

Silicon oxide particles size evolution during CVD graphene growth on Cu substrates

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Abstract. Chemical vapor deposition (CVD) on metal substrates is presently the remarkably route for the synthesis of high-quality continuous graphene films at a large scale. Whereas, during the thermal processing procedure in the quartz tube, the formation of silicon oxide particles would degrade the performance of graphene. To better understand the origin of these particles, a series of CVD graphene growth experiments were conducted on the Cu substrates. In this paper, we investigated the main component and morphology of the particles by X-Ray photoelectron spectroscopy (XPS), energy dispersive spectrometry (EDS) measurement in scanning electron microscopy (SEM) and revealed that the silicon oxide particles gradually increased in diameter across the graphene films on the Cu surface, which was found to be correlated with the working time of the quartz products. Raman spectroscopy was also applied to prove the drawback consequence of the contamination on the quality of the CVD graphene film. To mitigate this issue, we further propose a modification of the CVD system that a coaxial alumina or BN tube inside the quartz tube to screen the contaminants bringing about improved graphene growth.

Keywords: CVD; graphene; Silicon oxide.

1. Introduction

Chemical vapor deposition (CVD) is a brilliant technique as the preparation of graphene films on the Cu substrate after this approach was first proposed more than a decade ago [1]. The CVD reactor can usually be divided into two types, cold-wall and hot-wall, the latter being the most widespread due to its uniform temperature distribution, easy gas flow control and simple equipment [2-3]. Fused quartz is frequently used as the reaction chamber and supporter of metal substrate in hot-wall CVD system, silicon oxide particles become mobile when the temperature above 800 °C [4]. Therefore, silicon oxide impurities may appear as particle contaminations during high temperature processing either at low or atmospheric pressure [5-6]. In the subsequent experimental work, CVD refers specifically to atmospheric pressure hot-wall CVD.

To date, a great deal of work has been devoted to optimizing the CVD manufacturing conditions to improve the quality of the CVD graphene film growth [7-11]. Nonetheless, the CVD graphene film's mechanical and electrical properties are still far from the theoretical value. Consequently, the understanding of the CVD graphene defects, such as grain boundaries (GBs), wrinkles, point defects and impurities, etc. are the crucial factors for high-quality CVD graphene growth [12-15]. Hence, numerous researches on CVD graphene growth had focused on reducing graphene defects, although significant development in recent years, the growth of high-quality CVD graphene film and its applications are still impeded by contamination impurities [8]. Impurities on the CVD graphene have two possible sources, one is from the metal substrate, the other is from the CVD system component [5, 8, 13, 16].

Granular impurities normally existing on the films of CVD growth graphene, and even though the transferred graphene film is also present, could be easily detected as “white particles” by scanning electronic microscopy (SEM), moreover, energy dispersive X-ray spectroscopy (EDS) results manifest that the particles contain silicon element [4, 8, 12, 16-17]. These particles could serve as nucleation centers for bilayer graphene growth and the continuous growth of the adlayer

beneath the top layer graphene from the free region between the particles and graphene like the inverted wedding cake [18]. In addition, silicon oxide particles also have a momentous impact on the capability of graphene-based devices as these contaminants are ubiquitous [7]. Consequently, silicon oxide particles have a significant influence on the graphene film growth mechanism and properties [8]. Currently, several works have reported the related findings, while a systematic analysis of the detail of silicon oxide particles scale variation during fabrication remains to be unraveled.

In the present work, a series of experiments were conducted to explore the silicon oxide particles size evolution during atmospheric pressure CVD graphene growth in associated with the system process times. The element composition and microstructure variation of the particles were analyzed by the results of XPS, EDS and SEM. In addition, the quality of CVD graphene films with these particles was investigated by Raman spectroscopy line scanning.

2. Experimental

2.1 Sample preparation

Cu foil (50 μm thick, 99.9 %, Lingbao Zhaohui Copper Co. Ltd) was first cleaned with acetone, isopropyl alcohol, and deionized (DI) water. Then, the foils were dried by Nitrogen gas stream. After the Cu foil cleaning procedure, the Cu foils were placed on the quartz plate full spread, and put into 10 cm quartz tube furnace (Anhui BEQ furnace, BTF 1200C). The CVD system was evacuated for 20 min by dry pump (Edward XDS 35i). By introducing an Argon and Hydrogen mixture gas to recover atmospheric pressure. This process repeated for 3 times to minimize the trapped air in the CVD chamber. The sample was heated up to 1030 $^{\circ}\text{C}$ within 60 min with 200 standard cubic centimeters per minute (sccm) Argon flow and 5 sccm Hydrogen flow. The purity of all gases used in our work is 5N (99.999 %). After reaching 1030 $^{\circ}\text{C}$, the Cu foil annealed under same gas atmosphere for 120 min. After Cu foil thermal treatment, the furnace was maintained at the same temperature for graphene growth with 600 sccm Argon flow and 8 sccm Hydrogen flow, 5 sccm diluted methane (1% CH_4 in Argon) was introduced to the quartz tube for 60 min growth. Finally, the CVD furnace was quickly slid away to rapidly cool down the Cu substrate by fan, until the sample cool to room temperature, the gas flow was shut down.

After graphene growth, the film was transferred onto 285 nm SiO_2/Si substrate using spin-coating PMMA(poly-methyl methacrylate) to the Cu foil with graphene film and heated at 90 $^{\circ}\text{C}$ for 5 min. Then, The 1 mol/L FeCl_3 with 5% (vol%) HCl solution was used to etch Cu foil. The PMMA/graphene sample was rinsed by deionized water twice and transferred onto SiO_2/Si substrate. After air dry under room temperature, the PMMA layer was dissolved with acetone at 45 $^{\circ}\text{C}$ for 20 min. Finally, the graphene film was rinsed with ethanol and isopropyl alcohol respectively.

2.2 Samples characterization

Nikon Eclipse LV100 ND was used to collect optical microscope (OM) images. Scanning electron micrograph (SEM) photographs and energy dispersive X-ray spectroscopy (EDS) were collected using a FEI Nova Nano 450 equipped with Ametek EDAX detector with 5 kV voltage. Raman spectra were collected by a Renishaw inVia Reflex with an excitation line of 532 nm (2.33 eV) with a 100x objective lens. X-Ray photoelectron spectroscopy (XPS) analysis was aquired using a Kratos (Shimadzu) Axis Supra with monochromatic $\text{Al K}\alpha$ radiation (1486.6 eV) with detection limits of about 0.2 % (atomic percentage).

3. Results and discussion

CVD graphene films were grown on the Cu foils after reducing atmosphere annealed in a hot-wall horizontal quartz reactor system at 1030 $^{\circ}\text{C}$. The surfaces of the as-received Cu foil and the

CVD graphene growth Cu substrate were characterized for elemental composition by XPS. As seen in Fig.1A, Cu, C, O, N, and Al were present on the as-received Cu foil surface. After the graphene growth treatment, the Si element 2p peak was detected, indicating the existence of Si element (Fig. 1B). The possible sources of the Si impurity could be from the quartz tube, quartz plate, or the intrinsic impurity in the bulk Cu segregation to the surface [19].

After obtaining the CVD graphene films, they were transferred onto 285 nm SiO₂/ Si and microgrid carbon film coated Cu mesh for OM and SEM analysis, respectively. As depicted in Fig. 2A, the silicon oxide particles were retained after the transfer process. Numerous white particles were observed as shown in Fig. 2B. From the above results, it can demonstrate that the particles are not only on the surface but also the particles had been integrated into the structure of the CVD graphene film [20].

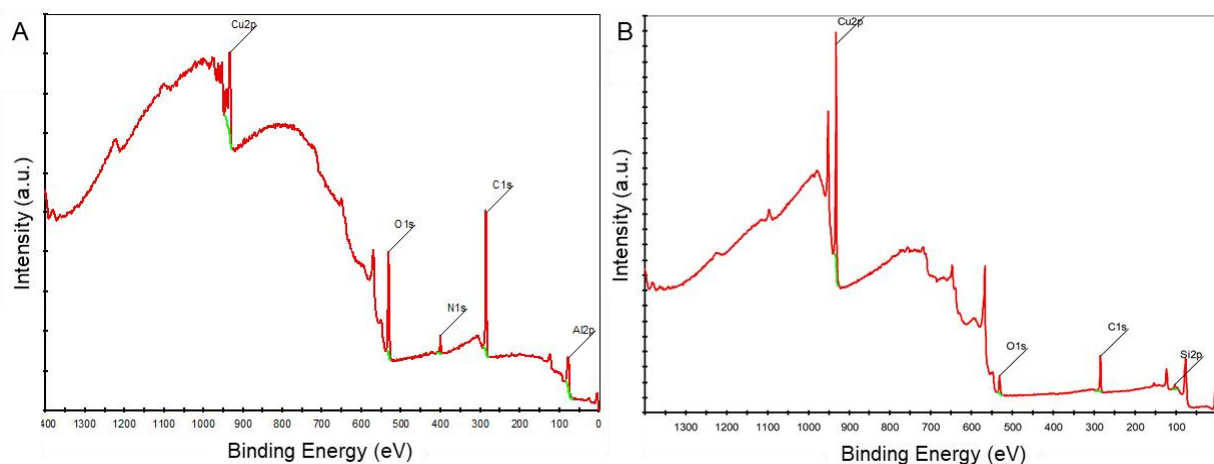


Fig. 1 XPS analysis of (A) as-received Cu substrate and (B) CVD graphene growth Cu substrate.

In order to clarify the main source of the Si impurity, a series of graphene growth experiments with Cu substrate were performed under the same conditions. A new quartz tube was installed and only one heating/cooling cycle was maintained to check the status of the CVD system before the first graphene preparation procedure. The SEM images of Fig. 3 (A1-A13) successively show the microstructure of the Cu foils surface after graphene growth for 13 times. The area with dark color is graphene, and the area with light color is Cu substrate with no graphene film coverage [8, 17], and the silicon oxide particles could be found in all samples. Fig. 3 (A1) demonstrates that the contaminations appear as small white dots with uniformly particle size about 100 nm dispersed along the graphene domain boundaries or on the surface of Cu substrate [21]. As depicted in Fig.3 (A2-A13) that representative SEM pictures of the graphene growth under the same settings whereas from different growth batch samples, the bean-shaped particles gradually increase in diameter throughout the graphene films on the Cu surface. The largest particle almost reaches about 3.4 μm in diameter from the last film growth batch. However, it seems to be difficult to gradually increase in dimension with time and segregation from the bulk to reach such a large size for different as-received Cu substrates. Therefore, the most likely source of the impurity should be the quartz products in the CVD system. The EDS results provided accurately confined analysis of the chemical composition of the surface particles. Si, O and Cu were detected on the nanoscale particle (Fig.3 B1). Only Si and O were probed on the larger particle (Fig.3 B2). Thus, we explored that these particles mainly contain the elements of Si and O. These results further confirm that the impurity comes from the quartz products, such a significant level of contamination was detected that was related to the working time of the quartz products.

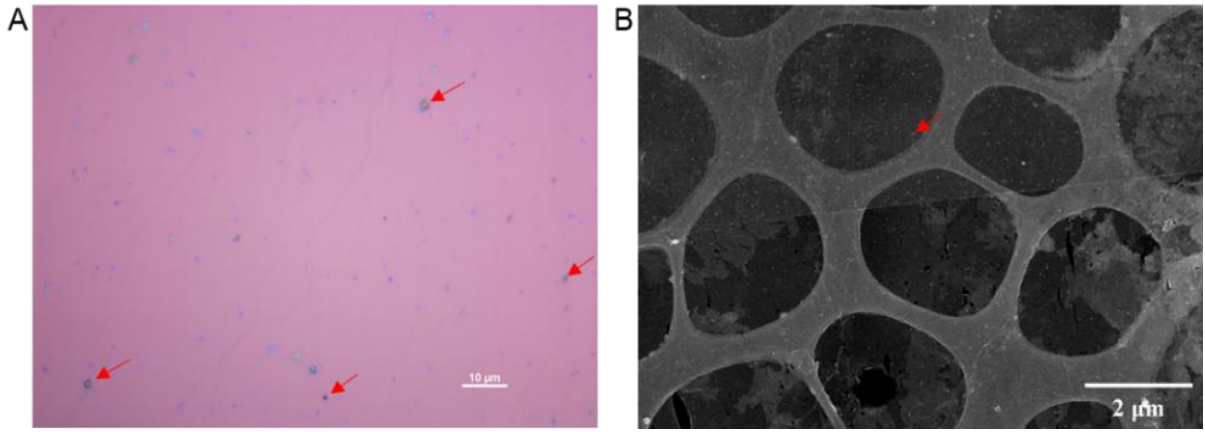


Fig. 2 (A) OM photograph of graphene transferred onto 285 nm SiO₂/Si, red arrows marked the particle impurities. (B) SEM photograph of graphene transfer to microgrid carbon film coated Cu mesh.

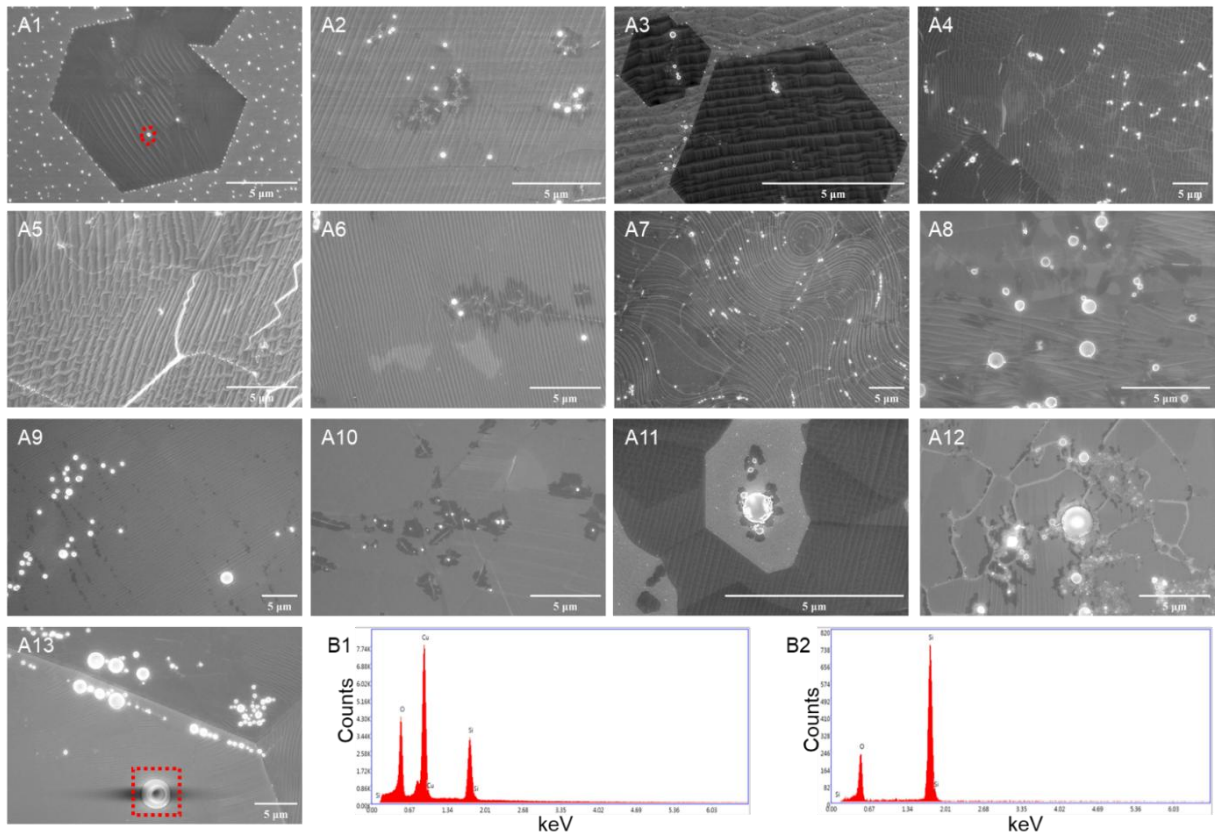


Fig. 3 (A) SEM sequential photographs of evolution of contaminations on the graphene grown on Cu substrate (A1-A13). (B) EDS energy spectra of silicon particles marked in red circle in A1 for B1, red square in A13 for B2, respectively.

In order to assess the contamination impact on the graphene quality, the Raman spectroscopy line scan was executed across a silicon oxide particle to evaluate the graphene structure variance. The silicon oxide particle was marked as No.6 indicated in the inset OM image in Fig. 4. It demonstrated a D peak intensity at 1342 cm⁻¹ higher than the other Raman spectra taken from the cleaner section, which manifested higher disorder or defects near the contamination particle [22-23]. The ratio of the G peak intensity (1586 cm⁻¹) and the D peak intensity is regularly used to determine the degree of defects present in graphene. The I_D/I_G ratios in the case of the clean and contaminated region (No. 6) are 0.013 and 0.22, respectively. Hence, the particles played an fundamental role in

the high-quality CVD graphene growth. So as to overcome the practical problem in the CVD graphene growth, we propose modifying the quartz tube reactor by adding an alumina, BN or other high melting point materials tube coaxial to the quartz tube to act as a screen for contaminants [2, 24].

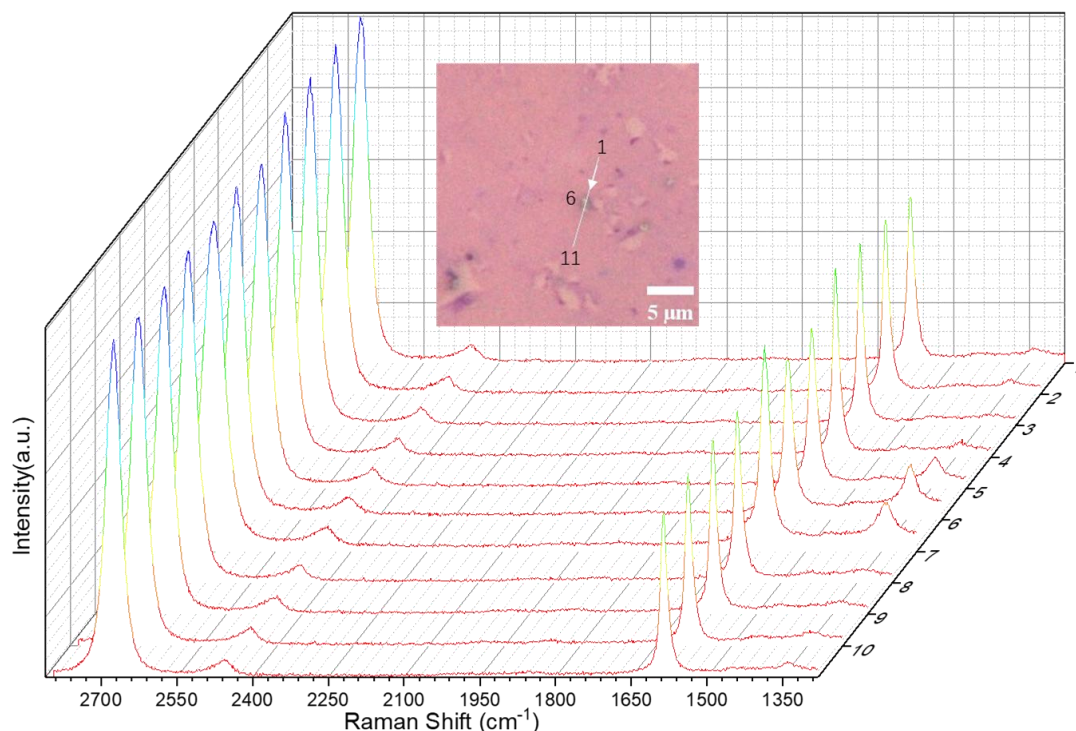


Fig. 4 Raman spectra of line scanning CVD graphene film with silicon oxide contamination, the corresponding region is indicated by the white line and number insert in the OM image, the No.6 represents the particle position.

4. Summary

In general, the silicon oxide particles are ubiquitous contaminations formed during the graphene synthesis in a CVD system. Even if a new quartz tube still contains contaminations, the quality of the graphene is degraded. Furthermore, a significant level of contamination was found to be connected to the operating time of the CVD system, and a considerable level of particles was discovered to be related to the working time of the quartz products in the CVD system. Finally, a simple solution by introducing alumina or BN tube to screen the contaminants was proposed to eliminate the contamination to promote the quality of synthesis the CVD graphene films.

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