Journal of Crystal Growth 425 (2015) 177–180

Contents lists available at ScienceDirect

Journal of Crystal Growth

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

Transferring-free and large-area graphitic carbon film growth by using molecular beam epitaxy at low growth temperature

Meng-Yu Lin [a,b], Cheng-Hung Wang [c], Chun-Wei Pao [b], Shih-Yen Lin [a,b,*]

[a] Graduate Institute of Electronics Engineering, National Taiwan Univeristy, Taipei, Taiwan, ROC
[b] Research Center for Applied Science, Academia Sinica, Nankang, Taipei, Taiwan, ROC
[c] Institute of Display, National Chiao-Tung University, Hsinchu, Taiwan, ROC

ARTICLE INFO

Available online 3 March 2015

Keywords:
A3. Molecular beam epitaxy
B2. Semiconducting materials

ABSTRACT

Graphitic carbon films prepared by using molecular beam epitaxy (MBE) on metal templates with different thicknesses deposited on SiO_2/Si substrates are investigated in this paper. With thick Cu templates, only graphitic carbon flakes are obtained near the Cu grain boundaries at low growth temperatures on metal/SiO_2 interfaces. By replacing the Cu templates with thin Ni templates, complete graphitic carbon films with superior crystalline quality is obtained at 600 °C on SiO_2/Si substrates after removing the Ni templates. The enhanced attachment of the graphitic carbon film to the SiO_2/Si substrates with reduced Ni thickness makes the approach a promising approach for transferring-free graphene preparation at low temperature by using MBE.

1. Introduction

Since the first discovery of graphene film obtained by the exfoliation method from graphite in 2004 [1], many researchers have studied methods to enlarge the film size and its crystalline quality. Unlike flakes of graphene obtained via the exfoliation method, SiC sublimation and chemical vapor deposition (CVD) on metal templates are two approaches, which have demonstrated large-area graphene growth [2–7]. In the SiC sublimation method, it requires high substrate temperature ~1400 °C during the process to desorb Si atoms from the substrate surface such that the remaining C atoms may undergo graphitization [2–4]. In this case, although the SiC sublimation method can achieve high quality graphene, the high growth temperature and high substrate price become a major concern on its practical application. For the CVD method, Ni and Cu are two metal templates commonly adopted for graphene growth. With the mechanism of C atoms dissolved and precipitated in the Ni templates, high quality graphene films can be observed on the metal surface after high-temperature annealing and fast cooling procedure [5]. However, because the C atoms would only precipitate from the defect locations on the Ni surface, un-uniform layer number of graphene films is usually obtained by using Ni templates. Unlike the growth mechanism of Ni templates, low solubility of the C atoms in Cu foil results in different graphene growth mechanisms of surface migration and self-align arranged construction on Cu foil by using CVD [6,7]. Due to the self-limited process of C atoms, uniform single layer graphene is usually obtained on Cu foil surface by using CVD. However, due to the requests of methane decomposition and C atom dissolution into Ni templates, the growth temperatures of the CVD methods based on Cu and Ni templates are usually up to 1000 °C. The high processing temperature would become a major drawback for the practical application of CVD-prepared graphene films. On the other hand, graphene film transferring from the metal templates to other substrates required for CVD-prepared graphene would usually bring defects such as wrinkles and small holes on the film surface. This would become the other disadvantage of CVD-prepared graphene for practical applications.

Since good crystalline quality and large-area films have been demonstrated on CVD-prepared graphene on metal templates, graphene grown on metal templates can still be very useful if both transferring-free and low growth temperature can be achieved. In one of our previous publications, graphene formation on the interface between Ni templates and the dielectric substrate is observed [8]. The underneath graphene formation mechanism is based on the C atom dissolution and precipitation to the two Ni template surfaces. Therefore, the growth temperature ~1050 °C is required and multilayer graphene is obtained by using this approach. Similar experiment result is also observed by replacing the metal with Cu [9]. Because of its low C solubility, Cu templates show different mechanisms on underneath graphene formation. The C atoms would migrate along the grain boundaries and reach

* Correspondence to: 128 Sec. 2, Academia Rd., Nankang, Taipei 11529, Taiwan. Tel.: +886 2 27873187; fax: +886 2 27873122.
E-mail address: shihyen@gate.sinica.edu.tw (S.-Y. Lin).

http://dx.doi.org/10.1016/j.jcrysgro.2015.02.039
0022-0248/

the interface between metal templates and dielectric substrates. From their result, the processing temperature is reduced to 900 °C, which is mainly due to the request of methane decomposition. Although the growth temperature has decreased 150 °C after replacing the metal from Ni to Cu, the growth temperature is still too high for applications. To decrease the growth temperature, supplying C atoms directly for graphene growth could be the solution. By using the molecular beam epitaxy technique (MBE), the C atoms can be directly supplied by using heated pyrolithic graphite (PG) filament or cracked ethylene and then reach the substrate in atomic form [10–12]. In this case, the growth temperature of the graphene films can be greatly depressed, which could be a major improvement for graphene preparation and applications.

In this paper, graphitic carbon films are prepared by using MBE on metal templates with different thicknesses. With thick Cu templates, C atoms would diffuse to the Cu/SiO_2 interfaces through the grain boundaries and form graphitic carbon films. However, only graphitic carbon flakes are obtained near the boundaries at low growth temperatures. By replacing the Cu templates with thin Ni templates, complete graphitic carbon films with superior crystalline quality is obtained. The results suggest that similar C migration and graphitic carbon film growth mechanisms observed on Cu foil could also be observed on Ni templates given lower carbon solubility at low growth temperatures.

2. Experiment

The samples prepared in this paper are fabricated by using a customer-designed MBE system linked with a thermal coater. The first part of the experiments is focused on the investigations of Cu templates for graphene growth. The preparation procedure is as following: (1) a 600 nm SiO_2/Si substrate is loaded to the thermal coater connected to the MBE chamber, (2) a 300 nm Cu template is deposited on the sample surface, (3) the sample is annealed at 750 °C for 30 min after transferring the sample into growth chamber without exposure to the environment, (4) depositing C atoms on the sample surface for 1 h with different substrate temperatures and (5) removing the Cu templates by using $FeNO_3$ solution after transferring the sample out of the MBE system. During the C atoms deposition, two growth temperatures 400 and 700 °C are adopted. The C source is supplied by using a Riber C filament effusion cell [10]. The other set of graphene growth is done on Ni templates with different thicknesses. The growth procedure is as following: (1) a 600 nm SiO_2/Si substrate is loaded to the thermal coater connected to the MBE chamber, (2) Ni templates with different thicknesses is deposited on the sample surface with exposure to the environment, (3) depositing C atoms on the sample surface for 20 min at 600 °C and (4) removing the Ni templates with HCl solution after transferring the sample out of the MBE system. The Raman spectrums of the films are measured by using a HORIBA Jobin Yvon HR800UV spectrum system equipped with 532 nm laser.

3. Result and discussion

The picture of the Cu template taken under an optical microscope after 750 °C annealing is shown in Fig. 1(a). As shown in the figure, Cu crystal grains are formed on the substrate surface, which would facilitate C atom migration and underneath graphitic carbon growth [9]. After removing the Cu templates, the pictures of the graphitic carbon films formed underneath the metal templates at growth temperatures 400 and 700 °C are shown in Fig. 1(b) and (c), respectively. As shown in Fig. 1(b), only strip-like

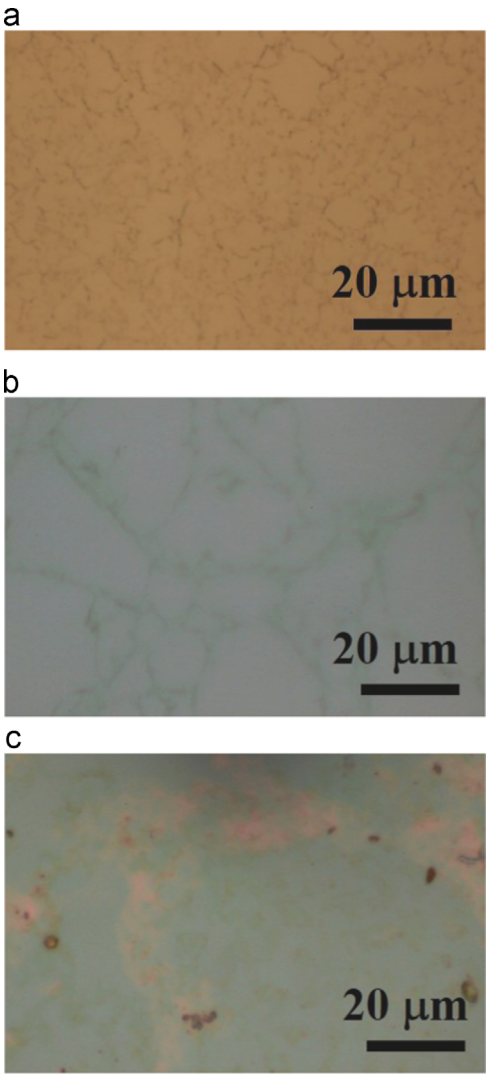

Fig. 1. The optical microscope pictures of (a) the 300 nm Cu template surface after 750 °C annealing and the graphene films formed underneath the metal templates at growth temperatures (b) 400 and (c) 700 °C.

graphitic carbon flakes are observed on the surface for the sample grown at 400 °C. With growth temperature raised up to 700 °C, denser graphitic carbon flakes are obtained on the sample surface. The results suggest that although C source decomposition is no longer required by using the atomic C source in the MBE chamber, higher growth temperature is still required for C atom migration on the Cu/SiO_2 interface for complete film formation [9]. Therefore, when the substrate is grown at 400 °C, the C atoms could only migrate through the grain boundary and accumulate along the grain boundary without further migration away the boundaries. When the growth temperature is raised up to 700 °C, enhanced C atom migration length would be obtained. In this case, instead of accumulating near the grain boundaries, the C atoms would migrate further on the Cu/SiO_2 interface and form denser graphitic carbon flakes.

To further investigate the crystalline quality of the graphitic carbon films, the Raman spectrums of the two samples are shown in Fig. 2. As shown in the figure, for the sample grown at 400 °C, except for the D and G peaks observed at around 1350 and 1590 cm^{-1}, dispersed G peak is also observed at around 1500 cm^{-1} [13]. The results indicate that both sp^2 and sp^3 bonding C structures are observed on the graphitic carbon film. The result indicates that most C atoms are accumulated near the grain