FINAL REPORT

Investigation of the Electron Interactions in Graphene

Grant Number : DE-FG02-05ER46215

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ABSTRACT

In graphene, combined with the real spin degree of freedom, which exhibits SU(2) symmetry, the total internal degrees of freedom of graphene carriers is thus described by a larger SU(4) symmetry, which produces a richer space for potential phenomena of emergent correlated electron phenomena. The major part of this proposal is exploring this unique multicomponent correlated system in the quantum limit. In the current period of DOE BES support we have made several key advances that will serve as a foundation for the new studies in this proposal. Employing the high-mobility encapsulated graphene heterostructures developed during the current phase of research, we have investigated spin and valley quantum Hall ferromagnetism in graphene and discovered a spin phase transition leading to a quantum spin Hall analogue. We have also observed the fractal quantum Hall effect arising from the Hofstadter's butterfly energy spectrum. In addition, we have discovered multiband transport phenomena in bilayer graphene at high carrier densities.

1. Introduction

In this project, we have developed experimental fabrication processes to create extremely high quality graphene samples by encapsulating graphene into hexagonal boron nitride (hBN) single crystal layers, forming van der Waals (vdW) heterostructures. Due to their extremely high mobility, approaching 10^6 cm^2/vsec, our samples display exotic and unique phases of electronic states formed by electron interaction that have been probed using various experimental tools including electric, magneto-transport, thermoelectric transport, and magneto-electromechanical measurements. As summarized below, we have achieved most of the goals we laid down in the current phase of proposal. A total of 6 publications are already published in high profile journals (1 *Nature*, 3 *Nature Physics*, 1 *PRL*, and 1 *PRB rapid*). In the following sections, we will describe our experimental progress in more detail.

2.1. Investigation of spin and valley quantum Hall ferromagnetism in graphene

Electronic systems with multiple degenerate degrees of freedom can support a rich variety of broken symmetry states. In a graphene Landau level (LL), strong Coulomb interactions and the fourfold spin/valley degeneracy lead to an approximate SU(4) multi-component spin symmetry. At partial filling, exchange interactions can break this symmetry, manifesting as additional Hall plateaus outside the normal integer sequence. In this period of work, we reported the observation of a number of these quantum Hall isospin ferromagnetic (QHIFM) states, which we classified according to their real spin structure using tilted field magnetotransport. The large activation gaps confirm the Coulomb origin of all the broken symmetry states, but the order depends strongly on LL index. In the high energy LLs, the Zeeman effect is the dominant aligning field, leading to real spin ferromagnets hosting skyrmionic excitations at half filling, whereas in the 'relativistic' zero LL, lattice scale interactions drive the system to a density wave.

In addition, we also observed intriguing hierarchical structure in the fractional quantum Hall effect (FQHE) in single layer graphene. The FQHE in an electron gas with multiple internal degrees of freedom provides a model system to study the interplay between symmetry breaking and emergent topological order. Due to the excessively stronger Coulomb interaction of electrons in graphene, the combination of spin and pseudo spin can be described in terms of larger SU(4) symmetry. Many body correlated states, such as FQHE, thus reflect this additional symmetry imprinted in graphene. Experimentally, we report the observation of the FQHE in substrate-supported graphene multi-terminal devices which manifest spin/pseudospin textures in the many body wave function producing a hierarchy of structures among the observed FQHE states. We found that the even multiples of 1/3 FQH states are strongly developed for both the lowest and second lowest Landau levels at fields up to 35 T. Despite significant disorder broadening, the measured FQHE gaps are an order of magnitude larger than those reported in the best semiconductor devices. The measured energy gaps are large, particularly in the second Landau level, where they are up to 10 times larger than those reported in the cleanest conventional systems. In the lowest Landau level the hierarchy of FQH states reflects the additional valley degeneracy

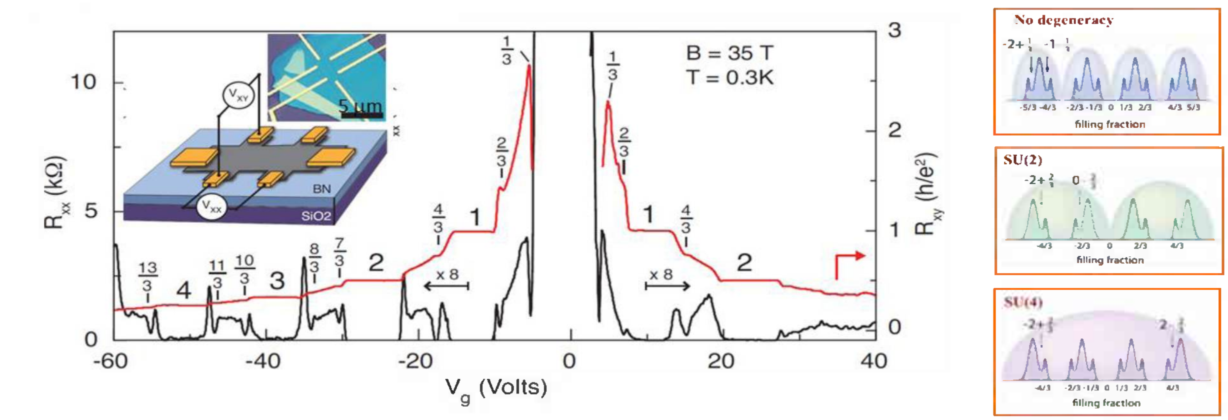

Fig. 2. Magnetoresistance (left axis) and Hall resistance (right axis) versus gate voltage acquired at magnetic field B=35 T. Inset shows a schematic and optical image of the graphene etched Hall bar device on hBN substrate. Integer QH effect, including symmetry broken QHF, and FQH effect are clearly marked by the corresponding filling fraction values. The bottom panels are schematic representation of the FQHE hierarchy observed in our sample. Shown is the expected electron–hole symmetry assuming (i) full lifting of all internal degeneracies, (ii) full breaking of only one degeneracy, leaving SU(2) symmetry, (iii) schematic diagram of the experimental situation, corresponding SU(4).

Two publications [1,2], resulted from this part of project, were published in *Nature Physics*. The PI's DOE support was the major supporting source, responsible for the sample preparation, measurement and data analysis performed in this work. The other funding sources acknowledged in this work were responsible for microfabrication usages (NSEC, NYSTAR, and FENA) and other collaborators' support (DARPA, AFOSR MURI).

2.2. Spin phase transition at charge neutrality in graphene

The QHE appearing at the charge neutral point (CNP) presents an unusual experimental observation, as it is not marked by the usual longitudinal resistance minima that typify all other filling factors. Theoretically, various models of symmetry breaking and ordering underlying this insulating state have been proposed, including quantum hall ferromagnetism, magnetic catalysis,

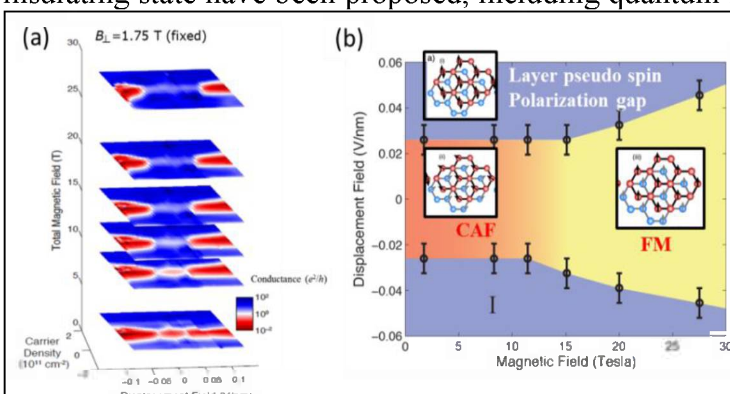

Fig. 3. (a) Conductance of bilayer graphene as a function of total magnetic field (B_T), carrier density (n) and perpendicular electric displacement fields (D). Perpendicular magnetic field (B_P) is fixed at 1.75 T. Developing insulating states (red in color) are clearly visible. (b) Different phases of the ν=0 QH state mapped as a function of D and B_T at B_p =1.75 T. The phase boundaries between layer-polarized, ferromagnetic (FM), and canted antiferromagnetic (CAF) is determined by the conductance spike separating the two insulating phases.

and sublattice charge density waves. Models for the edge state conductance have examined counter-propagating spin states, with local magnetic impurities on the edge providing a mechanism for dissipation to explain the diverging resistance at the CNP. An unanswered experimental question related to these models, and the nature of the symmetry breaking at the CNP, was whether this state is spin-polarized. In this period of time, we performed transport measurements of the insulating state at the CNP of graphene in a magnetic field. Using both conventional two-terminal measurements, sensitive to bulk and edge conductance, and Corbino measurements, sensitive only to the bulk conductance, we observed a vanishing conductance with increasing magnetic fields. By examining the resistance changes of this insulating state with varying perpendicular and in-plane fields, we probed the spin-active components of the excitations in total fields of up to 45 T. Our results indicate that the zero energy quantum Hall state in single layer graphene is not spin-polarized.

Extending the investigation of the QHE at CNP in bilayer, we also observed a very peculiar quantum Hall state in BLG that mimics a topologically unique quantum spin Hall effect. The quantum spin Hall effect is characterized by spin-polarized counter-propagating edge states. It has been predicted that this edge state configuration could occur in graphene when spin-split electron- and hole-like Landau levels are forced to cross at the edge of the sample. In particular, a quantum spin-Hall analogue has been predicted in bilayer graphene with a Landau level filling factor $\nu = 0$ if the ground state is a spin ferromagnet. Previous studies have demonstrated that the bilayer $\nu = 0$ state is an insulator in a perpendicular magnetic field, although the exact nature of this state has not been identified. In our study we presented measurements of the $\nu = 0$ state in a dual-gated bilayer graphene devices in a tilted magnetic field. We mapped out a full phase diagram of the $\nu = 0$ state as a function of experimentally tunable in-plane magnetic field and perpendicular electric field. At large in-plane magnetic fields we observed a quantum phase transition to a metallic state with conductance on the order of $4e^2/h$, consistent with predictions for a ferromagnetic state.

Two publications [3, 4] reporting these discoveries resulted from this part of the project were published in *PRL* and *Nature Physics*. The DOE was the sole source of support for the work published in PRL, and was the major supporting source for the other work as well. The other funding sources acknowledged were responsible for sample fabrication (INDEX) and support for other collaborators (ONR MURI and FENA).

2.3. Observation of the fractal quantum Hall effect in Hofstadter's butterfly spectrum

Electrons moving through a spatially periodic lattice potential develop a quantized energy spectrum consisting of discrete Bloch bands. In two dimensions, electrons moving through a magnetic field also develop a quantized energy spectrum, consisting of highly degenerate Landau energy levels. In 1976 Douglas Hofstadter theoretically considered the intersection of these two problems and discovered that 2D electrons subjected to both a magnetic field and a periodic electrostatic potential exhibit a self-similar recursive energy spectrum. Known as Hofstadter's butterfly, this complex spectrum results from a delicate interplay between the characteristic lengths associated with the two quantizing fields, and represents one of the first quantum fractals discovered in physics. In the decades since, experimental attempts to study this expected spectrum have been limited by difficulties in reconciling the two length scales. Typical crystalline systems (< 1 nm periodicity) require impossibly large magnetic fields to reach the commensurability condition, while in artificially engineered structures (~100 nm), the corresponding fields are too small to completely overcome disorder.

In this period of time, we used Bernal-stacked bilayer graphene (BLG) Hall bars fabricated on hBN substrates (Fig. 4a, b) using mechanical exfoliation followed by co-lamination. Figure 4b shows a non-contact atomic force microscopy (AFM) image acquired from an example device. In the magnified region, a triangular moire´ pattern is visible with wavelength ~15 nm. This is comparable to the maximal moire´ wavelength of ~14nm expected for graphene on hBN, suggesting that in this device the BLG lattice is oriented relative to the underlying hBN lattice with near-zero angle mismatch. We confirm that quantum Hall effect features associated with the fractal gaps are described by two integer topological quantum numbers, and report evidence of their recursive structure. Observation of Hofstadter's spectrum in graphene provides the further opportunity to investigate emergent behavior within a fractal energy landscape in a system with tunable internal degrees of freedom.

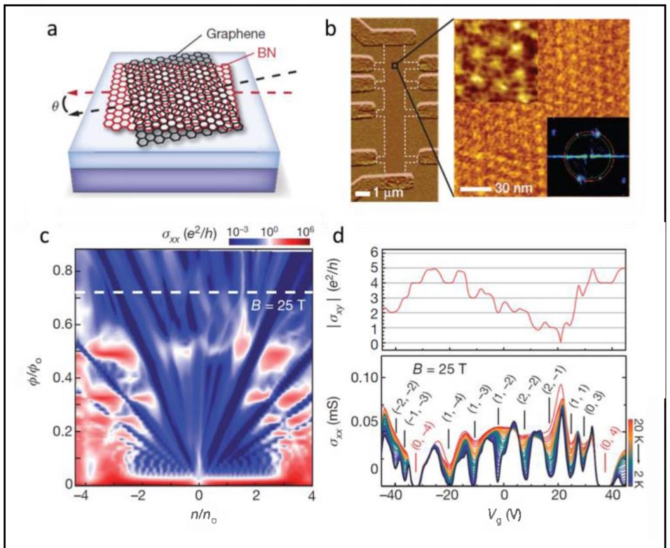

Fig. 4. (a) Sketch of graphene on hBN showing the emergence of a moire pattern. (b) An AFM image of the device with a high resolution image of a magnified region. The inset shows a fast Fourier transform of the scan area. (c) Landau fan diagrams demonstrating unusual quantum Hall effect appeared in moire supperlattice. (d) Bottom: the evolution of magnetoconductivity with temperature varying between 2 and 20 K, acquired at constant B =25 T. Top: the corresponding Hall conductivity. The bracketed numbers label the (s, t) values of the corresponding fractal gaps according to the Diophantine equation.

A paper has been published in Nature [5] reporting this discovery. The DOE support was the PI's sole supporting source for this work. The other funding sources acknowledged were responsible for supporting other collaborators (AFOSR, ONR, and DARPA).

2.4. Multiband transport in bilayer graphene at high carrier densities

Multiband transport is common in many complex metalswhere different types of carriers on different pieces of the Fermi surface (FS) carry electrical currents. Conduction in this regime is controlled by the properties of the individual subbands, each of which can have distinct mobilities, band masses, and carrier densities. Other changes to the single-band conduction model include interband scattering processes and mutual electrostatic screening of carriers in different subbands, which alters the effective strength of the Coulomb potential and hence adjusts the strength of electron-electron and electroncharged impurity interactions.

Bilayer graphene (BLG), with its multiband structure and strong electrostatic tunability, offers a unique model system to investigate multiple-band transport phenomena. BLG's fouratom unit cell yields a band structure described by a pair of low-energy subbands (LESs) touching at the charge neutrality point (CNP) and a pair of high-energy subbands (HESs) whose onset is~±0.4 eVaway from the CNP (Fig. 5(a)). Using an electrolytic gate (Fig. 5(b-c)), we were able to populate the HES of bilayer graphene, allowing for both the LES and HES to be occupied simultaneously.

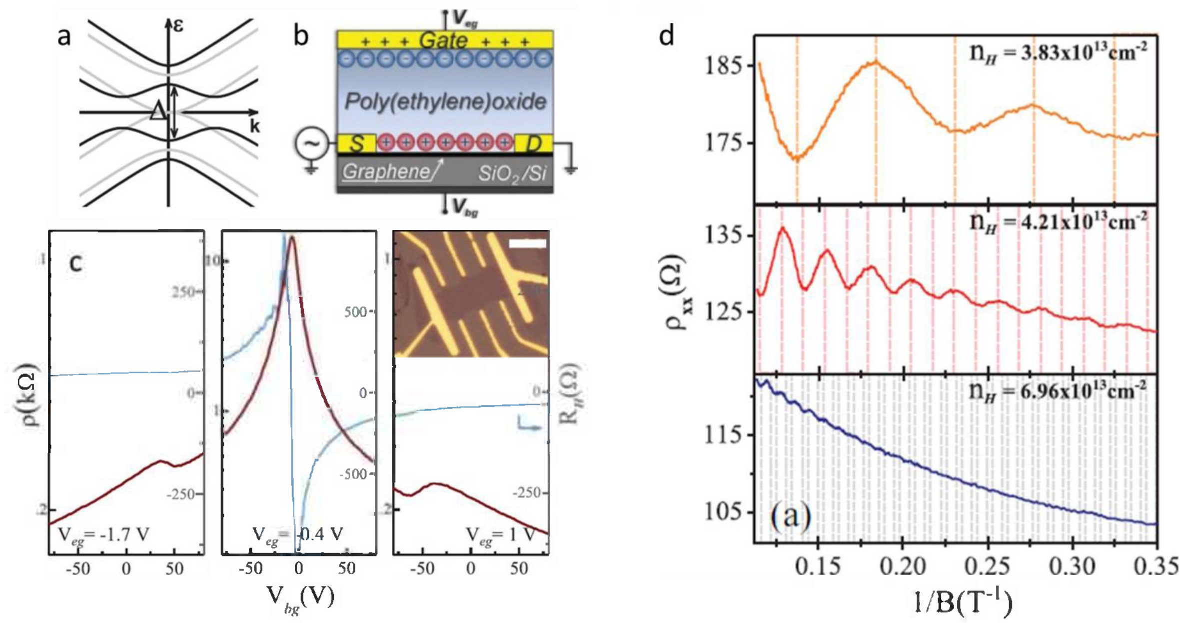

Fig. 5. (a) The tight-binding band structure of bilayer graphene for no interlayer asymmetries (gray) and finite interlayer asymmetry (black). (b) Schematic view of the double-gated device, consisting of the SiO2/Si back gate and the electrolytic top gate. Debye layers of Cs+ or ClO4− ions are formed d ~ 1 nm above the bilayer and the gate electrode, respectively. (c) Longitudinal resistivity and Hall resistance of the bilayer graphene device at $T = 2$K as a function of back gate voltage V_{bg} for three different fixed electrolyte gate voltage (denoted by V_{eg}). The inset shows an optical microscope image of a typical Hall bar device (the scale bar corresponds to 5 μm). (b) Exemplary traces of the longitudinal resistivity as a function of inverse magnetic field at fixed values of n_H beyond the onset of the high energy subband.

We reported a multiband transport study of bilayer graphene at high carrier densities. Employing a poly(ethylene)oxide-$CsClO_4$ solid polymer electrolyte gate we demonstrated the filling of the high-energy subbands in bilayer graphene samples. We observed a sudden increase of resistance and the onset of a second family of Shubnikov–de Haas (SdH) oscillations as these high-energy subbands are populated (Fig. 5(d)). From simultaneous Hall and magnetoresistance measurements, together with SdH oscillations in the multiband conduction regime, we deduced the carrier densities and mobilities for the higher-energy bands separately and found the mobilities to be at least a factor of 2 higher than those in the low-energy bands.

A paper has been published in Physical Review B, rapid communication [6]. The PI's DOE grant was one of the major supporting sources, responsible for sample preparation and device fabrication. The other funding source acknowledged MURI, FENA, and DARPA for personnel support for this work.

Publications supported by ER46215 during the budget period (7/14/11 – 7/15/14)

Acknowledgements and Author contributions are from the published papers with the emphasis related to the DOE funding marked in bold characters

[1] C. R. Dean, A. F. Young, P. Cadden-Zimansky, L. Wang, H. Ren, K. Watanabe, T. Taniguchi, P. Kim, J. Hone, and K. L. Shepard, "Multicomponent Fractional Quantum Hall Effect in Graphene", Nature Physics **7**, 693-696 (2011).

Acknowledgements
We thank J. K. Jain, C. Toke, N. Shibata, M. O. Goerbig and M. Foster for discussions, J. Sanchez-Yamagishi and P. Jarillo-Herrero for fabrication advice regarding the PVA, and I. Meric, Z. Kagan, A. Tsoi, N. Baklitskaya and I. Mendonca for help with the device preparation. A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by National Science Foundation Cooperative Agreement No. DMR-0654118, the State of Florida and the US Department of Energy. This work is supported by DARPA CERA, AFOSR MURI, FCRP through C2S2 and FENA, NSEC (No. CHE-0117752) and NYSTAR. **P.K. and A.F.Y. acknowledge support from DOE (DE-FG02-05ER46215).**

Author contributions
C.R.D. and **A.F.Y. performed all experiments including sample fabrication and measurement, and wrote the paper**. P.C-Z. contributed to sample measurement. L.W. and H.R. contributed to sample fabrication. K.W. and T.T. synthesized the h-BN samples. J.H., **P.K.** and K.L.S. **advised on experiments**.

Additional Comments
The DOE support was the PI's sole supporting source for this work. The other funding sources acknowledged were responsible for supporting other collaborators (AFOSR, ONR, and DARPA).

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[2] A. F. Young, C. R. Dean, L. Wang, H. Ren, P. Cadden-Zimansky, K. Watanabe, T. Taniguchi, J. Hone, K. L. Shepard, and P. Kim, "Spin and Valley Quantum Hall Ferromagnetism in Graphene", Nature Physics **8**, 550-556 (2012).

Acknowledgements
We acknowledge discussions with I. Aleiner, A. Macdonald, Y. Barlas, R. Cote, W. Luo and M. Kharitonov. The measurements were made at NHMFL, which is supported by National Science Foundation Cooperative Agreement DMR-0654118, the State of Florida and the US Department of Energy. We thank S. Hannahs, T. Murphy, J.-H. Park and S. Maier for experimental assistance at NHMFL. This work is supported by the US Defense Advanced Research Projects Agency Carbon Electronics for RF Applications, the Air Force Office of Scientific Research Multidisciplinary University Research Initiative, the Focus Center Research Program through the Center for Circuit and System Solutions and Functional Engineered Nano Architectonics, the Nanoscale Science and Engineering Center (CHE-0117752) and the New York Division of Science, Technology and Innovation. **P.K. and A.F.Y. acknowledge support from the US Department of Energy (DE-FG02-05ER46215)**.

Author contributions
A.F.Y., C.R.D. and **P.K. conceived the experiment and analysed the data**. **A.F.Y.,** C.R.D., L.W. and H.R. **fabricated the samples. A.F.Y.,** C.R.D., L.W., H.R. and P.C-Z. made the measurements. **A.F.Y.,** C.R.D. and **P.K. wrote the paper**. T.T. and K.W. synthesized the hBN crystals. J.H., K.L.S. and **P.K. advised on experiments**.

Additional Comments
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in this work were responsible for microfabrication usages (NSEC, NYSTAR, and FENA) and other collaborators' support (DARPA, AFOSR MURI).

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[3] Y. Zhao, P. Cadden-Zimansky, F. Ghahari, and P. Kim, "Magnetoresistance Measurements of Graphene at the Charge Neutrality Point", Physical Review Letters **108**, 5, 106804 (2012).

Acknowledgements
The authors thank I. Aleiner, Y. Barlas, E. A. Henriksen, Z. Jiang, and A. F. Young for helpful discussions and thank S. T. Hannahs, E. C. Palm, and T. P. Murphy for their experimental assistance. **This work is supported by DOE (No. DEFG02-05ER46215)**. A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by NSF Cooperative Agreement, by the State of Florida, and by the DOE (No. DMR-0654118).

Additional Comments
The DOE was the sole source of support for the work published in PRL.

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[4] P. Maher, C. R. Dean, A. F. Young, T. Taniguchi, K. Watanabe, K. L. Shepard, J. Hone, and P. Kim, "Evidence for a Spin Phase Transition at Charge Neutrality in Bilayer Graphene", Nature Physics **9**, 154-158 (2013).

Acknowledgements
The authors thank M. Kharitonov for useful discussions. Portions of this experiment were conducted at the National High Magnetic Field Laboratory, which is supported by National Science Foundation Cooperative Agreement No. DMR-0654118, the State of Florida and the US Department of Energy. We thank S. Hannahs, T. Murphy and A. Suslov for experimental assistance at NHMFL. This work is supported by AFOSR MURI. P.M. acknowledges support from ONR MURI and FENA. **A.F.Y. and P.K. acknowledge support from DOE (DE-FG02-05ER46215) for carrying out experiments and INDEX for sample fabrication**

Author contributions
P.M., C.R.D. and **A.F.Y. designed and conceived the experiment**. T.T. and K.W. synthesized hBN samples, P.M. fabricated the samples. P.M., C.R.D. and **A.F.Y. performed the measurements**. P.M., C.R.D. and **P.K. analysed the data and wrote the paper**. J.H., K.L.S. and **P.K. advised on experiments**.

Additional Comments
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[5] C. R. Dean, L. Wang, P. Maher, C. Forsythe, F. Ghahari, Y. Gao, J. Katoch, M. Ishigami, P. Moon, M. Koshino, T. Taniguchi, K. Watanabe, K. L. Shepard, J. Hone, and P. Kim, "Hofstadter's butterfly in moire superlattices: A fractal quantum Hall effect," *Nature* **497**, 598-602 (2013)

Acknowledgements

We thank A. MacDonald for discussions. A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by US National Science Foundation cooperative agreement no.DMR-0654118, the State of Florida and the US Department of Energy. This work is supported by AFOSR MURI. J.K. and M.I. were supported by the US National Science Foundation under grant no. 0955625. K.L.S. was supported by DARPA under Office of Naval Research contract N00014-1210814. **P.K. and F.G. acknowledge sole support from the US Department of Energy (DE-FG02-05ER46215).**

Author contributions

C.R.D., P. Maher, L.W., C.F., **F.G.** and Y.G. **performed device fabrication and transport measurements.** J.K. and M.I. performed AFM measurements. P. Moon and M.K. provided theoretical support. K.W. and T.T. synthesized the hBN samples. K.L.S., J.H. and **P.K. advised on experiments.** C.R.D., P. Maher, P. Moon, M.K., J.H. and **P.K. wrote the manuscript** in consultation with all other authors.

Additional Comments

The DOE was the sole supporting source for the PI's participation in this work. The other funding sources acknowledged were responsible for the support for other collaborators (AFOSR, NSF and DARPA) and facilities (NHMFL).

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[6] D. K. Efetov, P. Maher, S. Glinskis, and P. Kim, "Multiband Transport in Bilayer Graphene at High Carrier Densities", Physical Review B **84**, 4, 161412 (2011).

Acknowledgements

The authors thank I. L. Aleiner, E. Hwang, and K. F. Mak for helpful discussion. This work is supported by the AFOSR MURI, FENA, and DARPA CERA. **Sample preparation was supported by the DOE (Contract No. DE-FG02-05ER46215).**

Additional Comments

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