



Safe growth of graphene from non-flammable gas mixtures via chemical vapor deposition



Ying Feng ^{a,b,*}, Daniel J. Trainer ^a, Hongshang Peng ^c, Ye Liu ^d, Ke Chen ^a

^a Department of Physics, Temple University, Philadelphia, Pennsylvania 19122, USA

^b Department of Electrical and Computer Engineering, Temple University, Philadelphia, Pennsylvania 19122, USA

^c College of Science, Minzu University of China, Beijing 100044, China

^d Anhui Provincial Key Laboratory of Photonics Devices and Materials, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei 230031, China

ARTICLE INFO

Article history:

Received 22 August 2016

Received in revised form

29 September 2016

Accepted 29 September 2016

Available online 21 December 2016

Keywords:

Graphene

Safe growth

Non-flammable

Chemical vapor deposition (CVD)

Contact resistance

Transfer length method

Chemical vapor deposition has emerged as the most promising technique for the growth of graphene. However, most reports of this technique use either flammable or explosive gases, which bring safety concerns and extra costs to manage risk factors. In this article, we demonstrate that continuous monolayer graphene can be synthesized via chemical vapor deposition technique on Cu foils using industrially safe gas mixtures. Important factors, including the appropriate ratio of hydrogen flow and carbon precursor, pressure, and growth time are considered to obtain graphene films. Optical measurements and electrical transport measurements indicate graphene films are with comparable quality to other reports. Such continuous large area graphene can be synthesized under non-flammable and non-explosive conditions, which opens a safe and economical method for mass production of graphene. It is thereby beneficial for integration of graphene into semiconductor electronics.

Copyright © 2017, The editorial office of Journal of Materials Science & Technology. Published by Elsevier Limited.

1. Introduction

Nano-carbon materials, one-dimensional carbon nanotubes (CNTs) [1,2] and two-dimensional (2D) graphene [3,4], conduct electricity far more easily than silicon used in computer chips. Studies on such materials hold promise to drive the semiconductor industry to new heights [5–8]. As a single sheet of carbon honeycomb lattice with unique properties and promising potential for applications, graphene has attracted a great deal of research attention over the past decade. The 2D material has been widely investigated from the focus of basic science to its applications in silicon electronics, photonics, and bio-sciences [9–11]. To meet the high demand of graphene material, there are several popular synthesis methods, including mechanical exfoliation of graphite [12], chemical exfoliation of graphite [13], reduction of graphene oxide [14], epitaxial growth on silicon carbide [15], and chemical vapor deposition (CVD) [16]. Among them, CVD approach has been proven the most effective one, as it enables the roll-to-roll industrial scale

graphene production, accurate control of spatial uniformity and coverage, and compatibility with semiconductor manufacturing.

This CVD method involves thermal decomposition of hydrocarbons in the presence of catalysts at high temperature (~1000 °C), which has also been widely used to achieve both vertically and parallel aligned CNTs [17–19]. For graphene, CVD of methane (CH₄) or ethyne (C₂H₂) gases on copper (Cu) or nickel substrates has been the most widely explored. To synthesize continuous large area graphene films, the carbon source gas is introduced into the CVD system along with an inert gas, such as argon (Ar) as a dilution gas while hydrogen (H₂) is introduced in a co-catalyst role [20]. The concentrations of the gases are varied from a low value to 100%, which increases the risk of fire and explosion. Take H₂ for example, the explosive limits of H₂ in air range from about 18% to 60%, and the flammable limits are from 4% to 75%. Pure H₂ and H₂ mixture beyond the flammable limit are also dangerous, because the H₂ is a small and light molecule that diffuses fast. In addition, H₂ tends to accumulate under the ceiling due to much lighter molar mass than air. Thus, H₂ can easily reach a zone where the gas and air mixture is explosive or flammable. Similar to H₂, CH₄ has a flammability limit in air of 5%–15%. Therefore, ventilation must be sufficient and safety control equipment has to be installed for the CVD method to grow graphene, resulting in a substantial cost.

* Corresponding author.

E-mail address: y_feng@outlook.com (Y. Feng).

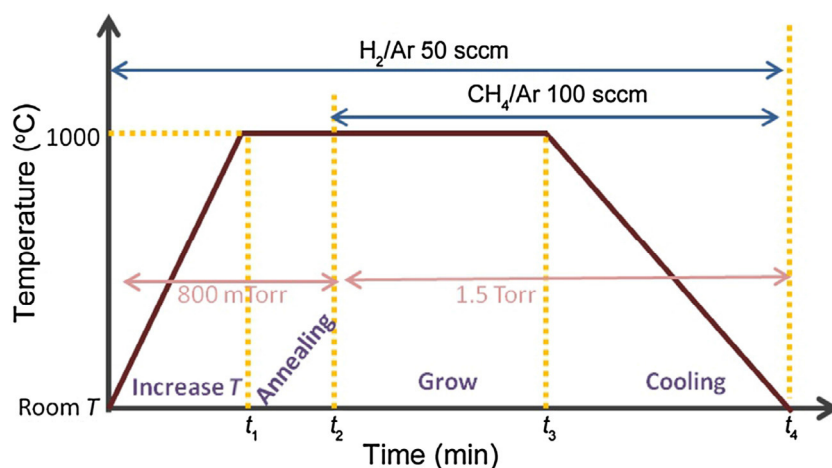


Fig. 1. Schematic of a typical graphene CVD grown process (T : temperature).

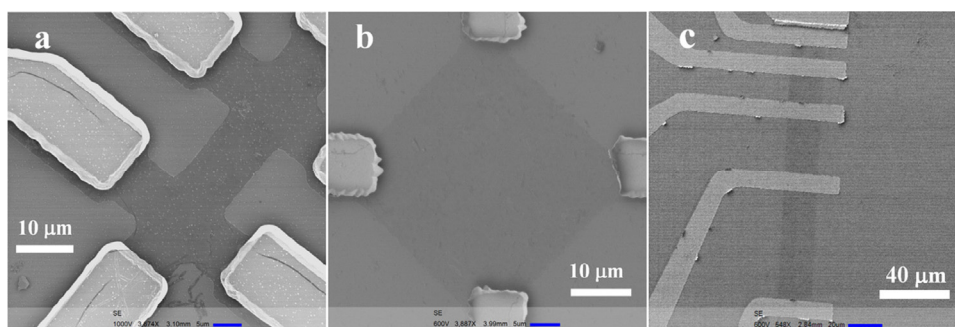


Fig. 2. SEM images of electronic devices for graphene electrical property measurements. (a) six-terminal Hall bar; (b) square shape of van der Pauw device; (c) graphene strip for TLM.

Recipes of graphene growth that could overcome the flammability issues have been reported. Sun et al. focused on developing routes for obtaining graphene through solid carbon sources, such as poly(methyl methacrylate), fluorene and sucrose [21]. Vlasiouk et al. used much diluted H_2 , which is 2.5% (below the lower flammable limit 4%) [22]. Jessica et al. investigated liquid alcohols to replace the gas phase carbon source [23]. However, the above reports still chose flammable H_2 and CH_4 mixtures when using safe carbon source and safe H_2 mixture, respectively.

Here, we report a recipe using industrially safe gas mixtures to synthesize continuous monolayer graphene by CVD on Cu foils. The gases are 2% H_2 balance Ar (H_2/Ar) and 10% CH_4 balance Ar (CH_4/Ar). The quality of the as grown graphene films was confirmed by scanning electron microscopy (SEM), optical microscopy, and Raman spectroscopy. The electrical properties were investigated by devices such as six-terminal Hall bars and van der Pauw configurations. Contact properties between metal and graphene were revealed via transfer length method (TLM). The results indicate that our approach using low concentration and nonflammable gas mixtures is able to obtain graphene materials with comparable quality with the graphene grown by high concentration and flammable gas mixtures.

2. Experimental

Graphene was synthesized on commercially available 25 μm thick Cu foils using the CVD method. Cu foils were cut into small pieces to fit to a quartz tube. Before placing the Cu foils into the quartz tube, the Cu samples were pre-cleaned with acetone and isopropyl alcohol. Acetic acid was also used to remove the surface oxide if the Cu foils

were placed in humid air for a while. The quartz tube as the CVD growth reactor chamber was then loaded into a single-zone tube furnace. Base pressure as low as a few millitorr was achieved by a mechanical pump. Then 2% H_2/Ar was introduced into the CVD chamber at a flow rate of 50 standard cubic centimeters per minute (sccm). The Cu foils were heated to 1000 $^{\circ}C$ and held for 30 minutes while the chamber pressure was kept at around 800 mTorr. After annealing, 100 sccm 10% CH_4/Ar was introduced into the CVD tube to carry out the graphene growth. The chamber pressure was kept at around 1.5 Torr. The cooling process started 30–60 min after the growth was started. The chamber was firstly cooled below 600 $^{\circ}C$ at a slow cooling rate of around 30 $^{\circ}C/min$ without opening the furnace and further cooled below 200 $^{\circ}C$ with furnace open. Finally, before taking out the Cu foils, both H_2/Ar and CH_4/Ar gas lines were closed. Fig. 1 shows a typical graphene CVD grown process.

To separate graphene from Cu foils, transfer procedures, such as our previously reported method [16], were performed, in which a methyl methacrylate (MMA) layer and $FeCl_3$ were used as a carrying layer and the Cu etchant, respectively. Silicon wafers with a thickness of 285 nm thermally grown silicon oxide (SiO_2/Si) were used as a graphene receiving substrate. The Raman spectra were measured using a Raman system with 514 nm Ar laser. Electronic devices were fabricated by forming graphene patterns by photolithography first and then forming electrode patterns for sputtered chrome and gold (Cr/Au) (5 nm/60 nm). The geometry of a six-terminal Hall bar was 8 μm wide and 48 μm long, while the square geometry of van der Pauw devices were 65 μm wide, as shown in Fig. 2(a) and (b), respectively. Hall measurements were conducted in a physical property measurement system, in which tempera-

Download English Version:

<https://daneshyari.com/en/article/5451609>

Download Persian Version:

<https://daneshyari.com/article/5451609>

[Daneshyari.com](https://daneshyari.com)