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The Effect of Bilayer Regions on the Response of Epitaxial Graphene Devices to Environmental Gating

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The effect of a bilayer area on the electronic response to environmental gating of a monolayer graphene Hall bar device is investigated using room temperature magnetotransport and scanning Kelvin probe microscopy measurements in a controlled environment. The device is tuned through the charge neutrality point with n-p-n- junctions formed. Scanning Kelvin probe measurements show that the work function of the monolayer graphene decreases more than that of the bilayer area however magnetotransport measurements show a larger change in carrier concentration for bilayer graphene with environmental gating. Interface scattering at the boundary between the monolayer and bilayer regions also affects device response with field-dependent suppression of the conductivity observed near the charge neutrality point. Simultaneous electronic and environmental scanning Kelvin probe measurements are used to build nano-scale maps of the work function of the device surface revealing the areas of greatest work function change with environmental gating.

1. Introduction

Bilayer (2LG) regions are often observed in nominally monolayer (1LG) graphene however, relatively little is understood regarding how 2LG patches affect device response to gating. While the production of epitaxial graphene (EG)¹ on silicon carbide (SiC) with little or no 2LG growth is becoming tangible, ² 2LG islands are, at present, occasionally observed and their effect on device response warrants study. EG is often termed metrology grade graphene

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due to the uniform 1LG graphene produced over the surface and the uniformity of the electronic properties, as such, EG is useful for quantum Hall metrology and has recently been used to verify the universality of the quantum Hall effect.³ At low temperatures magnetotransport measurements of EG devices⁴ show 2LG regions can be either conductive or insulating in the quantum Hall regime depending on the initial and gated carrier density. At room temperature scanning Kelvin probe microscopy (SKPM) has been used to demonstrate the different changes in the work function of 1LG and 2LG on gating due to their different band structure.⁵ We investigate environmental gating effects on the carrier concentration of 1LG and 2LG and the controlled formation of p-n- junctions on a device where 2LG is present. Tuning graphene to near the CNP enables the study of transport where electronic screening is reduced.⁶ For devices with a mean free path approaching the dimensions of the device the probability of scattering from phonons, defects and charged impurities is reduced and scattering at interfaces becomes more dominant,⁷ allowing the study of interface scattering.

Conventional back gating is challenging in EG which is not removed from the SiC substrate, with transfer of the graphene to other substrates altering the electronic properties⁸ and potentially adding structural disorder and contamination with transfer polymers.⁹ EG on the Si- face of SiC is electron doped due to interaction with the underlying buffer layer¹⁰ which is partially bonded to the SiC substrate¹¹. Tuning of the electronic properties of EG has focused on intercalation of graphene; a dramatic reduction in sheet resistivity is observed on intercalation of electron donating FeCl₃ molecules.¹² Angle resolved photoemission spectroscopy of hydrogen intercalated, quasi-freestanding graphene has shown that the buffer layer becomes monolayer graphene and monolayer graphene becomes p-type bilayer graphene after intercalation treatment.¹³ Graphene sensor devices have been demonstrated as ultra-sensitive sensors¹⁴ with the potential to be single molecule detectors.¹⁵ This sensitivity of graphene to environmental gating makes it an attractive method of tuning the carrier concentration.

Environmental gating involves the donation and withdrawal of electrons by the controlled adsorption of gas molecules which shift the Fermi level of graphene. Environmental gating does not require a dielectric giving large effective fields as the distance between the graphene and the gate is reduced. The effective gate voltage is determined by the concentration of adsorbates and the amount of charge transferred by each adsorbed species. The effective

charge (q) or equivalent gate voltage on the graphene device can be tuned from electron doped (net positive q) through the charge neutrality point (net $q = 0$) to hole doped (net negative q) by the adsorption of electron withdrawing gases which counteract the electron donation from the buffer layer.

Controlled environment SKPM of devices allows unparalleled access to the device surface enabling the changing work function of the device to be mapped as it is tuned through the charge neutrality point. While gated transport measurements can be used to show the overall response of the device they do not show nano-scale effects of inhomogeneity on the device response. A combination of controlled environment transport and SKPM measurements is thus useful for understanding the effect of 2LG inclusions and changing contact resistance for sensing applications and enable a nanoscale understanding of gating effects for all graphene devices.

We investigate graphene Hall bar devices fabricated by e- beam lithography from EG on the Si face of 4H SiC. The devices have a carrier concentrations (n) of the order of $\sim 2 \times 10^{12} \text{ cm}^{-2}$ in vacuum and a Hall mobility (μ) on the order of $3000 \text{ V}^{-1} \text{ s}^{-1} \text{ cm}^2$ in ambient conditions at room temperature. The measured devices comprise 1LG and 2LG crosses. A Hall bar was selected with a 2LG region which covers the entire 2LG cross marked in Figure.1. The n was tuned by the controlled desorption of atmospheric oxygen and water vapour and the adsorption of NO_2 in N_2 . The devices were tuned to, and through the charge neutrality point (CNP) with the longitudinal voltages (V_{xx}) between crosses and the Hall voltage (V_{xy}) of each measured cross.

2. Experimental

Hall bar devices were defined by e-beam lithography and plasma etching of the graphene. Markers were deposited onto the graphene film and the enclosed areas were imaged using optical microscopy¹⁶ to determine the location of areas of 2LG. Hall bars were then positioned over areas of 2LG. The devices were cleaned by contact mode atomic force microscopy (AFM) to remove any residual photo resist from the fabrication process and then annealed in vacuum to desorb gaseous adsorbates.

Hall measurements were carried out in controlled environments in field with constant applied current through the device ($I_{channel}$). In order to correct for contact misalignment offsets in the measurements taken on the purely 1LG cross the Hall or transverse voltage (V_H) values at magnetic field $B = 0$ were subtracted and values were averaged for positive and negative

applied $I_{channel}$ for each data point. The effects of contact misalignment and sample inhomogeneity were corrected for crosses with mixed 1 and 2LG by sweeping B between 0 and 0.7T. The Hall coefficient (R_H) is calculated from the slope of the measured V_H for each cross. Due to the time taken to sweep B , each R_H measurement point takes 3 minutes. During gas exposure the V_H changes rapidly during each R_H measurement, as such, the best linear fit was used to calculate R_H .

SKPM measurements were carried out on a NT-MDT environmentally controlled chamber with Bruker PFQNE Si on SiN probes. In order to calibrate the surface potential (SP) measurements it was assumed that the work function of the gold leads did not change. Changes in the measured SP of the gold leads were assumed to be due to a change in the work function of the Si tip and were subtracted from the measured SP values of the device.

3. Results and Discussions

3.1. Device characterization

The device was characterized by AFM and SKPM measurements see Figure. 1 which shows a 2LG area indicated by a brighter region on the SKPM map and outlined in blue on the topography map. The 2LG region covers one cross of the graphene Hall bar device. The topography map shows the step edges of the SiC substrate running at an angle of $\sim 45^\circ$ across the device, the Ti/Au electrodes and the edges of the device which are highlighted in Figure. 1a). For measurements of the 1LG cross a constant $I_{channel}$ was applied with V_{xx} measured between the two 1LG crosses and V_{xy} measured over the central 1LG cross. For whole device measurements $V_{channel}$ was monitored and V_{xy} measured over the central 1LG cross and the right hand side 2LG cross.

Figure 1. a) topography with outline of device and 2LG area highlighted in blue b) SKPM (unbiased) of graphene Hall bar device showing brighter areas corresponding to bilayer regions and darker areas corresponding to gold leads

3.2. Environmental Hall measurements on 1LG cross

Figure 2 shows the 1LG R_{xx} , n and mobility (μ) from Hall measurements taken in increasing concentrations of NO_2 . The large initial response to 250 part per billion (ppb) of NO_2 demonstrates the sensitivity of these devices; a 50% change in resistance is observed in 30 minutes and a 20% increase in resistance in 5 minutes. The device demonstrates a 450% increase in resistance at the CNP when exposed to 42 parts per million (ppm) NO_2 . Increasing surface coverage of NO_2 increases the equivalent positive charge (q^+) in the graphene counteracting the q^- from the buffer layer. When $q^+ = q^-$ the net carrier concentration (n), = 0. For 1LG the R_{xx} passes through a maximum as the n passes through zero. The μ initially increases however, as the n nears zero the μ decreases due to less screening of charge inhomogeneity and electron hole puddle formation.¹⁷ μ passes through zero with n , increasing with further gating and increasing number of holes.

Figure 2.a) 1LG R_{xx} with NO_2 conc. b) 1LG n and μ , (NO_2 concentrations are as in Figure 2a)

3.3. Mean free path of monolayer graphene

The mean free path (l) of the 1LG was calculated using eq. (1)¹⁸ where e is the elemental charge and $\hbar$ is the reduced Planck's constant

$$l = \frac{\hbar}{2e} \frac{\mu}{\sqrt{\frac{n}{\pi}}} \quad (1)$$

If $l < l_{CH}$ the channel length (l_{CH}) transport through the device is expected to be diffusive. Figure 3 shows the calculated conductivity changes ($\sigma = en\mu$) with NO_2 exposure time with values taken from data plotted in Figure, 2b. Figure. 3b shows the relation between the calculated value of l for this device and n . The calculated l of ~ 10 nm indicates that transport through the device and through the n-p- junction is expected to be diffusive rather than ballistic. Mean free paths on the order of 10 nm have been demonstrated for EG devices¹⁹ in agreement with the data presented here.

Figure 3. a) conductivity (σ), mean free path (l) and carrier concentration (n) with time in NO_2 . b) mean free path (l) and conductivity (σ) with varying n . Data is not plotted for the region where divergence of n is observed.

3.4 Effect of 2LG on transport: SKPM measurements

Measuring a 2LG inclusion on a 1LG device has the advantage that the conditions of growth and the post growth processing of the areas are identical for both regions and the difference in the response of each cross is due purely to the difference in layer thickness.

SKPM maps of the device when grounded (Figure 4b) and biased (Figure 4c.) are plotted in Figure 4 along with the topography of the device (Figure 4a). The voltage drop across the device can be visualized as a change in color gradient along the channel. Figure 4d shows potential line profiles taken across the SKPM maps b) and c) from the regions marked with a blue line. The slope of the voltage drop across the channel is linear even in the region of the 2LG area indicating that the 2LG region does not affect the resistance of the channel significantly at this equivalent gating voltage.

Figure 4. a) topography of device b) SKPM of grounded device c) SKPM of biased device, d) extracted line profiles from Figures. 4. a), b) and c)

3.5 Effect of 2LG on transport: Hall measurements

Transport measurements were measured at room temperature; the longitudinal and transverse voltages ($V_{channel}$ and V_H respectively) were recorded. $V_{channel}$ was recorded over the channel length and V_H was simultaneously measured over the central 1LG cross and the 2LG cross while sweeping the magnetic field between 0 and 0.7 T in a controlled environment. R_H is calculated from the slope of the line of the measured V_H with field (B). For each plotted R_H point 20 $R_{channel}$ points in increasing B and 20 in decreasing B were measured. $R_{channel}$ is plotted as a continuous line in Figures 5a) and b). The R_H and the calculated n of the central 1LG cross and the 2LG cross are plotted as a linked scatter plot. The device resistance was monitored in a vacuum environment at $\sim 1 \times 10^{-7}$ mbar until the resistance stabilized ~ 48 hours. Clean, dry nitrogen (Air products, BIP⁺) was introduced into the chamber as a carrier gas. 1ppm NO₂ in N₂ was used to tune the Fermi level of the device from n-type through the CNP to p-type while monitoring the R_H and calculating n for the 1LG and 2LG crosses.

Figure 5. a) $R_{channel}$, R_{H-1LG} and R_{H-2LG} with circled area showing suppression of conductivity with field, b) $R_{channel}$, n_{1LG} and n_{2LG} ,

Figure 5a) shows the $R_{channel}$ and R_H of the central 1LG cross and the 2LG cross. The resistance of the device reaches a maximum when the 2LG area, which dissects the channel, reaches the CNP. Figure 5b shows that the 2LG area reaches the CNP at a shorter time in NO_2 than the 1LG demonstrating a larger change in n , but a smaller change in R_H than the 1LG. SKPM measurements⁵ have shown a larger $\Delta\Phi$ for 1LG than 2LG in increasingly electron withdrawing NO_2 environments due to the narrower density of states of 1LG compared to 2LG.

The overall series resistance of the device is dominated by the most resistive part, with a change in the slope of R_{xx} observed in Figures 5a and b when the 1LG area nears the CNP. The resistance of the device begins to stabilize as the rate of NO_2 adsorption and desorption reaches equilibrium. The R_{xx} increases rapidly on evacuating the chamber and desorption of NO_2 until the CNP is reached. For graphene free from impurities and disorder the Fermi level is expected to lie at the Dirac point with a maximum resistance of e^2/h .²⁰ However, the conductivity at the Dirac point is calculated to be affected by impurity scattering. The presence of disorder leads to the formation of electron and hole puddles¹⁷ which, in turn, leads to non zero conduction at the Dirac point for 1LG²⁰ and 2LG.²¹ Here we show that with environmental gating the maximum measured resistance of the device depends on the speed at which the gating species is adsorbed or desorbed. Different maximum resistivity values are observed when the CNP is reached by introducing NO_2 and when the NO_2 is slowly desorbed in vacuum.

3.6 Field induced conductivity suppression

Suppressed conductivity is observed along the channel with applied B when the device contains an n-p-n- junction and, to a lesser extent, when one area of the device (1LG or 2LG) is close to the CNP, the conductivity change with field is highlighted in Figure 5a and also shown in figure 6). The field induced conductivity suppression is observed as one oscillation in $R_{channel}$ for each V_H measurement point where the field is swept from 0 to 0.66T and back to zero with $R_{channel}$ measured at 40 points. The effect of field on the continuous $R_{channel}$ measurements is enlarged in figure 6a. The increasing V_H and $V_{Channel}$ with field is plotted in Figure 6b when the 2LG is p-type and the 1LG is n-type. The resistance of the device is changing rapidly at this time leading to changing values of V_H and $V_{Channel}$ at zero field.

At the CNP screening is reduced and the effects of scattering become more pronounced.⁶ The observed increase in resistance with field may indicate magnetic scatterers with

paramagnetic, vacancies and adatoms²² reported. Ferromagnetic domain walls²³ and zigzag edge states have also been predicted for graphene.²⁴ The magnetic moment of defects in graphene has been reported to be affected by doping,²⁵ with magnetic moments near the charge neutrality point reversibly switched off by shifting the Fermi energy away from neutral. Conductivity through the device may also be affected by band gap opening which has been reported in bilayer graphene in a perpendicular magnetic field.^{26, 27}

Figure 6. a) enlargement of circled region of figure 5a) b) Response of V_{H-1LG} , V_{H-2LG} and V_{xx} to magnetic field when the 2LG region is p-type and the 1LG region is n-type

Scanning potentiometry measurements²⁸ have demonstrated local perturbations located at 1-2LG boundaries with first principle calculations²⁸ showing an intrinsic 1-2LG wave function mismatch leading to localised high resistance. The doping dependant nature of these localised resonant scattering mechanisms has been proposed²⁹. Conductive atomic force microscopy observations and first principle calculations²⁹ indicate that this wave function mismatch gives rise to strong conduction suppression for energies within a ± 0.48 eV range from the Dirac point. Within this energy range weak wave function coupling of the 1LG π/π^* bands with the first bands of the 2LG region is observed however, matching between the 1LG π/π^* bands and the second bands of the bilayer region is calculated to be almost ideal²⁹.

3.7 NO₂ adsorption: effective gate voltage and NO₂ density of adsorption

The adsorption energy and electron transfer when an NO₂ molecule binds to a graphene supercell has been calculated to be $\sim 0.1e$ per molecule.³⁰ Various configurations of oxygen up or oxygen down type adsorption give relatively similar amounts of charge transfer and similar graphene – NO₂ distances, however the total amount of charge transfer may vary with supercell size.³¹

At the CNP the q^+ from the adsorbed NO₂ is equal and opposite to the q^- from the buffer layer ($q_{BL} = q_{NO_2}$). The density of adsorbed NO₂ molecules (γ_{NO_2}) required to tune the 1LG and

the 2LG to the CNP is calculated along with the effective gate voltage at the CNP. The initial n_{1LG} is $\sim 3 \times 10^{12} \text{cm}^{-2}$, assuming a charge transfer (Δe) per molecule of $0.1e$ per $\text{NO}_{2\text{ads}}$ ³⁰ gives a density of adsorbates $\gamma_{\text{NO}_2} = 3 \times 10^{13} \text{cm}^{-2}$. Using theorized NO_2 –graphene distances (d) of $3.6 \text{\AA}$ ³⁰ the effective gate voltage (V_{eff}) due to the transfer of charge to the NO_2 molecules is calculated; $V_{\text{eff}} = \Delta Q/C$, where C is the capacitance. Assuming a value of $\epsilon_r = 1$ then $V_{\text{eff}} = d\gamma_{\text{NO}_2}\Delta e/\epsilon_0$ giving a $V_{\text{eff}} 1\text{LG} = 19.5 \text{mV}$ and a $V_{\text{eff}} 2\text{LG} = 65 \text{mV}$ assuming a $n_{2\text{LG}}$ of $1 \times 10^{13} \text{cm}^{-2}$. For a SiO_2 dielectric of 300nm thickness and an ϵ_r value of 3.9 the equivalent q required to reach the CNP for 1LG would give a gate voltage of 4.17V , and a gate voltage of 13.91V for 2LG. The larger calculated V_{eff} required for tuning the 2LG area to the CNP and the more rapid change in n of the 2LG suggests either that NO_2 transfers more q to 2LG than 1LG or that more NO_2 is adsorbed on 2LG than 1LG. Different chemical reactivity rates have been reported for 1LG and 2LG^{32, 33}

3.8 Combined electronic and SKPM measurements

The response of the device to NO_2 was investigated with combined electrical and SKPM measurements. Figure 6 a) shows the resistance of the device with V_{xx} applied along the channel and I_{xx} measured along the channel in order to maintain a constant voltage drop over the device during exposure to 1ppm NO_2 in nitrogen. The colored numbers in Figure 6a indicate where scans were taken during environmental gating. The initial vacuum pressure was $\sim 1 \times 10^{-6} \text{mbar}$, 1ppm NO_2 in N_2 was flowed into the chamber the NO_2 concentration was increased to 100ppm after 2 hours. The higher concentration NO_2 was used as the chamber is larger (~ 8 liters) than the chamber used for the Hall measurements (~ 0.5 liters). The resistance of the device increases with NO_2 concentration until the CNP is reached for the 2LG area, the resistance then decreases until the chamber is evacuated. On evacuation the device resistance increases rapidly reaching a maximum at the CNP from which point the resistance decreases again. The increase in resistance on exposure to lab ambient ($20\% \text{ O}_2$ and $70\% \text{ RH}$) is smaller than the increase observed for 100ppm NO_2 demonstrating the smaller charge transfer between O_2 /water vapour and graphene than NO_2 and graphene.

The SKPM maps (Figure 7b) taken at points marked on Figure 7a) show the SP change over the device. In vacuum the 2LG appears darker indicating a larger work function than 1LG. The change in SKPM contrast between 1LG and 2LG in different environmental conditions has been discussed⁵ and is assigned to the faster changing work function of 1LG than 2LG due to the narrower DOS of 1LG. Here we show that the change in SKPM contrast

occurs not at the CNP but at a much higher n , with the contrast inversion occurring between vacuum and very low NO_2 concentrations.

Figure 7c) shows extracted line profiles taken from Figure 7b (marked in blue). The line profiles show the relative decrease in SP of the graphene with NO_2 exposure. The SP of the 2LG remains relatively constant in vacuum, N_2 and in low $\sim 1\text{ppm}$ NO_2 in N_2 whereas the SP of the 1LG drops by 0.25V , the larger change in SP for 1LG than 2LG causes an inversion of the observed SKPM contrast. The contact resistance between the 1LG and the grounded Au contact pad drops with NO_2 exposure as the work function of the graphene become more similar to that of the gold electrode. The difference in measured voltage drop between the graphene and the Au electrode when the device is unbiased and biased is used to calculate a contact resistance of $\sim 4\text{k}\Omega$ in vacuum. The contact resistance lowers with NO_2 exposure with a 0.01V drop measured in 100ppm NO_2 giving a resistance of $\sim 1.5\text{k}\Omega$.

Figure 7. a) R_{channel} measured during environmental SKPM, b) SKPM maps of the device taken at points 1 to 6 marked in Figures. a), c) extracted line profiles from the SKPM maps in b) showing the changing SP with environmental gating.

4. Conclusion

An overview of the room temperature effects of bilayer areas on the response of graphene devices to gating has been presented. Using simultaneous transport and SKPM measurements we have demonstrated nanoscale mapping of the response of the device to gating indicating the areas of fastest change in Φ and mapping resistance as a function of device position in each environment. The effect of non-uniform response to gating in a device where 2LG is present is demonstrated by the formation of p-n-junctions, in this region field dependent interface scattering effects are observed. Hall measurements demonstrate the greater sensitivity of R_{H-1LG} to gating than that of R_{H-2LG} , despite the n of 2LG changing to a greater extent than that of 1LG, making 1LG the preferred material for sensitive chemical sensors. The larger change in n_{2LG} than n_{1LG} indicates that gaseous species interaction with graphene may be thickness dependent.

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