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Copper substrate as a catalyst for the oxidation of chemical vapor deposition-grown graphene

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ABSTRACT

We report the catalytic effect of copper substrate on graphene–oxygen reaction at high temperature. Previous studies showed that graphene grown on copper are mostly defect-free with strong oxidation resistance. We found that a freshly prepared copper-supported graphene sample can be completely oxidized in trace amount of oxygen (<3 ppm) at 600 °C within 2 h. Both X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) suggest that upon ambient air exposure, oxygen molecules diffuse into the space between graphene and copper, resulting in the formation of copper oxide which acts as catalytic sites for the graphene-oxygen reaction. This result has important implications for the characterization, processing, and storage of copper-supported graphene samples.

1. Introduction

The copper-catalyzed chemical vapor deposition (CVD) of graphene is widely used in the research community because it offers high quality graphene with controlled thickness, high transferability and low cost [1–4]. Given its importance, a complete understanding of the interaction between graphene and the underlying copper substrate is highly desirable for both fundamental and practical considerations [5].

Among the many studies of graphene–copper interaction, a substantial portion was devoted to understand the effect of copper surface during the CVD growth of single layer graphene. Many of these studies were motivated by the need to grow high quality, defect-free graphene samples. For example, Yan et al. decreased the graphene nucleus density through electrochemical polishing and high pressure annealing copper surface [1]. Lyding and coworkers explored the effects of copper crystal structure on graphene synthesis, they observed that the copper (111) facet, having a hexagonal crystalline structure and the best match to that of graphene, facilitates graphene growth in the highest quality [6]. More recently, Hao et al. reported that oxygen-rich copper surface enabled the growth of single-crystal graphene in centimeter scale [7].

A smaller number of studies have also investigated the interaction between copper and graphene after the CVD synthesis. For example, graphene has been recently observed to play a dual role in the underlying copper corrosion process, in which graphene works as an anti-corrosion barrier under aggressive chemical environment but promotes the long-term corrosion process in ambient atmosphere at room temperature [8–10]. On the other hand, copper substrate shows very weak influence on the interaction between graphene and H_2O/O_2 at low temperature [11]. Because graphene grown on a copper substrate is mostly defect-free, it is generally assumed that the copper substrate does not impose negative impact on its post-synthesis characterization and processing. However, this assumption has never been experimentally confirmed.

Copper is known to catalyze the oxidation of graphite. Several studies have investigated the copper-catalyzed oxidation of graphite since the 1970s [12–15]. For example, McKee et al. reported that the ignition temperature/activation energy for graphite–oxygen reaction decreased from 740 °C/54 kcal mol^{-1} to 600 °C/34 kcal mol^{-1} with very small addition of Cu (<0.3 wt%) [14]. In their experiments, a copper salt solution was used as the metal source, which produced copper oxide particles 1–5 μm in size during the catalytic oxidation process. These particles moved rapidly above 600 °C and cut channels on the graphite surface by reacting with graphite:

$$CuO + C \rightarrow Cu + CO$$

These studies suggested that the underlying copper substrate may facilitate the oxidation of graphene surface. However, to the best of our knowledge, the copper catalyzed oxidation of graphene has not been systematically investigated.

Compared to the copper-catalyzed oxidation of graphite, the copper foil supported graphene is quite different in many ways. On one hand, all carbon atoms on graphene surface are in direct contact with the underlying copper substrate, which could result

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in a significant enhancement of the catalytic efficiency. On the other hand, unlike graphite surface, which has substantial amount of step edges acting as reactive center, [12] graphene grown on a copper foil is mostly defect-free without almost no step edge. In addition, the fact that graphene covers the copper substrate may suggest the absence of any catalytic effect of copper. Given these considerations, it is difficult to predict whether the graphene-oxygen reaction can be enhanced by the underlying copper substrate.

Herein, we report our studies on the effect of copper substrate during the thermal annealing of copper/graphene sample in high purity Ar having tracing amount of O_2. Graphene on copper substrate undergoes a complete oxidation at 600 °C within 2 h in the presence of < 3 ppm of O_2. The reaction was characterized by Raman, XPS, and AES. Our results suggest that ambient oxygen can diffuse into the interlayer of copper/graphene upon air exposure, resulting in the formation of copper oxide which catalyzes the graphene–oxygen reaction at high temperature.

2. Materials and methods

2.1. Synthesis of single-layer graphene on copper foil (copper/graphene)

The synthesis process was reported by Li et al. [2] and briefly described as follows: (i) a copper foil (Alfa Aesar, 25 μm thick, purity of 99.8%) was cut into small strips (1.5 cm × 3 cm), rinsed with 1% HCl and placed on a quartz substrate inside a hot wall furnace, (ii) the tube furnace was evacuated for 10 min followed by H_2 gas flow at a flow rate of 2.0 standard cubic centimeters per minute (SCCM), (iii) the copper foil in the tube furnace was then heated to 1000 °C under H_2 flow for 30 min, followed by a CH_4/H_2 gas mixture at 500 m Torr and 1000 °C for another 30 min, (iv) the copper foil was cooled to room temperature under H_2 and CH_4 gas flow (500 m Torr) and then taken out of the furnace.

2.2. Synthesis of multi-layer graphene on Ni foil (nickel/graphene)

The CVD growth of multi-layer graphene on nickel foil was analogous to the case of single layer graphene growth on copper, except the reaction temperature was 800 °C. The sample was determined to be 2–3 layers of graphene based on its Raman spectrum (see discussion below).

2.3. Graphene transferred onto different substrates

Copper/silicon substrate preparation: a copper film was vacuum deposited onto a silicon wafer with 300 nm of SiO_2 (University Wafers). The deposition was carried out on a Thermionics VE-180 e-beam evaporator at a pressure of 2×10^{-6} Torr. A total thickness of 5 nm of Ti layer was first deposited followed by a 300 nm of Cu layer onto the silicon substrate. The copper/silicon substrate was soaked in acetone for 30 min then rinsed with deionized (DI) water before use.

The graphene film grown on a copper foil was transferred onto different substrates following the procedures reported by Li et al. [16]. The transfer process began with spin-coating of poly methylmethacrylate (PMMA (Aldrich, M_w 996000)) layer on one side of the copper/graphene surface, followed by etching Cu foil in 1 M $FeCl_3$ (Sigma-Aldrich, 97%)/3.5 M HCl (Fisher Scientific, 37.1%) aqueous solution for 20 min. After the copper foil being completely etched, PMMA/graphene film was transferred to a DI water bath for cleaning and then carefully collected onto different substrates. The PMMA film was then dissolved in acetone for 8 h followed by immersion in a dichloromethane bath for another 8 h. To further remove the surface contamination, the graphene covered substrate was then annealed in Ar atmosphere at 400 °C for 30 min.

2.4. Thermal annealing of copper/graphene sample

After CVD synthesis, a copper/graphene sample was taken out of tube furnace and exposed in air for 5 h. The sample was then put back to the tube furnace under Ar (99.999%) flow at a flow rate of 1.5 L/min for 30 min to ensure removal of air in the chamber. The sample was then annealed at 600 °C in Ar for 2 h, followed by a fast cooling process to room temperature before taken out of the chamber.

2.5. Optical microscopy

Optical microscopy imaging of both copper and silicon substrates surface was conducted using a Nikon Eclipse Ti – U in reflectance mode with an Ample Scientific 3.0 M pixel camera.

2.6. Raman spectroscopy

Room temperature micro-Raman spectra were collected on a custom-built setup using 532 nm single-longitudinal mode solid-state laser with a spot size less than 1 μm. A 40× objective (NA: 0.60) was used in all the micro-Raman experiments. Laser power was kept less than 1 mW at the sample to avoid laser induced thermal damage on graphene. Raman spectra were shifted on the y-axis for clarity.

2.7. XPS

XPS measurements were carried out in a UHV chamber (base pressure $\sim 1 \times 10^{-10}$ Torr) with a custom built multi-technique surface analysis instrument. Spectra were collected using the Al-Kα X-ray line and a Leybold-Heraeus EA-10 hemispherical energy analyzer (HSA). The characterization was typically operated with a bandpass of 50 eV for both survey scans (1.0 eV/step) and multiple scans (0.1 eV/step). After raw data collection, XPS-peak software was used in data analysis.

2.8. AES

AES was performed on a Perkin-Elmer 10–155 cylindrical Auger electron optics in the same UHV chamber as XPS, operated with an electron multiplier supply under 2-kV-mode. The spectra were collected using the same HSA with a bandpass of 50 eV for multiple scans (0.5 eV/step).

3. Results and discussion

3.1. Oxidation of copper-supported graphene

We found that that the underlying copper substrate can enhance the oxidation of graphene at > 600 °C in the presence of trace amount of O_2. In a typical experiment, we exposed a freshly prepared copper/graphene sample to air at room temperature for several hours and then annealed it in an Ar (99.999% purity, $O_2 < 3$ ppm, $H_2O < 5$ ppm) atmosphere at 600 °C for 2 h. During the 2 h thermal annealing in Ar flow (1.5 L/min), $\sim 2.41 \times 10^{-5}$ mol oxygen molecules will flow into the tube furnace compared to only $\sim 1.72 \times 10^{-9}$ mol carbon atoms located on 1 × 1 cm copper surface. Therefore, the oxidation is not limited by the supply of oxygen.