Applied Surface Science 307 (2014) 327–332

Contents lists available at ScienceDirect

Applied Surface Science

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

Facile synthesis of graphene on single mode fiber via chemical vapor deposition

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ARTICLE INFO

Article history:
Received 16 February 2014
Received in revised form 2 April 2014
Accepted 2 April 2014
Available online 13 April 2014

Keywords:
Graphene
Single mode fiber
Chemical vapor deposition
Gas flow
Carbon nanotubes

ABSTRACT

Direct deposition of graphene film on the standard single mode fiber is offered using a Cu-vapor-assisted chemical vapor deposition system. The gas flow of H_2 and Ar before the growth process plays a crucial role for the direct deposition of the graphene film and the layers of the graphene can be controlled by the growth time. With a large gas flow, Cu atoms are carried off with the gas flow and hard to deposit on the surface of the single mode fiber before the growth process. Consequently, uniform graphene film is obtained in this case. On the contrary, with a lower one, Cu atoms is facile to deposit on the surface of the single mode fiber and form nanodots acting as active catalytic sites for the growth of carbon nanotubes. This method presents us a promising transfer-free technique for fabrication of the photonic applications.

1. Introduction

Graphene as typical sp^2 hybridized carbon has been attracting extensive scientific interest from both experimental and theoretical communities in the recent years. Graphene has been reported by numerous papers on the growth [1–6], properties [7–11], and applications [12–16]. Graphene also shows an extensive range of promising photonic applications. Quite recently, Bao et al. proposed that graphene due to Pauli blocking can provides the ultrafast nonlinear saturable absorption and verified that passive mode-locked fiber laser was obtained by using graphene as saturable absorber [17]. Compared with conventional saturable absorber, such as semiconductor saturable absorber mirror and saturable absorbers based on carbon nanotubes (CNTs), graphene saturable absorber has significant advantages: (1) an ultrafast recovery time (~200 fs); (2) a lower threshold level of the saturable absorption; (3) a broad operating spectral range (covering 300–2500 nm) [18]; (4) a higher damage threshold [18,19]. Up to date, various bulk and fiber lasers have been demonstrated to generate ultrashort pulse using graphene as a saturable absorber [17–27]. With the advantages of facile fabrication, low cost, compact structure and easy integration, fiber laser has caused great attention in the filed of mode locking. To fabricate a graphene saturable absorber serving for the mode locking of fiber laser, there are mainly two different mechanisms: transfer the graphene film to the end fiber facet [22–24] and deposit graphene-polymer composites on the side-polished or tapered fiber with evanescent field interaction [25–27]. However, the fabrication of the graphene saturable absorber with these methods is challengeable and not so straightforward. Before transfer graphene to the fiber, graphene must be fabricated by means of mechanical exfoliation, exfoliation in the liquid phase or chemical vapor deposition (CVD). Consequently, a simple method to directly deposit graphene film on the fiber is much needed.

In this article, an approach for direct deposition of graphene on the standard single mode fiber (SMF) is offered based on the CVD growth route. To the best of our knowledge, it is the first demonstration that the direct deposition of graphene on the surface of SMF, which shows the possibility that the mode locking of fiber laser based on this facilely fabricated graphene saturable absorber can be achieved. The evanescent field interaction mechanism between the oscillated beam and the graphene can be used in this case for the mode locking of the fiber laser.

2. Experimental

As shown in Fig. 1, the experiment was performed in the horizontal quartz tube, where the temperature was set as 1000 °C. A $8 \times 10\,cm^2$ strip of Cu foil serving on the catalyst for the thermal

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http://dx.doi.org/10.1016/j.apsusc.2014.04.035
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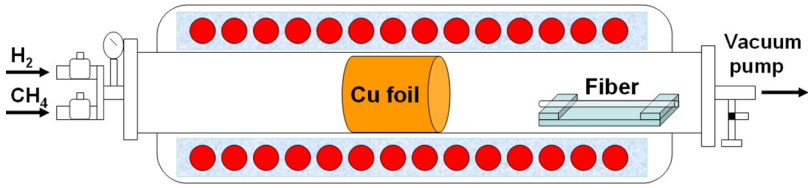

Fig. 1. Schematic of the hot-wall CVD system used in this study.

dissociation of CH_4 was located in the constant-temperature zone and a SMF (silica fiber, ~12 cm in length, 125 μm in diameter) after being treated with acetone and deionized water was located in the downstream zone (~450 °C). Next the horizontal quartz tube was pumped to 1.0×10^{-6} Torr and heated in the meanwhile. When the temperature reached 300 °C, the Cu foil surrounding the tube was annealed in the flow of H_2 and Ar (100 sccm/500 sccm) to remove the remaining copper oxide and prevent the evaporated Cu atoms deposit on the SMF. Subsequently, CH_4 (50 sccm) and H_2 (50 sccm) were introduced for 30 min growth at 1000 °C. Finally, the furnace was cooled down to the ambient temperature rapidly by simply opening the furnace.

Following the growth, the morphology of graphene grown on the SMF was characterized by optical microscopy (Olympus MX51) and scanning electron microscope (SEM, Zeiss Gemini Ultra-55). In order to characterize the crystalline quality and identify the single- and few-layer graphene, we carried out the Raman spectra on the sample with a Horiba HR Evolution 800 Raman microscopy system (laser wavelength 532 nm). We also characterized the sample with a transmission electron microscopy system (TEM, JEM-2100F) and X-ray photoelectron spectroscopy (XPS, ThermoFisher SCIENTIFIC ESCALAB 250).

3. Results and discussion

Fig. 2(a) exhibits the optical image of the SMF after the direct growth of the graphene. A relatively uniform color is appreciated and no rippled or wrinkles structures are detected on the SMF. The color difference between the middle region and the edge is caused by the imperfect focus mode due to the cylinder-shaped structure of the SMF. Typical SEM images of the SMF after the CVD also give us persuasive and striking evidence of the uniform structure of the prepared graphene film. Fig. 2(b) and (c) shows SEM images of the prepared sample under different magnification factor. It is clear that the graphene film still possesses a uniform structure even under a high magnification (Fig. 2(b)). When we further magnify the SEM image, some light-colored dots are detected (Fig. 2(c)). We classify these light-colored dots to the deposited Cu atoms on the SMF. As we known, the color of the SEM image changes with the atomic number in the same sample, a large atomic number corresponding to a bright color. In order to demonstrate our estimate, XPS was carried out on the same sample. Just as expected, a small amount of Cu element was found within the detectable resolution limit (Fig. 2(d)). Although the large flow of H_2 and Ar before the growth process can prevent the evaporated Cu atoms settle on the surface of SMF, it is unavoidable that small amount of Cu atoms deposit on the SMF in the growth process due to the lower flow of H_2 and CH_4. The XPS results are well consistent with our judgment based on the SEM image. Nonetheless, the small amount of Cu element does not reduce its value for applications as a saturable absorber employing the evanescent field interaction [25,26]. We also monitored the transmission characteristic of the SMF by an optical power-meter. There is no obvious change of the output power after the CVD treatment, which implies that the SMF still maintains perfect transmission characteristics.

Raman spectra were performed to detect and characterize the presence of graphene in the surface of the SMF. Fig. 3(a) and (b) shows the $10 \times 10\ \mu m^2$ Raman G and 2D band mappings of a continuous graphene film directly deposited on the SMF. As can be seen from Fig. 3(a) and (b), a relatively smooth G and 2D band mapping with only a little black region indicates that the prepared graphene film features a uniform structure and a micro-scale inhomogeneity. What's more, the Raman G band mapping corresponds well with the 2D band mapping. The Raman spectrum in Fig. 3(c) was taken from the region marked by the yellow dot and arrow in Fig. 3(a). It presents typical characteristics of graphene film: obvious D, G, and 2D bands at 1349, 1583 and 2698 cm^{-1}. The I(G)/I(2D) intensity ratio is ~2.2, and the full width at half maximum (FWHM) of 2D band is ~59 cm^{-1}, which represents three-layer graphene film [28]. Compared with the Raman spectrum of the monolayer graphene [1], the 2D band of the tri-layer graphene is broader and can be fitted into multipeaks, which can be explained by the double resonance theory: the electronic band structure and electron-phonon interactions changes with the number of the graphene layers [29]. The presence of the high D band ~1349 $cm^{-1}$is reasonable. The distance between defects can be estimated, based on the formula $L_a(\text{nm}) = 2.4 \times 10^{-10} \times \lambda^4 \times [I(G)/I(D)]$ [30], to be ~30 nm, where the λ is the excitation laser wavelength (532 nm) and the $I(G)/I(D)$ is 1.6. The laser spot in our case is ~1 μm and covers numerous defects of the nanocrystalline graphene, which spontaneously results in the high D band. The inset in Fig. 3(c) is the Raman spectrum of the SMF before the CVD treatment. As can be seen clearly, there is no related bands of the graphene or graphite, just the bands of the quartz are detected. Combined with the Raman results shown in Fig. 3(c), it is convincible to confirm the graphene deposition on the fiber surface after the CVD treatment. Fig. 3(d) shows the $I(G)/I(2D)$ mapping of the same area in Fig. 3(a) and (b). In most of the directly prepared sample, the Raman $I(G)/I(2D)$ ratios are ~2, which can be accounted as a thin film (~3 layers). These Raman results indicates that the uniform, tri-layer graphene film can be directly fabricated on the SMF substrate. It should be noted that the layers of graphene can be controlled by adjusting the growth time. The monolayer graphene can be obtained with the growth time of 15 min, which can be demonstrated from the Raman spectrum and SAED pattern inserted in Fig. 3(e). The $I(G)/I(2D)$ ratio (~0.41) combined with the SAED pattern (the inner peaks are more intense than the outer ones) confirms the presence of the monolayer graphene [29]. When we further increase the growth time to 22 min, bilayer graphene can be fabricated in this case. The $I(G)/I(2D)$ ratio (~1) and the more intense outer peaks than the inner ones in the SAED pattern (Fig. 3(f)) exhibit us convincible evidences for the presence of the bilayer graphene [29]. As we known, the modulation depth of graphene absorber is reduced with the increase of the layers and the controllable modulation depth allows one to adjust the pulse duration. Graphene films with different thickness have their specific virtue, multilayer graphene is usually favorable for the energy storage and low laser threshold, while monolayer graphene is beneficial to the lower scattering and pulse stability.

It is also possible to investigate the state of the graphene by transferring it to a small holey copper grid using TEM. The graphene