Synthesis of multi-layer graphene films on copper tape by atmospheric pressure chemical vapor deposition method

Van Tu Nguyen\textsuperscript{1}, Huu Doan Le\textsuperscript{2}, Van Chuc Nguyen\textsuperscript{1}, Thi Thanh Tam Ngo\textsuperscript{1}, Dinh Quang Le\textsuperscript{1}, Xuan Nghia Nguyen\textsuperscript{1} and Ngoc Minh Phan\textsuperscript{1}

\textsuperscript{1}Institute of Materials Science, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet Road, Cau Giay District, Hanoi, Vietnam
\textsuperscript{2}Hanoi National University of Education, 136 Xuan Thuy Road, Cau Giay District, Hanoi, Vietnam

E-mail: chucnv@ims.vast.ac.vn

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Abstract
Graphene films were successfully synthesized by atmospheric pressure chemical vapor deposition (APCVD) method. Methane (CH\textsubscript{4}) gas and copper (Cu) tapes were used as a carbon source and a catalyst, respectively. The CVD temperature and time were in the range of 800–1000 \textdegree C and 10 s to 45 min, respectively. The role of the CVD temperature and time on the growth of graphene films was investigated in detail via scanning electron microscopy (SEM) and Raman spectroscopy techniques. The results of SEM images and Raman spectra show that the quality of the graphene films was improved with increasing of CVD temperature due to the increase of catalytic activity.

Keywords: graphene, atmospheric pressure chemical vapor deposition, Cu tape

Classification number: 5.15

1. Introduction

Graphene is a two-dimensional material composed of carbon atoms arranged in a hexagonal atomic structure. Its theoretical thickness is about 0.34 nm \cite{1, 2}. However, graphene has a number of properties which make it interesting for several different applications. It is the thinnest, mechanically very strong, transparent and flexible conductor \cite{3}. The electron mobility of graphene is very high at room temperature (15000 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}) which makes this material very interesting for electronic high-frequency applications such as high-frequency transistor and modulator \cite{4}. Since graphene is the transparent electrode, it may be widely used in liquid crystal display (LCD), organic light-emitting display (OLED), where it can replace the rather fragile and expensive indium–tin–oxide (ITO) \cite{5}. Established on large specific surface area, graphene is also used in gas detectors and biosensors \cite{6, 7}. Besides, new types of composite material based on graphene with great strength and low weight could also become interesting for use in satellites and aircraft \cite{8}.

Most of these promising applications require the growth of graphene films in large areas on a suitable substrate. Graphene can be prepared by many methods. The first method is micromechanical cleavage from graphite. This method can only produce very small graphene films \cite{9}. Recently, graphene has been produced by exfoliation and dispersion of graphite in organic solvents but the yield is very low \cite{10}. The chemical exfoliation is an effective method to produce graphene film in large quantities \cite{11}. However, chemical exfoliation involves complex chemical processes using heavily functionalized organic groups. Another way is epitaxial growth of graphene on silicon carbide (SiC) \cite{12}. However, graphene grown on SiC substrates is difficult to transfer to other substrates. At present, thermal chemical vapor deposition (CVD) is one of the major methods to fabricate graphene \cite{13}. With this method, the area and shape of graphene films are variable. In the thermal CVD process, at
high temperature, hydrocarbon gases are decomposed, which leads to the formation of carbon atoms on the metal surface. These carbon atoms segregate and form graphene film.

In this work we report on APCVD method to grow large-area graphene films on copper (Cu) tape. There are a few reasons for the selection of Cu metal as a substrate: (i) carbon has a low solubility in Cu substrate, (ii) absence of a copper carbide and (iii) chemical etchant selectivity to graphene. Several parameters of APCVD such as time and temperature, which play important roles in graphene formation, were studied.

2. Experiment method

The graphene films were synthesized by thermal CVD method under high temperature (850–1000 °C) in argon (Ar) environment (1000 sccm). The Cu tapes with a thickness of 35 µm and a size of 0.5 cm × 0.5 cm were used as substrates for graphene-films synthesis process. To reduce the native copper oxide and to facilitate Cu grain growth on the Cu tape surface, the samples were annealed at CVD temperature for 30 min in a flow of Ar and hydrogen (H₂, 300 sccm). After 30 min, a flow of methane (CH₄, 30 sccm) was introduced for growth process (figure 1). The time for the CVD process ranged from 10 s to 45 min. After a preset graphene growth time, the samples were cooled rapidly under a flow of Ar (1000 sccm). The grown graphene films were then characterized using SEM, Raman spectroscopy and atomic force microscopy (AFM) techniques.

3. Results of synthesis of graphene

3.1. Effect of growth temperature

One of the critical factors in synthesis of graphene is growth temperature because high energy is necessary to dissociate methane so that it reacts with the catalyst. To study the influence of the growth temperature on the synthesis of graphene, we executed the CVD process at different temperatures 850, 900, 950 and 1000 °C for the same time and gas flow (30 min and Ar/H₂/CH₄ = 1000/300/30 sccm flow rates). The shape and the size of graphene patches referred to as domains can be imaged by SEM. Figure 2 is the SEM images which shows the effect of growth temperature on the formation of the graphene while keeping time and gas flow rates unchanged. Figure 2 shows that the density and size of graphene domains increase with increasing temperature.
Figure 4. SEM images of graphene films grown on the Cu tape’s surface after CVD process for (a) 10 s, (b) 30 s, (c) 1 min, (d) 5 min, (e) 30 min and (f) 45 min.

3.2. Effect of growth time

Figure 4 shows SEM images of graphene films grown on Cu tape surface with the growth time ranging from 10 s to 45 min at 1000 °C under flow of CH$_4$ and H$_2$ (CH$_4$/H$_2$ = 30/300 sccm). The dark features in the SEM images in figures 4(a)–(c) correspond to the graphene domains and the bright regions are the bare Cu. It is clear that the graphene domains grown during 10 s are smaller than that grown during 30 s (figures 4(a) and (b)). The formed graphene area increases with the growth time increasing. Figure 4(d) indicates that after 5 min of growing, the entire surface of the copper foil is covered with graphene. This shows that the carbon atoms actively move in and out of the edges of the graphene sheet till all the growth domains are linked, forming a solid and stable graphene sheet.

Figure 5 shows a comparison of the Raman spectra of the graphene films grown on the surface of the Cu and graphite measured at 632.8 nm. The ratio $I_{2D}/I_G$ of the intensity $I_{2D}$ and $I_G$ of the bands 2D and G is dependent on the number of graphene layers [14, 15]. The ratio $I_{2D}/I_G \sim 2$–3 is for monolayer graphene, $2 > I_{2D}/I_G > 1$ for bilayer graphene and $I_{2D}/I_G < 1$ for multilayer one. Based on the ratio $I_{2D}/I_G$ of Raman spectra, it can be concluded that the graphene films grown on the Cu tape at 950 and 1000 °C are multilayers. The graphene films grown at 1000 °C have higher ratio $I_{2D}/I_G$ and lower ratio $I_D/I_G$ compared to those of the graphene films grown at 950 °C. These results show that the CVD temperature of 1000 °C is the optimum temperature for growing high-quality graphene films on the Cu tape surface.
Figure 6. SEM image (a) and Raman spectra (b) of the graphene domains on the surface of the Cu tape after CVD process at 1000 °C for 30 min.

Figure 7. (a) Photo and (b) AFM image of the graphene film after transferring from the Cu tape to the glass substrate.

steps) to form nucleation centers. Detailed description on the effect of Cu surface to the growth of high-quality graphene was also published in [16].

Figure 6(a) shows the SEM image of the graphene domains on the surface of the Cu tape after CVD process at 1000 °C for 30 min. There are two different visibly contrasting regions in the SEM image. The regions with A circle and with B circles are few-layer and multilayer structures, respectively. Figure 6(b) shows the Raman spectra measured on two different points of graphene film. The ratio of $I_{2D}/I_G$ is 0.84 and 0.44 for the few-layer and multilayer graphene film, respectively. The 2D band of the few-layers graphene shifts to short wavelength (at 2650 cm$^{-1}$) compared to wavelength (at 2660 cm$^{-1}$) of the multilayer graphene.

To estimate clearly the thickness of the graphene film, we transferred the graphene film from the Cu tape to glass substrate (figure 7(a)) and measured the difference between the height of the graphene film and the glass substrate using AFM. Figure 7(b) shows the AFM image of the graphene film after transferring from the Cu tape to silicon substrate. AFM image indicates that the thickness of the graphene film was about 5 nm; this means that the grown graphene films are multilayer (about 15 layers). The thickness of the graphene is only 5 nm, so the transmission of the graphene film is very high. We can see clearly the word of IMS-VAST covered by the graphene film (figure 7(a)).

4. Conclusion

Multilayer graphene films were successfully synthesized on the Cu tapes by APCVD method. The quality of the graphene films was improved with increasing CVD temperature. The growth time does not much affect the number of layers of graphene films. CVD temperature of 1000 °C and CVD time of 30 min are the optimum temperature and time for growing high-quality graphene films on the Cu tape, respectively. The graphene films were successfully transferred from the Cu tape to other substrates by wet etching Cu with a solution of iron(III) nitrate. This opens a promising way for application of graphene films in LCD, OLED electronic devices, in gas detectors and biosensors.

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