious (i) gas precursor adsorption, (ii) formation of active carbon species (dehydrogenation), (iii) diffusion of active carbon on the surface and (iv) critical size nuclei formation that competes with (v) desorption.[28] Desorbed species may include

Table 1. D and G peak ratios for different growth times.

Growth time (s)	I_G/I_{2D}
30	0.39
60	0.27
120	0.37
150	0.297
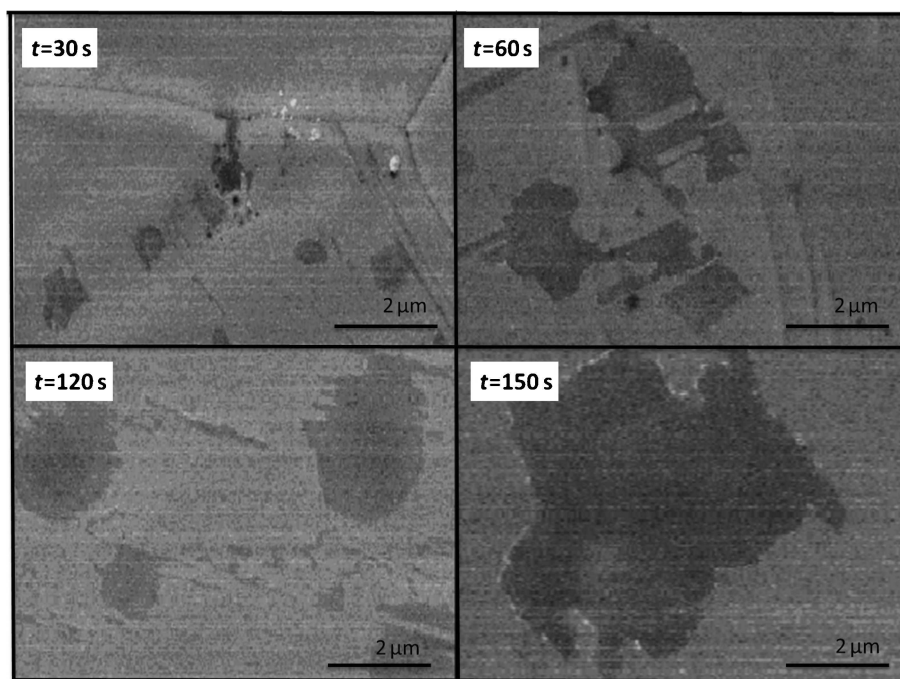
Figure 3. SEM images of graphene grown on Cu foils for different growth times.

different hydrocarbons and, consequently, substantially different desorption energies at low and atmospheric conditions. It is well known that depending on CVD parameters, the quality of as-produced graphene films can differ significantly in terms of graphene domain size and film coverage.[29]

4. Conclusion

In this paper, the synthesis of high-quality monolayer graphene with the controllable grain size on Cu foil by the LPCVD method has been investigated. Raman spectroscopy and SEM imaging of the grown graphene indicate that the quality and the large-area of monolayer graphene improved by increasing the growth time. Raman spectroscopy indicates a $\sim$1584 cm^{-1} G peak and a $\sim$2699 cm^{-1} 2D peak with a I_G/I_{2D} $\sim$0.2 ratio. We found that the I_G/I_{2D} measurements do not increase with increasing the growth time. The values of I_G/I_{2D} are always lower than 0.5, which indicates that all samples are single-layer graphene; it means that the increase in growth time cannot cause multilayer growth. The control over the grain size of synthesized graphene by adjusting the growth time (achieved in this work) provides useful insights for understanding the growth mechanism of LPCVD of graphene and for optimization of the growth process to further improve the quality of graphene. Finally, with investigation on all analyses as explained before, we found that the quality and the large-area of monolayer graphene improved by increasing the growth time and it is very important consequence for all those who do research on graphene.

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