

Control of the nucleation and quality of graphene grown by low-pressure chemical vapor deposition with acetylene



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ABSTRACT

Although many studies have reported the chemical vapor deposition (CVD) growth of large-area monolayer graphene from methane, synthesis of graphene using acetylene as the source gas has not been fully explored. In this study, the low-pressure CVD (LPCVD) growth of graphene from acetylene was systematically investigated. We succeeded in regulating the domain size, defects density, layer number and the sheet resistance of graphene by changing the acetylene flow rates. Scanning electron microscopy and Raman spectroscopy were employed to confirm the layer number, uniformity and quality of the graphene films. It is found that a low flow rate of acetylene (0.28 sccm) is required to form high-quality monolayer graphene in our system. On the other hand, the high acetylene flow rate (7 sccm) will induce the growth of the bilayer graphene domains with high defects density. On the basis of selected area electron diffraction (SAED) pattern, the as-grown monolayer graphene domains were analyzed to be polycrystal. We also discussed the relation between the sheet resistance and defects density in graphene. Our results provide great insights into the understanding of the CVD growth of monolayer and bilayer graphene from acetylene.

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1. Introduction

Graphene, a single atomic layer composed of carbon hexagonal network, has attracted tremendous attention due to its unusually superior characteristics in mechanical strength, electrical carrier mobility and thermal conductivity [1–4]. Utilizing these features, graphene has shown great potential for electronic and Micro/Nano Electro Mechanical Systems (MEMS/NEMS) applications [5–8]. Considering its application of electronic devices, large-area monolayer and bilayer graphene films are desirable. Chemical vapor deposition (CVD) of graphene on the transition metal catalysts has become the most promising method, which can form large-area and high quality graphene sheets [9,10]. Metal foils such as Cu, Ni, Pt, etc., have been used to grow graphene in the CVD process [11,12]. Growth of graphene on Cu has many advantages such as low cost and ease of transfer [13]. The growth mechanism has been proved to be a surface adsorption process due to the low solubility of carbon species in Cu, which make it easy to control the layer number [14].

Methane is the most commonly used precursor gas for the growth of graphene in low-pressure CVD (LPCVD) and atmospheric-pressure CVD (APCVD) process [15,16]. The dissociation of methane is higher than that of ethylene and acetylene, so it is easy to control the growth rate and layer number [17,18]. In addition, the adsorption energy of methane on Cu is very low, which can efficiently reduce the carbon species supply [19]. To date, single-crystal graphene domains up to 10 mm can be synthesized from methane by LPCVD [20]. However, in this process very low partial pressure of methane is required to lower the nucleation density. The decrease in carbon species supply also leads to the low graphene growth rate. As a result, several hours of growth duration is required to grow millimeter-scale graphene domains, which consumes large amounts of energy and precursor gas. On the other hand, the growth of high-quality bilayer graphene depends on the lateral diffusion of carbon species underneath the monolayer graphene islands, so it is very difficult to grow the second layer without bare Cu [21]. Thus, the hydrocarbon source with high reactivity such as acetylene should be considered to shorten the growth time. Compared to methane, the surface adsorption energy of acetylene is much higher, which should promote the graphene growth [22]. In addition, it has been demonstrated that acetylene can efficiently heal the divacancy defects in graphene [23]. However, there are limited studies investigating the CVD growth of graphene from acetylene.

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Qi et al. investigated the effect of hydrogen in the APCVD process using acetylene as the precursor and found that the hydrogen serves as an activator of the surface bound carbon and exhibits etching effect on the multilayer graphene domains [24]. Mueller et al. reported the nucleation process of graphene in the acetylene-based process using ultrahigh vacuum CVD (UHVCVD) and succeeded in the growth of monolayer graphene for the first time [22]. However, due to the low partial pressure of acetylene gas, a long growth time up to 1 hour is required. In this study, for the first time, we succeeded in the rapid LPCVD growth of monolayer and bilayer graphene sheets using acetylene as the precursor gas. By using pre-oxidized Cu pockets, LPCVD growth of monolayer graphene is realized. Raman spectroscopy measurement results show that the flow rates of acetylene are a key factor to control the layer number and the quality of graphene films. The Graphene domains characterized by selected area electron diffraction (SAED) measurements showed polycrystallinity, which is different from that of graphene grown from methane.

2. Experimental

2.1. LPCVD growth of graphene

Synthesis of graphene films was performed by using the CVD (ULVAC QH-P610CP) apparatus with a quartz tube furnace. 50- μm -thick Cu foils (CU-113263, 99.9% in purity, Nilaco) served as the catalyst. Before CVD process, the Cu foils were dipped into a 5% aqueous solution of nitric acid for 60 s, and rinsed by deionized water. Subsequently, The Cu foils were cleaned by an ultrasonic cleaner for 10 min in acetone and ethanol, respectively, and folded into pockets with the remaining three sides carefully crimped with a pincer as reported by Li et al. [25]. In order to suppress the nucleation of carbon species, before the CVD growth, the Cu pockets were heated using the hotplate in air for 90 min at 250 °C to form a catalytic inactive Cu_2O layer [26]. Pure H_2 (99.9999 vol.%) and acetylene (C_2H_2) (99.999 vol.%) gas were used as the reaction gas. In the CVD process, the pre-oxidized Cu pockets were heated to 1035 °C for 20 min in vacuum, followed by annealing for 40 min under the constant flow rate of 14 sccm H_2 to increase the Cu grain size. During the CVD growth, the flow rates of hydrogen is increased to 80 sccm, and acetylene at different flow rates was imported into the quartz tube to grow graphene with a total pressure of 0.8 torr. After CVD growth, the samples were rapidly cooled down to 600 °C

at a rate of 100 °C/min under the same H_2 atmosphere but without acetylene supply. Then the samples were cooled down to room temperature in 30 min.

2.2. Transfer process of graphene

Graphene films were transferred from the Cu foils to 300 nm SiO_2/Si substrates based on the reported wet transfer process [27]. Polymethylmethacrylate (PMMA) resist (PMMA, Microchem 950 K A2, 2% in anisole) was spin-coated onto the graphene surface at 3000 rpm for 20 s, followed by baking at 120 °C for 2 min. Graphene layers and impurities on the backside was etched by reactive ion etching (RIE) equipment (Anelva L-201D) with oxygen plasma at 50 W for 5 s. 1 M FeCl_3 solution was used to dissolve the Cu foils in 3 h. The samples were then immersed in 10% HCl solution for 1 h to remove any residuals. The PMMA/graphene film was scooped out from the solution by the SiO_2/Si substrate and dried by heating it at 80 °C for 5 min. The PMMA layer was removed by acetone followed by cleaning with ethanol and deionized water.

2.3. Characterization of as-grown and transferred graphene

Field emission scanning electron microscopy (FE-SEM; Hitachi SU-70) was used to observe the nucleation of graphene domains and perform the electron backscatter diffraction (EBSD) analysis of Cu foils. X-ray diffraction (XRD) measurement was performed using an X-ray diffractometer (SHIMAZU XRD-7000) to evaluate the crystallinity of the Cu foils. Optical microscopy (KEYENCE VK-X100) was employed to characterize the transferred graphene films on SiO_2/Si substrates. Raman spectroscopy and mapping was performed to characterize the carbon bonding states by micro-Raman spectroscopy apparatus (Jasco NRS-5100) with an excitation wavelength of 532 nm. Sheet resistance of graphene films was measured using four-point probe measurement system (Kyowariken K-705RS). SAED (selected area electron diffraction) measurement was employed to evaluate the crystalline structure by the Transmission electron microscopy (TEM, 200 KV, TOPCON EM-002B).

3. Results and discussion

First, we investigated the effect of pre-oxidation process on the nucleation density of graphene in our LPCVD process. Graphene was grown on the inner surface of the Cu pockets at an acetylene

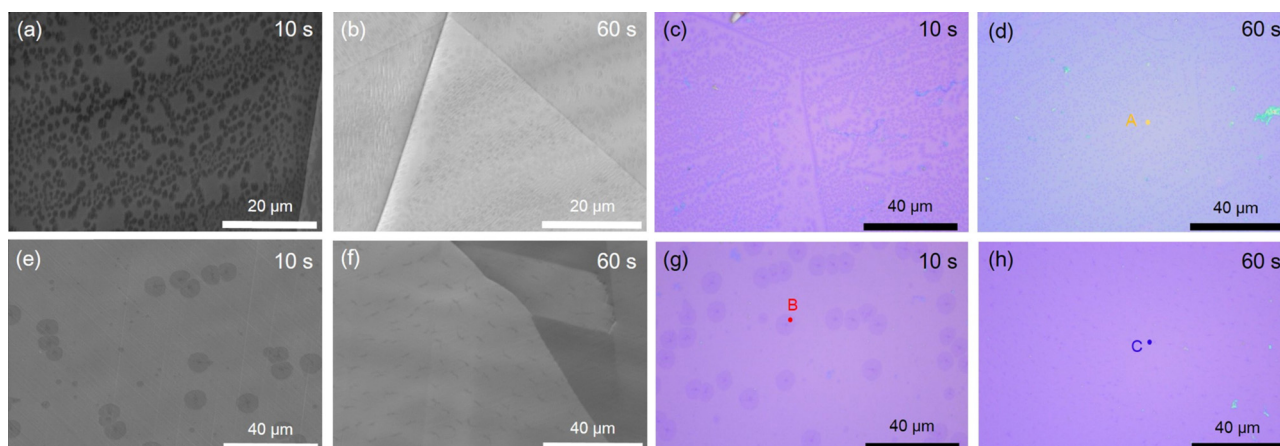


Fig. 1. SEM images and optical images of graphene grown on the inner surface of unoxidized Cu pockets and pre-oxidized Cu pockets at an acetylene flow rate of 7 sccm. (a), (b) SEM images of the inner surface of Cu pockets after the CVD growth for 10 s and 60 s, respectively. (c), (d) Optical image of graphene transferred onto 300 nm SiO_2/Si substrates, which was deposited on the inner surface of Cu pockets for 10 s and 60 s, respectively. (e), (f) SEM images of the inner surface of pre-oxidized Cu pockets after the CVD growth for 10 s and 60 s, respectively. (g), (h) Optical image of graphene transferred onto 300 nm SiO_2/Si substrates, which was deposited on the inner surface of pre-oxidized Cu pockets for 10 s and 60 s, respectively.

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