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Controllable growth of 1–7 layers of graphene by chemical vapour deposition

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ABSTRACT

We report that graphene films with thickness ranging from 1 to 7 layers can be controllably synthesized on the surface of polycrystalline copper by a chemical vapour deposition method. The number of layers of graphene is controlled precisely by regulating the flow ratio of CH_4 and H_2, the reaction pressure, the temperature and the reaction time. The synthesized graphene films were characterized by scanning electron microscopy, transmission electron microscopy, selected area electron diffraction, X-ray diffraction and Raman spectroscopy. In addition, the graphene films transferred from copper to other substrates are found to have a good optical transmittance that makes them suitable for transparent conductive materials.

1. Introduction

Graphene, a novel two-dimensional monolayer material consisting of a hexagonal crystal structure of sp^2-bonded carbon atoms, is gaining much attention due to its particular structure and great potential for a wide range of applications [1–4]. For instance, though graphene is as thin as one layer, it is also one of the strongest materials. Besides, enormous surface area of graphene with excellent conductivity and high carrier mobility can be grown. Literature survey shows that numerous methods have been developed to produce graphene, including the micromechanical cleavage of highly oriented pyrolytic graphite [1], epitaxial growth on a SiC substrate [5], reduction of graphite oxide [6], chemical vapour deposition (CVD) [7] and arc discharge [8]. Among all the developed synthesis methods, the CVD method has received significant attention for growing high-quality graphene films with large area. Up to now, this relatively simple and low-cost method has been used to produce graphene samples that can reach spectacular sizes [9], and can be easily transferred to other substrates [9,10].

Different transition metals, including nickel [11], copper [12], rhodium [13], iridium [14], platinum [15], and cobalt [16], have been used in CVD system for graphene synthesis. In order to get wafer-scale single-layer graphene, special substrates such as a binary metal alloy, single-crystal metal surface on sapphire or others were designed [17,18]. The growth of graphene on a metal is influenced by a number of factors, including crystal structure of metal surface, carbon solubility in metals, thermodynamic and kinetic parameters. From an industrial viewpoint, polycrystalline non-noble metal substrates will be preferable. During the growth of graphene on copper foils, a self-limiting mechanism was proposed [12]. Also, the previous reports reveal that under atmosphere pressure chemical vapour deposition (APCVD), graphene growth on copper surface is not self-limiting any more [19–22],

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therefore, controllable synthesis of graphene with different layer number on copper might be possible. Interestingly, the various properties of materials made of more than one layer of graphene vary significantly with the number of layers, thus opening a new range of applications for carbon-based materials. However, the research on precisely controlling the number of graphene layers is still in the early stage, and needs to be discussed in detail.

Up to now, there are several reports about the controlled synthesis of few-layer graphene, which mainly focussed on the growth mechanism and the catalyst of graphene manufacture. Moreover, researchers prefer using Ni substrates owing to their larger carbon solubility, thus avoiding the problem of self-limitation. For example, Liu et al. reported a segregation approach to achieve precise layer control by using Cu–Ni alloy, which is a combination of the well-behaved Cu and Ni substrates for graphene growth [23]. Another method to synthesize few-layer graphene also based on Ni substrates, published by Gong et al., is carried out by modulating simplified CVD process conditions and hydrogen exposure [24]. Herein, we employ a simple CVD method to investigate the relationship between the growth parameters and the number of layers of graphene, thus providing a promising approach to control the thickness of few-layer graphene films on Cu substrates. Our results demonstrate that some factors such as the flow ratio of CH_4 and H_2 and the reaction pressure play key roles during the formation of graphene with different layers.

2. Experimental section

2.1. Synthesis of 1–7 layers of graphene by a CVD method

Graphene films with different number of layers were grown on 25-μm-thick copper foil (Alfa Aesar, item No. 046365, cutting into 2×2 cm square plates) using the CVD method in a 4-inch chamber quartz reactor. In the case of the synthesis of the monolayer graphene film, a pretreatment by acetic acid and ethanol on the copper foil was first performed. Then the copper foil was sent to the centre of the furnace chamber. With argon flowing at a 300 sccm/min rate, the quartz tube was heated to 940 °C, and the pressure was maintained at about 1.5×10^3 Pa. At this growth temperature, the flow ratio of CH_4:H_2 was maintained at 5:35 for 5 min. After this step, CH_4 was cut off and the furnace was cooled down to room temperature under a 300 sccm/min flow of Ar and a 35 sccm/min flow of H_2. The heating rate was 12 °C/min, while the cooling rate was 10 °C/min.

Similarly, the other layered graphene films (2–7 layers) on Cu were fabricated by changing the synthesis recipe, as shown in Table 1. For instance, in order to obtain the bilayer graphene film, the flow ratio of CH_4:H_2 was changed to 10:30, while the other experiment conditions remained the same as for the growth of monolayer graphene. In contrast to the synthesis process for monolayer and bilayer graphene, the preparation of 3–7 layers graphene films was carried out under atmospheric pressure, and the flow ratio of CH_4:H_2 was the same as for the bilayer synthesis. The reaction temperature for trilayer graphene growth was 960 °C, and the reaction time was 5 min. When synthesizing the four-layer and five-layer graphene films, the optimal temperature was found to be 920 °C, while the reaction times were 10 and 20 min, respectively. The six and seven layers graphene films were synthesized at 940 °C, and the reaction times were 10 and 20 min, respectively, which could be controlled similarly to the case of the four- and five-layer graphene films.

2.2. Graphene transfer onto Si substrate

Typically, the graphene films grown on the copper foil were coated with poly-methyl methacrylate (PMMA) before etching. Then graphene films with different number of layers on copper foils were etched in an aqueous solution of ferric chloride. After the etching process, the films were transferred to deionized water. The PMMA/graphene stack was then lifted by the silicon. In order to smooth the wrinkles caused during the transfer process, ethanol was sprayed to the surface of the stack, which could make a full contact between PMMA/graphene and silicon. Water molecules were vaporized by drying the films in an oven at 50 °C for about 3 h. Afterwards, acetone was used to dissolve the PMMA and clean graphene on silicon was finally obtained.

2.3. Characterisation of graphene

After transferring process, the prepared graphene films with different number of layers were characterized by scanning electron microscopy (SEM, FEI Quanta 200 F), transmission electron microscopy (TEM, FEI Tecnai G^2 F20), Raman spectroscopy (HORIBA JY T64000) and X-ray diffraction (XRD, Bruker D8 Advance). The optical transmittance of the transferred graphene films in the visible and near infrared range were measured by using a UV756CRT spectrophotometer in the 400–1100 nm wavelength range. For the measurement of the electrical conductivity, graphene films were directly

Table 1 – Summary of the growth conditions of few-layer graphene films.

Layers	Temperature (°C)	Pressure (Pa)	Time (Min)	CH_4:H_2 (Sccm)
Monolayer	940	1.5×10^3	5	5:35
Bilayer	940	1.5×10^3	5	10:30
Three layers	960	1.01×10^5	5	10:30
Four layers	920	1.01×10^5	10	10:30
Five layers	920	1.01×10^5	20	10:30
Six layers	940	1.01×10^5	10	10:30
Seven layers	940	1.01×10^5	20	10:30