Carbon 105 (2016) 205–213

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Large-area layer-by-layer controlled and fully bernal stacked synthesis of graphene

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ARTICLE INFO

Article history:
Received 29 February 2016
Received in revised form
9 April 2016
Accepted 17 April 2016
Available online 19 April 2016

ABSTRACT

As semi-metallic monolayer graphene is limited in broadening the applications, synthesis of multi-layer graphene has recently attracted intense interests to enable functional optoelectronic devices. However, controlling the growth of multiple graphene layers is still quite challenging since the process critically depends on self-limited growth and interaction between graphene nucleation and Cu substrate. Herein, we report a layer-by-layer growth of large area graphene with precisely controlled number of layers and stacking order using a novel two-step two-heating zone low pressure chemical vapor deposition. The layered epi-growth on initially grown monolayer graphene limits the effect of underlying metal catalyst, thus leading to fully Bernal stacked bi-layer graphene as indicated by Raman spectra and electron diffraction patterns. Atomic resolution images with optical and electrical measurements verify the successful demonstration of the layer-by-layer synthesis by controlling growth time as a key parameter with other variables at their optimal process conditions.

1. Introduction

Graphene, a sp^2-bonded two-dimensional (2D) carbon material with honeycomb lattice structure, has gained tremendous interests due to its unique and superior characteristics compared to conventional three dimensional (3D) materials [1,2]. Even though the graphene is just one atom thick layer, it provides an excellent conductivity, ultrahigh carrier mobility [3,4], and outstanding mechanical and optical properties [5,6]. Therefore, many researchers have regarded graphene as a candidate for the next generation materials in various applications [7,8]. To produce a graphene layer, various methods have been investigated such as mechanical exfoliation from graphite, epitaxial growth on the silicon carbide, reduction of graphene oxide, and chemical vapor deposition (CVD) [1,9–11]. Among these processes, recent approach with the enhanced CVD method is able to produce a large area and high quality monolayer graphene with high yield, which is suitable for industrial applications [12]. Due to the self-limited growth in the CVD process, graphene tends to grow predominantly as a single layer, not as multi-layers on the Cu substrate [13]. However, single layer graphene has semi-metallic properties and zero-energy band gap structure, limiting its wide electrical and optical applications [13–15]. On the contrary, this zero energy gap structure of graphene has been shown to change in the Bernal-stacked bi-layer graphene and rhombohedral-stacked tri-layer graphene [16,17]. Also, multiple layers of stacked graphene effectively tune the optical and electrical properties of graphene such as transmittance and sheet resistance [12,18]. From the above reasons, the synthesis of multi-layer graphene with well-defined stacking order allows complementary strength to the properties of monolayer graphene, thus opening up further optoelectronic applications. Therefore, numerous studies for controlling the number of layers of graphene have been conducted [19–22]. Recently, researchers have demonstrated layer-stacked growth of graphene with suggested mechanisms such as wedding cake [20,23–25], inverted wedding cake [26–29], and graphitic seed edge-growth model [30,31]. Each of these studies has presented completely different result depending on the experimental parameters such as growth temperature, chamber pressure, and gas flow ratio of CH_4 and H_2 [32]. Also, those growth models are critically associated with the origin of haphazard seed layer formation [23,33], *i.e.*, the seed initially formed as a mono-, bi-, or tri-layer resulting in a mono-, bi-, or tri-layer graphene, respectively. Consequently, it is still quite a challenge to control the layered growth and their relative stack orientation for multi-layer graphene.

Here, we report completely layer-controlled growth with well-

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http://dx.doi.org/10.1016/j.carbon.2016.04.039
0008-6223/

defined stacking order for large area graphene ranging from a mono- to multi-layers by a novel two-step growth using two-heating zone low pressure chemical vapor deposition (LPCVD) as shown in Fig. 1a For the schematic process developed in our experiments, we also propose a new multi-layer growth model of layer-by-layer (LBL) growth controlled only through the growth time at the optimized growth conditions such as temperature, chamber pressure, and CH_4/H_2 gas flow ratio. This layer-by-layer process is originated from the van der Waals epi-growth of 2D layered materials [34]. The method of multi-layer synthesis using the two-heating zone consists of two-step procedures.

The first one is the growth step for a conventional monolayer graphene and the following step is a van der Waals epi-growth of graphene on the already grown monolayer. In the van der Waals epi-growth, atoms within an unit layer are connected by strong covalent bond while adjacent layers are held only with weak van der Waals force. This leads to the relaxation of a lattice-matching condition forming an energetically stable structure such as Bernal stacking in the case of graphene [35,36]. Therefore, the presence of Bernal stacked graphene layers can indicate the characteristic of van der Waals epi-growth as verified with selected area electron diffraction (SAED).

After the growth of monolayer graphene, temperatures of zone 1 and zone 2 are tuned to low and high to set the optimized condition for layer-by-layer growth, respectively as shown schematically in Fig. 1b. Activated carbon species CH_n ($n < 4$) formed from the high temperature heating zone 2 are observed to nucleate on the already grown monolayer graphene located in the lower temperature heating zone 1. In other words, the firstly grown monolayer acts as a substrate enabling the van der Waals epi-growth of

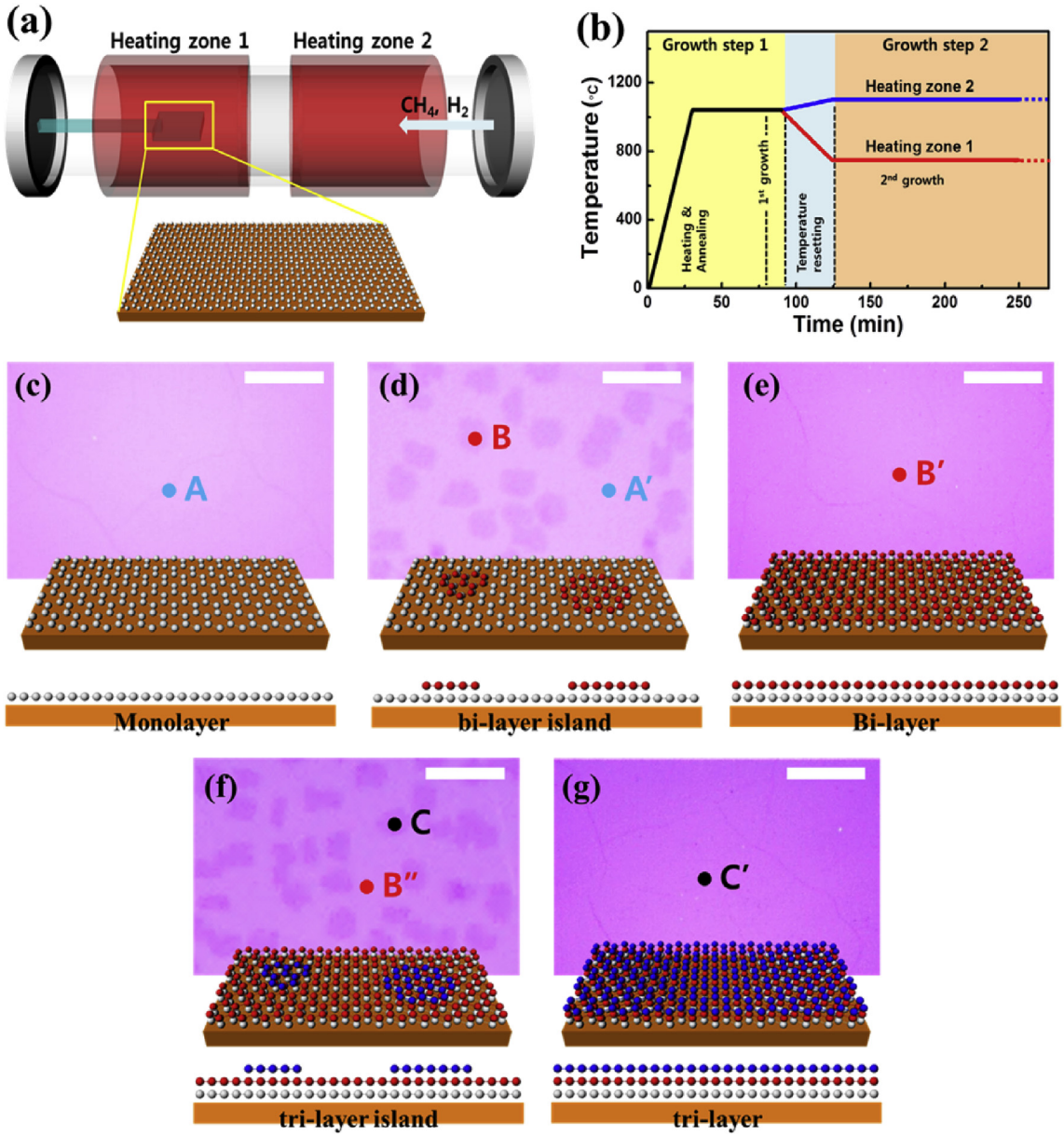

Fig. 1. Layer-by-layer growth process for multi-layer graphene. (a) Schematic illustration of two heating zone LPCVD for the graphene growth. (b) Diagram of two step process as a function of growth time. Optical images of graphenes transferred onto the SiO_2 (280 nm)/Si after the growth for (c) 10 min only with the growth step 1, and (d–g) for 20 min, 60 min, 80 min and 120 min with the growth step 2 following the growth step 1. Schematic figures located below the optical images (c–g) are proposed to illustrate the mechanism for the layer-by-layer multi-layer graphene growth. All scale bars are 5 μm. (A color version of this figure can be viewed online.)