AFRL-AFOSR-VA-TR-2020-0178

PROBING THE ATOMIC ORIGINS OF ELECTRONIC STATES IN LOW DIMENSIONAL MATERIALS AND INTERFACES

Pinshane Huang
UNIVERSITY OF ILLINOIS

09/15/2020
Final Report

Air Force Research Laboratory
AF Office Of Scientific Research (AFOSR)/ RTB1
Arlington, Virginia 22203
Air Force Materiel Command

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
24-09-2020

2. REPORT TYPE
Final Performance

3. DATES COVERED *(From - To)*
21 Apr 2017 to 20 Apr 2020

4. TITLE AND SUBTITLE
PROBING THE ATOMIC ORIGINS OF ELECTRONIC STATES IN LOW DIMENSIONAL MATERIALS AND INTERFACES

5a. CONTRACT NUMBER

5b. GRANT NUMBER
FA9550-17-1-0213

5c. PROGRAM ELEMENT NUMBER
61102F

6. AUTHOR(S)
Pinshane Huang

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
UNIVERSITY OF ILLINOIS
506 S WRIGHT STREET SUITE 364
URBANA, IL 61801-3649 US

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AF Office of Scientific Research
875 N. Randolph St. Room 3112
Arlington, VA 22203

10. SPONSOR/MONITOR'S ACRONYM(S)
AFRL/AFOSR RTB1

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-AFOSR-VA-TR-2020-0178

12. DISTRIBUTION/AVAILABILITY STATEMENT
A DISTRIBUTION UNLIMITED: PB Public Release

13. SUPPLEMENTARY NOTES

14. ABSTRACT

During this three-year grant, we have published five manuscripts, given nine conference talks and invited seminars, and been awarded six awards in recognition of my group's research. Our main work has focused on studying doping and strain in 2D materials and the impact that these structures have on the electronic properties of 2D materials and devices. As part of this work, we developed electron microscopy methods to measure picometer-scale displacements of individual atoms near point defects in 2D materials. Using this approach, we demonstrated methods to measure atomic displacements with 0.3 picometer precision, representing more than an order of magnitude improvement over conventional imaging of 2D materials with aberration-corrected STEM (C.-H. Lee et al., Nano Letters 2020). This new level of precision allowed us to uncover previously unseen features in the strain field around vacancies in WSe2-2xTe2x, including atomic-scale, radial strain oscillations around a vacancy, a phenomena first predicted in the 1950s. These results are significant because they point to methods to detect localized electronic rearrangements through high-precision electron microscopy, and because they demonstrate the coupling between strain and electronic charge at defects in 2D systems. In addition to the above research focus, we also completed four collaborative projects in nanoelectronic materials and devices. This work includes the development of a new fabrication method using graphene etch stops (J Son et al., Nature Communications 2018) to produce complex integrated 3D device structures with high electrical mobilitiesthe highest ever reported for graphene at the time of our publication. In addition, our collaborative project on strained 2D materials (Y. Zhang et al., Nano Letters 2018) demonstrates spatially periodic strain tuning of up to 2 percent in graphene and MoS2 using arrays

15. SUBJECT TERMS

2D materials, transmission electron microscopy, molecular-scale materials

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** SAYIR, ALI
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			
Unclassified	Unclassified	Unclassified	UU		**19b. TELEPHONE NUMBER** *(Include area code)* 703-696-7236

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

DISTRIBUTION A: Distribution approved for public release.

During this three-year grant, we have published five manuscripts, given nine conference talks and invited seminars, and been awarded six awards in recognition of my group's research. Our main work has focused on studying doping and strain in 2D materials and the impact that these structures have on the electronic properties and design of 2D nanoelectronic devices. Most recently, we published a manuscript on "Deep Learning Enabled Measurements of Single-Atom Defects in 2D Transition Metal Dichalcogenides with Sub-Picometer Precision" (C.-H. Lee et al., Nano Letters 2020). By applying machine learning to analyze atomic defects from scanning transmission electron microscopy images, we demonstrated that convolution neural networks can be trained to identify single atom dopants in a 2D transition metal dichalcogenides such as $Mo_{1-x}W_xTe_2$ and $WS_{2-x}Se_x$. These data allow us to probe large numbers of defects in order to extract information about local strains, deformation, and atomic-scale interactions between defects. For example, by locating, classifying, and aligning, and summing images from hundreds of identical defects, we produce very high signal-to noise images of atomic defects without damage to the structure. Using the resulting data, we can measure local strains around defects with sub-picometer precision: for example, we observed a local 0.4% (1 pm) lattice contraction at W dopants in $Mo_{1-x}W_xTe_2$. To our knowledge, these measurements are the highest precision structural measurements of defects in 2D materials, and they are comparable to the highest precision structural measurements ever acquired using atomic resolution electron microscopy.

Using this new characterization technique, we discovered the presence of point defect-induced, radially oscillating strain fields (Figure 1). This phenomenon was predicted for metals in 1950s but has never been previously observed. These oscillations cannot be explained by either classical discrete or continuum mechanics theories but are present in density functional theory simulations. We proposed that these oscillations in 2D semiconductors results from quantum mechanical charge oscillations, a topic we are continuing to explore. These results are significant because they point to methods to detect localized electronic rearrangements through high-precision electron microscopy, and because they demonstrate the coupling between strain and electronic charge at defects in 2D systems.

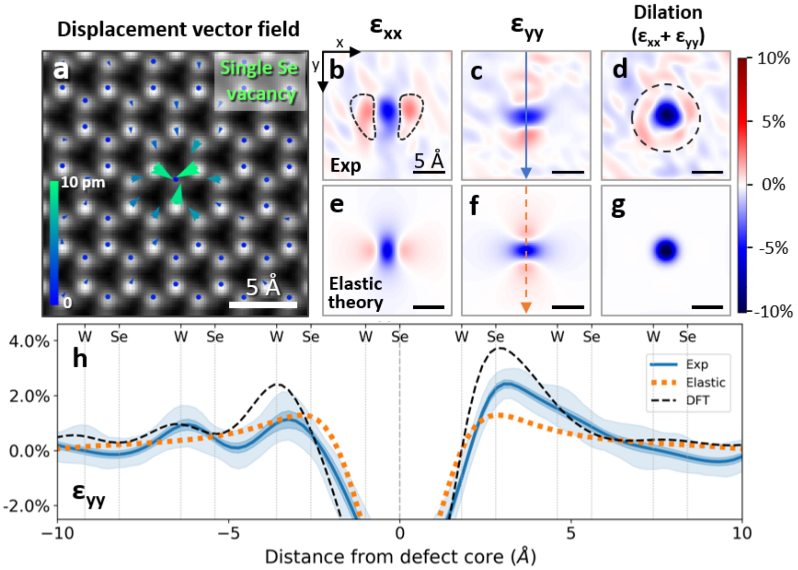

Figure 1: Displacement and strain fields of single Se vacancy. (a) Displacement vectors from a single Se vacancy. (b-d) Experimental strain fields induced by the vacancy (a). (e-g) Best-fit strain fields calculated by continuum elastic theory. (h) Line profiles of experimental, elastic theory, and DFT-derived ε_{yy} across the vacancy, as marked by the solid (blue) and dashed (orange) arrows on (c and f). In contrast to the monotonically decaying strain field predicted by continuum elastic theory, both experimental and DFT profiles show strong radial oscillations in the strain field. From C.H. Lee et al, Nano Letters (2020).

We have also contributed to four projects more broadly in nanoelectronic materials and devices. First, we, completed a collaborative project on graphene etch stops (J Son et al., Nature Communications 2018) demonstrated a new method to fabricate complex integrated 3D device structures with high electrical mobilities—the highest ever reported for graphene at the time of our publication. This method uses graphene, which is chemically inert and impermeable to gasses, to select with atomic precision the etch depth of patterning using otherwise conventional semiconductor patterning methods. This work addresses a major challenge in creating electronic devices from 2D materials—how to pattern and electrically address individual atomic layers while also protecting them from exposure to air and residues from nanopatterning procedures in order to achieve high performance devices. Second, our collaborative project on strained 2D materials (Y. Zhang et al., Nano Letters 2018) demonstrates spatially periodic strain tuning of in the 2D materials graphene and MoS_2 using arrays of silica nanospheres as a patterned substrate. Using this approach, strains were achieved up to an average of 0.3 percent and local strains up to 2 percent, enough to induce changes in the conductance these materials at low temperatures. Third, we contributed to a collaborative work on understanding the microstructural evolution of Cu-Nb oxide nanocomposite alloys (Q. Li et al., Journal of Materials Research 2019). The goal of this work was to develop bulk nanocomposites with high strength and radiation resistance. Our work in this area was to use electron energy loss spectroscopy and STEM imaging to understand the oxidation states of the Cu-Nb oxide nanoinclusions, and how they can be manipulated through ball milling. Finally, in a collaborative project on ferrimagnetic materials (J Finley et al., Advanced Materials 2018) demonstrates highly efficient spin-torque switching in the Heusler alloy $Mn_2Ru_{1-x}Ga$, indicating their potential for high density, low power magnetic memories.

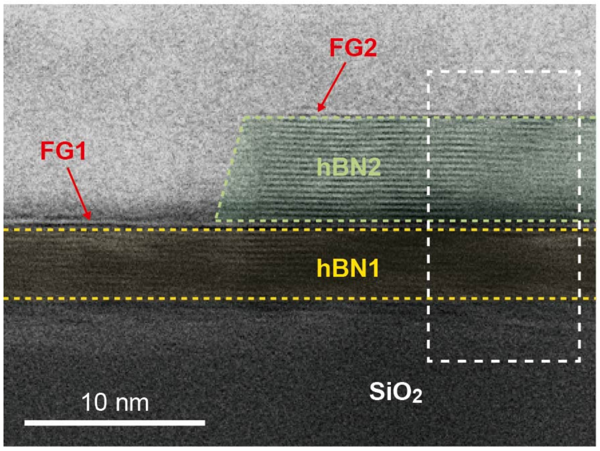

Figure 2: STEM image of a h-BN encapsulated graphene device fabricated using an atomically thin graphene etch stop. This novel fabrication method enables complex devices with 3D geometries to be fabricated in 2D materials, including the fabrication of graphene transistors with exceptionally high electron mobilities (40,000 cm^2/Vs at room temperature). From J. Son et al., Nature Communications (2018).

Publications

1. *Deep Learning Enabled Strain Mapping of Single-Atom Defects in Two-Dimensional Transition Metal Dichalcogenides with Sub-Picometer Precision*, C.-H. Lee, A. Khan, D. Luo, T. P. Santos, C. Shi, B. E. Janicek, S. Kang, W. Zhu, N. A. Sobh, A. Schleife, B. K. Clark, and P. Y. Huang, Nano Letters, **20**, 3369–3377 (2020).
2. *Evolution of Nb oxide nanoprecipitates in Cu during reactive mechanical alloying*, Q. Li, X. Shang, B. Janicek, P. Y. Huang, P. Bellon and R. S. Averback J. Mater. Res. **35**, 98–111 (2019).
3. *Atomically precise graphene etch stops for three dimensional integrated systems from two dimensional material heterostructures*, Son, J., Kwon, J., Kim, S., Lv, Y., Yu, J., Lee, J.-Y., Ryu, H., Watanabe, K., Taniguchi, T., Garrido-Menacho, R., Mason, N., Ertekin, E., Huang, P. Y., Lee, G.-H. & van der Zande, A.M. Nature Communications 9, 3988 (2018).
4. *Strain modulation of graphene by nanoscale substrate curvatures: a molecular view*, Zhang, Y., Heiranian, M., Janicek, B., Budrikis, Z., Zapperi, S., Huang, P.Y., Johnson, H. Aluru, N., Lyding, J., Mason, N., Nano Letters 18 2098–2104 (2018).
5. S*pin–Orbit Torque Switching in a Nearly Compensated Heusler Ferrimagnet*, Finley, J., Lee, C. H., Huang, P. Y. & Liu, L. Advanced Materials 1805361 (2018).

Presentations

1. *Deep Learning Enabled Measurements of Single-Atom Defects in 2D Transition Metal Dichalcogenides with Sub-Picometer Precision*, Chia-Hao Lee, Chuqiao Shi, Di Luo, Abid Khan, Blanka E. Janicek, Sangmin Kang, Wenjuan Zhu, Bryan Clark, and Pinshane Y. Huang, Baltimore, MD, Microscopy & Microanalysis, (2019)
2. *Deep Learning Enabled Measurements of Single-Atom Defects in 2D Transition Metal Dichalcogenides with Sub-Picometer Precision,* Chia-Hao Lee, Chuqiao Shi, Di Luo, Abid Khan, Nahil A. Sobh, Blanka E. Janicek, Sangmin Kang, Wenjuan Zhu, Bryan K. Clark, and Pinshane Y. Huang, Materials Research Society Fall meeting Boston, MA, (2019)
3. *Probing the Picometer-Scale Oscillating Strain Fields of Single-Atom Defects via Deep Learning,* Chia-Hao Lee, Abid Khan, Di Luo, Tatiane P. Santos, Chuqiao Shi, Blanka E. Janicek, Sangmin Kang, Wenjuan Zhu, Nahil A. Sobh, Andre Schleife, Bryan K. Clark, and Pinshane Y. Huang, Microscopy & Microanalysis, virtual, (2020)
4. *2D materials for single atom science in electron microscopy*, P.Y. Huang, Microscopy & Microanalysis, St. Louis, MO (2017)
5. *Electron Microscopy of 2D materials: A Platform for Solid State Research at the Single Atom Scale*, P.Y. Huang, University of Ulm, SALVE conference, Ulm, Germany, (2017)
6. *Materials at the atomically thin limit*, P.Y. Huang, Kavli Frontiers of Science Symposium, Irvine, CA (2019)
7. *Measuring atomic-scale strain, deformation, and bending in 2D materials with aberration-corrected STEM*, P.Y. Huang, Midwest Microscopy and Microanalysis Society Meeting, Madison, WI (2019)
8. *Characterizing Unconventional Strain and Bending in 2D materials with aberration-corrected STEM*, P.Y. Huang, Center for Integrated Nanotechnologies user meeting, Santa Fe, NM (2019)
9. *Characterizing Unconventional Strain and Bending in 2D materials with aberration-corrected STEM*, P.Y. Huang, Lawrence Berkeley National Laboratory, Berkeley, CA (2019)

Awards

The PI received the following awards during the course of this grant: Kavli Fellow of the National Academy of Sciences (2019), ISI Global Highly Cited Researcher (2018), Center for Advanced Study Fellow from the University of Illinois (2018-2019), Sloan Fellowship in Physics (2018), Packard Fellowship (2018), and the Presidential Early Career Award for Scientists and Engineers (2019).