

## Gateless $p$ - $n$ Junction Sharpness in Centimeter-Scale Epitaxial Graphene

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We have demonstrated the centimeter-scale fabrication of monolayer epitaxial graphene  $p$ - $n$  junction devices using simple ultraviolet photolithography, thereby significantly reducing device processing time compared to that of electron beam lithography typically used for obtaining sharp junctions. This work presents measurements yielding nonconventional, fractional multiples of the typical quantized Hall resistance at  $\nu = 2$  ( $R_H \approx 12906 \Omega$ ) that take the form:  $a/b \cdot R_H$ . Here,  $a$  and  $b$  have been observed to take on values such 1, 2, 3, and 5 to form various coefficients of  $R_H$ . Additionally, we provide a framework for exploring future device configurations using the LTspice circuit simulator as a guide to understand the abundance of available fractions one may be able to measure. These results support the potential for simplifying device processing time and may possibly be used for other two-dimensional materials.

## I. Introduction

We demonstrate how standard ultraviolet photolithography (UVP) and the photoresist ZEP520A were used to build  $p$ - $n$  junctions ( $pnJs$ ) that have junction widths smaller than 200 nm on devices made from centimeter-scale epitaxial graphene (EG) growths [1-4]. Quantum Hall transport measurements were performed and simulated for various  $p$ - $n$ - $p$  devices to verify expected behaviors of the longitudinal resistances in a two-junction device despite junction roughness [5]. Furthermore, we use the LTspice current simulator [see notes] to examine the various rearrangements of the electric potential in the device when injecting current at up to three independent sites. We find that nonconventional fractions of the typical quantized Hall resistance,  $R_H$ , can be measured, thus validating the simulations. These results have strong importance in the field of resistance standards and general fabrication techniques for other two-dimensional materials [6-8].

## II. Device Fabrication

The growth of high-quality epitaxial graphene can be found in Refs. [9-11]. EG is formed when Si atoms sublime from the silicon face of SiC. Samples were grown on square SiC chips diced from on-axis 4H-SiC(0001) semi-insulating wafers (CREE) [see notes]. SiC chips were submerged in a 5:1 diluted solution of hydrofluoric acid and deionized water prior to the growth process. Chips were placed, silicon face down, on a polished graphite substrate (SPI Glas 22) [see notes] and processed with another photoresist (AZ5214E) to utilize polymer-assisted sublimation growth techniques. The face-down configuration promotes homogeneous growth, and the annealing process was performed with a graphite-lined resistive-element furnace (Materials Research Furnaces Inc.) [see notes]. The heating and cooling rates were about 1.5 °C/s, with the growth performed in an ambient argon environment at 1900 °C.

The grown EG was evaluated with confocal laser scanning and optical microscopy as an efficient way to identify large areas of successful growth [13]. Protective layers of Pd and Au are deposited on the EG to prevent organic contamination. While protected, the EG is etched into the desired device shape, with the final step being the removal of the protective layers from the Hall bar using a solution of 1:1 aqua regia to deionized water. Some variants of this device included electrical contact pads made from NbTiN for lower contact resistances [14-15]. To fabricate the *pnJs*, completed Hall bars were functionalized with Cr(CO)<sub>3</sub> to reduce the electron density to a value close to the Dirac point and on the order of 10<sup>10</sup> cm<sup>-2</sup> [16]. A S1813 photoresist spacer layer was then deposited on a region intended to be preserved as an *n* region. Finally, a 100 nm layer of polymethyl methacrylate (PMMA/MMA) and an approximately 350 nm layer of ZEP520A were deposited. The 100 nm layer was intended to be a mild protectant for EG since ZEP520A is very photoactive and known to reduce the mobility of EG when in direct contact with it (see Figure 1).

### III. Characterization

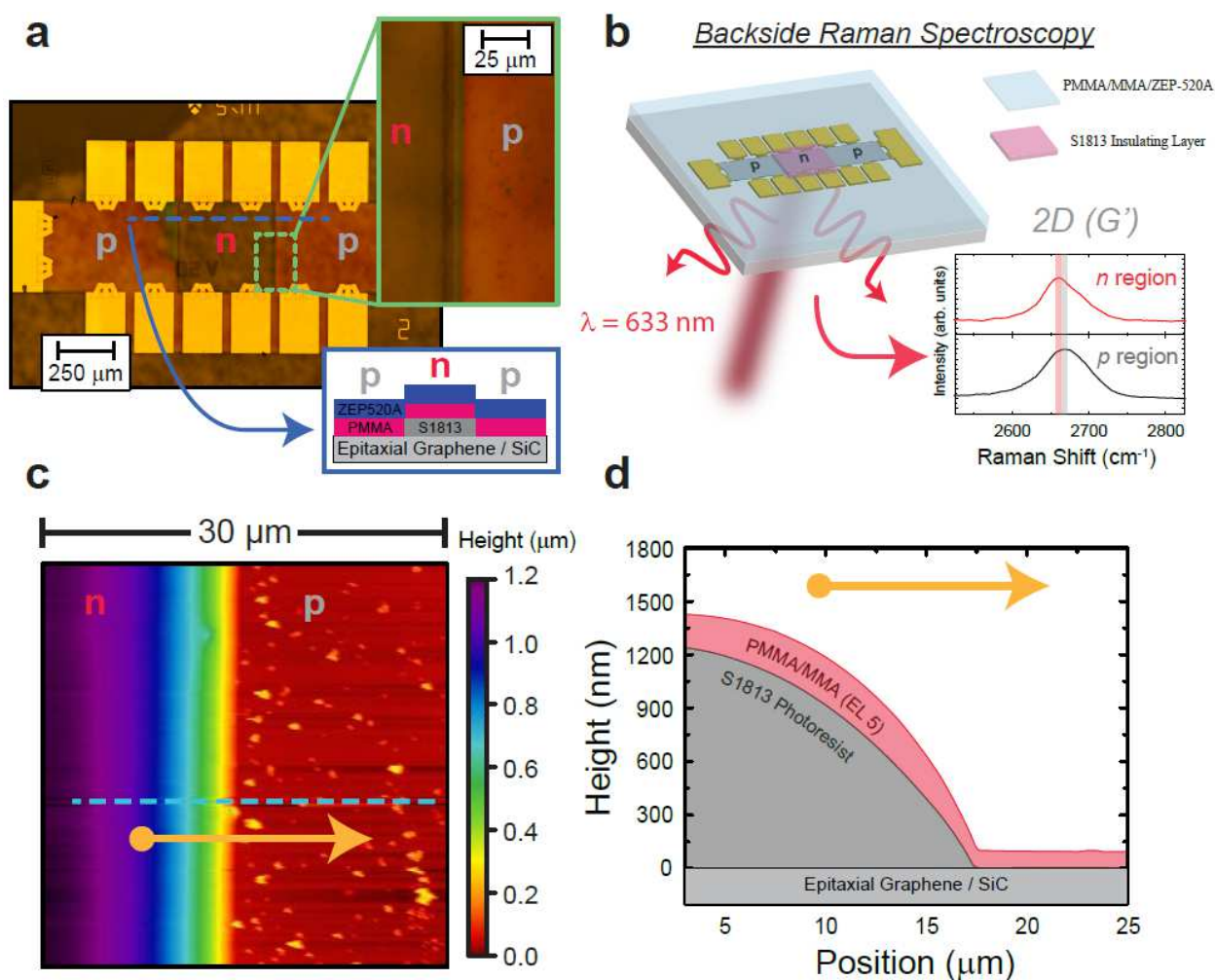


FIG. 1. (Color online) (a) The optical image of the device after processing is shown with labels indicating the intended charge polarity. A cross section of the device is also depicted for clarity. (b) An illustration of the Raman acquisition and a map-averaged 2D ( $G'$ ) spectrum are shown for the  $n$  (red) and  $p$  (gray) regions. The transparent red and gray bands indicate the range (for the corresponding polarity) of 2D ( $G'$ ) peak positions to within  $1\sigma$  of the average. (c) An atomic force microscope image was acquired to gain some insight into how the boundary between the intended  $p$  and  $n$  regions formed. (d) An extracted profile prior to ZEP520A deposition is shown.

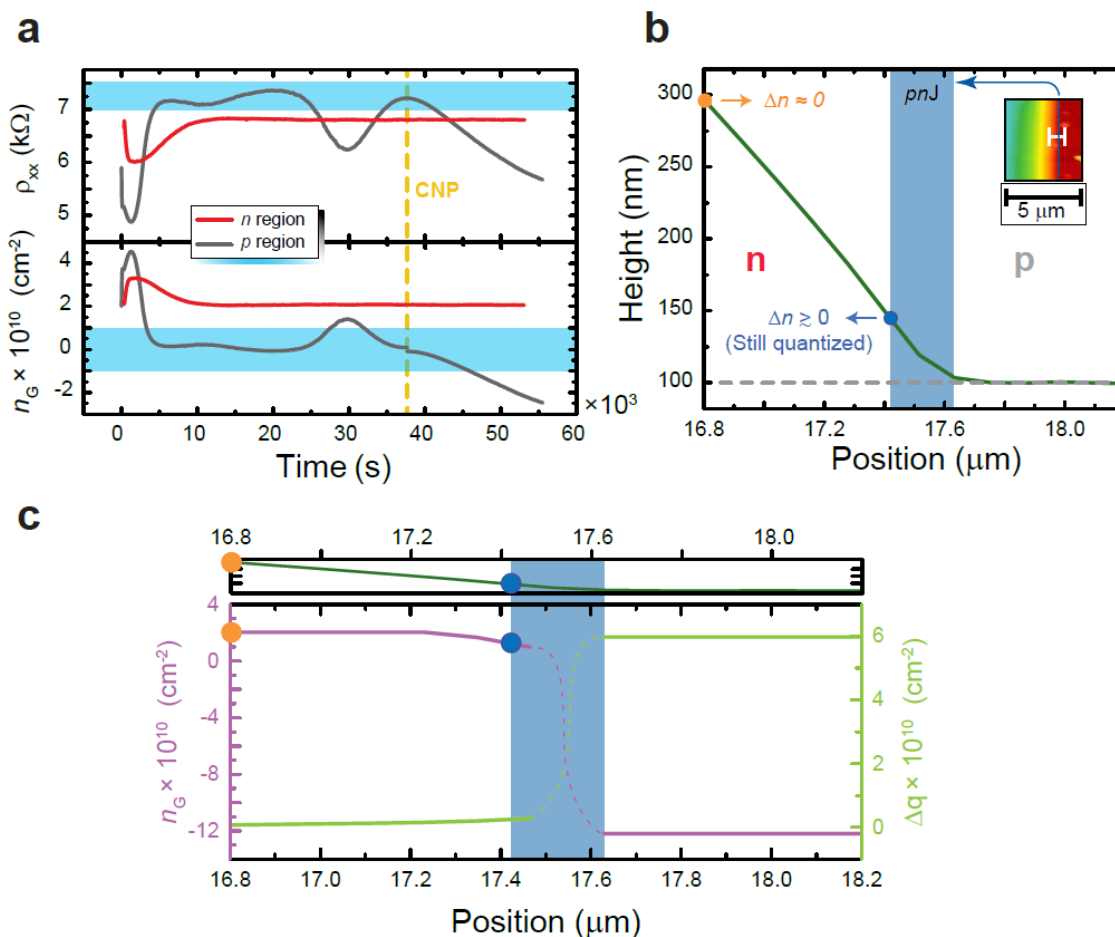


FIG. 2. (Color online) ((a) The longitudinal resistivity  $\rho_{xx}$  and electron density in EG  $n_G$  are monitored as a function of time in the upper and lower panel, respectively, while the region is being exposed to 254 nm UV light. The  $\text{Cr}(\text{CO})_3$  helps the carrier density transition from  $n$ -type to  $p$ -type despite an extensive time of transient lingering close to the Dirac point. The charge neutrality point (CNP) is marked by a gold dashed line. The cyan shading approximates a range where the electrical properties of the EG would not yield quantized plateaus. (b) The AFM profile and magnified image of the  $pn$ J are shown after PMMA/MMA copolymer deposition (totaling 100 nm). The green curve is taken along the white line in the inset. To validate the junction width, multiple devices with various thicknesses of S1813 were measured, as indicated by the orange and blue dot along the profile representing the two example thicknesses of 300 nm and 42.4 nm, respectively. The shaded blue region indicates the bounds within which the carrier density is expected to switch polarity. (c) The same profile and shaded region is projected onto the calculated charge transfer  $\Delta q$  to the ZEP520A layer and profile of  $n_G$ .

To assess device quality, the charge configuration of the device needed to be known and the width of the  $pnJs$  needed to be estimated. It is also important to approximate how the carrier densities in the regions change with exposure to 254 nm, 17 000  $\mu\text{Wcm}^{-2}$  UV light (distinct from the UV light used in photolithography), and this is primarily done by monitoring the longitudinal resistivity in all three regions of a  $p-n-p$  device during a room temperature exposure, with two polarities shown in the upper panel of Figure 2 (a). For the  $p$  region, the expected  $p$ -type doping mechanism resulting from the deposition of a ZEP520A layer on the whole device persists to the point where the carrier density crosses the Dirac point. This crossing is most evident during the room temperature UV exposure when the longitudinal resistivity of the device exhibits a similar value to when the exposure was started, but instead with a negative time derivative. The S1813 successfully prevents the  $n$  region from becoming a  $p$  region, as exhibited by the flat resistivity (and electron density). Though the idea of using ZEP520A as a dopant for EG has been demonstrated [17], accessing the  $p$  region with that mechanism is challenging due to the intrinsic EG Fermi level pinning from the buffer layer below. However, the reduction of the electron density from the order of  $10^{13} \text{ cm}^{-2}$  to the order of  $10^{10} \text{ cm}^{-2}$  by the presence of  $\text{Cr}(\text{CO})_3$  considerably assists the  $p$  region to undergo its transition.

## NOTES

Commercial equipment, instruments, and materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology or the United States government, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

## REFERENCES

- [1] Rigosi AF, Patel D, Marzano M, Kruskopf M, Hill HM, Jin H, Hu J, Walker AR, Ortolano M, Callegaro L, Liang CT. Atypical quantized resistances in millimeter-scale epitaxial graphene pn junctions. *Carbon*. 2019 Dec 1;154:230-7.
- [2] Patel D, Marzano M, Liu CI, Hill HM, Kruskopf M, Jin H, Hu J, Newell DB, Liang CT, Elmquist R, Rigosi AF. Accessing ratios of quantized resistances in graphene p–n junction devices using multiple terminals. *AIP Advances*. 2020 Feb 1;10(2):025112.
- [3] Rigosi AF, Marzano M, Levy A, Hill HM, Patel DK, Kruskopf M, Jin H, Elmquist RE, Newell DB. Analytical determination of atypical quantized resistances in graphene pn junctions. *Physica B: Condensed Matter*. 2020 Apr 1;582:411971.
- [4] Liu CI, Patel DK, Marzano M, Kruskopf M, Hill HM, Rigosi AF. Quantum Hall resistance dartboards using graphene p-n junction devices with Corbino geometries. *AIP Advances*. 2020 Mar 1;10(3):035205.
- [5] Hu J, Rigosi AF, Lee JU, Lee HY, Yang Y, Liu CI, Elmquist RE, Newell DB. Quantum transport in graphene p–n junctions with moiré superlattice modulation. *Physical Review B*. 2018 Jul 12;98(4):045412.
- [6] Rigosi AF, Panna AR, Payagala SU, Kruskopf M, Kraft ME, Jones GR, Wu BY, Lee HY, Yang Y, Hu J, Jarrett DG, Newell DB, Elmquist RE. Graphene devices for tabletop and high-current quantized Hall resistance standards. *IEEE transactions on instrumentation and measurement*. 2019 Jun;68(6):1870-8.
- [7] Hu J, Rigosi AF, Kruskopf M, Yang Y, Wu BY, Tian J, Panna AR, Lee HY, Payagala SU, Jones GR, Kraft ME, Jarrett DG, Watanabe K, Taniguchi T, Elmquist RE, Newell DB. Towards epitaxial graphene pn junctions as electrically programmable quantum resistance standards. *Scientific reports*. 2018 Oct 9;8(1):1-1.
- [8] Rigosi AF, Elmquist RE. The quantum Hall effect in the era of the new SI. *Semiconductor science and technology*. 2019 Aug 27;34(9):093004.
- [9] Hill HM, Rigosi AF, Chowdhury S, Yang Y, Nguyen NV, Tavazza F, Elmquist RE, Newell DB, Walker AR. Probing the dielectric response of the interfacial buffer layer in epitaxial graphene via optical spectroscopy. *Physical Review B*. 2017 Nov 28;96(19):195437.
- [10] Rigosi AF, Liu CI, Wu BY, Lee HY, Kruskopf M, Yang Y, Hill HM, Hu J, Bittle EG, Obrzut J, Walker AR. Examining epitaxial graphene surface conductivity and quantum Hall device stability with Parylene passivation. *Microelectronic engineering*. 2018 Jul 5;194:51-5.
- [11] Rigosi AF, Hill HM, Glavin NR, Pookpanratana SJ, Yang Y, Boosalis AG, Hu J, Rice A, Allerman AA, Nguyen NV, Hacker CA. Measuring the dielectric and optical response of millimeter-scale amorphous and hexagonal boron nitride films grown on epitaxial graphene. *2D Materials*. 2017 Dec 13;5(1):011011.
- [12] Rigosi AF, Glavin NR, Liu CI, Yang Y, Obrzut J, Hill HM, Hu J, Lee HY, Hight Walker AR, Richter CA, Elmquist RE. Preservation of surface conductivity and dielectric loss tangent in large-

scale, encapsulated epitaxial graphene measured by noncontact microwave cavity perturbations. *Small*. 2017 Jul;13(26):1700452.

[13] Panchal V, Yang Y, Cheng G, Hu J, Kruskopf M, Liu CI, Rigosi AF, Melios C, Walker AR, Newell DB, Kazakova O. Confocal laser scanning microscopy for rapid optical characterization of graphene. *Communications physics*. 2018 Nov 20;1(1):1-7.

[14] Kruskopf M, Rigosi AF, Panna AR, Patel DK, Jin H, Marzano M, Berilla M, Newell DB, Elmquist RE. Two-terminal and multi-terminal designs for next-generation quantized Hall resistance standards: contact material and geometry. *IEEE transactions on electron devices*. 2019 Jul 18;66(9):3973-7.

[15] Kruskopf M, Rigosi AF, Panna AR, Marzano M, Patel D, Jin H, Newell DB, Elmquist RE. Next-generation crossover-free quantum Hall arrays with superconducting interconnections. *Metrologia*. 2019 Oct 10;56(6):065002.

[16] Rigosi AF, Kruskopf M, Hill HM, Jin H, Wu BY, Johnson PE, Zhang S, Berilla M, Walker AR, Hacker CA, Newell DB. Gateless and reversible Carrier density tunability in epitaxial graphene devices functionalized with chromium tricarbonyl. *Carbon*. 2019 Feb 1;142:468-74.

[17] Lara-Avila S, Moth-Poulsen K, Yakimova R, Bjørnholm T, Fal'ko V, Tzalenchuk A, Kubatkin S. Non-Volatile Photochemical Gating of an Epitaxial Graphene/Polymer Heterostructure. *Advanced Materials*. 2011 Feb 15;23(7):878-82.