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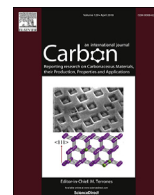
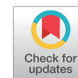


Transfer-free growth of graphene on Al_2O_3 (0001) using a three-step method



Chitengfei Zhang [a], Jin Huang [a, 1], Rong Tu [a], Song Zhang [a, *], Meijun Yang [a], Qizhong Li [b], Ji Shi [a, c], Haiwen Li [a, d], Lianmeng Zhang [a], Takashi Goto [a, e], Hitoshi Ohmori [a, f]

[a] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, 122 Luoshi Road, Wuhan, 430070, People's Republic of China
[b] Hubei Key Laboratory Advanced Technology of Automobile Parts, Wuhan University of Technology, 122 Luoshi Road, Wuhan, 430070, People's Republic of China
[c] School of Materials and Chemical Technology, Tokyo Institute of Technology, Tokyo, 152-8552, Japan
[d] International Research Center for Hydrogen Energy, Kyushu University, Fukuoka, 819-0395, Japan
[e] Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, 980-8577, Japan
[f] Institute of Physical and Chemical Research, 2-1 Hirosawa, Wako, Saitama, 351-0198, Japan

A R T I C L E I N F O

Article history:

A B S T R A C T

The transfer process before graphene device fabrication could worsen the performance of graphene device greatly, so a transfer-free growth method for preparing graphene films is demanded urgently. Herein, we propose a novel three-step method to achieve transfer-free graphene films on Al_2O_3 (0001) substrates. Cu (111) films and carbon source were co-deposited on α-Al_2O_3 (0001) substrates by metal-organic chemical vapor deposition (MOCVD) at one step, then graphene was synthesis by a rapid annealing process, transforming the carbon source in copper into graphene films. Finally, a transfer-free graphene film with an ultra-smooth surface (~3.49 nm) is achieved by etching the copper film on Al_2O_3(0001). Crystallographic characterization demonstrated the as-deposited Cu films show a nature of epitaxial single crystal, with a smooth surface (~6.89 nm). Few layer graphene films (3–4 layers) with least defect concentration were grown at annealing time of 20 min.

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1. Introduction

Graphene, honeycomb crystal lattices with one-atom thickness, has raised countless attentions of scientists all over the world, because of its unique properties [1–3]. It has been reported that the charge carrier mobility of graphene field-effect transistors (FET) can reach almost 200000 $cm^2 V^{-1} s^{-1}$, which makes it possible to break Moore's law in semiconductor industry [4]. Graphene has been achieved by different methods, such as mechanical exfoliation [5], epitaxial growth of SiC [6], reduction of graphene oxide [7] and chemical vapor deposition (CVD) [8–10]. Recently, high-quality graphene films achieved by roll-to-roll CVD method reveals CVD method is the most promising method for industrial production [11,12].

Graphene on transition metal cannot be used to fabricate electric device directly. An additional transfer step is essential. Usually, a wet chemical transfer method and bubbling transfer method are used [13–15]. However, this additional step always induces wrinkles, cracks, polymer residues and defects, which worsen the performance of CVD graphene greatly [16]. In order to avoid these shortcomings, transfer-free technologies are developed in recent year. In general, transfer-free technologies can be divided into two types: metal-free method and metal-assisted method. Metal-free method can obtain graphene film on insulated substrates directly. However, graphene with only nanometer-scale crystallites was produced, unless higher temperature [17] or longer process times were conducted [18]. As for metal-assisted method, higher-quality graphene was produced with mild experimental condition. There are four steps for metal-assisted method: (1) Transition metal films are prepared on insulated substrate by physical vapor deposition method. (2) Solid carbon source (sputtering carbon films or spin-coating polymer films) are grown on the as-prepared transition metal films. (3) A rapid thermal annealing process under Ar/H_2

* Corresponding author.
E-mail addresses: kobe@whut.edu.cn, superkobe0104@gmail.com (S. Zhang).
[1] This author contributed equally to this work and should be considered co-first authors.

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atmosphere. (4) Etch the transition metal films by etching solution [19–21].

Herein, we propose an efficient three-step method to obtain transfer-free graphene films. Copper film and carbon source are deposited at one step by metal organic chemical vapor deposition (MOCVD). Schematic of synthesis route is shown as Fig. 1. We co-deposited Cu (111) films and amorphous carbon (AC) arisen from the decomposition of $Cu(acac)_2$ on *c*-plane sapphire by MOCVD, and then a rapid annealing was conducted in order to graphitize the AC under the catalysis of copper. Finally, transfer-free graphene films on *c*-plane sapphire were achieved by an etching step. Compared to the conventional four-step method, this three-step method simplifies the synthetic method and decreases the production cost without affecting the quality of graphene, thereby opening up a new method for transfer-free graphene films on insulated substrates broadly.

2. Experimental methods

2.1. Synthesis of copper film and graphene

Growth of copper film by MOCVD: Cu (111) film was deposited on single crystalline Al_2O_3 (0001) substrate 15×10×0.5 mm in size (Hefei Department of Crystal Material Technology Co Ltd., China), which was ultrasonically washed by acetone (98%, Alfar Aesar) for 15 min, deionized water for 1 min, and solution of hydrochloric acid (98%, Alfar Aesar) (HCl: DI = 1: 1) for 2 min. Then, the cleaned Al_2O_3 (0001) substrate was placed on an alumina made boat and inserted at the center of the CVD quartz tube with 60 mm in diameter (the equipment illustrator is shown in Fig. 2). The quartz tube was evacuated to 1 Pa before heating and then heated to 350 °C at a heating rate of ~10 °C min^{-1}. The chamber was kept at 5 kPa during the deposition. $Cu(acac)_2$ precursor (98%, Alfar Aesar) was heated to 240 °C. Ar gas was divided into Ar gas and Ar carrier gas. During the deposition process, the flow rate of H_2 (99.999%, WuHanShi XiangYun Industry CO., Ltd.) and carrier Ar (99.999%, WuHanShi XiangYun Industry CO., Ltd.) was fixed at 1000 sccm and 50 sccm, respectively. Deposition time was 60 min. After deposition of copper film, the $Cu(acac)_2$ precursor was cooled down and shut off by a valve.

The as-deposited copper film was moved to cold region in order to prevent evaporation of copper. The chamber was increased to graphitization temperature of 1000 °C at a heating rate of 12 °C min^{-1}, 10 sccm H_2 was flowed to protect copper film from oxidation. Then, the furnace was heated from 350 to 1000 °C at a heating rate of 12 °C min^{-1}. After furnace temperature rose to 1000 °C, copper film was moved back to the center of quartz tube. During graphitization, H_2 flow was fixed at 20 sccm. The graphitization time was varied from 10 to 60 min. Finally, the specimen was cooled down to room temperature at cool region at the flow of 2 sccm H_2 and 100 sccm Ar to prevent oxidation. Illustration of the fabrication processes of Cu (111) and graphene is shown in Fig. 3. As for the copper etching process, the copper films were etched by an aqueous $(NH_4)_2S_2O_8$ (98%, Alfar Aesar) solution. The graphene/Cu/Al_2O_3 was put in a 0.5 M $(NH_4)_2S_2O_8$ solution, and the copper films were etched away one hour later. Then, the graphene/Al_2O_3 wafer should be cleaned in DI water for several times.

2.2. Characterization

Crystallographic, preferred orientation and in-plane orientation were examined by X-ray diffraction (XRD) with Pole Figure device (Ultima III, Rigaku, Japan) using Cu *Kα* under 40 kV and 40 mA. The surface and cross-sectional morphology of copper film was observed by scanning electron microscopy (Quanta FEG250, FESEM, USA) at an accelerating voltage of 20 kV and the surface orientation was examined by the equipped electron backscatter diffraction (EBSD, NordlysNano, Oxford, UK). Atomic force microscopy (AFM) (Nanoscope V, Veeco, USA) was used to characterize surface roughness of copper film. The TEM sample in Fig. 7 was prepared by scraping the copper film. The copper film was scraping in DI water, and then was caught up by a TEM grid. The TEM sample in Fig. 8 (e) was prepared by a focused ion beam (FIB, FEI Helios Nanolab 600i, USA). The cross-section of the graphitized specimen was sliced with a FIB and observed by transmission electron microscopy (TEM, JEM-2100UHR, Tokyo, Japan) at 200 kV acceleration voltages. Raman spectra of graphene on copper film were measured by an inVia Raman microscopy (Renishaw, USA) using 633 nm excitation wavelength.

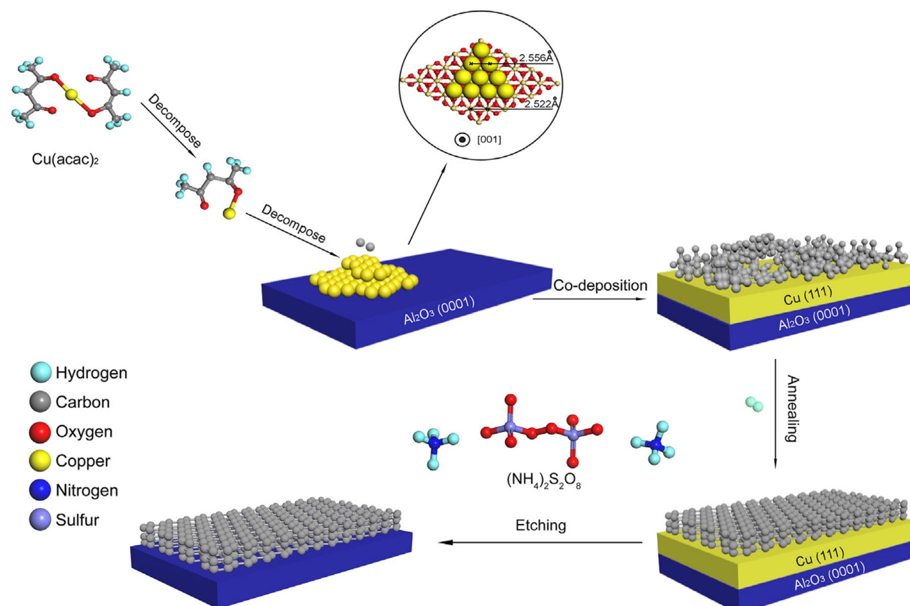

Fig. 1. Schematic of synthesis route. (A colour version of this figure can be viewed online.)

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