Mechanism of Growth of Graphene Grains on Copper during Low Pressure Chemical Vapor Deposition

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Graphene grown by chemical vapor deposition (CVD) on Cu is very promising for future graphene applications, as it meets the two requirements for batch production, namely: 1) large size and self limitation to a single-layer of graphene and 2) easy transfer onto arbitrary substrates [1-4]. New insights for controlling CVD processes, e.g. leading to dendritic growth of graphene flakes [5], or allowing for controlling the size of hexagonal islands [6], were recently demonstrated.

Although extensive studies have been conducted on the CVD of graphene on Cu, some of the processes involved during growth remain to be elucidated. Two important remaining issues are: (1) the parasitic formation of multilayer regions [7-8], and (2) the occurrence of both hexagonal-shaped and dendritic flakes

In this work, we report on a systematic study of the CVD growth mechanism of graphene on Cu under low gas pressure (1 mbar total pressure of a $Ar/H_2/CH_4$ mixture). Before graphene islands merge into a continuous layer, various shapes can be found for graphene flakes, ranging from hexagonal ones to flower-like dendritic ones, depending on the growth conditions (inset of Figure 1). Besides flower-shaped islands coexist with smaller ones, hexagonally-shaped (Figure 2a). We found no indication for two preferential crystallographic orientations which would each correspond to one type (larger or smaller) of islands. Neither do we find any correlation between the island size and the distance to the nearest neighbor island. We analyzed the roughness of the edges of graphene islands with different sizes by measuring the perimeter of the islands against their area (Figure 1). A plot of hexagonal shape is shown in Figure 1 as a reference. One can see that the smallest islands have almost hexagonal shape, and the larger the islands, the more they diverge from the hexagonal shape, which reveals the that graphene growth begins with the nucleation of hexagonal islands latter evolving into dendritic lobe-shaped islands, which is illustrated by our model in Figure 3a, as well as the model proposed in other works [9,10].

Interestingly, the larger lobe-shaped islands are very likely comprising in their center a two- (or even more) layer region (Figure 2) as already observed in previous reports [8,11,12]. The shape and size of the second layer centered in the large islands are strikingly similar to that of smaller islands in between larger islands. This bimodality in island shapes and sizes can be explained by the fact that the larger islands are the result of surface growth from an adatom carbon gas at high temperature, and that the smaller islands develop upon cooling down after growth, *via* segregation of carbon atoms stored at Cu defects extending out of the surface plane (Figure 3b). Moreover, a recent study suggests that the central layer is underneath the first larger layer [13]. Actually, it is known that multilayer and inhomogeneous graphene results from enhanced carbon segregation, which is favored at defects such as screw dislocations or grain boundaries [14]. In the light of all above, there are two routes to suppress these carbon inhomogeneities: either by suppressing the surface defects *via* graphene deposition on top of high quality metallic surfaces (single crystal metal, epitaxial thin films), or by keeping standard low-cost copper foil but depleting nucleation at defects upon cooling.

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Figures

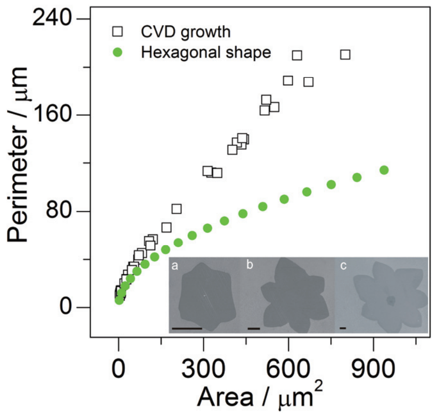

Figure 1: Plot of the perimeter of graphene islands as a function of their area. Squares represent for graphene islands prepared by CVD growth. The green dots correspond to perfect hexagonal islands. Inset: a, b, c, are SEM images of graphene islands found on one single Cu foil obtained via CVD growth (2 sccm CH_4, 20 min, 1 mbar), which presents three different stages of the growth: start of the hexagonal nucleation, diffusive lobe-shape flower, flower with a "seed" in the center. Scale bars for the inset are 3 μm.

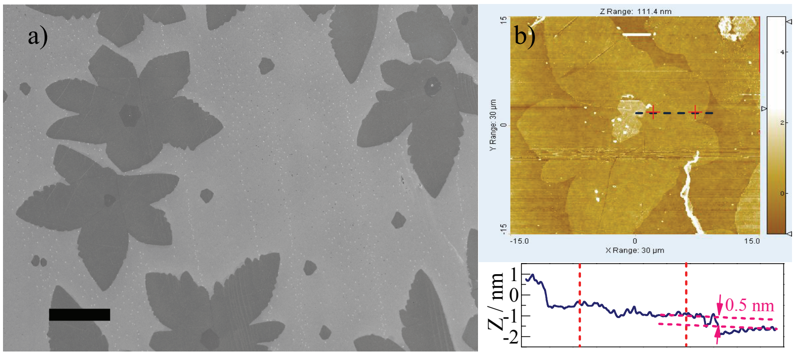

Figure 2: a) Scanning electron micrograph images of graphene flakes grown on Cu under the condition of 1000 ^{o}C, 2 sccm CH_4, 1 mbar, for 20 minutes. Scale bar is 10 μm; b) AFM image of one of the flowers shown in a. A profile of the cross section of this flower is given below.

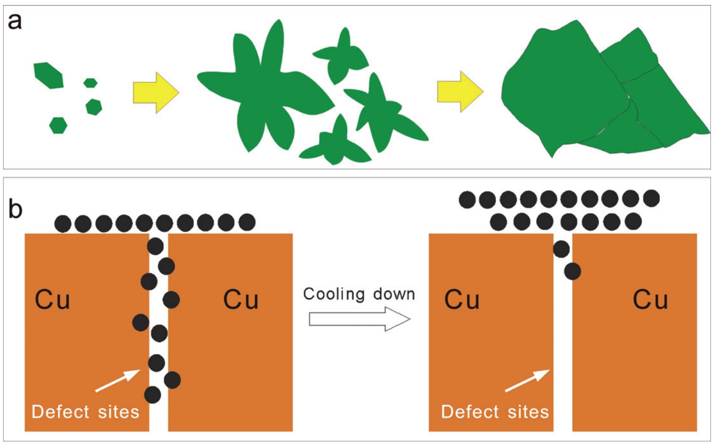

Figure 3: a) A simple model showing the formation of graphene islands from the beginning of their nucleation to the final continuous layer; b) Schematic of the flower centers formed at the defect sites during cooling down.