Anomalous photoresponse in the deep-ultraviolet due to resonant excitonic effects in oxygen plasma treated few-layer graphene

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Abstract
Graphene holds great promise for novel optoelectronic devices due its exceptional optical properties. Here we report an anomalous photoresponse due to resonant excitonic effects in oxygen functionalized epitaxial graphene (EG) with gain exceeding $10^4$ in the deep-ultraviolet (DUV) region. The method used to introduce the oxygen adatoms is via mild oxygen plasma treatment. Upon oxygen adsorption, spectral weight transfer occurs and a photoresponse emerges. The photoresponse in the oxygen plasma treated EG (OPTEG) is attributed to the enhancement of the resonant exciton in the DUV and suppression of optical conductivity below it, as evidenced in our spectroscopic ellipsometry measurements. Our result shows that the OPTEG produces large photoconductive gain, high selectivity, and detectivity in excess of $10^{12}$ Jones in the DUV spectral range and can be harnessed to fabricate tunable graphene-based high-gain DUV photodetectors.

1. Introduction

Graphene has been an attractive research field for fundamental science and applications, such as novel photonic and optoelectronic devices, due to its fascinating electronic and optical properties [1–4]. In particular, epitaxial graphene (EG) prepared on silicon carbide (SiC) is a promising substrate material for the development of carbon-based electronics [5,6] and optoelectronics [7] due to its compatibility with large-scale semiconductor processing techniques. High-speed photodetectors based on EG materials have been reported previously [7,8]. Infrared (IR) and ultraviolet (UV) photoconductors based on thin films of reduced graphene oxide (RGO) or graphene nanoribbons have also been demonstrated with device photoreponsivity up to 4 mA W$^{-1}$ for IR light and up to 0.12 A W$^{-1}$ for UV light [9]. RGO is a promising candidate in organic or plastic electronics [10,11]. However, compared to pristine graphene, the electrical property of RGO is poor, thus limiting its ultimate utility in high-performance electronics [12,13]. It has been observed that the attachment of quantum dots on the graphene surface enhances the photoconductivity in the visible range [14–16]. An electro-oxidized multilayer EG based device has shown photoreponsivity up to 200 A W$^{-1}$ in the UV region [17]. However, the acid solution method used could be detrimental to the device performance and the photoreponsivity mechanism is not known. Therefore, an alternative simple, dry method of oxidation to functionalize graphene in devices is needed.

For fundamental science, graphene has been used as a model system to study electronic correlations, i.e. electron-electron (e-e) and electron-hole (e-h) interactions [18]. It has been shown both experimentally [19–25] and theoretically [25–28] that the optical properties of graphene are determined by strong electron-electron...
(e-e) and electron-hole (e-h) interactions yielding resonant excitonic effects in the deep ultraviolet (DUV). Indeed, resonant excitons have been observed in the DUV range and depend on the number of layers [19–21], substrate [21–23,25] or doping with adatoms [24]. However, till now there is no mechanistic study of the photoresponse of functionalized graphene in devices, particularly in the DUV range.

Here, we discover an anomalous photoresponse in the DUV of few layer EG (4–layer) based devices by modifying its optical conductivity using mild dry oxygen plasma treatment. This method, namely oxygen plasma treated EG (OPTEG), introduces a low coverage of oxygen adatoms on EG, which then generates spectral weight transfer in a broad energy range. Such a spectral weight transfer strongly modifies the resonant excitonic effects and activates an anomalous photoconductive response in the DUV range. This new physical phenomenon can be harnessed to produce high-gain, and large area processable graphene based DUV photoductive devices. The controlled low power plasma used in this study does not produce substantial lattice damage in EG. The high-gain, large energy selectivity, and high detectivity (a measure of signal to noise ratio) in the DUV spectral range highlights its potential advantages over Si or other semiconductor DUV photodetectors.

2. Results and discussion

The OPTEG samples were investigated using Raman spectroscopy, synchrotron-based high resolution photoelectron spectroscopy (PES), electrical I-V and spectroscopy ellipsometry measurements. The photoconductive characteristics of OPTEG devices were studied under illumination of white light, and subsequently the spectral photoresponses were investigated.

In Fig. 1, we show the characterization of pristine EG and OPTEG samples using atomic force microscopy (AFM), synchrotron-based photoelectron spectroscopy (PES), and Raman measurements. AFM surface morphology imaging shows similarity between EG and OPTEG samples with no significant peeling or damage of OPTEG sample as compared to pristine EG (Fig. 1a-b). Synchrotron-based high-resolution (energy \( h\nu = 650 \text{ eV} \)) light was used for core level PES measurements of EG and OPTEG samples for wide-scan (Fig. 1c) and C 1s spectra (Fig. 1d-e). We observe the emergence of the O 1s peak (at 532.18 eV) in OPTEG and it indicates the population of oxygen species on the surface. Furthermore, detailed analysis of the C 1s peak (at ~284.6 eV) shows chemisorbed C–O (at ~286.0 eV) and C=O (at ~287.3 eV) species [29,30] on the OPTEG surface. In particular for our OPTEG devices, as representatives for this study, the oxygen plasma treated with relatively longer (40 s) exhibits an enhancement in DUV-detection-gain by a factor of ~2.4. The significant performance characteristics of OPTEG photodetectors are summarised in Table 1. Our findings suggest that the oxygen plasma treated device is most sensitive to DUV light. The gain of our OPTEG devices are several orders of magnitude higher than many photodetectors based on pristine graphene [31], reduced graphene oxide (RGO) materials [32], and many other organic/inorganic semiconducting materials [33–40].

An important figure of merit of a photodetector is detectivity (or sensitivity), which refers to the minimum impinging optical signal that is distinguishable above noise. It is denoted as \( D^* \), and is measured in units of Jones (cm Hz\(^{1/2}\) W\(^{-1}\)). If noise from the dark current is the dominant contribution, the detectivity can be expressed as:

\[
D^* = \left(\frac{A^{1/2}PR}{2qI_d}\right)^{1/2}
\]  

Where \( I_d \) is the dark current, \( q \) is the electron charge. Under illumination at 4.133 eV (DUV light, Fig. 2b), the calculated detectivities of OPTEG1 and OPTEG2 devices (at fixed 2 V bias) are ~1.3 × 10\(^{12}\) Jones and 3.2 × 10\(^{12}\) Jones respectively (see Table 1). The detectivity of our OPTEG device is much higher compared to the detectivity of previously reported photodetectors based on organic (5TmDCA)/inorganic(ZnO) [40] hybrid systems [10\(^{12}\) Jones], many other organic/inorganic systems [34,41,42], and comparable to a commercial InGaAs (10\(^{12}\) Jones) [43] photodetector or high performance AlGaN (3 × 10\(^{12}\) Jones) UV detector, however the OPTEG is much thinner (4-layer graphene only) [44].

We turn now to reveal the physical origins of the anomalous photoresponse observed in the OPTEG devices. The electronic structure and optical conductivity of graphene, which are determined by the interplay of e-h and e-e interactions, can be revealed directly using spectroscopic ellipsometry. We perform spectroscopic ellipsometry measurements on pristine EG, OPTEG1 and OPTEG2 samples, as shown in Fig. 3. For pristine EG, we observe a prominent peak centered ~4.4 eV, which is attributed to the resonant exciton [26]. The resonant exciton in EG is found to be red-shifted as compared to free standing graphene which occurs ~4.6 eV [19]. This suggests that the strength of e-h interactions for pristine EG is ~800 meV yielding to a larger exciton binding energy compared to ~600 meV for free standing graphene, given the interband transition of ~5.2 eV [24,26].
A new, important phenomenon from spectroscopic ellipsometry is that upon oxygen plasma treatment, we observe spectral weight transfer in a broad energy range (Fig. 3). Upon oxygen adsorption, spectral weight transfer occurs from below ~4.5eV to higher energies. As a result, the resonant excitonic peak enhances and shifts toward higher photon energy (or blue-shifted) and the optical conductivity below the resonant exciton is suppressed. Such an anomalous spectral weight transfer is a fingerprint of strong electronic correlations [45-47]. This implies that the oxygen adatoms introduce strong electronic correlations. We note that such optical properties are also rule out the role of other impurities such as OH because the presence of OH might shift the resonant exciton peak toward lower energy accompanied by states at and near Fermi energy as opposed to our observations [48]. Based on our synchrotron PES core level spectra (Fig. 1), various C and O bonds are observed and this may lead to such a spectral weight transfer due to hybridizations [25]. Intriguingly, for the OPTEG2 sample, the optical conductivity is nearly visible around 1.5 eV and thus resonant exciton excitation is dominant. This itself is a new observation and the behaviour of optical conductivity in oxygen-modified epitaxial graphene is different than for single layer graphene previously reported [24]. Furthermore, in contrast to bandgap in graphene oxide (GO) material, we realize that graphene layers in our case are partly oxidized, and it does not result in bandgap creation in OPTEG. Absence of bandgap in OPTEG is further confirmed by electrical measurements (Fig. S2 and Fig. S3, Supplementary) and ultraviolet photoelectron spectroscopy (UPS) measurements (Fig. S4, Supplementary). As such, OPTEG is different from semiconducting GO and photoconductive mechanism in OPTEG can be explained as follows.
The conventional photoresponse in semiconductors is known to occur due to e-h pairing (or exciton formation). When light shines on doped semiconductors, the e-h pairs, which arise from the doping, are created and quickly dissociated generating (local) current. This photoresponse is what has been normally detected in conventional doped semiconductors. The anomalous photoresponse observed in OPTEG is somewhat different. It can be explained by the presence of the resonant exciton. Since the resonant exciton is an intrinsic property of graphene and occurs without any additional doping (hole or electron), the resonant exciton is dominant in optical transitions. However, we do not observe such a photoresponse in pristine EG. This may be because the optical conductivity below the resonant exciton is very high, which may hinder the dissociation of e-h pairs due to interband transitions at lower energies. Furthermore, carrier transition and recombination in pristine graphene is ultrafast (fs or ns), which result in high speed but limits the efficiency in graphene based photodetectors. The adsorbed oxygen molecules in OPTEG can hinder the ultrafast recombination (extending the life time of carriers to the order of one second, Fig. 4) and suppress the optical conductivity below the resonant exciton, leaving the resonant exciton as the dominant optical excitation in the DUV range. Thus, this generates a good platform for the dissociation of resonant excitons, generating a huge photoresponse. Such a scenario is consistent with experimental observations. For OPTEG1 (20 s oxygen plasma treatment), the resonant exciton shifts toward higher energy accompanied by suppression of optical conductivity at lower energy (Fig. 3), while an anomalous photoresponse is then generated (Fig. 2b). For OPTEG2 (40 s oxygen plasma treatment), the resonant exciton shifts toward even higher energy accompanied by further suppression of optical conductivity at lower energy, and this further enhances the photoresponse in the DUV range.

The electrical and photoconductive characteristics of the OPTEG devices are further elaborated (see Fig. S2, Supporting Information). Our findings show that the device undergoes changes in channel resistance (resistance increases ~3 e5 times in treated devices with respect to the pristine EG channel) after oxygen plasma treatments for 20 s and 40 s, and this is expected due to modification of the sp2 graphene network. Fig. 4a-b show the time response of OPEG1 and OPTEG2 devices (at fixed bias 2 V) illuminated with white light (intensity ~ 30 mW cm⁻²). We obtain that the time constants for

<table>
<thead>
<tr>
<th>Active material</th>
<th>Oxygen plasma treatment time (second)</th>
<th>Gain</th>
<th>Photoresponsivity (A W⁻¹)</th>
<th>Detectivity (Jones)</th>
<th>Bias voltage (V)</th>
<th>Reference</th>
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<tr>
<td>OPTEG1</td>
<td>20</td>
<td></td>
<td>1.00 × 10⁴</td>
<td>2.42 × 10³</td>
<td>1.3 × 10¹²</td>
<td>2</td>
</tr>
<tr>
<td>rGO</td>
<td>40</td>
<td>2.23 × 10⁴</td>
<td>5.39 × 10³</td>
<td>3.2 × 10¹²</td>
<td>2</td>
<td>This work</td>
</tr>
<tr>
<td>rGO/TiO₂</td>
<td>–</td>
<td>0.40</td>
<td>0.12</td>
<td>–</td>
<td>–</td>
<td>1</td>
</tr>
<tr>
<td>AlGaN</td>
<td>–</td>
<td>0.75</td>
<td>0.18</td>
<td>6.82 × 10¹¹</td>
<td>5</td>
<td>[42]</td>
</tr>
<tr>
<td>GaN</td>
<td>–</td>
<td>1.2 × 10⁻²</td>
<td>1.2 × 10⁻²</td>
<td>3 × 10¹²</td>
<td>4</td>
<td>[44]</td>
</tr>
<tr>
<td>SiC</td>
<td>–</td>
<td>0.52</td>
<td>0.15</td>
<td>–</td>
<td>–</td>
<td>2</td>
</tr>
<tr>
<td>AlGaN/GaN</td>
<td>–</td>
<td>0.47</td>
<td>0.10</td>
<td>–</td>
<td>50</td>
<td>[50]</td>
</tr>
<tr>
<td></td>
<td>–</td>
<td>2.78 × 10⁴</td>
<td>7.0 × 10⁴</td>
<td>–</td>
<td>100</td>
<td>[51]</td>
</tr>
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</table>

Fig. 2. (a) A schematic of the device showing the OPTEG active region and pristine EG protected underneath two Cr/Au electrodes. (b) Spectral photoresponse acquired from pristine EG (inset), OPTEG1 (red), and OPTEG2 (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Optical conductivity data acquired from pristine EG (Black), OPTEG1 (red), and OPTEG2 (blue) materials. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
rising \(t_r\) and decay \(t_d\) are 7 and 12 s for OPTEG1 and increase to 21 and 41 s for OPTEG2, respectively (Fig. 4a-b). Our findings show that OPTEG photodetector is faster as compared to RGO based UV photodetectors (response time is of the order of minute) reported previously.\(^{32}\) The speed of the OPTEG photodetectors may further be improved by adopting strategies that include i) reduction of device length scale, and ii) coupling high mobility pristine graphene with OPTEG active layers. Fig. 4c shows the photogenerated current \(I_{ph}\) at 2 V bias under different light intensities. The photocurrent grows with light intensity, and tends to saturate at higher intensity of \(~30\ m\ A\) \((\text{Fig. 4d})\). The photocurrent \(I_{ph}\) and light intensity \(F\) can be expressed by \(I_{ph} \propto F^n\), where \(n\) is an exponent, and has a fitted value \(~0.49\) \((\text{Fig. 4d})\) for the OPTEG device. Furthermore, we also observe that the photocurrent in OPTEG devices is saturated (not presented here) at relatively low bias voltage \(~(2\text{–}2.5)\ V\), and we opt for a 2 V bias as an appropriate fixed value to present the photoconductive characteristics throughout the article. At higher bias voltage, the bias induced generation of dark current is enhanced, and can compete with the photogenerated current to saturate it.

### 3. Conclusion

In summary, we have demonstrated that mild oxygen plasma treatment in epitaxial graphene (OPTEG) based devices can be harnessed to produce high-gain deep-ultraviolet (DUV) photodetectors. The OPTEG device exhibits photoconductive gain as high as \(~2 \times 10^{12}\) at 4.133 eV spectral light. Upon oxygen adsorption, spectral weight transfer occurs. It enhances the resonant exciton and suppresses optical conductivity below it yielding an anomalous photoresponse in the OPTEG device. The tunable, large photoconductive gain, high selectivity, and detectivity in range of \(~1 \times 10^{12}\) to \(3 \times 10^{14}\) Jones of the OPTEG devices in the DUV spectral range highlight their potential advantages over Si and many other semiconductor DUV photodetectors. The plasma process on large area processable graphene is compatible with CMOS fabrication processes making it possible to scale up the fabrication of graphene-based high-gain DUV photodetectors.

### 4. Experimental

#### 4.1. Preparation and characterization of epitaxial graphene

Epitaxial graphene (EG) films (~4-layer) were prepared by annealing chemically etched (10% HF solution) high-purity, semi-insulating 4H–SiC (0001) (resistivity \(\geq 10^5\ \Omega\ cm\) and thickness \(~0.37\ mm\), CREE Research Inc.) in ultrahigh vacuum (UHV) above 1100 °C. The EG sample preparation and its characterization using scanning tunnelling microscopy (STM) and Raman measurements are published elsewhere\(^{[7,8]}\). A thermal evaporator was used to deposit Cr(10 nm)/Au(100 nm) metals through a shadow mask onto pristine EG to fabricate two-terminal devices. Subsequently, the EG device with two metal electrodes was mounted in a sample holder for wire-bonding (Fig. S1, Supplementary information). Two copper wires were soldered to the electrodes for device measurements.
4.2. Oxygen plasma treatment

Oxygen plasma (rf power: 6W, oxygen flow rate: 20 sccm) treatments of EG device were performed cumulatively (for 20 s and 40 s) using a reactive ion etching (NTI RIE-2321) system.

4.3. Temporal photocurrent measurements

Temporal photocurrent measurements were performed with an Agilent B2912A precision source/measure unit system, with a xenon arc lamp as white light source. The ON and OFF light switching was performed at 30 and 40 s intervals in OPTEG1 and OPTEG2 devices respectively.

4.4. Spectral photoresponse measurements

We performed spectral photoresponse measurements using a home-built photconductivity measurement setup which consists of a tungsten halogen lamp coupled with a monochromator (iHR320, HORIBA), mechanical chopper, a pyroelectric detector, a preamplifier and two lock-in amplifier (SR830). The light intensity was calibrated with a high sensitivity and spectrally fixed 2 V bias. All the measurements were performed at room-temperature and in ambient environment.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2016.05.026.