Journal of Alloys and Compounds 615 (2014) 415–418

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Letter

Large-area synthesis of high-quality and uniform monolayer graphene without unexpected bilayer regions

Jingbo Liu, Pingjian Li *, Yuanfu Chen *, Zegao Wang, Jiarui He, Hongjun Tian, Fei Qi, Binjie Zheng, Jinhao Zhou, Wei Lin, Wanli Zhang

State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, PR China

ARTICLE INFO

Article history:
Received 19 March 2014
Received in revised form 11 June 2014
Accepted 1 July 2014
Available online 9 July 2014

Keywords:
Semiconductors
Vapor deposition
Catalysis
Diffusion
Electronic properties

ABSTRACT

Chemical vapor deposition is a promising method to synthesize the large area monolayer graphene. However, unexpected bilayer regions are easily formed on the monolayer graphene, which will dramatically degrade the quality and uniformity of graphene. In this work, the large-area, high-quality and uniform monolayer graphene has been synthesized on the Cu foil. The studies reveal that the density of bilayer graphene regions decreases with increasing the growth time; when the growth time increases to 120 min, the formation of bilayer regions is effectively prevented. The corresponding growth mechanism was discussed. Further, the electrical studies reveal that by preventing the formation of bilayer regions, the mobility of graphene not only obviously increases, but also has a narrow distribution, indicating that the as-synthesized monolayer graphene has high quality and uniformity. We expect that this work is beneficial for not only potential applications, but also the fundamental understanding of the growth mechanism for graphene on Cu surface.

1. Introduction

Graphene, a one-atom-thick planar sheet of sp^2-hybridized carbon, has drawn much attention due to the outstanding properties and wide potential applications [1–3]. For practical applications, it is significant to achieve the large-area synthesis of monolayer graphene with high quality and uniformity. Recently, chemical vapor deposition (CVD) is considered as one of the most promising methods to synthesize large-area monolayer graphene film [4]. However, unexpected multilayer or bilayer regions are usually observed on the CVD monolayer graphene, which obviously influence the quality and uniformity of graphene [5,6].

Until now, there are many efforts to investigate the growth mechanism of CVD graphene films grown on Cu foils [6–8]. Liu et al. [6] demonstrated that the multilayer or bilayer regions were formed on the imperfection sites of Cu substrates with high chemical activation energy, and low pressure annealing in H_2 (before graphene growth) could make the Cu surface smoother and thereby prevent the formation of multilayer regions; however, some bilayer regions were still formed on the monolayer graphene. Herein, we report an effective way to synthesize the high-quality and uniform CVD monolayer graphene without bilayer regions. Optical microscope (OM), scanning electron microscope (SEM), Raman spectroscopy and electrical measurements were used to investigate the growth mechanism and evaluate the quality and uniformity of graphene.

2. Experimental

2.1. CVD synthesis of graphene

Firstly, the Cu foil was dipped into the dilute HCl/H_2O (1:10) solution for 3 min, and then washed by deionization (DI) water several times to remove the residual acid solution, and then was dried by nitrogen gas. Secondly, the Cu foil was loaded into the silica tube of the CVD system with a vacuum background of 7×10^{-4} Pa, and then the growth chamber was heated to 1000 °C and held for 20 min with 30 sccm pure H_2 (99.999%), and then the 15 sccm of CH_4 was introduced into the tube for graphene growth at 1000 °C for 20–180 min with the pressure of 340 Pa. Finally, cooled the system to room temperature with a cooling rate of 50 °C/min in CH_4/H_2 ambience. The as-synthesized graphene samples were denoted as G-X, where X represents the growth time (min).

2.2. Transfer process of graphene films

Firstly, the surface of graphene grown on the Cu foil was spin-coated with poly(methyl methacrylate) solution (PMMA, A4) at 3000 rpm for 30 s, and then the Cu foil was etched away in the iron trichloride solution ($FeCl_3$, 1 mol/L) for

* Corresponding authors. Tel.: +86 028 83202291 (P. Li), +86 028 83202710 (Y. Chen).
E-mail addresses: lyjw8813@sina.com (J. Liu), lipingjian@uestc.edu.cn (P. Li), yfchen@uestc.edu.cn (Y. Chen), xiaowzg2004@yahoo.com.cn (Z. Wang), 543994478@qq.com (J. He), 5419879589@qq.com (H. Tian), 493290586@qq.com (F. Qi), cloverbibi@vip.qq.com (B. Zheng), zhousuiyuan@163.com (J. Zhou), 459173874@qq.com (W. Lin), wlzhang@uestc.edu.cn (W. Zhang).

http://dx.doi.org/10.1016/j.jallcom.2014.07.003
0925-8388/

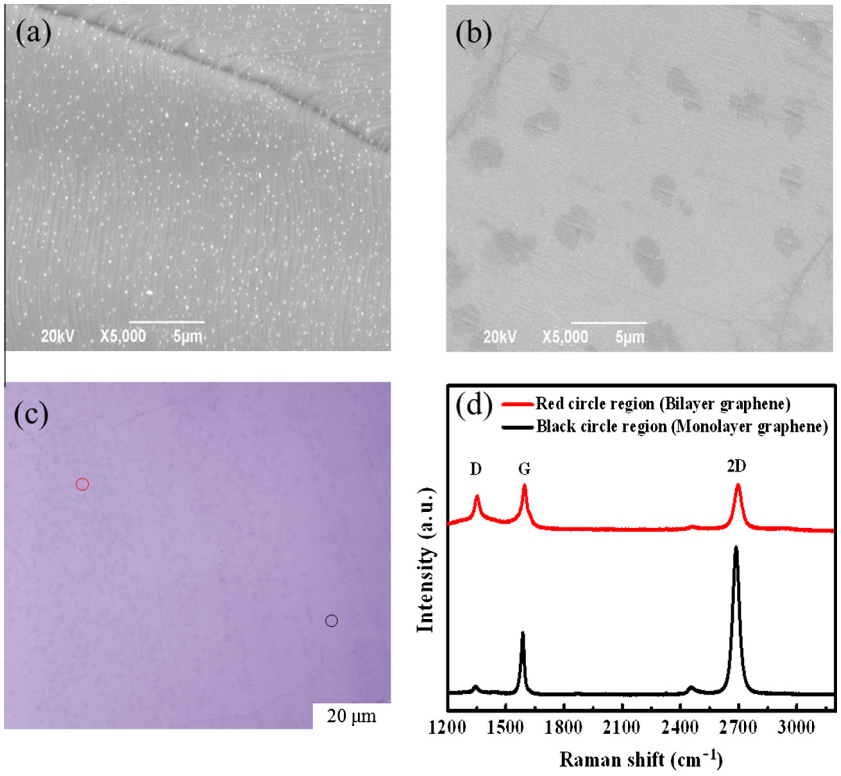

Fig. 1. SEM images of G-20 grown on the Cu foil (a) without and (b) with dilute HCl pretreatment. (c) OM image of G-20 transferred onto the SiO_2/Si substrate. (d) Raman spectra of the red and black circle regions in the (c). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

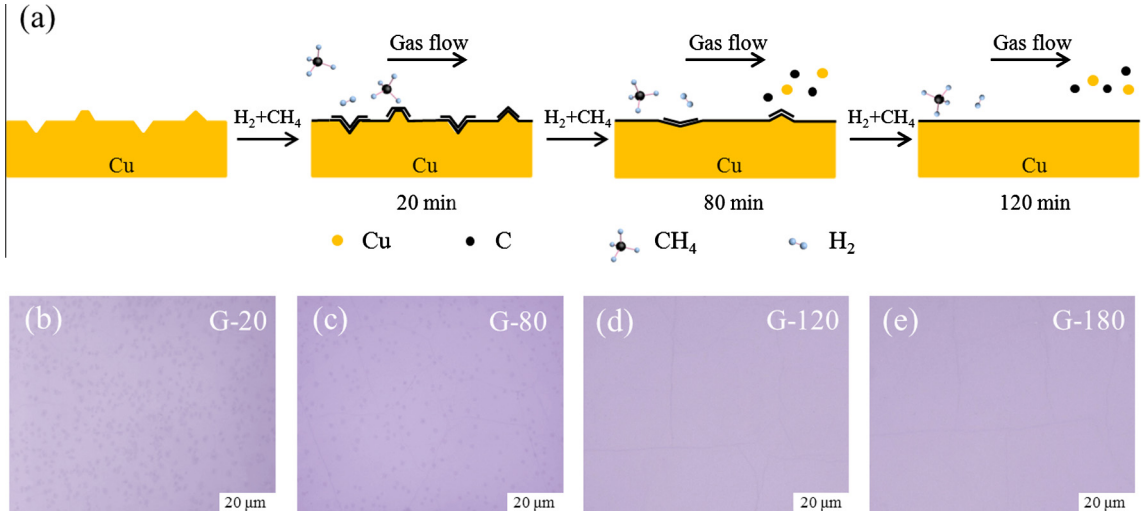

Fig. 2. (a) Schematic diagram of graphene grown on the Cu foil. (b–d) OM images of G-20, G-80, G-120 and G-180 transferred onto the SiO_2/Si substrates.

12 h. Secondly, after the PMMA/graphene film was rinsed repeatedly using the DI water (10 times), it was transferred to the $H_2O/HCl/H_2O_2$ (20:1:1) solution for 15 min for removing the residual metal particles, and then was transferred to the $H_2O/NH_4OH/H_2O_2$ (20:1:1) solution for 15 min for removing the insoluble organic contaminants. Note that the PMMA/graphene film was rinsed using the DI water to remove the residual solution after each cleaning step. Thirdly, the PMMA/graphene was transferred onto the target substrate (SiO_2/Si or PET substrates), and then was baked at 150 °C for 10 min after natural drying, and then the PMMA was removed using acetone [9].

2.3. OM, SEM, Raman and electrical measurements

The surface morphology and structure of graphene were studied by using OM (Olympus BX51M), SEM (JSM-6490LV) and Raman spectrometer (Renishaw, 514 nm) at room temperature.

The graphene field-effect transistors (FETs) were fabricated by using standard photolithography after transferring the graphene onto the 270 nm SiO_2/Si substrate. The Ni (30 nm) film was deposited as source and drain electrodes; the 270 nm SiO_2 and *n*++ silicon layers acted as the gate dielectric and back-gate electrode, respectively. The electrical measurements were carried out with an Agilent 4155B semiconductor parameter analyzer in air at room temperature.

3. Results and discussions

Before graphene growth, it is necessary to use dilute HCl to remove the native Cu-oxide layer on the Cu foil, otherwise the Cu-oxide nanoparticles will be formed on the graphene, as shown in Fig. 1a. Fig. 1b shows the SEM image of G-20 grown on the Cu foil with dilute HCl pretreatment. Although the graphene surface