Reconfigurable edge-state engineering in graphene using LaAlO₃/SrTiO₃ nanostructures

Cite as: Appl. Phys. Lett. 114, 123103 (2019); doi: 10.1063/1.5080251
Submitted: 6 November 2018 · Accepted: 10 March 2019 · Published Online: 26 March 2019

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ABSTRACT
The properties of graphene depend sensitively on doping with respect to the charge-neutrality point (CNP). Tuning the CNP usually requires electrical gating or chemical doping. Here, we describe a technique to reversibly control the CNP in graphene with nanoscale precision, utilizing LaAlO₃/SrTiO₃ (LAO/STO) heterostructures and conductive atomic force microscope (c-AFM) lithography. The local electron density and resulting conductivity of the LAO/STO interface can be patterned with a conductive AFM tip [Cen et al., Nat. Mater. 7, 298 (2008)] and placed within two nanometers of an active graphene device [Huang et al., APL Mater. 3, 062502 (2015)]. The proximal LAO/STO nanostructures shift the position of graphene CNP by ~10¹² cm⁻² and are also gateable. Here, we use this effect to create reconfigurable edge states in graphene, which are probed using the quantum Hall effect. Quantized resistance plateaus at ℎ/2 ℎ and ℎ/3 ℎ are observed in a split Hall device, demonstrating edge transport along the c-AFM written edge that depends on the polarity of both the magnetic field and direction of currents. This technique can be readily extended to other device geometries.

Graphene has proved to be a powerful and versatile platform for studying condensed matter phenomena due to the unique honeycomb crystal structure and Dirac fermion behavior of electrons. The unique Dirac cone band structure makes it possible to tune the carrier density continuously between electrons and holes. This duality of carriers in graphene results in many exotic properties of graphene, such as Klein tunneling, edge state mixing, and recently the “wedding cake” structure of quantum Hall states. Central to many of these experimental findings is the ability to control the charge neutrality point (CNP) by electrical gating. Another well-studied two-dimensional electronic system is the LaAlO₃/SrTiO₃ (LAO/STO) heterostructure, which supports a high mobility 2D electron layer with a wide range of additional properties including magnetism, tunable spin-orbit coupling, superconductivity, and BEC-like superconductivity. The two dimensional electron gas (2DEG) on the interface is globally tunable with a back-gate voltage and locally tunable from the top LAO surface using conductive atomic force microscope (c-AFM) tip, when the LAO thickness is close to a critical thickness of ~3 unit cells. Using c-AFM lithography, a wide range of devices on the LAO/STO interface can be fabricated, such as a single electron transistor, a broadband terahertz source and detector, a one-dimensional interference device, and an electron waveguide. This technique can also be applied to other complex oxide heterostructures as well.

There have been efforts to locally control the CNP of graphene on silicon or hexagonal boron nitride (h-BN) substrates using AFM or STM. However, those doping techniques are either non-reversible or can only be performed in ultra-high vacuum and low temperature, which limits the applications. In this work, we demonstrate how local control over the metal-insulator transition in LAO/STO can be used to reversibly pattern interacting edge channels in a proximal graphene layer under ambient conditions. The graphene used in this work is grown from chemical vapor deposition (CVD) on oxygen-free electronic grade copper flattened with a diamond turning machine. Then, graphene is coated with perfluoropolymer Hyflon AD60 and transferred onto the LAO/STO surface with the wet-transfer
Graphene is patterned into Hall bars by standard photolithography. Hylon is removed from graphene with FC-40 after patterning. Particles and contaminants on graphene from wet transfer and photolithography are brushed away using a contact-mode AFM scan sequence. After cleaning, the 4 Å atomic steps of the LAO surface underneath graphene are clearly resolvable. The quality of the graphene is similar to other samples prepared in similar methods, with the mobility $\mu > 10,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 2 K.

Figures 1(a) and 1(b) illustrate the c-AFM writing setup. Graphene is scanned with a conductive doped-silicon tip in the contact mode with a contact force of 15–20 nN and scanning speed between 1 mm/s and 10 mm/s. The bias voltage applied on the tip is set to +17 V (for creating a conductive LAO/STO interface) or −5 V (for restoring an insulating LAO/STO interface while avoiding damage to graphene). After each raster scan of the graphene area, the CNP of the graphene in the written region is shifted. The mechanism for shifting the CNP is believed to be essentially the same as for tuning the LAO/STO interface without graphene. Under ambient conditions, when a positive voltage is applied to the tip while graphene is grounded, water molecules adsorbed on the graphene surface are dissociated into protons and transferred through the graphene and mediate the metal-insulator transition in the LAO/STO while contributing to a shift in the chemical potential in the graphene layer. The CNP can be further shifted by dynamically changing the electron density in the LAO/STO layer.

STO has high dielectric permittivity at low temperature ($\varepsilon_r \sim 10,000$), which enables the graphene to be easily tuned with a back-gate voltage $V_{bg}$ applied to the bottom of the LAO/STO substrate [Fig. 1(b)]. However, this gating method is subject to significant hysteresis [Fig. S1(a), inset], and hence, the back-gate voltage is not a reliable indicator of the doping level with respect to the CNP. In addition, the c-AFM lithography itself will dope the graphene, even when the back-gate voltage is held fixed. For these reasons, we rely on the four-terminal resistance of the graphene to monitor the carrier density change in situ during the c-AFM writing process, which takes place under the condition $V_{bg} = 0$ V (more details are discussed in the supplementary material). Once the c-AFM writing is finished, the sample is immediately stored in vacuum and cooled to cryogenic temperatures, where the writing is known to persist indefinitely.

To directly illustrate the effect of c-AFM writing, we scan half of the graphene device with $V_{tip} = +17$ V, as shown in Fig. 1(c). The graphene resistance is then measured as a function of back-gate voltage at $T = 2$ K. Figure 1(d) shows a control measurement where the resistance is measured before c-AFM scanning. The peak at $V_{bg} = 5$ V clearly indicates the CNP. Figure 1(e) is measured after c-AFM writing shown in Fig. 1(c), and two peaks can be observed. The additional peak on the left-hand-side is attributed to the c-AFM writing.

The graphene doping from the positively biased c-AFM tip is reversible. After the c-AFM writing and the change in four-terminal resistance are observed, a scan with $V_{tip} = −5$ V voltage on the c-AFM tip will partially remove the previous writing effect. Scans with negative $V_{tip}$ need to be carefully conducted and the c-AFM tip should be connected in series with a 1 MΩ resistor, due to the fact that graphene can be oxidized as the anode.

The carrier density in the LAO/STO-doped graphene device is quantified using the Hall effect. As shown in the inset of Fig. 2(a), a graphene/LAO/STO device is prepared with one graphene Hall cross (Hall B) scanned in the contact mode with the c-AFM tip biased at +17 V 15 times. A second Hall cross device (Hall A) is measured as a control, where no c-AFM lithography is performed. An electrical gate connected to the back of the 1 mm thick STO substrate is used to adjust the overall carrier density of the graphene device. Magnetotransport experiments are performed at $T = 2$ K, in an out-of-plane magnetic field ($B = 1$ T), in order to determine the carrier densities of the two regions. A shift of $\Delta n = 7 \times 10^{11} \text{ cm}^{-2}$ is observed, with the patterned area being more $n$-type. Because Hall Device B is locally gated positively, the CNP is shifted to a lower $V_{bg}$ value (green curve). The carrier densities on both regions can be tuned by the back-gate up to $1 \times 10^{13} \text{ cm}^{-2}$ at $V_{bg} = −10$ V, in part due to the large dielectric constant of STO ($\varepsilon_r \sim 10,000$) at 2 K. The right ends of the curves are less linear and tend to be saturated, due to the shielding effect of the 2DEG on the LAO/STO interface induced by a high positive back-gate voltage. For $V_{bg} < 5$ V, the interface of LAO/STO outside the previously written area is insulating, so the back-gate voltage will not be shielded.

![Diagram](image-url)
When the two adjacent regions have different Berry phase and fourfold degeneracy from electron spin and valley and vanishing longitudinal resistance, as a result of the non-trivial Landau level filling factors, for example, a quantum Hall regime, the mixing and equilibration of edge states from higher filling factors are reflected on the boundary in the middle, and recombined with the state coming from the right on the bottom. When the back-gate voltage is set at the value where the carriers are bipolar, the directions of current are the opposite of each other. As shown in Fig. 3(a), when the back-gate voltage $V_{bg}$ is between $-2$ V and $+6$ V, the resistance $R_{xx1}$ transitions from $h/3e^2$ to 0 and then to $h/3e^2$, while $R_{xx2}$ transitions from 0 to $h/3e^2$ and then to 0, as predicted by the Landauer-Buttiker formalism. When the magnetic field is reversed, the quantization of $R_{xx1}$ and $R_{xx2}$ is switched, because of the reversing of current directions. Figures 3(c) and 3(d) show the swapping of quantization between $R_{xx1}$ and $R_{xx2}$, when the magnetic field is reversed. These results are consistent with the graphene edge-state mixing reported in the literature. The values of resistance plateaus are quite close to theoretical values when the magnetic field is higher than 2 T, suggesting well-defined edge-state quantization.

At sufficiently large magnetic fields, graphene would exhibit quantized Hall resistance of $R_H = \frac{h}{(4n + 2)e^2}$ ($n = 0, 1, 2, \ldots$) and vanishing longitudinal resistance, as a result of the non-trivial Berry phase and fourfold degeneracy from electron spin and valley pseudo-spin. When the two adjacent regions have different Landau level filling factors, for example, a $p-n$ junction in the quantum Hall regime, the mixing and equilibration of edge states will produce a non-zero longitudinal resistance, which follows the Landauer-Buttiker formalism. In our sample, the $\Delta n = 7 \times 10^{11}$ cm$^{-2}$ carrier density difference on the two sides is enough to keep them at adjacent Landau level filling factors. Consequently, these two regions have different edge-channel occupancies. As shown in Fig. 2(b), when both regions have the same polarity, the channels present in both regions would travel across both regions, while the ones from higher filling factors would only circulate in one region. The longitudinal resistances $R_{xx1}$ and $R_{xx2}$ measured from the top and bottom of the sample can be described using the Landauer-Buttiker formalism (details of derivations can be found in the supplementary material).
equilibrium. The quantization features experience a negligible change over the course of the measurement (>10h), indicating that the graphene doping is stable in vacuum, similar to the c-AFM writing on bare LAO/STO.22

In summary, we developed a reversible, spatially controllable graphene doping technique by c-AFM tips on LAO/STO substrates. Graphene edge state mixing in the quantum Hall regime can be observed from with the c-AFM writing. In the future, this technique can be used to locally dope high-mobility graphene with feature sizes as small as 20 nm² and create a new family of reconfigurable graphene metamaterials.

See supplementary material for the details of hysteresis from back-gate voltage sweep, resistance and carrier density of graphene as functions of the back-gate voltage, graphene resistance change during the c-AFM writing process, and the derivations of longitudinal resistances for edge-state mixing.

This research was supported by the Office of Naval Research (N00014-16-1-3152), National Science Foundation and US-Israel Binational Science Foundation (DMR-1609519), and Vannevar Bush Faculty Fellowship program sponsored by the Basic Research Office of the ASD (R&E) and funded by the ONR (N00014-15–1-2847). The work at University of Wisconsin-Madison was supported by the National Science Foundation (DMR-1629270) and the Air Force Office of Scientific Research (FA9550-15–1-0334).

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