Low Energy Electron Microscopy Study of Tiered 'Wedding-cake' Island Formation of Bi-layer Graphene by Using Chemical Vapor Deposition Technique

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Abstract: Mono-layer graphene shows zero-bandgap dispersion relation which differ from bi- and multi-layer graphene that open up its energy bandgap.Therefore, bi- and multi-layer grapheneare preferable in electronics and photonics applications. It is known that chemical vapor deposition (CVD) technique produces high-quality graphene, however the major challenge will be to fabricate a large area bi-layer graphene. Herein, we report a study of the mechanism of uniform tiered 'wedding-cake' graphene island growth by using copper oxide nanoparticle as a nucleation seed. The stacking order of the multi-layer graphene island is clearly depicted through Low Energy Electron Microscopy (LEEM). The growth can be controlled by changing the hydrogen flow rate which affects the etching of graphene edges. By implying the vapor trapping mechanism, the seeding can be done simultaneously with the bi-layer graphene growth by using a novel single-step CVD fabrication process.

Keywords: *Graphene, chemical vapor deposition, Cu_2O, nanoparticle, growth mechanism*

INTRODUCTION

Typically, FESEM and Raman spectroscopy (including Raman mapping) have been used to map the morphology and growth of graphene films. However, FESEM imaging only observed the topmost layer of graphene and cannot view the presence of adlayers or under-layer graphene while, micro-Raman mapping is so time consuming and it has major drawback from a low lateral resolution (micron scale). Most of previous study had reported that the graphene grown by conventional CVD on copper are suggested to be surface mediated and self-limiting [1]. It means that once the mono-layer graphene is completed, the process does not propagate further, since the catalytic Cu surface (topochemical site) were blocked. Recently, a study of graphene growth using isotopic labeling aided with Raman mapping has shown that the mono-layer graphenemay consists of small regions with bi- or multi-layers growth stacked like an inverted 'wedding-cake' configuration [2]. However, the mechanism of the formation of a multi-layer region is not well understood yet or even controversial. On the other hand, Low Energy Electron Microscopy (LEEM) can be utilized to study the adlayers between graphene layer and metal substrate (as well as number of graphene layers) with a higher lateral resolution (sub-micron scale) [3].

MATERIALS AND METHODS

Graphene was fabricated on Cu foils (25 lm thick, 99.99% purity from Alfa Aesar) in a Hot-filament Thermal Chemical Vapor Deposition (HFTCVD) system. An alumina tube with one closed end was wound with a Tungsten; (W) filament (99.95% purity, 0.5 mm diameter from Kurt J. Lesker) with the substrate rolled and fitted inside it. This will give the vapor trapping condition that promotes the growth of graphene nucleated by copper oxide nanoparticle. The base pressure of the system was 5.0 x 10^{-5} mbar. Prior to the fabrication process, the W hot-filament was used to heat the Cu foils to the fabrication temperature of ~1000 °C. The filament temperature was measured at ~1750 °C by using an external optical pyrometer. The growth of the graphene films was carried out in a 10 sccm of CH_4 while varying the H_2 at 10, 25 and 50 sccm for 30 min. Subsequently, the sample was cooled to 200°C (~2 °C/s) by reducing the external power supply. Finally, the sample were convectively cooled by adding 100 sccm N_2 gases until achieved a room temperature.

RESULTS AND DISCUSSION

The number of bottom stated at the upper right edge of Fig. 1. corresponds to the number of graphene layer(s); for example, 1 bottom means mono-layer graphene and so on. Interestingly, the number of bi-layer and tri-layer graphene covers about ~60% and ~25%, respectively of the 7.5 µm FOV area. This further supported the idea of the first graphene layer is formed by surface adsorption around the nucleation seed and followed up by the consecutive layers on top of the first graphene layer.

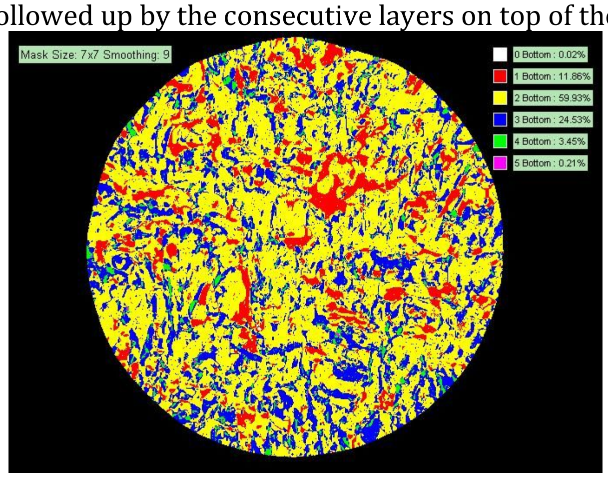

Fig. 1. The color coding of 10 sccm H_2 flow rate sample in 7.5 µm FOV. The dominant yellow color resembles a bi-layer graphene with the coverage up to ~60 % of total area.

CONCLUSIONS

In summary, the surface morphology of mono- and bi-layer graphene island on a micron scale have been observed. Good correlation has been found for Raman, FESEM and LEEM measurement with the determination for number of graphene layers. The growth of uniform tiered 'wedding-cake' graphene island has been shown by the I-V LEEM analysis which signifies the role of Cu_2O nanoparticle seed for the growth of subsequent graphene layer. Therefore, with the optimization in the growth duration as well as H_2 flow rate, it is believed that the growth of predetermined number of graphene layer coverage is achievable.

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