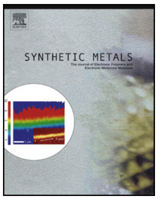
Synthetic Metals 174 (2013) 50–53

Contents lists available at SciVerse ScienceDirect

Synthetic Metals

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



Chemical vapor deposition of amorphous graphene on ZnO film

Xing-ao Li[a], Zhong-ru Liu[b], Bo-lin Wang[b], Jian-ping Yang[a], Yan-wen Ma[a,*], Xiao-miao Feng[a], Wei Huang[a,*], Min-fen Gu[c]

[a] *Institute of Advanced Materials, Nanjing University of Posts and Telecommunications, Nanjing 210046, China*
[b] *School of Optoelectronics Engineering, Nanjing University of Posts and Telecommunications, Nanjing 210046, China*
[c] *Analytical & Testing Center of Nanjing Normal University, Nanjing 210046, China*

ARTICLE INFO

Article history:
Received 28 April 2012
Received in revised form 17 March 2013
Accepted 20 April 2013
Available online 16 May 2013

Keywords:
Amorphous graphene
Zinc oxide
RF magnetron sputtering
Chemical vapor deposition

ABSTRACT

Using ZnO film as catalytic substrate and template, honeycomb-like amorphous graphene film could be prepared from chemical vapor deposition of benzene at 700–800 °C. The special structure of the amorphous graphene film is inherited from the ZnO film since the film grown on Si wafer by radio frequency magnetron sputtering is composed of numerous ZnO nanocrystals. The topography of the as-prepared graphene film was well depicted by scanning electron microscopy and atomic force microscopy. The amorphous characteristic is clearly revealed by the combination of Raman spectrum, transmission electron microscopy and selected area electron diffraction. The possible growth process is also discussed.

1. Introduction

Graphene, a single atomic layer of graphite, is a remarkable carbon material with some unique physical properties and many fascinating applications [1]. To fulfill its practical usage, numerous research efforts have been focus on graphene synthesis and a number of different methods have been developed including mechanical cleavage [1], epitaxial growth on SiC [2], chemical exfoliation [3], and chemical vapor deposition (CVD) [4–10]. Whereas the CVD process is regarded as the most promising approach to large-scale, large-area and low-cost synthesis by the aiding of the catalytically metal substrate, such as Ni and Cu foils. However, the CVD grown graphene on the metal foils needs to transfer to the target substrate after dissolving the metals when applied to electronic and optical devices. This process is complicated and additional contamination is difficult to avoid. In order to eliminate the transfer operation, Rummeli et al. [11] have directly grown graphene-like materials on MgO substrates. Recently, Liu et al. [12] have realized the synthesis of high-quality polycrystalline graphene on SiO_2 films. These intrigue progresses match well with the today's transistor technology in which an oxide layer acts as insulators to separate the transistor gate from the channel. Apart from the dielectric substrate, the direct synthesis of graphene on semiconductor film is also attractive because graphene could act as metal electrode and some novel properties may be found. For example, the graphene/ZnO hybrid structures prepared by the adhesion of graphene on ZnO films have been shown to be a type of surface plasmon resonance materials in the violet-frequency region [13]. Considering the wide optoelectronic applications owned by ZnO, in this study, we attempt to synthesize graphene upon ZnO films by CVD using benzene precursor. At the reaction temperature of 800 °C, amorphous graphene with ~5 layers and corrugated morphology was synthesized. Since amorphous graphene is transparent and metallic [14–16], the so obtained amorphous graphene/ZnO structure is promising for the design of optoelectronic devices.

2. Experimental

2.1. Preparation of ZnO films

100 nm ZnO films were deposited on Si(1 1 1) substrates by radio-frequency (RF) magnetron sputtering (MS500B). Zn (99.999%) was used as target and Si wafer without silicon oxides etched by hydrofluoric acid solution was used as substrates. Before deposition, the base gas pressure inside the chamber was pumped down to less than 1.8×10^{-5} Pa and a pre-sputtering process employed to eliminate the surface pollution. During the deposition processing, pure argon and oxygen gases with the flow rates of 8 sccm and 12 sccm, respectively, were fed into the chamber and

---

* Corresponding authors. Tel.: +86 25 8586 6396; fax: +86 25 8586 6396.
E-mail addresses: iamywma@njupt.edu.cn (Y.-w. Ma), iamwhuang@njupt.edu.cn (W. Huang).

0379-6779/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.synthmet.2013.04.020

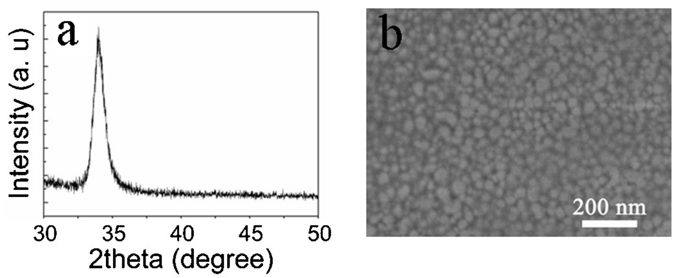


Fig. 1. XRD pattern (a) and SEM image (b) of ZnO films on Si substrates.

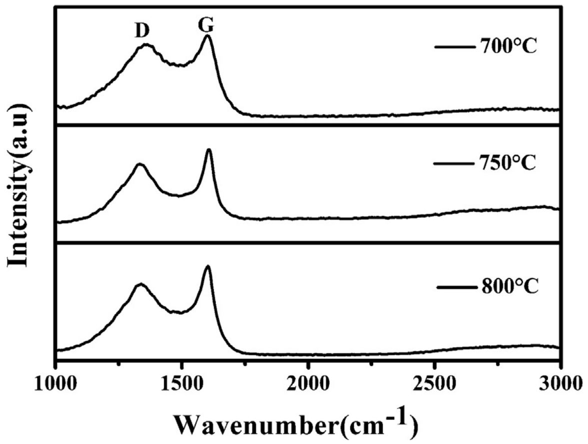


Fig. 2. Raman spectrum of the carbon–ZnO films obtained at 700, 750 and 800 °C.

the gas pressure was maintained at 3 Pa. The RF power is 250 W and the deposition time is 1.5 h.

2.2. Growth of graphene on ZnO films

Graphene deposited onto ZnO film was synthesized by the CVD method. Briefly, ZnO film/Si wafer was placed in a quartz tube furnace and then heated under Ar (40 sccm) from room temperature to target temperature of 700, 750 and 800 °C, respectively at a rate of 10 °C/min. Then 150 μL benzene was injected continuously into the reactor at a rate of 10 μL/min and carried to the reaction zone by the mixture gas for 15 min. After reaction, the reactor was cooled in Ar to room temperature and the product was obtained.

2.3. Characterization

The films were characterized by X-ray diffractomer (D/max-2500/PC), Raman (LABRAM 800) with laser excitation wavelength of 538 nm, scanning electron microscopy (SEM, Hitachi S-4800) and atomic force microscopy (AFM, Nanoscpoe-IIIa). Graphene nanosheet was exfoliated by dissolving the ZnO film in HCl solution (0.5 mol/L), which was used for transmission electron microscopy (TEM, JEM2000EX) characterization.

3. Results and discussion

Fig. 1a shows the XRD pattern of the ZnO film on Si substrate. Only a diffraction peak at 34.00° appears in the pattern, which comes from the (0 0 0 2) plane of a hexagonal wurtzite crystal structure of ZnO, indicating the highly preferential growth of ZnO film along the *c*-axis orientation (perpendicular to the substrate surface). The full width at half maximum (FWHM) of the XRD peak is 1.0°, suggesting that ZnO film comprises many crystallites. The surface morphology of the ZnO film was depicted by SEM image in Fig. 1b. It is seen that the ZnO film is composed of many compacted grains with sizes ranged from 10 to 80 nm, forming a rough surface.

After CVD process, the as-prepared films at 700, 750 and 800 °C were detected by Raman spectrum at first due to its sensitivity to carbon microstructure. Each curve for the three samples shown in Fig. 2 displays two distinct peaks located at around 1350 and 1601 cm^{-1}, ascribing to the D-band and G-band of carbon. The G-band is assigned to one of the two E_{2g} modes originates from stretching vibrations in the carbon–carbon bonds in graphene sheets (sp^2 domains) while the D-band is usually attributed to the amorphous or disordered carbon [17]. The D-band is broad and the G-band significantly shifts to high wavenumber with respect to that of graphite (1582 cm^{-1}) [18], which suggests that all the three carbon films deposited on the ZnO films have low degree of graphitization.

The SEM image of the sample prepared at 800 °C is given in Fig. 3a. It is seen that a large part of ZnO nanocrystals are invisible with respect to the uncoated ones in Fig. 1b. Moreover, some film cracks appear on the surface, clearly indicating that carbon film could grow on the coarse ZnO films. To acquire the topography of the carbon film, we carried out AFM measurements (Fig. 3b). The height variation is about 20 nm, which should come from the template effect of the ZnO nanocrystals and the wrinkles of the carbon film.

The microstructure of the graphene films exfoliated from ZnO films were studied by TEM observation. Fig. 4a–c shows the TEM images of graphene nanosheets prepared at 700, 750 and 800 °C. It is seen that for each sample, a large graphene nanosheet is supported on the holey carbon film. The typical features of these graphene nanosheets are their honeycomb-like film that shown in Fig. 4a and d. The top-view image in Fig. 4d shows that the honeycomb-like graphene film is composed of many bowl-like graphene walls, matches well with the surface topography revealed by AFM image (Fig. 3b). The hole sizes enclosed by the graphene walls are 10–100 nm, similar to the grain sizes of the ZnO crystallites. But the graphene nanosheets are completely amorphous and disorder, which further confirmed by the selected area electron diffraction (SAED, Fig. 4e). The SAED pattern of the carbon film shows only diffraction rings without any diffraction dots, unambiguously suggesting that the graphene sheets are amorphous. The cross-section of the graphene sheets prepared at 800 °C can be observed from its edge and the TEM image is shown in Fig. 4f. It is seen that the curled graphene walls are supported by a graphene flake and an undissolved ZnO nanocrystal is embraced by the graphene walls. These indicate that ZnO is a powerful template to govern the formation of amorphous graphene. The thickness of these walls are 4–5 nm, corresponding to 12–14 graphene layers. The underside amorphous graphene flake is composed of ~5 layers as depicted by the image inserted in Fig. 4f. According to our recent study on the growth of graphene on MgO substrate [19], we can deduce that the layer thickness of graphene depends on synthesis temperature, i.e., higher temperature produce thicker layers. In this case, the layer thickness for the samples prepared at 700,

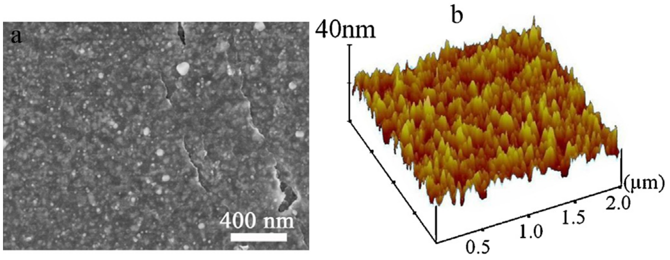


Fig. 3. SEM (a) and AFM images (b) of the carbon–ZnO film prepared at 800 °C.