Nano Energy 27 (2016) 114–120

Contents lists available at ScienceDirect

Nano Energy

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

Self-aligned graphene oxide nanoribbon stack with gradient bandgap for visible-light photodetection

Yann-Wen Lan [a,b,c,*], Carlos M. Torres Jr.[b,1], Xiaodan Zhu [b], Chia-Liang Sun [d,e], Shuanglin Zhu [f], Chii-Dong Chen [c,**], Kang L. Wang [b]

[a] National Nano Device Laboratories, Hsinchu 30010, Taiwan, ROC
[b] Department of Electrical Engineering, University of California at Los Angeles, Los Angeles, CA 90095, United States
[c] Institute of Physics, Academia Sinica, Taipei 115, Taiwan, ROC
[d] Department of Chemical and Materials Engineering, Chang Gung University, Tao-Yuan 333, Taiwan, ROC
[e] Department of Neurosurgery, Chang Gung Memorial Hospital, No. 5, Fu-Shing Rd., Guishan, Taoyuan 333, Taiwan, ROC
[f] Department of Materials Science and Engineering, University of California at Los Angeles, Los Angeles, CA 90095, United States

ARTICLE INFO

Article history:
Received 23 February 2016
Received in revised form
12 May 2016
Accepted 21 June 2016
Available online 25 June 2016

Keywords:
Photodetector
Multi-bandgap
Graphene oxide nanoribbon (GONR)
Visible-light
Stacking structure

ABSTRACT

In this work, we demonstrate multi-bandgap photodetectors with an inherently lattice-matched structure by the natural stacking of graphene oxide nanoribbons. The stacked multilayer graphene oxide nanoribbons are produced by unzipping multi-walled carbon nanotubes. A correlation study between image inspection and photoelectrical characterization of stacked graphene oxide nanoribbon devices is performed in specific chips. Transmission electron microscopy images reveal the presence of a multilayer graphene oxide nanoribbon with gradually increasing widths, suggesting that multilayer graphene oxide nanoribbons with decreasing bandgaps could innately act as low-pass photon energy filters and serve to increase the spectral absorption window in these photodetectors. Photoelectrical measurements show visible-light spectrum absorption, which suggests that the various energy bandgaps of the multi-layer graphene oxide nanoribbons contribute toward the increased bandwidth in photon absorption. Furthermore, photo-responsivities on the order of 10 A/W with a stable photo-switching behavior as well as fast response times are observed. The response times range from 2 ms in the membrane devices down to a few hundred of μs in the suspended devices due to elimination of the substrate effect. Based upon this correlation study, we believe that this stacked multilayer graphene oxide nanoribbon structure with gradually varying widths is a promising candidate towards the development of novel high performance photodetectors and optoelectronics.

Published by Elsevier Ltd.

1. Introduction

A wide variety of photoactive semiconductors with appropriate bandgaps are able to detect photons across specific wavelength regimes. For instance, GaN, silicon, and InGaAs are usually utilized for sensing in the ultraviolet, visible, and near-infrared regimes, respectively. The detection of mid-infrared photons typically relies on small-bandgap semiconductor compounds such as HgCdTe, PbS, PbSe, or graphene. In contrast to these conventional bulk semiconductor photo-responsive materials, graphene has attracted significant attention in recent years for its potential applications in next generation optoelectronics, photodetectors in particular, due to its broadband absorption and high carrier mobility [1–3]. Electrons travelling through graphene act as massless Dirac fermions, with carrier mobilities up to 10^6 cm^2/Vs for the suspended case, thus making graphene especially suitable for high-speed applications [4]. The intrinsic response time of graphene photodetectors has been experimentally determined to be 2.1 ps, which translates into a bandwidth of 262 GHz [5], and photodetectors with operational frequencies up to 40 GHz have been demonstrated [6]. Graphene consists of a single monolayer of carbon atoms, which is ideal for applications in ultra-thin, lightweight and flexible electronics. However, the absorption of single layer graphene is limited to 2.3%. Due to this limited absorption, the photo-responsivity of single-layer graphene based photodetectors is restricted to a few mA/W, which is too small for most practical applications [1].

To increase the photo-responsivity, Schottky junctions between graphene and semiconductor materials were implemented with the semiconductor material acting as the absorber, resulting in

* Corresponding author at: National Nano Device Laboratories, Hsinchu 30010, Taiwan, ROC.
** Corresponding author.
E-mail addresses: ywlanblue@gmail.com (Y.-W. Lan), chiidong@phys.sinica.edu.tw (C.-D. Chen).
[1] Present Address: Space and Naval Warfare (SPAWAR) Systems Center Pacific, San Diego, California 92152, United States.

http://dx.doi.org/10.1016/j.nanoen.2016.06.039
2211-2855/Published by Elsevier Ltd.

photo-responsivities on the order of A/W [7,8]. Sensitizing graphene with quantum dots is also effective in significantly improving its photo-responsivity, with reported values up to 10^7 A/W [9]. The response time of these graphene-semiconductor photodetectors are much slower, however, limited by the carrier mobility of the semiconductors. An alternative strategy for improving the photo-responsivity is to utilize the unique electronic property of graphene nanoribbons (GNRs) featuring a bandgap that varies with the nanoribbon width: the larger its width, the smaller its bandgap [10]. This advantage of customizable bandgaps has recently been proposed for the development of GNR-based phototransistors and photodetectors [3,11]. One example of a derivative of graphene materials is graphene oxide nanoribbon (GONR), which also shares similar properties to GNRs. In this work, a novel approach based on the natural stacking of highly transparent GONRs with increasing width layers is proposed to realize broadband absorption for photodetection. The GONRs are produced from unzipping multi-walled carbon nanotubes (MWCNT). Due to the unique multilayer structure with gradually increasing widths, these naturally stacked GONRs feature decreasing bandgaps which results in a higher bandwidth in photon absorption of the incident light. Photodetectors based on these self-aligned gradient bandgap GONR stacks exhibit broadband photodetection in the visible range, featuring a photo-responsivity on the order of 10 A/W with a fast response time of a few hundred μs.

2. Experiment

In this work, two kinds of device platforms were used: the membrane chip (unsuspended) and the through-hole chip (suspended). The membrane chip was constructed by means of photolithography and KOH wet etching to form an area of $40 \times 40\ \mu m^2$ Si_3N_4 membrane (75 nm-thick) locally, without an underlying silicon substrate in the central region of the silicon chip. Based upon this membrane chip platform, the through-hole chip was fabricated by further processing with *e*-beam lithography, dry etching, and thermal evaporation in order to achieve a micron-sized hole with suspended electrodes on a Si_3N_4 membrane. These two kinds of chips allow us to perform a correlated study between image inspection and photoelectrical characterization. The detailed information pertaining to these two chip platforms is referred to in our previous work [15,16]. In order to precisely place carbon nanotubes or GONRs on specific positions, a scanning electron microscope (SEM) based probe station was utilized. In this process, one of the electrodes was grounded beforehand. As the materials attached to the Au-probe were brought closer to the top surface of the grounded electrode, these materials were attracted to and then laid upon the electrodes. Details concerning the SEM-based manipulation method have been described in a previous work [16,17]. Electrical transport was studied using a two-terminal symmetrical circuitry so as to take advantage of the common mode noise rejection. In this measurement setup, a bias voltage (V_b) was applied between the source and drain electrodes, and a source-drain current (I) was measured. Furthermore, a JEOL JEM-2000V UHV TEM was utilized for TEM analysis, while a FEI XL30 Sirion equipped with a Zyvex S100 nanomanipulator was used for the SEM characterization and nanomaterial manipulation.

We commence the study with a control experiment based on a suspended MWCNT device as shown in Fig. 1(a), where the pristine nanotubes were placed on top of parallel metallic electrodes (see the lower inset of Fig. 1(a)). The reason we begin with the MWCNT control experiment is to illustrate that the main difference between the MWCNT and the multi-layered multi-bandgap GONR case is that the photoresponse can be extended to a broader spectral range by unzipping the MWCNTs into GONRs with multiple bandgaps. The active area of the MWCNT device is suspended in air, which eliminates the influence of the substrate on its intrinsic properties. The upper inset of Fig. 1(a) shows the corresponding transmission electron microscopy (TEM) image, which displays a MWCNT with a regular crystalline structure. The main panel of Fig. 1(a) shows the current-voltage (I–V_b) characteristics with and without illumination. Note that the two curves overlap very well, which implies the lack of photoresponse in the pristine MWCNT device. One possible reason for the absence of photoresponse from the MWCNTs could be the involvement of a metallic shell in the carbon nanotubes. Fig. 1(b) shows the formation of naturally-stacked GONRs via the unzipping of MWCNTs. The nanotube-to-nanoribbon transformation was assisted with microwave energy. Based upon a previously published method [12–14], MWCNTs were unzipped to form naturally-stacked GONRs. In order to anticipate light absorption in the visible spectrum, MWCNTs with inner diameters of 2∼4 nm were implemented (see Fig. 1(a)), which roughly corresponds to 10 nm-width nanoribbons ($W = 2\pi r$) that exhibit a bandgap of a few eV after unzipping. The bottom inset of Fig. 1(b) shows a scanning electron microscopy (SEM) image of one of the naturally-stacked GONRs. Since many edges are present in stacked GONRs, both sides of stacked nanoribbons appear bright in the SEM image. Fig. 2(a)–(e) are typical TEM

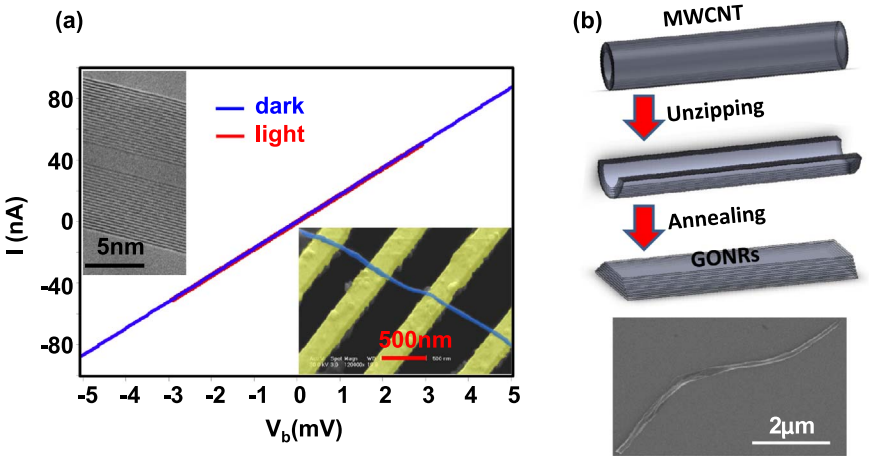

Fig. 1. (a) I–V_b characteristic for the pristine MWCNT with and without illumination. The lower inset shows the false-colored SEM image of the measured suspended device. The upper inset is the corresponding TEM image, showing a regular crystal structure. (b) Representation of the gradual unzipping of the MWCNT to form a multilayer GONR. The bottom SEM image pertains to one of the unzipped MWCNT samples.