High-responsivity turbostratic stacked graphene photodetectors using enhanced photogating

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High-responsivity graphene photodetectors were fabricated using turbostratic stacked graphene, which provided enhanced photogating. Photogating is a promising means of increasing the responsivity of graphene photodetectors, and this effect is proportional to carrier mobility. Turbostratic stacked graphene exhibits higher carrier mobility than conventional monolayer graphene because it has the same band structure as monolayer graphene while preventing scattering by the underlying SiO2 layer. The photoresponse of these devices at a wavelength of 642 nm was approximately twice that obtained for a conventional monolayer graphene photodetector. The results reported show the feasibility of producing high-responsivity graphene-based photodetectors using a simple fabrication technique.

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Graphene is a unique material comprising two-dimensional carbon films with atomic-scale thicknesses, and possesses exceptional optoelectrical characteristics, such as a high carrier mobility and broadband photoresponse. Graphene produced via chemical vapor deposition (CVD) is also much less expensive than compound semiconductors. Thus, it has been proposed that inexpensive, broadband photodetectors exhibiting rapid responses and operating over a wide range of frequencies (from the terahertz to the ultraviolet regions of the electromagnetic spectrum) are feasible. Unfortunately, graphene shows low responsivity, as its optical absorbance is just 2.3%, and so the real-world applicability of this material will require improvements to this property. Dissimilar electrodes, pn-junctions, bolometers, thermopiles, optical cavities, plasmonic resonance, tunneling structures based on dual graphene sheets, nanoribbons, and photogating have all been assessed as means of improving the responsivity of graphene-based photodetectors. Among these, photogating perhaps has the most potential, since this technique can improve the responsivity to a degree that is not possible with standard approaches, including increasing the quantum efficiency. Photogating can be induced by positioning photosensitizers in the proximity of a graphene channel. In this scenario, coupling occurs between incident light and the photosensitizers, which modifies the gate voltage of the channel. Exceptional changes in the electrical signal obtained from the graphene and in the carrier density are possible using this technique. Such devices typically incorporate either quantum dots or Si substrates (n-type or p-type) as photosensitizers. As an example, our group has recently reported the use of InSb and LiNbO3 as substrates for the fabrication of graphene photodetectors based on photogating. These devices exhibit high responsivity and function in the near, middle and long wavelength infrared regions of the spectrum, in addition to the visible region.

The responsivity of graphene photodetectors based on photogating is known to exhibit a high degree of correlation with the graphene carrier mobility. It is therefore important to improve the mobility so as to increase the responsivity. The mobility is mainly determined by the crystallinity of the graphene and the extent of carrier scattering in the support substrate, which can reduce the mobility. Mechanical exfoliation of graphene tends to increase mobility, but it is difficult to exfoliate large surface areas, while the growth of graphene on a single crystal substrate is costly. Various techniques for suppressing carrier scattering by the substrate have also been proposed, such as the use of hexagonal boron nitride (h-BN) or suspended graphene as substrate materials. Unfortunately, neither of these alternatives are suitable for mass production at present. High-quality h-BN can currently only be obtained via mechanical exfoliation, and this technique cannot provide substrates having sizes sufficient for use in actual devices, whereas suspended graphene requires a complicated fabrication procedure and tends to show poor uniformity. For these reasons, our own work has focused on the use of turbostratic stacked CVD graphene. Although multilayered graphene having an orderly AB-type stacked structure tends to exhibit parallel conduction, and hence is highly conductive, this material is also associated with nonlinear band dispersion (as is also the case for bulk graphite), and so the carrier mobility is limited. In contrast, theoretical analyzes have demonstrated that turbostratic multilayer graphene should have a linear band dispersion similar to that for monolayer graphene. In fact, turbostratic stacked graphene transistors have demonstrated higher carrier mobility and greater conductivity values than CVD monolayer graphene. Graphene fabricated using CVD typically comprises grains having random orientations and is polycrystalline. Turbostratic stacking can then be accomplished simply by repeated transfer of graphene monolayers produced by CVD, and it is relatively easy to obtain graphene having the sizes required for mass production of electronic devices (a few inches or more) using CVD. For the above reasons, turbostratic stacked graphene is a viable candidate for use in devices that make use of performance enhancement via photogating, although to date there have been no reports of its application to photodetectors. In the present study, we therefore fabricated turbostratic...
stacked graphene photodetectors enhanced by the photogating effect, with the aim of demonstrating that this method can be employed to obtain high-responsivity, low-cost graphene photodetectors.

Photodetectors incorporating turbostratic stacked CVD graphene were fabricated by first employing CVD to synthesize monolayer graphene on Cu foil. The synthesis was performed over a period of 45 min with a 10 sccm flow of 5% CH₄/95% Ar and a 1600 sccm flow of 3% H₂/97% Ar at 1010 °C. The parameters employed during this CVD step were determined to provide essentially only monolayers of graphene. Poly(methyl methacrylate) (PMMA) was subsequently used to transfer the resulting monolayer to a substrate made of SiO₂/p-type-Si, after which the unit was heated for 1 h at 330 °C in conjunction with a flow of Ar/H₂ to remove any remaining PMMA or other impurities. Following this step, a second graphene monolayer was formed in the same manner on top of the first monolayer on the same substrate. This process was simply repeated to build up the turbostratic stacked graphene. This process is both cost-effective and facile and could potentially be employed on an industrial scale. Using this technique, turbostratic stacked graphene photodetectors having different numbers of layers were fabricated for experimental study. In preparation for experimental trials, four-terminal electrodes consisting of 15 nm thick Ni and 30 nm thick Au layers were deposited on the graphene by thermal evaporation and a lift-off process. The graphene channel (15 μm wide and 7 μm long) in each device was formed by a conventional photolithography process and O₂ plasma etching.

The photoresponse characteristics were investigated by monitoring the source-drain voltage, V_{sd}, and back-gate voltage, V_{bg}, of each unit. All data reported herein were obtained at room temperature by four-terminal measurements, which are not affected by the resistances of the graphene/metal contacts. The photoresponse of each unit was determined in a vacuum chamber at a pressure of 10⁻⁶ Pa, using a 642 nm diode laser with an intensity of 9.66 mW and a spot size of 1 mm. Each unit was irradiated from overhead at a frequency of 0.5 Hz and a duty ratio of 0.6.

Figure 1(a) presents a schematic diagram of the turbostratic stacked graphene photodetector based on photogating fabricated in this work. Figures 1(b) and 1(c) show planar views of the structures of AB stacked and turbostratic stacked graphene. AB stacked multilayer graphene is a stable crystal that exists in nature, while turbostratic stacked graphene does not possess periodicity, as the layers are misaligned with one another either by translation or rotation. The crystal structure of the turbostratic stacked CVD graphene was analyzed using Raman spectroscopy. Previous studies have reported that in the case of AB stacked multilayer graphene, the G’ peaks become asymmetric and broad with an increasing number of layers.⁴⁰⁻⁴² In the case of our turbostratic stacked graphene, the G’ peaks are symmetrical and narrow. Therefore, our turbostratic stacked graphene exhibits linear band dispersion like monolayer graphene, as shown in previous studies.⁴⁰

Figure 2(a) plots the experimentally determined gating responses for CVD monolayer graphene and for two-layer, three-layer, and four-layer turbostratic stacked CVD graphene at V_{sd} = 0.1 V. Note that both the monolayer graphene and two-layer turbostratic stacked graphene photodetectors were modified by vacuum annealing for 32 h so that the maximum field effect mobility was obtained in the vicinity of V_{bg} = −10 V. This was necessary because p-type Si substrates were used, such that enhancement of the light response by photogating was achieved when applying a negative back-gate voltage. The slopes of these plots are seen to increase significantly with an increasing number of layers.

Figure 2(b) plots the field effect mobility, μ_{FE}, for the graphene as a function of V_{bg} at V_{sd} = 0.1 V. These data were calculated using the standard formula:

\[
\mu_{FE} = \frac{dI_{sd}}{dV_{bg}} \times \frac{L}{W \cdot C_{OX} \cdot V_{sd}},
\]

where C_{OX} is the capacitance of the insulator (defined as \(\varepsilon_{SiO_2}\varepsilon_0/t\), where \(\varepsilon_1 = 3.9\) is the relative permittivity of SiO₂, \(\varepsilon_0\) is the permittivity of a vacuum, and \(t = 290\) nm is the insulator layer thickness), W and L are the width and length of the graphene channel (W = 15 μm, L = 7 μm), respectively, and \(I_{sd}\) is the source-drain current. Figure 2(c) plots the hole μ_{FE} as a function of the layer number at V_{bg} = −10 V. The hole μ_{FE} values were determined to be 2000, 2900, 3000 and 3100 cm² V⁻¹ s⁻¹ for the monolayer graphene and the two-layer, three-layer, and four-layer turbostratic stacked graphene, respectively. Previous studies have established that monolayer graphene typically exhibits higher mobility than
multilayer graphene produced via mechanical exfoliation and having well-ordered stacking. The lower mobility of the latter material is attributed to its nonlinear band dispersion, which is similar to the case for a standard semiconductor. In contrast, $\mu_{FE}$ for the turbostratic graphene obtained in the present study through CVD was found to greatly increase as the number of layers was increased [Fig. 2(c)]. Specifically, an increase of approximately 50% in mobility was observed in the case of two or more layers compared to monolayer graphene. This greatly improved mobility is believed to result from reduced carrier scattering and from linear band dispersion. Previous studies have reported that graphene is strongly affected by Coulomb scattering from charge impurities, such as charge inhomogeneity on SiO$_2$ surfaces. In turbostratic stacked graphene photodetectors, carrier scattering caused by SiO$_2$ is suppressed by the lower graphene layers, and so the hole $\mu_{FE}$ saturates after the application of three or more layers. It should be noted that the electron $\mu_{FE}$ is higher for the two-layer device than for the three or more layer devices in Fig. 2(b). This is due to the effect of the removal of water molecules and resist residue, which act as hole dopants on the graphene surface, by vacuum annealing. However, after vacuum annealing the three- and four-layer devices would also exhibit a similar electron $\mu_{FE}$ as that of the two-layer device.

Figure 3(a) shows the gated photocurrent response, $I_p$, as a function of $V_{bg}$, where $I_p$ is the difference between the source-drain current, $I_d$, with and without light illumination. $I_p$ is significantly affected by $V_{bg}$ and is clearly enhanced in the $-V_{bg}$ region as the number of graphene layers increases. The effect of $V_{bg}$ on $I_p$ seen here is consistent with the $\mu_{FE}$ values in the $-V_{bg}$ region shown in Fig. 2(b), and it is also evident that $I_p$ and $\mu_{FE}$ are correlated. These results provide direct evidence that the photoresponse of our devices is enhanced by the photogating effect. The photogating mechanism can be summarized as follows. Upon the application of a negative $V_{bg}$, holes (acting as the majority carriers) migrate to the back gate to form a depletion layer at the interface between the SiO$_2$ and the p-Si. Photocarriers are subsequently generated in this depletion layer by incident light, leading to a slight modulation of the $V_{bg}$ value for the graphene channel. The mobility of carriers in the graphene is extremely high and each layer has an atomic-scale thickness. Therefore, a slight change in the gate voltage can produce an extremely large variation in $I_p$.

Figure 3(b) graphs the variation in $I_p$ with time for the monolayer graphene and the two-layer, three-layer, and four-layer turbostratic stacked graphene photodetectors at $V_{bg} = -10$ V and $V_{sd} = 0.1$ V, which gives the maximum value of $I_p$. The $I_p$ values for the monolayer graphene and two-layer, three-layer, and four-layer turbostratic stacked graphene photodetectors were determined to be 2.6, 3.7, 4.8 and 4.8 $\mu$A, respectively. Thus, the values obtained when using three or more layers of the turbostratic stacked graphene were almost double that for the monolayer. The $I_p$ values are also seen to saturate at three layers, similar to the $\mu_{FE}$ values at $V_{bg} = -10$ V. These results indicate that the carrier scattering caused by SiO$_2$ is suppressed by the lower graphene layers, but that the photogating effect was not shielded by the lower graphene layers. This is because the impact of the change in gate voltage caused by the photogating effect is much larger than the impact of the carrier scattering.

Subsequently, the effect of $V_{sd}$ and the light intensity on the photoresponse was assessed. In all such trials, $V_{bg}$ was constant at $-10$ V. Figure 4(a) summarizes the effect of $V_{sd}$ on $I_p$ for the monolayer graphene and the two-layer, three-layer, and four-layer turbostratic stacked graphene photodetectors. As shown in Fig. 4(a), $I_p$ increased with increasing...
Figure 4(b) shows the dependence of $I_p$ on $V_{sd}$ at different light intensities for the sample with three-layer turbostratic stacked graphene. These data demonstrate that $I_p$ is proportional to $V_{sd}$ and that the responsivity of the device can be effectively tuned. It is evident that turbostratic stacked graphene photodetectors using photogating can maintain a linear relationship between responsivity and $V_{sd}$ regardless of the light intensity. This result indicates that the responsivity can be tuned using the bias voltage, which would be advantageous in the case of image sensor applications.

Figure 4(c) summarizes the effect of the light intensity on $I_p$ at various $V_{sd}$ values for the three-layer turbostratic stacked graphene photodetector. The measurement results are reproducible over the range of the laser powers used in the measurement; therefore, graphene does not undergo optical damage in this range. Figure 4(c) demonstrates that $I_p$ is a logarithmic function of light intensity. This relationship is ascribed to a saturation in the voltage change induced by photogating as the light intensity is increased. Since the photogating effect is based on the modulation of the back gate voltage due to photocarriers generated in the depletion layer of the Si substrate, the modulation effect of the back gate voltage becomes saturated when the light intensity increases. Interestingly, this logarithmic increase is similar to that exhibited by the human eye, suggesting that these turbostratic stacked graphene photodetectors based on photogating can be expected to have a high dynamic range.
In conclusion, this work investigated the fabrication and performance of turbostratic stacked CVD graphene photodetectors using the photogating effect, with the aim of demonstrating high responsivity. The strength of the photogating effect is proportional to the carrier mobility in the graphene. Therefore, improved carrier mobility is critically important for achieving high responsivity. In our devices, the photoresponse at a wavelength of 642 nm was increased roughly twofold compared to monolayer graphene photodetectors. This elevated responsivity of these turbostratic stacked CVD graphene photodetectors is attributed to the high mobility obtained by maintaining a linear band dispersion as well as a reduction in the carrier scattering by SiO2. In addition, the mobility improvement exhibited by the turbostratic stacked CVD graphene was found to saturate at three layers. Therefore, carrier scattering by the substrate can be suppressed by stacking three or more layers. It is apparent that the use of turbostratic stacked CVD graphene is an effective method for large area processing and increasing the responsivity of graphene photodetectors. This work is expected to contribute to the realization of low-cost and mass-producible high-responsivity graphene-based photodetectors.

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