Graphene Optoelectronics based on Antidot Superlattices

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ABSTRACT

Graphene is well known for its outstanding electronic, thermal, and mechanical properties, and has recently gained tremendous interest as a nanomaterial for optoelectronic devices. We review our recent efforts on exfoliated graphene with a particular focus on the influence of graphene’s chiral edges on the electronic and optical properties. We first show that Raman spectroscopy can not only be used for layer metrology but also to monitor the composition of graphene’s zigzag/armchair edges. To elucidate the role of the localized edge state density, we fabricated dye sensitized antidot superlattices, i.e. nanopatterned graphene. The fluorescence from deposited dye molecules was found to quench strongly as a function of increasing antidot filling fraction, whereas it was enhanced in unpatterned but electrically back-gated samples. This contrasting behavior is strongly indicative of a built-in lateral electric field of up to 260 mV accounting for p-type doping as well as fluorescence quenching due to dissociation of electron-hole pairs from attached dye molecules. Our study provides new insights into the interplay of localized edge states in antidot superlattices and the resulting band bending, which are critical properties to enable novel applications of nanostructured graphene for light harvesting and photovoltaic devices.

Keywords: Graphene, Antidot Superlattice, Optoelectronics, Raman Spectroscopy, Nanoribbon, Chirality.

1. INTRODUCTION

Graphene has been recently isolated [1] and shown to exhibit excellent electrical [2,3], thermal [4], mechanical [5] and optical [6] properties. Graphene is mostly known for its outstanding electrical properties such as ultra high mobilities and ballistic transport [7,8]. The addition of a second layer forms bilayer graphene with a largely changed electronic band structure resulting in field-tunable electronic band gaps [9] and strongly suppressed electronic noise [10], which is of interest for applications such as field-effect transistors. Optoelectronic properties and light matter interaction in nanostructured graphene gains increasingly more interest in the research community. Single layer graphene absorbs only 2.3% of the incident radiation in the visible spectrum [11], making it an ideal candidate for the ultimate transparent electrode material [6]. While the first demonstration of ultrafast (100GHz) graphene photodetectors is very promising [12], graphene’s low absorption strongly limits the achievable wall plug efficiency. Consequently, efficient photocarrier separation within graphene as well as exploration of new routes to enhance the device efficiencies becomes particularly important.

Silicon-based technology relies on controlled doping to form a p-n junction which creates a built-in electrical field that facilitates carrier separation. Physical doping of graphene has been previously achieved by addition of...
extrinsic atomic [13,14] or molecular [15,16] species either by adsorption or intercalation into the graphene lattice [14,17]. A potentially simpler way to make graphene a viable material for optoelectronics can be achieved by utilizing lateral electric fields created by Schottky barriers near the source and drain metal contacts [12,18,19] as was previously done in carbon nanotubes [20]. In the presence of such metal contacts it was also observed that nanotube fluorescence can be significantly enhanced [21]. While graphene does not display any exciton emission, quantum dots placed on unpatterned graphene were recently shown to undergo strong fluorescence quenching, which is indicative of energy transfer from the quantum dot exciton oscillator into graphene [22]. Such hybrids between graphene and light harvesting molecules can potentially overcome the low absorption efficiency of bare graphene. Here, nanostructured graphene offers further possibilities to explore light harvesting and carrier separation. One approach is to fabricate graphene nanoribbons (GNRs) which have been shown to display a bandgap. Another approach is to create so called antidot superlattices, i.e., lattices comprised of a periodic arrangement of perforations in the underlying graphene structure. These superlattices were predicted to possess a small band gap [23-26] that can be controlled by the antidot filling fraction [27,28] and an effective p-type doping [29]. In both cases the underlying edge chiralities, i.e. zigzag, armchair, or mixed type edges, are very important since the atomic edge composition influences the electronic structure and thus optical and transport properties [30,31] as well as chemical reactivity [32].

Raman spectroscopy is a nondestructive technique which can be utilized for edge state characterization in exfoliated flakes, GNRs, or antidot superlattices, since the chirality of graphitic edges and the orientation of the crystalline axis have a strong impact on phonon modes localized at the edges [33-36]. For the case of antidot superlattices it was shown that the G-Band in graphene’s Raman spectrum displays a stiffening as well as an energetic shift with increasing antidot filling fraction, which is commensurate with an effective p-type doping [29]. Furthermore, recent theoretical predictions show that the periphery of graphene possesses a nonnegligible density of states $N_{\text{edge}}$ that is spatially localized at the edges and is distinct from the bulk states $N_{\text{bulk}}$ that are present in graphene’s interior regions. Consequently, antidot superlattices provide a natural framework for studying these states and their properties, since the edge states in these systems coexist with the bulk states, unlike in dot lattices, where the ratio of edge to bulk states is small.

In this paper, we review our recent efforts with a particular focus on the influence of graphene’s chiral edges on the electronic and optical properties. We first show that Raman spectroscopy can be used to monitor the composition of graphene’s zigzag/armchair edges utilizing the varying polarization contrast of the G band [37]. To elucidate the role of the localized edge state density we fabricated dye sensitized antidot superlattices. Detailed investigations of the light-matter interaction indicative that the presence of antidot superlattices creates a built-in lateral electric field of up to 260 mV accounting for p-type doping as well as fluorescence quenching due to dissociation of electron-hole pairs from attached dye molecules [38].

2. MONITORING EDGE CHIRALITY WITH RAMAN SPECTROSCOPY

In order to investigate the correlation between graphene’s edge chirality and the corresponding Raman signatures, graphene flakes were mechanically exfoliated from natural graphite and deposited onto pre-patterned p$^+$ silicon wafer with a thermally grown 300 nm silicon oxide. Room temperature Raman spectra were obtained using a
2.33 eV laser diode focused down to about 2 μm spot size. Half wave plates were used to rotate the plane of polarization with respect to the sample in the laser excitation path and to rotate the plane of polarization in the collection path back to its original configuration in order to eliminate any errors introduced by the dependence of the spectrometer's grating and other optical components on the polarization of light. There are four prominent spectral bands of graphene in the wavelength range from 1300-2700 cm⁻¹. Each band can be used as a tool to probe different material characteristics. The G' band around 2700 cm⁻¹ (sometimes referred to as the 2D band) provides unambiguous information about the number of constituent graphene layers [37,39,40]. This phonon band originates from inter-valley scattering of two in-plane transverse optical (iTO) phonons at the K and K' points at the edges of the Brillouin zone [41,42]. The impact of the number of layers on the G' band is shown in Figure 1a. In single-layer graphene, the G' band can be approximated by a single Lorentzian function (Fig. 1a, lower panel), whereas several Lorentzian functions are required in the case of multilayer graphene (Fig. 1a, middle and upper panels), reflecting the splitting of the electronic bands and phonon branches [43]. After peak deconvolution we found that the difference in frequencies of the two dominant subcomponents of the G' band increases with the number of graphitic layers, with values comparable to the ones reported in the literature [39]. Our investigation focuses on exfoliated flakes which have been identified as bilayer graphene.

![Graphene Raman Spectra](image)

**Figure 1** a) Raman spectrum of the G’ band taken from a monolayer (bottom), bilayer (middle), and trilayer graphene flake. b) Polarization dependence of the G band recorded from the interior points of monolayer graphene (black dots), from a predominantly armchair edge (blue triangles), and a predominantly zigzag edge (red squares). c) Polarization dependence of the G band for three different armchair edges. All data are recorded at room temperature using an excitation wavelength of 532 nm.

While the G’ band is useful in layer metrology analysis, the D and D' bands can be used for edge chirality determination. Raman spectra of different edges of bilayer flakes were recorded under the same polarization conditions and selected from a single large area flake. One particular edge was identified as being zigzag using D / D' band spectroscopy (see discussion below) and used as a reference for measuring all subsequent edge angles Θ. Interestingly, several of the edges possess pronounced D (1350 cm⁻¹) and D' (1620 cm⁻¹) bands, while others lack both bands. The D band originates from inter-valley scattering that connects two adjacent K & K' points at the Brillouin zone boundary via a second order process that requires one iTO phonon and a symmetry breaking perturbation such as an armchair edge for its activation [42,44]. Similarly, the D' band is a weak intra-valley transition that requires one iLO phonon and a symmetry break [41,42]. The presence (absence) of these bands has been shown to correspond to armchair (zigzag) chiralities in both single layer graphene [34] as well as HOPG [45]. Based on the fact that the chirality of a given edge changes in multiples of 30°, odd multiples correspond to edges with opposite chirality and
even multiples correspond to edges with the same chirality [34]. Other edges can be identified as either predominantly zigzag or armchair depending if the angle they make with respect to the edge is closer to an even or an odd multiple of 30°. Thus the angle metrology and the correlation with the presence or absence of the D-band allows us to make a distinction between armchair and zigzag edges. However, the D band does not provide unambiguous information about edge purity since it does not change its oscillator strength accordingly and was found not to exhibit strong polarization dependence.

In contrast to the D band, we found that the G band around 1580 cm\(^{-1}\) does provide information about the fractional edge composition [37]. The G band arises from a doubly degenerate intra-valley process that originates from scattering of an iTO phonon or an iLO phonon at the center (Γ-point) of the Brillouin zone [41,42]. For pure zigzag edges, the intensity of the G band is expected to be maximum for an excitation beam polarization that is perpendicular to the edge. Conversely, for armchair edges its intensity maximizes for the incident excitation beam polarization that is parallel to the edge. This phenomenon is still present for mixed edges, however, the degree of the polarization contrast is diminished and is proportional to the amount of mixing of zigzag and armchair boundaries. Purely random edges, i.e. edges comprised of equal amounts of zigzag and armchair boundaries, are not expected to exhibit any polarization dependence [36]. We found that the intensity of the G band of the armchair and zigzag edges has a strong polarization dependence, that is 90° out of phase with respect to each other, as demonstrated in Figure 1b). Furthermore, the G band shows no polarization dependence far from the edges, as shown by the black circles in Figure 1b, obtained at the center of the flake. Similar non-polarized data were obtained at numerous different points away from the edges and across the entire flake. Previous experiments on the G band found a variation in amplitude when scanning across a flake at various interior points [33,46], which is related to Kohn anomalies and an underlying non-uniform strain or deformation potential [47]. Consequently, the lack of polarization dependence at interior points is indicative that the observed phenomenon in our experiments arises from the different allowed and forbidden phonon modes at the edges of the flakes and not from strain-related effects. The presence (absence) of the D band is strongly correlated to 30° multiplicity of the edges as discussed above. This effect originates from the fact that only the longitudinal (transverse) optical phonon mode is a Raman active mode near the armchair (zigzag) edge. Since the physical mechanism that gives rise to the G band originates from scattering of a doubly degenerate iTO and an LO phonon at the zone boundary, the G band should be better suited for mapping edge states with mixed chirality.

To this end we recorded the polarization contrast of the G band for 3 different edges, as shown in Figure 1c. We found strong correlation of the relative intensity change with the multiplicity of those edges. In contrast, the intensity of the D band showed little sensitivity on the incident photon polarization. More precisely, the particular edge which is 90° to the dominant zigzag edge has the highest (50 %) polarization contrast (purple squares in Fig.1c) while edges with 78° and 72° tilt angle display a polarization contrast of 26% (green dots) and 10% (red triangles), respectively. It should be noted that, in all cases, the polarization dependence of the G-band tends to a minimum value, but never vanishes, suggesting that although the edge is comprised of mostly armchair constituents, it is not atomically clean within the detection area. This verifies prior experimental results [34], which show that atomically smooth edges are very rarely obtained using micromechanical exfoliation. As a result, for mixed-state edges we observe that the G band polarization contrast reflects the fractional composition of armchair and zigzag edges and provides thus information about the purity of the edge, which serves as a convenient process monitor to characterize the degree of edge state purity in patterned graphene [37].
3. GRAPHENE ANTIDOT SUPERLATTICES

To elucidate the role of the localized edge state density and its influence on the electronic and optical properties, we introduced a controlled amount of edges by nanopatterning of graphene. Various antidot superlattices were etched onto the exfoliated flakes using electron beam lithography, following an initial Raman characterization to identify the number of layers. Figure 2a shows an antidote superlattice and illustrates the filling fractions \( F = \phi/s \) of antidots, where \( \phi \) is the antidote diameter and \( s \) is the dot separation. In accordance with previous experimental results [29,48,49], the corresponding Raman spectra display an energetic shift and linewidth narrowing of the G-band with increasing filling fraction [38]. The observed stiffening of the G band from initial 16.7 cm\(^{-1}\) in unpatterned graphene to 6.6 cm\(^{-1}\) at a filling fractions of two can be understood in terms of the Landau damping of the phonon mode, while the energetic shift arises from a renormalization of the phonon energy [48,50]. Furthermore, we observed that the energetic shift of the G-band is positively correlated with the shift of the G’-band, which is indicative of an effective p-doping of the underlying graphene layer [51,52]. In contrast, a negative correlation in the energetic shifts of the G and G’ bands would imply n-doping. In order to correlate shift and stiffening of the G-band in antidot superlattices to an underlying carrier density, we fabricated electrically contacted devices without an antidot lattice, as shown schematically in Figure 2b. Using the electrical field effect of the back gate, the sheet carrier density \( \Delta n \) was modulated and the stiffening and energetic shift of the G-band in the unpatterned samples was used to estimate the edge state density in the antidot superlattice. From these data the amount of p-doping in the antidot samples was determined to reach up to 4·10\(^{12}\) cm\(^{-2}\) at a filling fraction of two, and was not found to depend on the number of graphene layers. The large amount of effective p-doping is rather remarkable since neither extrinsic dopants, nor an external gate potential were applied to the antidot samples.

**Figure 2** a) Scanning electron microscope (SEM) image of a graphene antidot superlattice fabricated by electron beam lithography. b) SEM of an unpatterned 2 micron long stripe of graphene with the corresponding contacting scheme to study optical emission and Raman signals under applied source-drain and back-gate bias. c) Schematic explanation Fermi-level pinning which occurs at the periphery were the localized edge states \( N_{edge} \) are located together with a sketch of the resulting band bending.

The remarkable amount of free carriers in the presence of an antidote lattice might originate from an effective electrical field created by the presence of localized edge states. To further investigate the microscopic origin of the observed p-doping we fabricated graphene-dye hybrids. The idea is that the fluorescence and Raman emission of the attached dye molecules can act as an optical monitor for the underlying changes in carrier dynamics and/or the electrical field profile in the nanopatterned graphene flakes. Both, antidot flakes and electrically contacted devices were soaked in a 15 nanomol solution of Rhodamine 6G (R6G). In these experiments, the R6G Raman peaks, the R6G fluorescence, and the Raman signal from graphene were monitored as a function of the antidot filling fraction \( F \) as well as different backgate and source-drain biases on the unpatterned flakes. Our results indicate that the R6G
fluorescence emission around 577 nm is moderately quenched on the unpatterned graphene substrate as compared to the fluorescence on the bare SiO$_2$ wafer. Remarkably, the fluorescence is quenched even more strongly in the region where the antidot superlattices are located. It was found that the amount of R6G fluorescence quenching increases with increasing filling fraction of the antidots. When the relative intensity of the broad fluorescence signal was normalized to the intensity of R6G fluorescence on the bare SiO$_2$ substrate a quenching up to a factor of five for the largest realized filling fraction was estimated. In contrast to the quenching fluorescence signal, the intensity of the Raman signals from both R6G and graphene were found to increase six-fold with increasing filling fraction, i.e. increasing density of edge states $N_{\text{edge}}$. The fluorescence quenching may be understood as follows. The incident laser light creates electron-hole pairs in the R6G dye. In the absence of the graphene substrate the electron hole pairs in the dye molecules recombine radiatively, thereby giving rise to the fluorescence signal on the bare SiO$_2$ wafer. It was previously shown that placing quantum dots on top of graphene results in an energy transfer from the dots into the underlying graphene layer [53], resulting in a suppression of blinking from the quantum dots. A similar effect is expected to occur for the R6G molecules on graphene, where the radiative recombination of the excitons in the R6G molecule is suppressed. In our experiments, additional quenching of the fluorescence signal in the antidot regions was observed as described above. The additional quenching can thus be understood to arise from the extra states at the edges $N_{\text{edge}}$, that effectively prevents radiative recombination of the electron-hole pairs, and therefore quench the fluorescence signal. The amount of quenching observed in our experiments is rather remarkable since increasing the antidot filling fraction decreases graphene’s surface area and introduces larger areas of SiO$_2$ into the excitation volume on which the fluorescence is not quenched.

In order to further elucidate the mechanism for fluorescence quenching and the nature of $N_{\text{edge}}$ we fabricated electrically contacted and back-gated graphene flakes, which did not contain an antidote superlattice, as shown in Figure 2b. Varying the backgate voltage, effectively moves the Fermi level in the device thereby affording the possibility of in-situ electron and hole doping of the graphene flake according to $\Delta n_s = C_g (V_g - V_{\text{Dirac}})/e$, where $C_g$ is the gate capacitance, $V_g$ is the applied gate voltage, $V_{\text{Dirac}}$ is the location of the Dirac point, and $e$ is the electron charge [54-56]. Modulating the Fermi level with the backgate creates a free sheet carrier density in the underlying graphene layer. It was found that the intensities of both the Raman peaks as well as the fluorescence signal can be either quenched or enhanced by the applied gate bias, and directly follow the free carrier density in the device. It is evident that the enhancement of the Raman peaks achieved in antidot devices occurs at comparable concentrations of $N_{\text{edge}}$ and sheet carrier densities $\Delta n_s$ in unpatterned samples. Unlike the Raman peaks, the R6G fluorescence is strongly quenched in the nanopatterned samples, whereas it is enhanced in the electrically gated samples. The contrasting behavior of the fluorescence signal is strongly indicative of the different nature of the carriers in the antidot superlattice as compared to unpatterned graphene, and can be used to establish a microscopic mechanism for the observed fluorescence quenching and p-doping in the nanostructured samples.

Two possible mechanisms could be responsible for fluorescence quenching: charge transfer from R6G into the trap states that are created by the additional edge state density or electrical field dissociation of the radiative R6G exciton, which leads to a strong decrease in the exciton recombination rate due to the reduced electron-hole wavefunction overlap in an electric field. Although charge transfer into trap states could account for the decrease of the fluorescence intensity, it cannot explain the observed stiffening and the energetic shift of the G-band phonon in graphene, both of which require an electric field effect [48,49]. In contrast, the field dissociation mechanism explains both phenomena, as well as the absence of fluorescence quenching in unpatterned graphene under back-gate sweeping.
Since the edge states create spatially localized carriers, which are immobile, they would not cause the G-band stiffening. However, their presence effectively pins the Fermi level at the edges, thereby bending the band structure throughout the entire antidot superlattice, since no localized states exist in graphene’s basal plane and the Fermi level must remain continuous, as shown schematically in Figure 2c. This band bending creates an effective potential, i.e. a built-in lateral electrical field, that accounts for the dissociation of the R6G excitons, resulting in the observed fluorescence quenching. In contrast, the vertical back-gate field of the unpatterned graphene device does not lead to band bending, while the created free carrier density can effectively feed the carrier capture into the R6G molecules, causing the observed fluorescence enhancement. The Raman signals are enhanced by the electrical field mechanism providing free carriers in both cases. Finally, the effect of the built-in electrical field may be estimated to first order from the amount of p-doping that it introduces. In graphene, doping is commensurate with the movement of the Fermi level into the conduction or valence bands by the electrical field. The band offset $\Delta E_F$ as a function of doping concentration $n$ is given by $\Delta E = \hbar v_F k_F$, where $\hbar$ is the Planck’s constant, $v_F$ is the Fermi velocity, and $k_F$ is the Fermi wave vector, which in graphene is given by $k_F = \sqrt{\pi n}$. The antidot lattices used in our experiments yielded doping concentrations on the order of $0.5-4 \cdot 10^{12} \text{ cm}^{-2}$, which correspond to band offsets of $\Delta E_F = 90-260 \text{ meV}$. The Fermi level pinning at the localized carrier density in the antidot superlattice is similar to Fermi level pinning of a Schottky barrier at an graphene-metal interface that is used to separate photogenerated carriers in optoelectronic devices based, for example, on carbon nanotubes [12,18,20]. In our case, however, no metal was deposited onto graphene and the pinning occurs at the localized edge states that are a direct consequence of the antidot superlattice.

4. CONCLUSIONS

In summary, we have investigated the influence of graphene’s chiral edges on the electronic and optical properties. It was found that the Raman G band (1580 cm$^{-1}$) in bilayer graphene is particularly sensitive to the laser polarization with its intensity dependence being out of phase by 90º in the armchair and zigzag case. Moreover, we found that the G band polarization contrast reflects the fractional composition of armchair and zigzag edges, providing a convenient optical monitor to characterize the degree of edge state purity in graphene. To elucidate the role of the localized edge state density we introduced a controlled amount of edges by nanopatterning graphene into antidot superlattices. The nanopatterning was found to result in an effective p-type doping which increases with larger filling fractions, as evident from the corresponding Raman signatures. Further, we showed that, after depositing dye molecules on these flakes, the corresponding fluorescence signal is strongly quenched with increasing antidot filling fraction, while the Raman signal is enhanced. These results are indicative to a microscopic mechanism in which the Fermi level becomes pinned at the antidot periphery giving rise to a built-in electric field, which accounts for the fluorescence quenching and the observed p-type doping in nanopatterned graphene. These findings make antidot superlattices of great interest for carbon-based optoelectronics and might be particularly useful for light-harvesting applications such as photodetectors and solar cells requiring efficient field separation of electron-hole pairs.

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