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

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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 10A/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.

KEYWORDS

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

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 cm²/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 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 10A/W with a fast response time of a few hundred μ s.

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 $40 \times 40 \text{ } \mu\text{m}^2$ 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-2000 V 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 Figure 1(a), where the pristine nanotubes were placed on top of parallel metallic electrodes (see the lower inset of Figure 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 Figure 1(a) shows the corresponding transmission electron microscopy (TEM) image, which displays a MWCNT with a regular crystalline structure. The main panel of Figure 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. Figure 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 ~ 4nm were implemented (see Figure 1(a)), which roughly corresponds to 10nm-width nanoribbons ($W = 2\pi r$) that exhibit a bandgap of a few eV after unzipping. The bottom inset of Figure 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. Figures 2(a)-(e) are typical TEM images of stacked GONRs samples, which reveal both the multilayer GONRs with gradually increasing widths (Figure 2(c)) and the central planar region away from the edges (Figure 2(a) and (b)). In addition, we note that there exist some GONRs with a small width in the central planar regions, as shown in Figure 2(d) and (e), in which case we expect that these narrow nanoribbons (width $\leq 20\text{nm}$) should exhibit large bandgaps ($E_g \geq 1\text{eV}$) in the multilayer GONR structure, corresponding to visible-light spectral range absorption.

Results and discussion

In order to confirm our speculation, we performed a correlation study between image inspection and photoelectrical characterization for each multi-bandgap GONR stack device. The GONRs were positioned on top of the Si_3N_4 membrane window for the membrane chip and on top of the suspended electrodes for the through-hole chip by using an SEM-based nano-manipulator [16,17]. Nano-scaled Ni/Au electrodes deposited by standard *e*-beam lithographic technique were subsequently placed on top of the stacked GONRs for the membrane chips. The substrate effect will be discussed later when we compare these two cases (e.g. membrane versus through-hole chip). The inset in Figure 3(a) shows two stacked GONR devices on the same membrane chip. The main panel of Figure 3(a) displays the rectified $I-V_b$ curves with and without illumination for one of the multi-bandgap GONR photodetectors in which the two measured electrodes are marked by a capital S (source) and D (drain) in the inset. The device geometry implemented

asymmetric contact areas which resulted in the rectified I - V_b characteristics, in contrast to the case of symmetric contacts. It is worth mentioning that similar types of structural-asymmetry induced rectification in the I - V_b characteristics of nanodevices with different contact areas were previously reported [18-21]. The photocurrent (I_{ph}) is the difference between the current measured in the dark condition and under illumination. Upon illumination, the stacked multi-bandgap GONR devices exhibit a significant photocurrent as shown in Figure 3(a). We note that since the typical breakdown current density is around $2.8 \times 10^4 \text{ A/cm}^2$ at $V_b = +1\text{V}$, the maximum applied drain bias is limited to $V_b = \pm 0.3\text{V}$ or below in this work in order to avoid electrical breakdown of our GONR devices. The TEM image of the measured multi-bandgap GONR stack device is shown in Figure 3(b), which clearly shows the multilayer structure with gradually increasing widths (see the enlarged region). For photocurrent generation to occur, the incident photon energy must be greater than the energy bandgap of the semiconductor. Incident photons with wavelengths corresponding to at least the energy bandgap can excite electrons from the valence band (V) to the conduction band (C) in a semiconductor as shown in the inset of Figure 3(c). Since the widths of the nanoribbons slightly increase in our stacked multilayer GONR photodetectors, this results in the presence of gradually decreasing energy bandgaps in our device structure. The narrower GONRs present in the higher layers of the stacked multilayer GONR structure act as low pass photon energy filters. Thus, a broader spectrum of incident light could be absorbed by the energy bandgaps of the individual GONRs of varying widths in our stacked multilayer GONR photodetectors. Figure 3(c) shows I_{ph} as a function of excitation wavelength at a fixed optical power without applying any bias voltages. Upon illumination in the visible spectral range, our

GONR devices exhibit a photoresponse by generating a photocurrent. Furthermore, the nanoribbons which absorb excitation wavelengths larger than 500 nm primarily dominate in the generation of photocurrent. Hence, there may exist many GONRs with bandgaps ($E_g = hc/\lambda$) smaller than 2.5eV. On the basis of previous theoretical and experimental results [4,22], these bandgaps should roughly correspond to GONR widths of 10nm or wider. Figure 3(d) plots the theoretical GONR widths in terms of their corresponding bandgap energies and cutoff wavelengths. The dashed black curve is the calculated curve described by $E_{gap} = \alpha / (W - W^*)$, where we obtained $\alpha = 9\text{eV nm}$ and $W^* = 8\text{ nm}$ [10]. The GONR widths ranging between 11nm and 14nm, highlighted in yellow in Figure 3(d), are the main contributors in the range of visible light. In our multi-bandgap GONR photodetectors, the corresponding image of the stacked multilayer GNR widths shown in the inset of Figure 3(d) directly corroborates this point. The correlation between these photoelectrical results and the GONR widths observed in the TEM image strongly suggest that the visible light absorption arises due to the presence of narrow widths in our GONRs. This result is reproducible in many devices and a similar correlation between the TEM image and the photoresponse of another stacked multi-bandgap GONR device is shown in Figure S1 (Supporting information). Furthermore, in order to study the photo-switching behavior and the photo-switching rate of our stacked multi-bandgap GONR photodetector, the rate of change of their photoresponse for I_{ph} was recorded at a fixed optical power of 10mW/cm^2 and incident wavelength of $\lambda=500\text{nm}$. The stability of this switching behavior is presented in Figure 4(a), which clearly displays a stable ON-OFF switching behavior for I_{ph} . Moreover, the observed switching duration is quite fast. Both

the rise and the decay times for the measured current are about 2 ms, as shown in Figure 4(b).

In order to exclude the substrate effect, the suspended multilayer GONRs were fabricated on a through-hole chip, as is shown in the inset of Figure 5(a). The dark regions are air gaps in which the active areas of the GONR devices are suspended. The enlarged portion of the leftmost inset of Figure 5(a) is a TEM image of the measured device, which clearly shows a multilayer GONR structure with widths ranging from 10nm to 14nm. Similarly, this range of widths contribute toward absorption in the visible spectral range according to the calculated relation between wavelength (bandgap energy) and ribbon size shown in the main panel of Figure 5(a). Upon illumination in the visible spectral range, the suspended GONR devices exhibit a photoresponse. Figure 5(b) shows the dependence of I_{ph} on the excitation wavelength at a fixed optical power of 100mW/cm^2 . The result is similar to that in membrane chips (e.g. unsuspended case). However, the photoresponse of the suspended multilayer GONR photodetectors is faster and more sensitive than that of the multilayer GONR devices fabricated on a membrane chip. The ON-OFF photo-switching behavior is shown in Figure 5(c). Both the rise and the decay times in the photoresponse are nearly the same, which is about $500\mu\text{s}$. This can be clearly seen in the rise time of the measured I_{ph} , as is shown in the inset of Figure 5(b). In particular, such prompt photo-switching behavior is observed at various optical power intensities. As shown in Figure 5(d), I_{ph} were reproducible for various optical intensities. I_{ph} increased with increasing light intensity when plotted in a logarithmic scale (see the inset of Figure 5(d)), indicating that it saturates at high intensities. More interestingly, upon comparing the two kinds of multilayer stacked GONR photodetectors (e.g.

membrane chip versus through-hole chip), the photoresponse time for the suspended devices is 4 times faster than that of the multilayer GONR devices fabricated on a membrane. We surmise that due to the elimination of some trap states between GONRs and the underlying substrate [23], the suspended multi-bandgap GONR photodetectors yield a faster photoresponse.

The main figures of merit for photodetectors are responsivity (R), specific detectivity (D^*), and signal-to-noise ratio (SNR) [24, 25]. In order to obtain the responsivity (R in A/W) of our GONR photodetectors, the relation between photocurrent and incident light intensity is listed below

$$R = I_{ph} / L_{light} \quad (1)$$

where I_{ph} is the photocurrent and L_{light} is the incident light intensity. To estimate the specific detectivity, we assume that the shot noise from the dark current is the main contribution to the noise[24]; the specific detectivity can be expressed as

$$D^* = R / (2qI_d)^{1/2} = (I_{ph} / L_{light}) / (2qI_d)^{1/2} \quad (2)$$

where q is the absolute value of electronic charge (1.602×10^{-19} Coulombs) and I_d is the dark current. For the SNR, since the signal and the noise are measured in Amperes (measures of amplitudes), SNR is given by

$$SNR_{dB} = 10 \log_{10} [(I_{signal} / I_{noise})^2] = 20 \log_{10} (I_{signal} / I_{noise}) \quad (3)$$

where $I_{signal} = I_{ph}$ is the photocurrent and $I_{noise} = I_d$ is the dark current. Based on the above formulas, R, D^* and SNR for both the unsuspended and suspended multi-bandgap GONR photodetectors are estimated while we fixed λ at 500nm and the voltage bias at zero bias for a device area of about $1.5 \times 10^{-10} \text{ cm}^2$ ($A = 50 \text{ nm} \times 300 \text{ nm}$) and a measured dark current of around 0.1pA. For the unsuspended case with an incident light intensity of

10mW/cm² (using the data in Figure 4(a)), R, D* and SNR are 13.3 A/W, 1.12×10^7 Jones (cm Hz^{1/2} W⁻¹) and 46dB, respectively. For the suspended case with an incident light intensity of 100mW/cm² (using the data in Figure 5(b)), R, D* and SNR are 16.7 A/W, 1.12×10^7 Jones (cm Hz^{1/2} W⁻¹) and 68dB, respectively. Compared to the typical R and D* in both silicon-based and graphene-based photodetectors, the responsivity R (~10A/W) in our multi-bandgap GONR photodetectors is higher than the values in silicon-based (~0.5 A/W) and graphene-based photodetectors (~0.05-0.1 A/W) [26; 27], whereas the specific detectivity (~ 1.12×10^7 Jones) is smaller than those values in both silicon-based (~ 1.52×10^{14} Jones) and graphene-based photodetectors (~ 3×10^{10} Jones) [28]. Furthermore, the concept of SNR is closely related to the linear dynamic range (the maximum linear response divided by the detector noise), which corresponds to photo-sensitivity linearity. The SNR in our multi-bandgap GONR photodetectors is ~ 70dB, which is close to that of InGaAs-based photodetectors (66dB) and slightly lower than that obtained from silicon-based photodetectors (120dB).

Finally, we notice that the photo-responsivities in these two kinds of GONR devices are almost of the same order of magnitude, which is in the range of A/W to a few tens of A/W throughout the entire visible spectral range. These values of photo-responsivity (e.g. $R_{\text{GONR}} \sim 10\text{A/W}$) are comparable with those in the case of Schottky junctions between graphene and silicon or CdSe semiconductor materials [7,8] and even higher than those in commercial silicon-based photodetectors (e.g. $R_{\text{Silicon}} \sim 0.5\text{A/W}$). Figure 6 shows the photo-responsivity versus the response time of commercial visible (e.g. silicon) and infrared (e.g. InGaAs) photodetectors as well as photodetectors based on graphene, monolayer MoS₂, and GONRs (both suspended and unsuspended). It is

evident that GONR-based photodetectors feature an order of magnitude larger photo-responsivity than commercial silicon and InGaAs based detectors, and over 3 orders of magnitude larger photo-responsivity than graphene and monolayer MoS₂-based photodetectors. However, the response time of the GONR-based photodetectors are about 7 orders of magnitude slower than the response time of graphene-based photodetectors and commercial silicon and InGaAs-based photodetectors, yet about 2 orders of magnitude faster than the response time of monolayer MoS₂-based photodetectors. The slow response times of GONR-based and monolayer-MoS₂-based photodetectors can be attributed to the existence of trap states at the interface between the layered materials and the underlying substrates or to the fact that both GONRs and monolayer MoS₂ feature lower carrier mobilities compared to graphene, silicon, and InGaAs. In addition, our GONR-based multi-bandgap photodetectors are quite stable with retainable performance of at least six months. With a fast photoresponse time on the order of a few hundred microseconds, we believe that this stacked multilayer graphene oxide nanoribbon structure with gradually varying widths is a potential candidate for the development of high performance photodetectors and optoelectronics.

In summary, we presented a novel multi-bandgap photodetector based on the innate stacking of GONRs. A correlation analysis between image inspection and photoelectrical characterization was performed. From the TEM images, multilayer stacked GONRs with gradually increasing widths were clearly observed. From the photoelectrical characterization, a photoresponse in the visible spectrum was measured. Based on this correlation study, it was revealed that there exist multi-bandgap GONRs in tune with the spectrally wide-ranged light absorption in our stacked multilayer GONR photodetectors.

In addition, our stacked multilayer GONR photodetectors exhibit photo-reponsivities on the order of 10A/W with stable and fast photoresponse times throughout the entire visible spectral range. Hence, we believe that these innately stacked multilayer multi-bandgap GONRs with gradually varying widths are a good candidate towards the development of novel high performance photodetectors and photo-devices.

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Figure Legends

Figure 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.

Figure 2. TEM images of multilayer graphene nanoribbons. (a) A typical TEM image of stacked multi-bandgap GONRs. (b) The enlarged blue window in (a), shows both the edges and the central planar regions of the GONRs. (c) The enlarged red window in (b), shows a multilayer nanoribbon. (d - e) The enlarged green and orange windows in (a), which shows multilayer nanoribbons with various widths. Blue dashed lines in (a), (d) and (e) indicate the geometric axes in the multilayer GONRs. The red arrows indicate some of the multilayer GONR edges.

Figure 3. Photoelectrical characterization of unsuspended multi-bandgap GONR photodetectors. (a) I - V_b curves for the stacked multi-bandgap GONR photodetectors fabricated on top of a Si_3N_4 membrane chip under white light illumination with a fixed optical power of $1\text{W}/\text{cm}^2$, and in darkness. The inset shows the SEM image of the multi-bandgap GONR devices fabricated on top of the membrane. (b) TEM image of the measured multi-bandgap GONR devices, showing multilayer GNRs with gradually increasing widths. The blue dashed line denotes the geometric axis of the multi-bandgap GONRs. The inset shows the corresponding GONR device indicated by the red window in the inset of (a). (c) I_{ph} as a function of excitation wavelength at a fixed optical intensity of $10\text{mW}/\text{cm}^2$. Inset shows that multilayer graphene nanoribbons with different bandgaps absorb different spectral regions of the incident light spectrum. (d) The calculated relation between wavelength (e.g. bandgap energy) and the ribbon width. The inset is the corresponding TEM image of the ribbon widths marked by the black dashed window in (b) for the measured GONR device.

Figure 4. Photoresponse of unsuspended GONR photodetectors fabricated on top of a Si_3N_4 membrane chip. (a) Photo-switching behavior and (b) photo-switching rate at $\lambda=500\text{nm}$ and a fixed optical power of $10\text{mW}/\text{cm}^2$ in separated devices.

Figure 5. Photoelectrical characterization of suspended multi-bandgap GONR photodetectors. (a) The calculated relation between wavelength (e.g. bandgap energy) and the GONR nanoribbon width. The dashed black curve is described by $E_{\text{gap}}=\alpha/(W - W^*)$ with $\alpha = 9\text{eV nm}$ and $W^*=8\text{ nm}$. The inset is an SEM image of the measured multi-bandgap GONR device and the enlarged image in the left is the corresponding TEM image, showing the multilayer GONR structure with gradually increasing widths. (b) I_{ph} as a function of the excitation wavelength at a fixed optical power of $100\text{mW}/\text{cm}^2$. The inset shows the rise time of the suspended multi-bandgap GONR photodetector. (c) Photo-switching behavior at a fixed optical intensity of $1\text{W}/\text{cm}^2$ and (d) at different optical intensities. The inset of Figure 5(d) shows the dependence of I_{ph} on the incident optical intensity. The blue lines are exponential fits.

Figure 6. Comparison of responsivity versus response time for various photodetectors. [Data points were cited from references 6, 29, 30, 31 and 32].

Fig.1

Fig.2

Fig.3

(b)

Fig.4

Fig.5

Graphical abstract

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

Multi-bandgap photodetectors with an inherently lattice-matched structure by the natural stacking of graphene oxide nanoribbons is demonstrated. TEM images reveal a multilayer graphene oxide nanoribbon with gradually increasing widths. Photoelectrical measurements show visible-light spectrum absorption, which indicates that the various energy bandgaps of the multi-layer GONRs contribute towards the increased bandwidth in photon absorption.