

Graphene Underlayer growth by chemical vapour deposition

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Abstract

Chemical vapor deposition (CVD) growth of graphene on copper foil has been regarded as more viable for obtaining monolayer graphene, mainly by a surface-controlled process [1, 2]. However, synthesizing uniform, defect-free multilayers has proved to be more difficult, and the growth mechanisms remain poorly understood. It has been observed that in the early stages of growth by CVD at atmospheric pressure, graphene on Cu foil forms as isolated “islands” which eventually coalesce to yield full, continuous monolayers. Occasionally these isolated islands are observed to have a second graphene layer which appears to nucleate at some sort of defect on the catalytic metal surface. It has often been assumed in the literature that the smaller islands are on top of the larger monolayer, and that they will grow and eventually form a second layer [3, 4–7]. However, Tontegode and co-workers [8, 9] had previously used Auger electron spectroscopy to suggest that graphene thick films grow in such a manner that the second and subsequent layers of graphene grow next to the substrate during segregation from Re-C solid solution and when carbon is deposited on Ir(111) in an inverted wedding cake fashion [10]. Recently, several groups have elucidated this underlayer growth mechanism of additional layers [11, 10, 12, 13]. However, the methods used in these studies were expensive and complex. For example, Nie *et al.*[11] proved that second-layer islands nucleate between the existing layer and the substrate. This they did by monitoring misalignment during growth on Ir(111) using a low energy electron diffraction (LEED) ultra-high vacuum chamber, angle-resolved photo-emission spectroscopy (ARPES) and low-energy electron microscopy (LEEM).

Here we present a simple and very convincing approach to visualizing that subsequent layers of graphene grow between the existing monolayer graphene and the copper catalyst in chemical vapor deposition (CVD). Graphene samples were grown by CVD and then transferred onto glass substrates by the *bubbling method* in two ways, either direct-transfer (DT) to yield poly (methyl methacrylate) (PMMA)/graphene/glass or (2) inverted transfer (IT) to yield graphene/PMMA/glass. Field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM) were used to reveal surface features for both the DT and IT samples. The results from Raman spectroscopy, FE-SEM and AFM topographic analyses of the surfaces revealed the underlayer growth of subsequent layers. The subsequent layers in the IT samples are visualized as 3D structures, where the smaller graphene layers lie above the larger layers stacked in a concentric manner (see figures 1, 2 and 3 below). The results support the formation of the so-called “inverted wedding cake” stacking in multilayer graphene growth.

References

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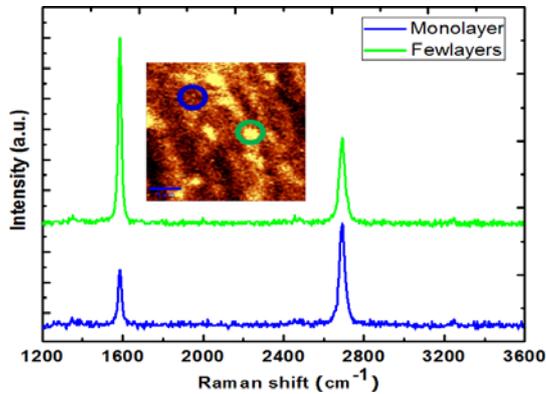


Fig. 3. Raman spectroscopy of the CVD graphene on glass substrate at two different spots indicated in the inset. (Inset) Raman map of the G-mode intensity showing a monolayer (blue circle) and few-layer graphene (green circle). Scale bar is 4 μm in the inset.

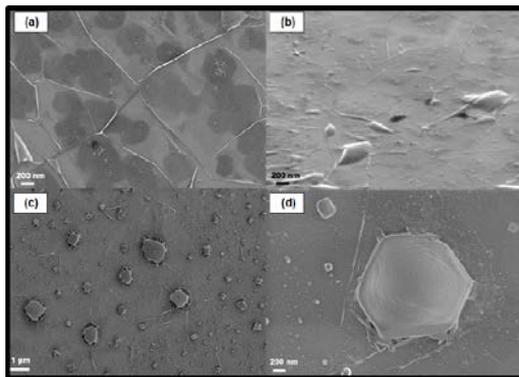


Fig.1. FE-SEM images of: (a) direct-transfer (DT) graphene; (b) DT graphene on glass substrate taken at 70° with respect to the sample plane; (c) inverse-transfer (IT) graphene; and (d) high magnification of one of the islands in (c).

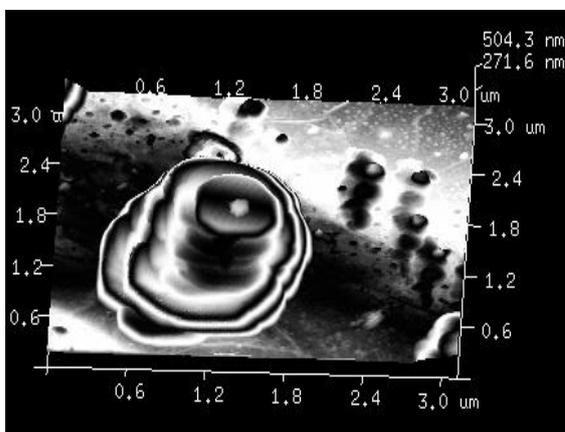


Fig. 2. 3D AFM image of one of the islands of the IT graphene sample.