AFRL-AFOSR-VA-TR-2023-0319

Investigating the Mechanisms of Electrical Contact Resistance between the Diffusive and Ballistic Limits

Baykara, Mehmet
UNIVERSITY OF CALIFORNIA MERCED
5200 N LAKE RD
MERCED, CA, 95343-5001
US

03/25/2023
Final Technical Report

DISTRIBUTION A: Distribution approved for public release.

Air Force Research Laboratory
Air Force Office of Scientific Research
Arlington, Virginia 22203
Air Force Materiel Command

REPORT DOCUMENTATION PAGE

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.

1. REPORT DATE 20230325	**2. REPORT TYPE** Final	**3. DATES COVERED** **START DATE** 20181215	**END DATE** 20221214

4. TITLE AND SUBTITLE
Investigating the Mechanisms of Electrical Contact Resistance between the Diffusive and Ballistic Limits

5a. CONTRACT NUMBER	**5b. GRANT NUMBER** FA9550-19-1-0035	**5c. PROGRAM ELEMENT NUMBER** 61102F
5d. PROJECT NUMBER	**5e. TASK NUMBER**	**5f. WORK UNIT NUMBER**

6. AUTHOR(S)
Mehmet Baykara

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
UNIVERSITY OF CALIFORNIA MERCED
5200 N LAKE RD
MERCED, CA 95343-5001
US

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Air Force 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-2023-0319

12. DISTRIBUTION/AVAILABILITY STATEMENT
A Distribution Unlimited: PB Public Release

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The original goal of this project was to investigate the mechanisms of electrical contact resistance (ECR) on small length scales through an interplay of conductive atomic force microscopy (C-AFM) experiments and atomistic simulations. This goal has been pursued, in the first half of the project period, by the following activities and accomplishments: (i) measuring ECR values between gold nano islands and graphite substrates, (ii) improving the C-AFM methodology in order to achieve more reliable and reproducible results, and (iii) understanding the physical mechanisms of the phenomenon of “conduction aging” we often observe in the experiments. In the second half of the project, our work evolved into the use of C-AFM as a powerful atomic-resolution imaging tool under ambient conditions, with exemplary results reported on various 2D materials as well as thin crystals of Mo2C, in collaboration with the TOBB University of Economics and Technology as well as Eskisehir Technical University (ETU). The results of the project have been shared with the scientific community by way of five journal publications and multiple invited as well as contributed presentations at conferences and research institutions.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT** UU	**18. NUMBER OF PAGES** 8
a. REPORT U	**b. ABSTRACT** U	**c. THIS PAGE** U		

19a. NAME OF RESPONSIBLE PERSON ALI SAYIR	**19b. PHONE NUMBER** *(Include area code)* 426-7236

Standard Form 298 (Rev.5/2020)
Prescribed by ANSI Std. Z39.18

Award Number: FA9550-19-1-0035

Report Type: Final Performance Report

Reporting Period: 12/15/2018 – 12/14/2022

Distribution Statement: *A – Approved for Public Release*

Program Officer Name: Dr. Ali Sayir

Principle Investigator Name: Mehmet Z. Baykara & Ashlie Martini

Project Title: Investigating the Mechanisms of Electrical Contact Resistance between the Diffusive and Ballistic Limits

Abstract:

The original goal of this project was to investigate the mechanisms of electrical contact resistance (ECR) on small length scales through an interplay of conductive atomic force microscopy (C-AFM) experiments and atomistic simulations. This goal has been pursued, in the first half of the project period, by the following activities and accomplishments: (i) measuring ECR values between gold nano islands and graphite substrates, (ii) improving the C-AFM methodology in order to achieve more reliable and reproducible results, and (iii) understanding the physical mechanisms of the phenomenon of "conduction aging" we often observe in the experiments. In the second half of the project, our work evolved into the use of C-AFM as a powerful atomic-resolution imaging tool under ambient conditions, with exemplary results reported on various 2D materials as well as thin crystals of Mo_2C, in collaboration with the TOBB University of Economics and Technology as well as Eskisehir Technical University (ETU). The results of the project have been shared with the scientific community by way of five journal publications and multiple invited as well as contributed presentations at conferences and research institutions.

1. Accomplishments

1.1 Research Objectives

The main research objectives of this project can be considered under two broad headings, separated into the first and second half of the project period.

(1) During the first half of the project period, the main research objective has been to investigate physical mechanisms of ECR at small length scales, and study the transition from the diffusive to the ballistic conduction regimes.

(2) During the second half of the project, the main research objective has been to utilize C-AFM as an atomic-resolution imaging tool under ambient conditions, to study the structure and electronic properties of defects on various 2D materials as well as thin crystals of Mo_2C grown via chemical vapor deposition (grown by Dr. Goknur Buke's group at TOBB University), a prominent member of the emerging material class of thin TMCs.

1.2 Research Accomplishments

We have been partially successful in meeting the goals associated with Research Objective (1) listed above. In particular:

(i) We have performed C-AFM-based ECR measurements on a sample system comprising atomically flat interfaces (up to several hundreds of nanometers in lateral size) formed between gold islands and a highly oriented pyrolytic graphite (HOPG) substrate. Proof-of-principle experiments performed on gold islands of varying size pointed toward an increasing contribution of the island-HOPG junction to the measured total resistance with decreasing island size. Atomistic simulations complemented and elucidated experimental results, revealing the maximum island sizes below which the electrical contact resistance at the island-HOPG junction can be feasibly extracted from the measured total resistance.

Publication: Vazirisereshk, M.R., Sumaiya, S.A., Martini, A., Baykara, M.Z., *Measurement of Electrical Contact Resistance at Nanoscale Gold-Graphite Interfaces*, Applied Physics Letters **115**, 091602 (2019).

(ii) We have improved our C-AFM methodology in order to achieve more reliable and reproducible results. In particular, we presented an approach aimed at improving the reliability of C-AFM measurements by addressing multiple sources of variability. Specifically, we performed current-voltage (*I-V*) spectroscopy on atomically flat terraces HOPG under an inert nitrogen atmosphere and at controlled temperatures. The sample was annealed before the measurements to desorb adsorbates, and conductive diamond tips are used to limit tip apex deformation. These precautions lead to measured ECR values that follow a Gaussian distribution with significantly smaller standard deviation than those obtained under conventional measurement conditions. The key factor leading

to this improvement was identified as the switch from ambient conditions to a dry nitrogen atmosphere.

Publication: Sumaiya, S.A., Martini, A., Baykara, M.Z., *Improving the Reliability of Conductive Atomic Force Microscopy-Based Electrical Contact Resistance Measurements*, Nano Express **1**, 030023 (2020).

(iii) We employed a combined experimental and computational approach to understand the physical mechanisms of the phenomenon of "electrical conduction aging" we often observe in the experiments. In particular, ECR was shown to decrease over time as measured using C-AFM and estimated using two approaches from MD simulations. The simulations show that time dependence of ECR is attributable to an increase in real contact area due to atoms diffusing into the contact. This diffusion-based aging was found to be a thermally activated process that depends on the local contact pressure.

Publication: Vazirisereshk, M.R., Sumaiya, S.A., Chen, R., Baykara, M.Z., Martini, A., *Time-Dependent Electrical Contact Resistance at the Nanoscale*, Tribology Letters **69**, 50 (2021).

Despite the accomplishments listed above, the superlubric (i.e., ultra-low friction) character of the gold-graphite sample we investigated in the project has prevented us from establishing robust and stable electrical contacts over small gold nano islands, which ultimately prevented us from studying the ballistic transport regime that would only be observable at miniscule contact areas.

On the other hand, the extensive experience we developed with the use of C-AFM throughout the first part of the project fueled an exciting, alternative research direction in the second half of the project, which culminated in the following accomplishment:

(iv) We showed the use of C-AFM as a powerful atomic-resolution imaging tool under ambient conditions, with proof-of-principle measurements performed on a variety of 2D materials (MoS_2, $PtSe_2$, WS_2), as well as CVD-grown thin crystals of Mo_2C. Our method delivered images of defects down to the single vacancy level. Using our method, we additionally reported the capability of in situ charge state manipulation of defects on MoS_2 and the observation of charge ordering on Mo_2C.

Publication: Sumaiya, S.A., Liu, J., Baykara, M.Z., *True Atomic-Resolution Surface Imaging and Manipulation under Ambient Conditions via Conductive Atomic Force Microscopy*, ACS Nano **16**, 20086 (2022).

1.3 Dissemination Activities

As already indicated in the previous sections, the results of our work have been shared with the scientific community by way of multiple journal articles in well-respected outlets, as well as invited and contributed talks at conferences and research institutions.

A list of **all invited talks** associated with this project is provided below:

1. Baykara, M.Z, *Atomic-Resolution Surface Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, Turkish Society of Electron Microscopy Webinar, Stanford Virtual, December 7, 2022.

2. Baykara, M.Z, *Make Measurable What is Not So: Atomic-Resolution Surface Imaging and Manipulation under Ambient Conditions*, Geballe Laboratory for Advanced Materials (GLAM) Special Seminar, Stanford University, Palo Alto, USA, November 2, 2022.

3. Baykara, M.Z., *Where Flatlands Meet: Mechanics and Electronics at Atomically Flat Interfaces*, UCLA, Department of Materials Science & Engineering Seminar, Los Angeles, USA, January 17, 2020.

4. Baykara, M.Z., *Measurement of Electrical Contact Resistance at Nanoscale Gold-Graphite Interfaces*, 15th Nanoscience and Nanotechnology Conference, Antalya, Turkey, November 6, 2019.

A list of **all contributed talks** associated with this project is provided below:

1. Vaziriseresk, M. *et al.*, *Insight into Dynamic Sliding Contacts from Conductive Atomic Force Microscopy*, STLE Virtual Student Conference, May 2020.

2. Vazirisereshk, M. *et al.*, *Electrical Contact Resistance at Gold/Graphene Interfaces,* Tribology Frontiers Conference, Chicago IL, October 2019.

3. Sumaiya, S.A. *et al.*, *True Atomic-Resolution Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, AVS 68th International Symposium & Exhibition, Pittsburgh, USA, November 2022.

4. Sumaiya, S.A. *et al.*, *True Atomic-Resolution Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, 2022 MRS Spring Meeting & Exhibit, Honolulu, USA, May 2022.

5. Sumaiya, S.A. *et al.*, *Atomically Resolved Imaging of Electronic Defects in a CVD Grown Transition Metal Carbide: α–Mo_2C*, 2021 MRS Fall Meeting & Exhibit, Boston, USA, November 2021.
6. Sumaiya, S.A. *et al.*, *Temporal Evolution of Electrical Contact Resistance Observed via Improved Conductive Atomic Force Microscopy*, AVS 67th International Symposium & Exhibition (*Virtual*), October 2021.

Both PIs have been active in general outreach activities throughout the duration of the project, whereby the main tools used during the course of the project (AFM and MD simulations) have been introduced to students from the elementary to the high school level via various events.

2. Impacts

2.1 Impact on the development of the principal discipline(s) of the project

The field of atomic-resolution surface imaging has been essentially confined to the pristine yet impractical conditions of ultra-high vacuum (UHV) and low temperatures. With our new C-AFM method being able to provide true atomic-resolution maps of surfaces under ambient conditions, without the need for expensive and hard-to-maintain UHV equipment, we expect the results of our project to have significant impact on the principal discipline of scanning probe microscopy (SPM). Perhaps equally importantly, having access to the structure and electronic properties of material surfaces under ambient conditions is projected to have important contributions for potential device applications based on emerging materials, which will, most of the time, operate under ambient conditions, as opposed to the pristine UHV environment.

2.2 Impact on the development of human resources

Three PhD students have been funded by the project throughout its existence as Graduate Student Researchers (GSRs), which provided significant opportunities for academic and professional growth. **Saima A. Sumaiya**, the GSR who worked on the project from the first day and performed all associated experiments, graduated recently with flying colors and has started a position as **Postdoctoral Fellow at Columbia University**. Saima won multiple awards during his time at UC Merced thanks to the AFOSR project, which include the *STLE Northern California Section Research Scholarship* as well as the *Graduate Dean's Dissertation Fellowship* at UC Merced. **Mohammad Vazirisereshk**, the first computational GSR to work on this project, obtained his PhD in May 2021 and then obtained a research position at Lam Research. **Karen Mohammadtabar**, who worked on the second half of the project, just successfully defended his PhD in December 2022. Both Mohammad and Karen won the *STLE Northern California Section Research Scholarship*, in 2019 and 2020, respectively. Also, Karen was among the ten finalists at UC Merced's GradSlam competition in 2022, where students present their research via three slides in three minutes.

3. Changes

3.1 Changes in approach

As explained in Section 1.2, the scope and goals of the project changed after about 2 years from its start. Specifically, instead of performing a detailed study of the transition between the electronic and ballistic electron transport regimes (which have been hampered by the superlubricity of the gold-graphite sample which prevented the formation of robust and stable electrical contacts on small gold islands), our efforts have been re-directed at the use of C-AFM for the atomic-resolution study of defects on 2D materials as well as thin, chemical-vapor-deposition-grown Mo_2C crystals (provided by Prof. Goknur Buke and her research group at TOBB University). This change in direction has been extensively discussed with and approved by the program officer.

4. Technical Updates

The progress associated with the 3-year reporting period between 12/2018 and 12/2021 has been covered in detail in prior progress reports. Here, we report on technical updates that have been realized in the last period of the project, from 12/2021 to 12/2022.

4.1 Electronic manipulation of defects via C-AFM

Going beyond imaging, we also investigated the capability of our method to electronically manipulate defects under ambient conditions. In particular, Figure 1A shows a current image on MoS_2 with two extended defects that exhibit higher conductivity than their surroundings. Magnified images on the defects allow their study with high spatial resolution (Figure 1B). By performing *I-V* sweeps for multiple cycles (Figure 1C), we found an emerging peak in the *I-V* curves at a bias voltage of about -1.7 V, which is first attenuated and then re-emerges during the *I-V* cycles. This is accompanied by a side peak appearing between -1.1 and -1.3 V. After the *I-V* sweeps, the high conductivity region associated with the defect disappears (see Figures 1D, E, to be compared with Figures1A, B). The possibility of surface contamination can be ruled out as roughness fluctuations are not observed in the corresponding topography images (Figures 1F-I). The negative differential resistance in Figure 1C, characterized by a decrease in current with increasing voltage, may be related to localized surface charging/discharging behavior. According to the passive sign convention, more electrons may flow out of the defect location, indicating a pre-existing negatively charged region. After *I-V* sweeping, more positive charge will accumulate in the region to compensate the non-uniform charge states, which may explain the slightly lower current detected on the defect location after the *I-V* sweeps (Figure 1E). These experiments demonstrate that our C-AFM method may provide a feasible strategy for localized manipulation/elimination of electrical surface defects on 2D materials under ambient conditions.

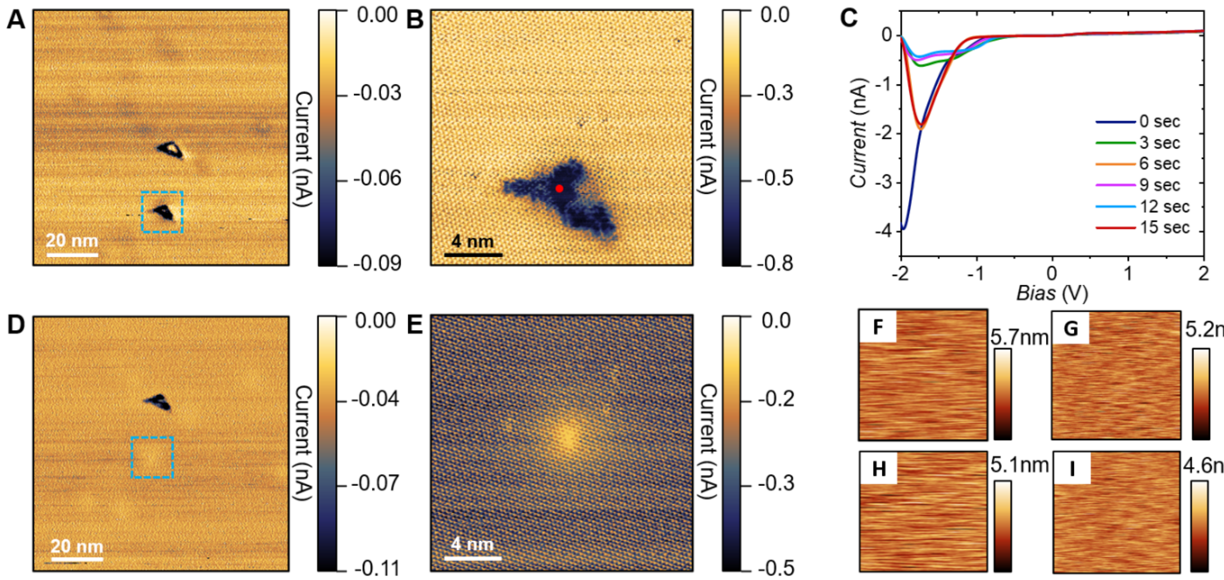

Figure 1. Electronic manipulation of a defect on MoS_2 via C-AFM under ambient conditions. (A) A large-scale current image showing two defects. **(B)** Zoom-in current image on the defect highlighted by the blue dashed square in (**A**). The defect features enhanced conductivity compared to its surroundings. **(C)** *I-V* curves recorded on top of the defect location marked with the red dot in **(B)**. **(D)** Current image of area **(A)** after the *I-V* sweeps. **(E)** Current image capturing the same defect in **(B)** after the *I-V* sweeps. The defect now features a slightly lower conductivity compared to its surroundings, with the uninterrupted atomic lattice overlaid on top of it. **(F-I)** Corresponding topographic images for **(A)**, **(B)**, **(D)**, and **(E)**, respectively. All images were obtained with an applied normal load of 0.0 nN, and at a scanning speed 15.62 Hz. Bias voltages: **(A)** -1.0 V, **(B)** -1.3 V, **(D)** -0.8 V, **(E)** -0.8 V.

4.2 Room-temperature charge ordering on Mo_2C

We employed our methodology to explore the surface electronic properties of thin Mo_2C crystals. In particular, C-AFM measurements revealed a periodic modulation (i.e., ordering) of charge, superimposed on the atomic lattice structure of Mo_2C (Figure 2A), in an area that includes two extended defects. The corresponding Fourier Transform (FT) shown in Figure 2B corroborates this observation, whereby the bright spots highlighted by red circles (with a periodicity of ~2.2 Å) represent the atomic structure of the Mo_2C surface, and the bright spots highlighted by green circles represent the periodic charge modulation with a periodicity of ~11.4 Å. Even more interestingly, the FT clearly shows the broken rotational symmetry between these two periodicities with an angular difference of ~13°. These results are supported by additional measurements on the material surface that show charge ordering (Figures 2C, E), with the corresponding FT again showing two periodicities corresponding to the lattice structure (~2.2 Å) and charge modulation (~11.1 Å), respectively, with an angular difference of ~12° between the two (Figure 2D). This discovery (which would need to be independently confirmed by angle-resolved photoemission spectroscopy (ARPES) measurements) has the potential to be important not only from a fundamental point of view) but also from a technological perspective as it may lead to the possibility of exciting electronic device applications at room temperature.

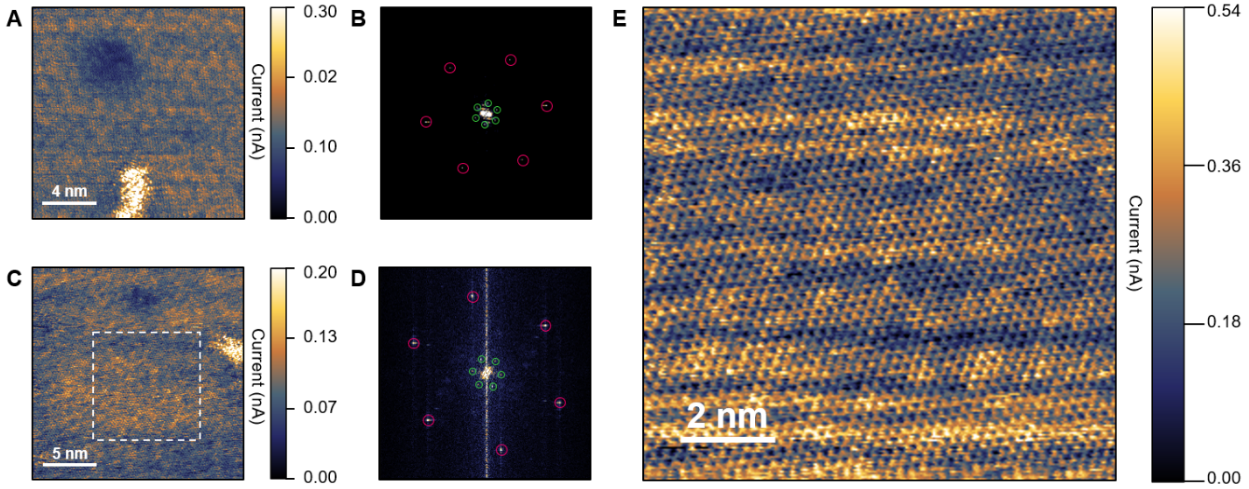

Figure 2. Observation of room-temperature charge ordering on Mo_2C via C-AFM. **(A)** Current image recorded on Mo_2C, showing periodic modulation of charge, along with two defects. **(B)** The corresponding FT of the image shown in **(A)**. The bright spots highlighted by red circles represent the lattice structure of α-Mo_2C with a periodicity of ~ 2.2 Å while the bright spots highlighted by green circles represent the charge modulation with a periodicity of ~11.4 Å. **(C)** Another current image recorded on α-Mo_2C exhibiting charge ordering. **(D)** The corresponding FT of the image shown in **(C)**. The bright spots highlighted by red and green circles represent lattice structure of α-Mo_2C (periodicity ~2.2 Å) and periodic modulation of charge (periodicity ~11.1 Å), respectively. **(E)** Zoom-in current image of the area highlighted by the white dotted rectangle in **(C)**, showing an ordering of charge superimposed on the atomic surface lattice. All images were obtained with an applied normal load of 0.0 nN, and at a scanning frequency of 15.62 Hz. Bias voltages: **(A)** 100 mV, **(C)** 1.3 V, **(E)** 1.3 V.

Award Number: FA9550-19-1-0035

Report Type: Final Performance Report

Reporting Period: 12/15/2018 – 12/14/2022

Distribution Statement: *A – Approved for Public Release*

Program Officer Name: Dr. Ali Sayir

Principle Investigator Name: Mehmet Z. Baykara & Ashlie Martini

Project Title: Investigating the Mechanisms of Electrical Contact Resistance between the Diffusive and Ballistic Limits

Abstract:

The original goal of this project was to investigate the mechanisms of electrical contact resistance (ECR) on small length scales through an interplay of conductive atomic force microscopy (C-AFM) experiments and atomistic simulations. This goal has been pursued, in the first half of the project period, by the following activities and accomplishments: (i) measuring ECR values between gold nano islands and graphite substrates, (ii) improving the C-AFM methodology in order to achieve more reliable and reproducible results, and (iii) understanding the physical mechanisms of the phenomenon of "conduction aging" we often observe in the experiments. In the second half of the project, our work evolved into the use of C-AFM as a powerful atomic-resolution imaging tool under ambient conditions, with exemplary results reported on various 2D materials as well as thin crystals of Mo_2C, in collaboration with the TOBB University of Economics and Technology as well as Eskisehir Technical University (ETU). The results of the project have been shared with the scientific community by way of five journal publications and multiple invited as well as contributed presentations at conferences and research institutions.

1. Accomplishments

1.1 Research Objectives

The main research objectives of this project can be considered under two broad headings, separated into the first and second half of the project period.

(1) During the first half of the project period, the main research objective has been to investigate physical mechanisms of ECR at small length scales, and study the transition from the diffusive to the ballistic conduction regimes.

(2) During the second half of the project, the main research objective has been to utilize C-AFM as an atomic-resolution imaging tool under ambient conditions, to study the structure and electronic properties of defects on various 2D materials as well as thin crystals of Mo_2C grown via chemical vapor deposition (grown by Dr. Goknur Buke's group at TOBB University), a prominent member of the emerging material class of thin TMCs.

1.2 Research Accomplishments

We have been partially successful in meeting the goals associated with Research Objective (1) listed above. In particular:

(i) We have performed C-AFM-based ECR measurements on a sample system comprising atomically flat interfaces (up to several hundreds of nanometers in lateral size) formed between gold islands and a highly oriented pyrolytic graphite (HOPG) substrate. Proof-of-principle experiments performed on gold islands of varying size pointed toward an increasing contribution of the island-HOPG junction to the measured total resistance with decreasing island size. Atomistic simulations complemented and elucidated experimental results, revealing the maximum island sizes below which the electrical contact resistance at the island-HOPG junction can be feasibly extracted from the measured total resistance.

Publication: Vazirisereshk, M.R., Sumaiya, S.A., Martini, A., Baykara, M.Z., *Measurement of Electrical Contact Resistance at Nanoscale Gold-Graphite Interfaces*, Applied Physics Letters **115**, 091602 (2019).

(ii) We have improved our C-AFM methodology in order to achieve more reliable and reproducible results. In particular, we presented an approach aimed at improving the reliability of C-AFM measurements by addressing multiple sources of variability. Specifically, we performed current-voltage (*I-V*) spectroscopy on atomically flat terraces HOPG under an inert nitrogen atmosphere and at controlled temperatures. The sample was annealed before the measurements to desorb adsorbates, and conductive diamond tips are used to limit tip apex deformation. These precautions lead to measured ECR values that follow a Gaussian distribution with significantly smaller standard deviation than those obtained under conventional measurement conditions. The key factor leading

to this improvement was identified as the switch from ambient conditions to a dry nitrogen atmosphere.

Publication: Sumaiya, S.A., Martini, A., Baykara, M.Z., *Improving the Reliability of Conductive Atomic Force Microscopy-Based Electrical Contact Resistance Measurements*, Nano Express **1**, 030023 (2020).

(iii) We employed a combined experimental and computational approach to understand the physical mechanisms of the phenomenon of "electrical conduction aging" we often observe in the experiments. In particular, ECR was shown to decrease over time as measured using C-AFM and estimated using two approaches from MD simulations. The simulations show that time dependence of ECR is attributable to an increase in real contact area due to atoms diffusing into the contact. This diffusion-based aging was found to be a thermally activated process that depends on the local contact pressure.

Publication: Vazirisereshk, M.R., Sumaiya, S.A., Chen, R., Baykara, M.Z., Martini, A., *Time-Dependent Electrical Contact Resistance at the Nanoscale*, Tribology Letters **69**, 50 (2021).

Despite the accomplishments listed above, the superlubric (i.e., ultra-low friction) character of the gold-graphite sample we investigated in the project has prevented us from establishing robust and stable electrical contacts over small gold nano islands, which ultimately prevented us from studying the ballistic transport regime that would only be observable at miniscule contact areas.

On the other hand, the extensive experience we developed with the use of C-AFM throughout the first part of the project fueled an exciting, alternative research direction in the second half of the project, which culminated in the following accomplishment:

(iv) We showed the use of C-AFM as a powerful atomic-resolution imaging tool under ambient conditions, with proof-of-principle measurements performed on a variety of 2D materials (MoS_2, $PtSe_2$, WS_2), as well as CVD-grown thin crystals of Mo_2C. Our method delivered images of defects down to the single vacancy level. Using our method, we additionally reported the capability of in situ charge state manipulation of defects on MoS_2 and the observation of charge ordering on Mo_2C.

Publication: Sumaiya, S.A., Liu, J., Baykara, M.Z., *True Atomic-Resolution Surface Imaging and Manipulation under Ambient Conditions via Conductive Atomic Force Microscopy*, ACS Nano **16**, 20086 (2022).

1.3 Dissemination Activities

As already indicated in the previous sections, the results of our work have been shared with the scientific community by way of multiple journal articles in well-respected outlets, as well as invited and contributed talks at conferences and research institutions.

A list of **all invited talks** associated with this project is provided below:

1. Baykara, M.Z, *Atomic-Resolution Surface Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, Turkish Society of Electron Microscopy Webinar, Stanford Virtual, December 7, 2022.

2. Baykara, M.Z, *Make Measurable What is Not So: Atomic-Resolution Surface Imaging and Manipulation under Ambient Conditions*, Geballe Laboratory for Advanced Materials (GLAM) Special Seminar, Stanford University, Palo Alto, USA, November 2, 2022.

3. Baykara, M.Z., *Where Flatlands Meet: Mechanics and Electronics at Atomically Flat Interfaces*, UCLA, Department of Materials Science & Engineering Seminar, Los Angeles, USA, January 17, 2020.

4. Baykara, M.Z., *Measurement of Electrical Contact Resistance at Nanoscale Gold-Graphite Interfaces*, 15th Nanoscience and Nanotechnology Conference, Antalya, Turkey, November 6, 2019.

A list of **all contributed talks** associated with this project is provided below:

1. Vaziriseresk, M. *et al.*, *Insight into Dynamic Sliding Contacts from Conductive Atomic Force Microscopy*, STLE Virtual Student Conference, May 2020.

2. Vazirisereshk, M. *et al.*, *Electrical Contact Resistance at Gold/Graphene Interfaces,* Tribology Frontiers Conference, Chicago IL, October 2019.

3. Sumaiya, S.A. *et al.*, *True Atomic-Resolution Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, AVS 68th International Symposium & Exhibition, Pittsburgh, USA, November 2022.

4. Sumaiya, S.A. *et al.*, *True Atomic-Resolution Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, 2022 MRS Spring Meeting & Exhibit, Honolulu, USA, May 2022.

5. Sumaiya, S.A. *et al.*, *Atomically Resolved Imaging of Electronic Defects in a CVD Grown Transition Metal Carbide: α–Mo_2C*, 2021 MRS Fall Meeting & Exhibit, Boston, USA, November 2021.
6. Sumaiya, S.A. *et al.*, *Temporal Evolution of Electrical Contact Resistance Observed via Improved Conductive Atomic Force Microscopy*, AVS 67th International Symposium & Exhibition (*Virtual*), October 2021.

Both PIs have been active in general outreach activities throughout the duration of the project, whereby the main tools used during the course of the project (AFM and MD simulations) have been introduced to students from the elementary to the high school level via various events.

2. Impacts

2.1 Impact on the development of the principal discipline(s) of the project

The field of atomic-resolution surface imaging has been essentially confined to the pristine yet impractical conditions of ultra-high vacuum (UHV) and low temperatures. With our new C-AFM method being able to provide true atomic-resolution maps of surfaces under ambient conditions, without the need for expensive and hard-to-maintain UHV equipment, we expect the results of our project to have significant impact on the principal discipline of scanning probe microscopy (SPM). Perhaps equally importantly, having access to the structure and electronic properties of material surfaces under ambient conditions is projected to have important contributions for potential device applications based on emerging materials, which will, most of the time, operate under ambient conditions, as opposed to the pristine UHV environment.

2.2 Impact on the development of human resources

Three PhD students have been funded by the project throughout its existence as Graduate Student Researchers (GSRs), which provided significant opportunities for academic and professional growth. **Saima A. Sumaiya**, the GSR who worked on the project from the first day and performed all associated experiments, graduated recently with flying colors and has started a position as **Postdoctoral Fellow at Columbia University**. Saima won multiple awards during his time at UC Merced thanks to the AFOSR project, which include the *STLE Northern California Section Research Scholarship* as well as the *Graduate Dean's Dissertation Fellowship* at UC Merced. **Mohammad Vazirisereshk**, the first computational GSR to work on this project, obtained his PhD in May 2021 and then obtained a research position at Lam Research. **Karen Mohammadtabar**, who worked on the second half of the project, just successfully defended his PhD in December 2022. Both Mohammad and Karen won the *STLE Northern California Section Research Scholarship*, in 2019 and 2020, respectively. Also, Karen was among the ten finalists at UC Merced's GradSlam competition in 2022, where students present their research via three slides in three minutes.

3. Changes

3.1 Changes in approach

As explained in Section 1.2, the scope and goals of the project changed after about 2 years from its start. Specifically, instead of performing a detailed study of the transition between the electronic and ballistic electron transport regimes (which have been hampered by the superlubricity of the gold-graphite sample which prevented the formation of robust and stable electrical contacts on small gold islands), our efforts have been re-directed at the use of C-AFM for the atomic-resolution study of defects on 2D materials as well as thin, chemical-vapor-deposition-grown Mo_2C crystals (provided by Prof. Goknur Buke and her research group at TOBB University). This change in direction has been extensively discussed with and approved by the program officer.

4. Technical Updates

The progress associated with the 3-year reporting period between 12/2018 and 12/2021 has been covered in detail in prior progress reports. Here, we report on technical updates that have been realized in the last period of the project, from 12/2021 to 12/2022.

4.1 Electronic manipulation of defects via C-AFM

Going beyond imaging, we also investigated the capability of our method to electronically manipulate defects under ambient conditions. In particular, Figure 1A shows a current image on MoS_2 with two extended defects that exhibit higher conductivity than their surroundings. Magnified images on the defects allow their study with high spatial resolution (Figure 1B). By performing *I-V* sweeps for multiple cycles (Figure 1C), we found an emerging peak in the *I-V* curves at a bias voltage of about -1.7 V, which is first attenuated and then re-emerges during the *I-V* cycles. This is accompanied by a side peak appearing between -1.1 and -1.3 V. After the *I-V* sweeps, the high conductivity region associated with the defect disappears (see Figures 1D, E, to be compared with Figures1A, B). The possibility of surface contamination can be ruled out as roughness fluctuations are not observed in the corresponding topography images (Figures 1F-I). The negative differential resistance in Figure 1C, characterized by a decrease in current with increasing voltage, may be related to localized surface charging/discharging behavior. According to the passive sign convention, more electrons may flow out of the defect location, indicating a pre-existing negatively charged region. After *I-V* sweeping, more positive charge will accumulate in the region to compensate the non-uniform charge states, which may explain the slightly lower current detected on the defect location after the *I-V* sweeps (Figure 1E). These experiments demonstrate that our C-AFM method may provide a feasible strategy for localized manipulation/elimination of electrical surface defects on 2D materials under ambient conditions.

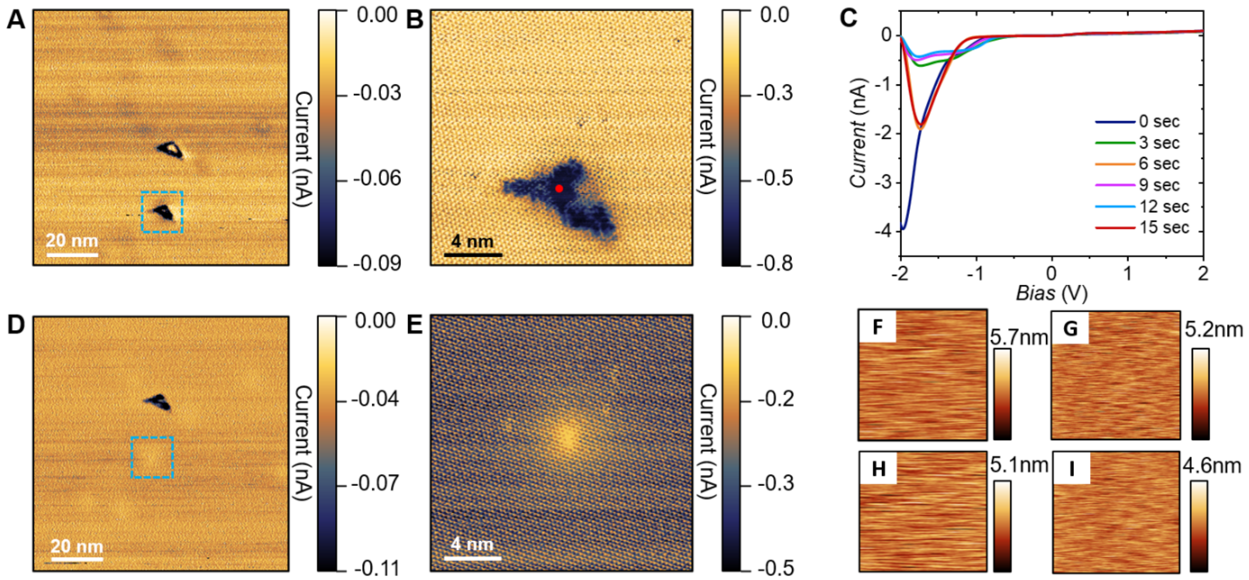

Figure 1. Electronic manipulation of a defect on MoS_2 via C-AFM under ambient conditions. (A) A large-scale current image showing two defects. **(B)** Zoom-in current image on the defect highlighted by the blue dashed square in (**A**). The defect features enhanced conductivity compared to its surroundings. **(C)** *I*-*V* curves recorded on top of the defect location marked with the red dot in **(B)**. **(D)** Current image of area **(A)** after the *I*-*V* sweeps. **(E)** Current image capturing the same defect in **(B)** after the *I*-*V* sweeps. The defect now features a slightly lower conductivity compared to its surroundings, with the uninterrupted atomic lattice overlaid on top of it. **(F-I)** Corresponding topographic images for **(A)**, **(B)**, **(D)**, and **(E)**, respectively. All images were obtained with an applied normal load of 0.0 nN, and at a scanning speed 15.62 Hz. Bias voltages: **(A)** -1.0 V, **(B)** -1.3 V, **(D)** -0.8 V, **(E)** -0.8 V.

4.2 Room-temperature charge ordering on Mo_2C

We employed our methodology to explore the surface electronic properties of thin Mo_2C crystals. In particular, C-AFM measurements revealed a periodic modulation (i.e., ordering) of charge, superimposed on the atomic lattice structure of Mo_2C (Figure 2A), in an area that includes two extended defects. The corresponding Fourier Transform (FT) shown in Figure 2B corroborates this observation, whereby the bright spots highlighted by red circles (with a periodicity of ~2.2 Å) represent the atomic structure of the Mo_2C surface, and the bright spots highlighted by green circles represent the periodic charge modulation with a periodicity of ~11.4 Å. Even more interestingly, the FT clearly shows the broken rotational symmetry between these two periodicities with an angular difference of ~13°. These results are supported by additional measurements on the material surface that show charge ordering (Figures 2C, E), with the corresponding FT again showing two periodicities corresponding to the lattice structure (~2.2 Å) and charge modulation (~11.1 Å), respectively, with an angular difference of ~12° between the two (Figure 2D). This discovery (which would need to be independently confirmed by angle-resolved photoemission spectroscopy (ARPES) measurements) has the potential to be important not only from a fundamental point of view) but also from a technological perspective as it may lead to the possibility of exciting electronic device applications at room temperature.

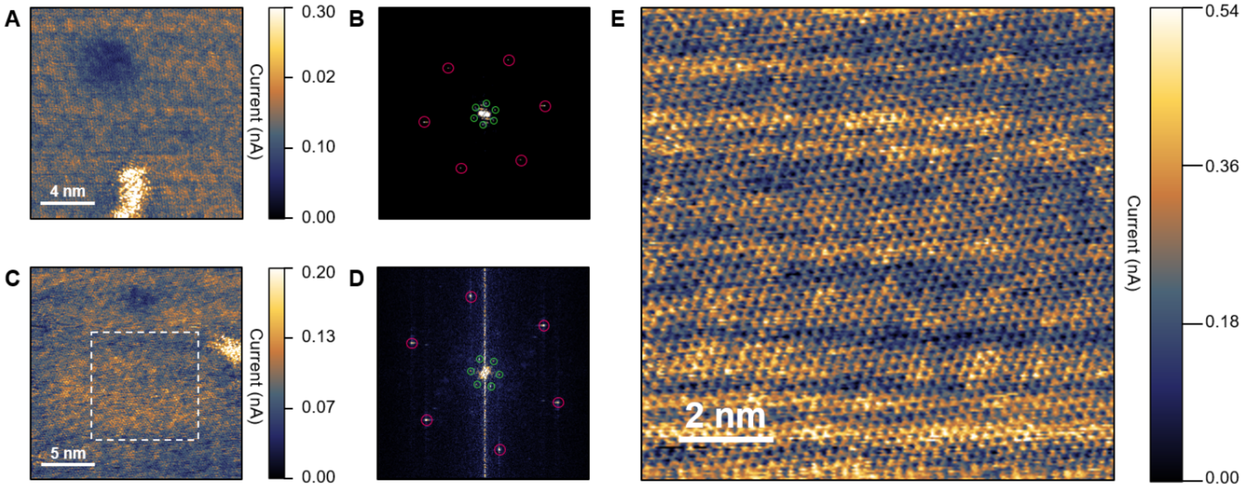

Figure 2. Observation of room-temperature charge ordering on Mo_2C via C-AFM. **(A)** Current image recorded on Mo_2C, showing periodic modulation of charge, along with two defects. **(B)** The corresponding FT of the image shown in **(A)**. The bright spots highlighted by red circles represent the lattice structure of α-Mo_2C with a periodicity of ~ 2.2 Å while the bright spots highlighted by green circles represent the charge modulation with a periodicity of ~11.4 Å. **(C)** Another current image recorded on α-Mo_2C exhibiting charge ordering. **(D)** The corresponding FT of the image shown in **(C)**. The bright spots highlighted by red and green circles represent lattice structure of α-Mo_2C (periodicity ~2.2 Å) and periodic modulation of charge (periodicity ~11.1 Å), respectively. **(E)** Zoom-in current image of the area highlighted by the white dotted rectangle in **(C)**, showing an ordering of charge superimposed on the atomic surface lattice. All images were obtained with an applied normal load of 0.0 nN, and at a scanning frequency of 15.62 Hz. Bias voltages: **(A)** 100 mV, **(C)** 1.3 V, **(E)** 1.3 V.

Award Number: FA9550-19-1-0035

Report Type: Final Performance Report

Reporting Period: 12/15/2018 – 12/14/2022

Distribution Statement: *A – Approved for Public Release*

Program Officer Name: Dr. Ali Sayir

Principle Investigator Name: Mehmet Z. Baykara & Ashlie Martini

Project Title: Investigating the Mechanisms of Electrical Contact Resistance between the Diffusive and Ballistic Limits

Abstract:

The original goal of this project was to investigate the mechanisms of electrical contact resistance (ECR) on small length scales through an interplay of conductive atomic force microscopy (C-AFM) experiments and atomistic simulations. This goal has been pursued, in the first half of the project period, by the following activities and accomplishments: (i) measuring ECR values between gold nano islands and graphite substrates, (ii) improving the C-AFM methodology in order to achieve more reliable and reproducible results, and (iii) understanding the physical mechanisms of the phenomenon of "conduction aging" we often observe in the experiments. In the second half of the project, our work evolved into the use of C-AFM as a powerful atomic-resolution imaging tool under ambient conditions, with exemplary results reported on various 2D materials as well as thin crystals of Mo_2C, in collaboration with the TOBB University of Economics and Technology as well as Eskisehir Technical University (ETU). The results of the project have been shared with the scientific community by way of five journal publications and multiple invited as well as contributed presentations at conferences and research institutions.

1. Accomplishments

1.1 Research Objectives

The main research objectives of this project can be considered under two broad headings, separated into the first and second half of the project period.

(1) During the first half of the project period, the main research objective has been to investigate physical mechanisms of ECR at small length scales, and study the transition from the diffusive to the ballistic conduction regimes.

(2) During the second half of the project, the main research objective has been to utilize C-AFM as an atomic-resolution imaging tool under ambient conditions, to study the structure and electronic properties of defects on various 2D materials as well as thin crystals of Mo_2C grown via chemical vapor deposition (grown by Dr. Goknur Buke's group at TOBB University), a prominent member of the emerging material class of thin TMCs.

1.2 Research Accomplishments

We have been partially successful in meeting the goals associated with Research Objective (1) listed above. In particular:

(i) We have performed C-AFM-based ECR measurements on a sample system comprising atomically flat interfaces (up to several hundreds of nanometers in lateral size) formed between gold islands and a highly oriented pyrolytic graphite (HOPG) substrate. Proof-of-principle experiments performed on gold islands of varying size pointed toward an increasing contribution of the island-HOPG junction to the measured total resistance with decreasing island size. Atomistic simulations complemented and elucidated experimental results, revealing the maximum island sizes below which the electrical contact resistance at the island-HOPG junction can be feasibly extracted from the measured total resistance.

Publication: Vazirisereshk, M.R., Sumaiya, S.A., Martini, A., Baykara, M.Z., *Measurement of Electrical Contact Resistance at Nanoscale Gold-Graphite Interfaces*, Applied Physics Letters **115**, 091602 (2019).

(ii) We have improved our C-AFM methodology in order to achieve more reliable and reproducible results. In particular, we presented an approach aimed at improving the reliability of C-AFM measurements by addressing multiple sources of variability. Specifically, we performed current-voltage (*I-V*) spectroscopy on atomically flat terraces HOPG under an inert nitrogen atmosphere and at controlled temperatures. The sample was annealed before the measurements to desorb adsorbates, and conductive diamond tips are used to limit tip apex deformation. These precautions lead to measured ECR values that follow a Gaussian distribution with significantly smaller standard deviation than those obtained under conventional measurement conditions. The key factor leading

to this improvement was identified as the switch from ambient conditions to a dry nitrogen atmosphere.

Publication: Sumaiya, S.A., Martini, A., Baykara, M.Z., *Improving the Reliability of Conductive Atomic Force Microscopy-Based Electrical Contact Resistance Measurements*, Nano Express **1**, 030023 (2020).

(iii) We employed a combined experimental and computational approach to understand the physical mechanisms of the phenomenon of “electrical conduction aging” we often observe in the experiments. In particular, ECR was shown to decrease over time as measured using C-AFM and estimated using two approaches from MD simulations. The simulations show that time dependence of ECR is attributable to an increase in real contact area due to atoms diffusing into the contact. This diffusion-based aging was found to be a thermally activated process that depends on the local contact pressure.

Publication: Vazirisereshk, M.R., Sumaiya, S.A., Chen, R., Baykara, M.Z., Martini, A., *Time-Dependent Electrical Contact Resistance at the Nanoscale*, Tribology Letters **69**, 50 (2021).

Despite the accomplishments listed above, the superlubric (i.e., ultra-low friction) character of the gold-graphite sample we investigated in the project has prevented us from establishing robust and stable electrical contacts over small gold nano islands, which ultimately prevented us from studying the ballistic transport regime that would only be observable at miniscule contact areas.

On the other hand, the extensive experience we developed with the use of C-AFM throughout the first part of the project fueled an exciting, alternative research direction in the second half of the project, which culminated in the following accomplishment:

(iv) We showed the use of C-AFM as a powerful atomic-resolution imaging tool under ambient conditions, with proof-of-principle measurements performed on a variety of 2D materials (MoS_2, $PtSe_2$, WS_2), as well as CVD-grown thin crystals of Mo_2C. Our method delivered images of defects down to the single vacancy level. Using our method, we additionally reported the capability of in situ charge state manipulation of defects on MoS_2 and the observation of charge ordering on Mo_2C.

Publication: Sumaiya, S.A., Liu, J., Baykara, M.Z., *True Atomic-Resolution Surface Imaging and Manipulation under Ambient Conditions via Conductive Atomic Force Microscopy*, ACS Nano **16**, 20086 (2022).

1.3 Dissemination Activities

As already indicated in the previous sections, the results of our work have been shared with the scientific community by way of multiple journal articles in well-respected outlets, as well as invited and contributed talks at conferences and research institutions.

A list of **all invited talks** associated with this project is provided below:

1. Baykara, M.Z, *Atomic-Resolution Surface Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, Turkish Society of Electron Microscopy Webinar, Stanford Virtual, December 7, 2022.

2. Baykara, M.Z, *Make Measurable What is Not So: Atomic-Resolution Surface Imaging and Manipulation under Ambient Conditions*, Geballe Laboratory for Advanced Materials (GLAM) Special Seminar, Stanford University, Palo Alto, USA, November 2, 2022.

3. Baykara, M.Z., *Where Flatlands Meet: Mechanics and Electronics at Atomically Flat Interfaces*, UCLA, Department of Materials Science & Engineering Seminar, Los Angeles, USA, January 17, 2020.

4. Baykara, M.Z., *Measurement of Electrical Contact Resistance at Nanoscale Gold-Graphite Interfaces*, 15th Nanoscience and Nanotechnology Conference, Antalya, Turkey, November 6, 2019.

A list of **all contributed talks** associated with this project is provided below:

1. Vaziriseresk, M. *et al.*, *Insight into Dynamic Sliding Contacts from Conductive Atomic Force Microscopy*, STLE Virtual Student Conference, May 2020.

2. Vazirisereshk, M. *et al.*, *Electrical Contact Resistance at Gold/Graphene Interfaces,* Tribology Frontiers Conference, Chicago IL, October 2019.

3. Sumaiya, S.A. *et al.*, *True Atomic-Resolution Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, AVS 68th International Symposium & Exhibition, Pittsburgh, USA, November 2022.

4. Sumaiya, S.A. *et al.*, *True Atomic-Resolution Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, 2022 MRS Spring Meeting & Exhibit, Honolulu, USA, May 2022.

5. Sumaiya, S.A. *et al.*, *Atomically Resolved Imaging of Electronic Defects in a CVD Grown Transition Metal Carbide: α–Mo_2C*, 2021 MRS Fall Meeting & Exhibit, Boston, USA, November 2021.
6. Sumaiya, S.A. *et al.*, *Temporal Evolution of Electrical Contact Resistance Observed via Improved Conductive Atomic Force Microscopy*, AVS 67th International Symposium & Exhibition (*Virtual*), October 2021.

Both PIs have been active in general outreach activities throughout the duration of the project, whereby the main tools used during the course of the project (AFM and MD simulations) have been introduced to students from the elementary to the high school level via various events.

2. Impacts

2.1 Impact on the development of the principal discipline(s) of the project

The field of atomic-resolution surface imaging has been essentially confined to the pristine yet impractical conditions of ultra-high vacuum (UHV) and low temperatures. With our new C-AFM method being able to provide true atomic-resolution maps of surfaces under ambient conditions, without the need for expensive and hard-to-maintain UHV equipment, we expect the results of our project to have significant impact on the principal discipline of scanning probe microscopy (SPM). Perhaps equally importantly, having access to the structure and electronic properties of material surfaces under ambient conditions is projected to have important contributions for potential device applications based on emerging materials, which will, most of the time, operate under ambient conditions, as opposed to the pristine UHV environment.

2.2 Impact on the development of human resources

Three PhD students have been funded by the project throughout its existence as Graduate Student Researchers (GSRs), which provided significant opportunities for academic and professional growth. **Saima A. Sumaiya**, the GSR who worked on the project from the first day and performed all associated experiments, graduated recently with flying colors and has started a position as **Postdoctoral Fellow at Columbia University**. Saima won multiple awards during his time at UC Merced thanks to the AFOSR project, which include the *STLE Northern California Section Research Scholarship* as well as the *Graduate Dean's Dissertation Fellowship* at UC Merced. **Mohammad Vazirisereshk**, the first computational GSR to work on this project, obtained his PhD in May 2021 and then obtained a research position at Lam Research. **Karen Mohammadtabar**, who worked on the second half of the project, just successfully defended his PhD in December 2022. Both Mohammad and Karen won the *STLE Northern California Section Research Scholarship*, in 2019 and 2020, respectively. Also, Karen was among the ten finalists at UC Merced's GradSlam competition in 2022, where students present their research via three slides in three minutes.

3. Changes

3.1 Changes in approach

As explained in Section 1.2, the scope and goals of the project changed after about 2 years from its start. Specifically, instead of performing a detailed study of the transition between the electronic and ballistic electron transport regimes (which have been hampered by the superlubricity of the gold-graphite sample which prevented the formation of robust and stable electrical contacts on small gold islands), our efforts have been re-directed at the use of C-AFM for the atomic-resolution study of defects on 2D materials as well as thin, chemical-vapor-deposition-grown Mo_2C crystals (provided by Prof. Goknur Buke and her research group at TOBB University). This change in direction has been extensively discussed with and approved by the program officer.

4. Technical Updates

The progress associated with the 3-year reporting period between 12/2018 and 12/2021 has been covered in detail in prior progress reports. Here, we report on technical updates that have been realized in the last period of the project, from 12/2021 to 12/2022.

4.1 Electronic manipulation of defects via C-AFM

Going beyond imaging, we also investigated the capability of our method to electronically manipulate defects under ambient conditions. In particular, Figure 1A shows a current image on MoS_2 with two extended defects that exhibit higher conductivity than their surroundings. Magnified images on the defects allow their study with high spatial resolution (Figure 1B). By performing *I-V* sweeps for multiple cycles (Figure 1C), we found an emerging peak in the *I-V* curves at a bias voltage of about -1.7 V, which is first attenuated and then re-emerges during the *I-V* cycles. This is accompanied by a side peak appearing between -1.1 and -1.3 V. After the *I-V* sweeps, the high conductivity region associated with the defect disappears (see Figures 1D, E, to be compared with Figures1A, B). The possibility of surface contamination can be ruled out as roughness fluctuations are not observed in the corresponding topography images (Figures 1F-I). The negative differential resistance in Figure 1C, characterized by a decrease in current with increasing voltage, may be related to localized surface charging/discharging behavior. According to the passive sign convention, more electrons may flow out of the defect location, indicating a pre-existing negatively charged region. After *I-V* sweeping, more positive charge will accumulate in the region to compensate the non-uniform charge states, which may explain the slightly lower current detected on the defect location after the *I-V* sweeps (Figure 1E). These experiments demonstrate that our C-AFM method may provide a feasible strategy for localized manipulation/elimination of electrical surface defects on 2D materials under ambient conditions.

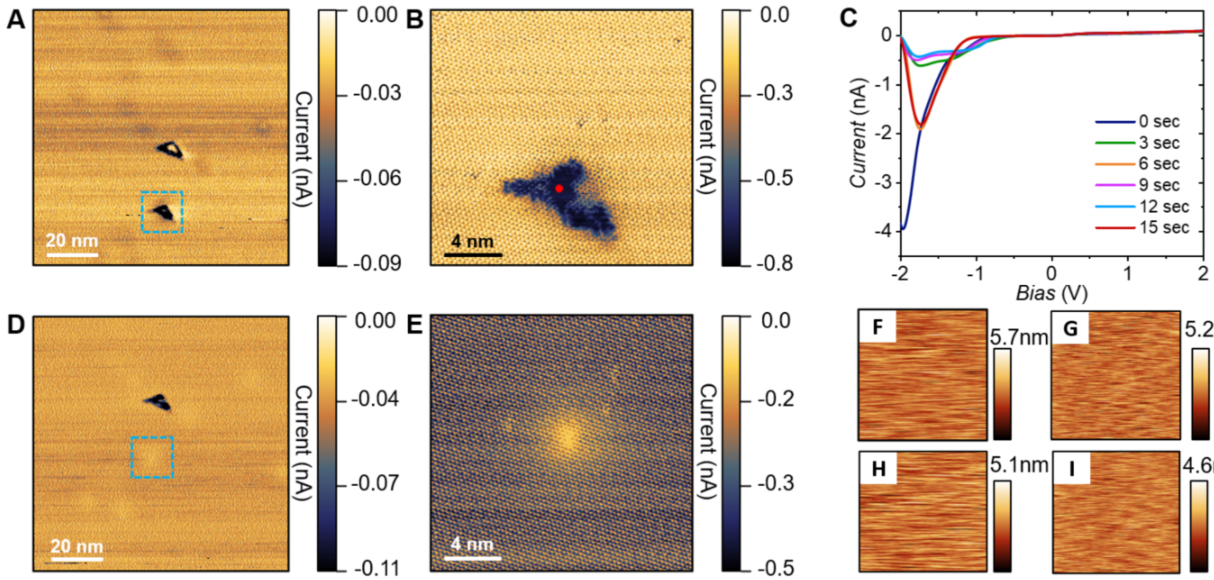

Figure 1. Electronic manipulation of a defect on MoS_2 via C-AFM under ambient conditions. (A) A large-scale current image showing two defects. **(B)** Zoom-in current image on the defect highlighted by the blue dashed square in (**A**). The defect features enhanced conductivity compared to its surroundings. **(C)** *I-V* curves recorded on top of the defect location marked with the red dot in **(B)**. **(D)** Current image of area **(A)** after the *I-V* sweeps. **(E)** Current image capturing the same defect in **(B)** after the *I-V* sweeps. The defect now features a slightly lower conductivity compared to its surroundings, with the uninterrupted atomic lattice overlaid on top of it. **(F-I)** Corresponding topographic images for **(A)**, **(B)**, **(D)**, and **(E)**, respectively. All images were obtained with an applied normal load of 0.0 nN, and at a scanning speed 15.62 Hz. Bias voltages: **(A)** -1.0 V, **(B)** -1.3 V, **(D)** -0.8 V, **(E)** -0.8 V.

4.2 Room-temperature charge ordering on Mo_2C

We employed our methodology to explore the surface electronic properties of thin Mo_2C crystals. In particular, C-AFM measurements revealed a periodic modulation (i.e., ordering) of charge, superimposed on the atomic lattice structure of Mo_2C (Figure 2A), in an area that includes two extended defects. The corresponding Fourier Transform (FT) shown in Figure 2B corroborates this observation, whereby the bright spots highlighted by red circles (with a periodicity of ~2.2 Å) represent the atomic structure of the Mo_2C surface, and the bright spots highlighted by green circles represent the periodic charge modulation with a periodicity of ~11.4 Å. Even more interestingly, the FT clearly shows the broken rotational symmetry between these two periodicities with an angular difference of ~13°. These results are supported by additional measurements on the material surface that show charge ordering (Figures 2C, E), with the corresponding FT again showing two periodicities corresponding to the lattice structure (~2.2 Å) and charge modulation (~11.1 Å), respectively, with an angular difference of ~12° between the two (Figure 2D). This discovery (which would need to be independently confirmed by angle-resolved photoemission spectroscopy (ARPES) measurements) has the potential to be important not only from a fundamental point of view) but also from a technological perspective as it may lead to the possibility of exciting electronic device applications at room temperature.

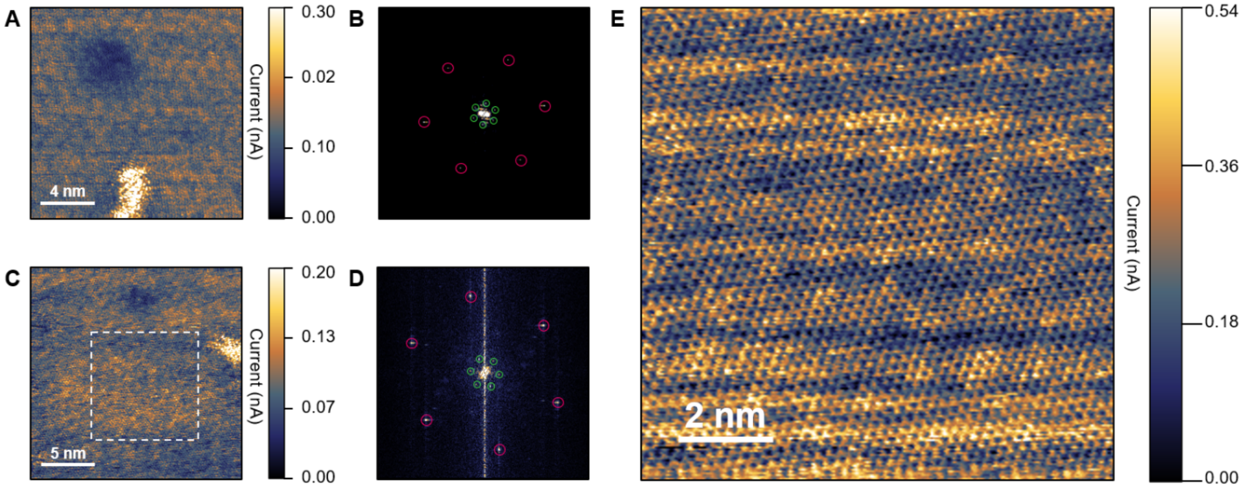

Figure 2. Observation of room-temperature charge ordering on Mo_2C via C-AFM. **(A)** Current image recorded on Mo_2C, showing periodic modulation of charge, along with two defects. **(B)** The corresponding FT of the image shown in **(A)**. The bright spots highlighted by red circles represent the lattice structure of α-Mo_2C with a periodicity of ~ 2.2 Å while the bright spots highlighted by green circles represent the charge modulation with a periodicity of ~11.4 Å. **(C)** Another current image recorded on α-Mo_2C exhibiting charge ordering. **(D)** The corresponding FT of the image shown in **(C)**. The bright spots highlighted by red and green circles represent lattice structure of α-Mo_2C (periodicity ~2.2 Å) and periodic modulation of charge (periodicity ~11.1 Å), respectively. **(E)** Zoom-in current image of the area highlighted by the white dotted rectangle in **(C)**, showing an ordering of charge superimposed on the atomic surface lattice. All images were obtained with an applied normal load of 0.0 nN, and at a scanning frequency of 15.62 Hz. Bias voltages: **(A)** 100 mV, **(C)** 1.3 V, **(E)** 1.3 V.

Award Number: FA9550-19-1-0035

Report Type: Final Performance Report

Reporting Period: 12/15/2018 – 12/14/2022

Distribution Statement: *A – Approved for Public Release*

Program Officer Name: Dr. Ali Sayir

Principle Investigator Name: Mehmet Z. Baykara & Ashlie Martini

Project Title: Investigating the Mechanisms of Electrical Contact Resistance between the Diffusive and Ballistic Limits

Abstract:

The original goal of this project was to investigate the mechanisms of electrical contact resistance (ECR) on small length scales through an interplay of conductive atomic force microscopy (C-AFM) experiments and atomistic simulations. This goal has been pursued, in the first half of the project period, by the following activities and accomplishments: (i) measuring ECR values between gold nano islands and graphite substrates, (ii) improving the C-AFM methodology in order to achieve more reliable and reproducible results, and (iii) understanding the physical mechanisms of the phenomenon of “conduction aging” we often observe in the experiments. In the second half of the project, our work evolved into the use of C-AFM as a powerful atomic-resolution imaging tool under ambient conditions, with exemplary results reported on various 2D materials as well as thin crystals of Mo_2C, in collaboration with the TOBB University of Economics and Technology as well as Eskisehir Technical University (ETU). The results of the project have been shared with the scientific community by way of five journal publications and multiple invited as well as contributed presentations at conferences and research institutions.

1. Accomplishments

1.1 Research Objectives

The main research objectives of this project can be considered under two broad headings, separated into the first and second half of the project period.

(1) During the first half of the project period, the main research objective has been to investigate physical mechanisms of ECR at small length scales, and study the transition from the diffusive to the ballistic conduction regimes.

(2) During the second half of the project, the main research objective has been to utilize C-AFM as an atomic-resolution imaging tool under ambient conditions, to study the structure and electronic properties of defects on various 2D materials as well as thin crystals of Mo_2C grown via chemical vapor deposition (grown by Dr. Goknur Buke's group at TOBB University), a prominent member of the emerging material class of thin TMCs.

1.2 Research Accomplishments

We have been partially successful in meeting the goals associated with Research Objective (1) listed above. In particular:

(i) We have performed C-AFM-based ECR measurements on a sample system comprising atomically flat interfaces (up to several hundreds of nanometers in lateral size) formed between gold islands and a highly oriented pyrolytic graphite (HOPG) substrate. Proof-of-principle experiments performed on gold islands of varying size pointed toward an increasing contribution of the island-HOPG junction to the measured total resistance with decreasing island size. Atomistic simulations complemented and elucidated experimental results, revealing the maximum island sizes below which the electrical contact resistance at the island-HOPG junction can be feasibly extracted from the measured total resistance.

Publication: Vazirisereshk, M.R., Sumaiya, S.A., Martini, A., Baykara, M.Z., *Measurement of Electrical Contact Resistance at Nanoscale Gold-Graphite Interfaces*, Applied Physics Letters **115**, 091602 (2019).

(ii) We have improved our C-AFM methodology in order to achieve more reliable and reproducible results. In particular, we presented an approach aimed at improving the reliability of C-AFM measurements by addressing multiple sources of variability. Specifically, we performed current-voltage (*I-V*) spectroscopy on atomically flat terraces HOPG under an inert nitrogen atmosphere and at controlled temperatures. The sample was annealed before the measurements to desorb adsorbates, and conductive diamond tips are used to limit tip apex deformation. These precautions lead to measured ECR values that follow a Gaussian distribution with significantly smaller standard deviation than those obtained under conventional measurement conditions. The key factor leading

to this improvement was identified as the switch from ambient conditions to a dry nitrogen atmosphere.

Publication: Sumaiya, S.A., Martini, A., Baykara, M.Z., *Improving the Reliability of Conductive Atomic Force Microscopy-Based Electrical Contact Resistance Measurements*, Nano Express **1**, 030023 (2020).

(iii) We employed a combined experimental and computational approach to understand the physical mechanisms of the phenomenon of "electrical conduction aging" we often observe in the experiments. In particular, ECR was shown to decrease over time as measured using C-AFM and estimated using two approaches from MD simulations. The simulations show that time dependence of ECR is attributable to an increase in real contact area due to atoms diffusing into the contact. This diffusion-based aging was found to be a thermally activated process that depends on the local contact pressure.

Publication: Vazirisereshk, M.R., Sumaiya, S.A., Chen, R., Baykara, M.Z., Martini, A., *Time-Dependent Electrical Contact Resistance at the Nanoscale*, Tribology Letters **69**, 50 (2021).

Despite the accomplishments listed above, the superlubric (i.e., ultra-low friction) character of the gold-graphite sample we investigated in the project has prevented us from establishing robust and stable electrical contacts over small gold nano islands, which ultimately prevented us from studying the ballistic transport regime that would only be observable at miniscule contact areas.

On the other hand, the extensive experience we developed with the use of C-AFM throughout the first part of the project fueled an exciting, alternative research direction in the second half of the project, which culminated in the following accomplishment:

(iv) We showed the use of C-AFM as a powerful atomic-resolution imaging tool under ambient conditions, with proof-of-principle measurements performed on a variety of 2D materials (MoS_2, $PtSe_2$, WS_2), as well as CVD-grown thin crystals of Mo_2C. Our method delivered images of defects down to the single vacancy level. Using our method, we additionally reported the capability of in situ charge state manipulation of defects on MoS_2 and the observation of charge ordering on Mo_2C.

Publication: Sumaiya, S.A., Liu, J., Baykara, M.Z., *True Atomic-Resolution Surface Imaging and Manipulation under Ambient Conditions via Conductive Atomic Force Microscopy*, ACS Nano **16**, 20086 (2022).

1.3 Dissemination Activities

As already indicated in the previous sections, the results of our work have been shared with the scientific community by way of multiple journal articles in well-respected outlets, as well as invited and contributed talks at conferences and research institutions.

A list of **all invited talks** associated with this project is provided below:

1. Baykara, M.Z, *Atomic-Resolution Surface Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, Turkish Society of Electron Microscopy Webinar, Stanford Virtual, December 7, 2022.

2. Baykara, M.Z, *Make Measurable What is Not So: Atomic-Resolution Surface Imaging and Manipulation under Ambient Conditions*, Geballe Laboratory for Advanced Materials (GLAM) Special Seminar, Stanford University, Palo Alto, USA, November 2, 2022.

3. Baykara, M.Z., *Where Flatlands Meet: Mechanics and Electronics at Atomically Flat Interfaces*, UCLA, Department of Materials Science & Engineering Seminar, Los Angeles, USA, January 17, 2020.

4. Baykara, M.Z., *Measurement of Electrical Contact Resistance at Nanoscale Gold-Graphite Interfaces*, 15th Nanoscience and Nanotechnology Conference, Antalya, Turkey, November 6, 2019.

A list of **all contributed talks** associated with this project is provided below:

1. Vaziriseresk, M. *et al.*, *Insight into Dynamic Sliding Contacts from Conductive Atomic Force Microscopy*, STLE Virtual Student Conference, May 2020.

2. Vazirisereshk, M. *et al.*, *Electrical Contact Resistance at Gold/Graphene Interfaces,* Tribology Frontiers Conference, Chicago IL, October 2019.

3. Sumaiya, S.A. *et al.*, *True Atomic-Resolution Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, AVS 68th International Symposium & Exhibition, Pittsburgh, USA, November 2022.

4. Sumaiya, S.A. *et al.*, *True Atomic-Resolution Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, 2022 MRS Spring Meeting & Exhibit, Honolulu, USA, May 2022.

5. Sumaiya, S.A. *et al.*, *Atomically Resolved Imaging of Electronic Defects in a CVD Grown Transition Metal Carbide: α–Mo_2C*, 2021 MRS Fall Meeting & Exhibit, Boston, USA, November 2021.
6. Sumaiya, S.A. *et al.*, *Temporal Evolution of Electrical Contact Resistance Observed via Improved Conductive Atomic Force Microscopy*, AVS 67th International Symposium & Exhibition (*Virtual*), October 2021.

Both PIs have been active in general outreach activities throughout the duration of the project, whereby the main tools used during the course of the project (AFM and MD simulations) have been introduced to students from the elementary to the high school level via various events.

2. Impacts

2.1 Impact on the development of the principal discipline(s) of the project

The field of atomic-resolution surface imaging has been essentially confined to the pristine yet impractical conditions of ultra-high vacuum (UHV) and low temperatures. With our new C-AFM method being able to provide true atomic-resolution maps of surfaces under ambient conditions, without the need for expensive and hard-to-maintain UHV equipment, we expect the results of our project to have significant impact on the principal discipline of scanning probe microscopy (SPM). Perhaps equally importantly, having access to the structure and electronic properties of material surfaces under ambient conditions is projected to have important contributions for potential device applications based on emerging materials, which will, most of the time, operate under ambient conditions, as opposed to the pristine UHV environment.

2.2 Impact on the development of human resources

Three PhD students have been funded by the project throughout its existence as Graduate Student Researchers (GSRs), which provided significant opportunities for academic and professional growth. **Saima A. Sumaiya**, the GSR who worked on the project from the first day and performed all associated experiments, graduated recently with flying colors and has started a position as **Postdoctoral Fellow at Columbia University**. Saima won multiple awards during his time at UC Merced thanks to the AFOSR project, which include the *STLE Northern California Section Research Scholarship* as well as the *Graduate Dean's Dissertation Fellowship* at UC Merced. **Mohammad Vazirisereshk**, the first computational GSR to work on this project, obtained his PhD in May 2021 and then obtained a research position at Lam Research. **Karen Mohammadtabar**, who worked on the second half of the project, just successfully defended his PhD in December 2022. Both Mohammad and Karen won the *STLE Northern California Section Research Scholarship*, in 2019 and 2020, respectively. Also, Karen was among the ten finalists at UC Merced's GradSlam competition in 2022, where students present their research via three slides in three minutes.

3. Changes

3.1 Changes in approach

As explained in Section 1.2, the scope and goals of the project changed after about 2 years from its start. Specifically, instead of performing a detailed study of the transition between the electronic and ballistic electron transport regimes (which have been hampered by the superlubricity of the gold-graphite sample which prevented the formation of robust and stable electrical contacts on small gold islands), our efforts have been re-directed at the use of C-AFM for the atomic-resolution study of defects on 2D materials as well as thin, chemical-vapor-deposition-grown Mo_2C crystals (provided by Prof. Goknur Buke and her research group at TOBB University). This change in direction has been extensively discussed with and approved by the program officer.

4. Technical Updates

The progress associated with the 3-year reporting period between 12/2018 and 12/2021 has been covered in detail in prior progress reports. Here, we report on technical updates that have been realized in the last period of the project, from 12/2021 to 12/2022.

4.1 Electronic manipulation of defects via C-AFM

Going beyond imaging, we also investigated the capability of our method to electronically manipulate defects under ambient conditions. In particular, Figure 1A shows a current image on MoS_2 with two extended defects that exhibit higher conductivity than their surroundings. Magnified images on the defects allow their study with high spatial resolution (Figure 1B). By performing *I-V* sweeps for multiple cycles (Figure 1C), we found an emerging peak in the *I-V* curves at a bias voltage of about -1.7 V, which is first attenuated and then re-emerges during the *I-V* cycles. This is accompanied by a side peak appearing between -1.1 and -1.3 V. After the *I-V* sweeps, the high conductivity region associated with the defect disappears (see Figures 1D, E, to be compared with Figures1A, B). The possibility of surface contamination can be ruled out as roughness fluctuations are not observed in the corresponding topography images (Figures 1F-I). The negative differential resistance in Figure 1C, characterized by a decrease in current with increasing voltage, may be related to localized surface charging/discharging behavior. According to the passive sign convention, more electrons may flow out of the defect location, indicating a pre-existing negatively charged region. After *I-V* sweeping, more positive charge will accumulate in the region to compensate the non-uniform charge states, which may explain the slightly lower current detected on the defect location after the *I-V* sweeps (Figure 1E). These experiments demonstrate that our C-AFM method may provide a feasible strategy for localized manipulation/elimination of electrical surface defects on 2D materials under ambient conditions.

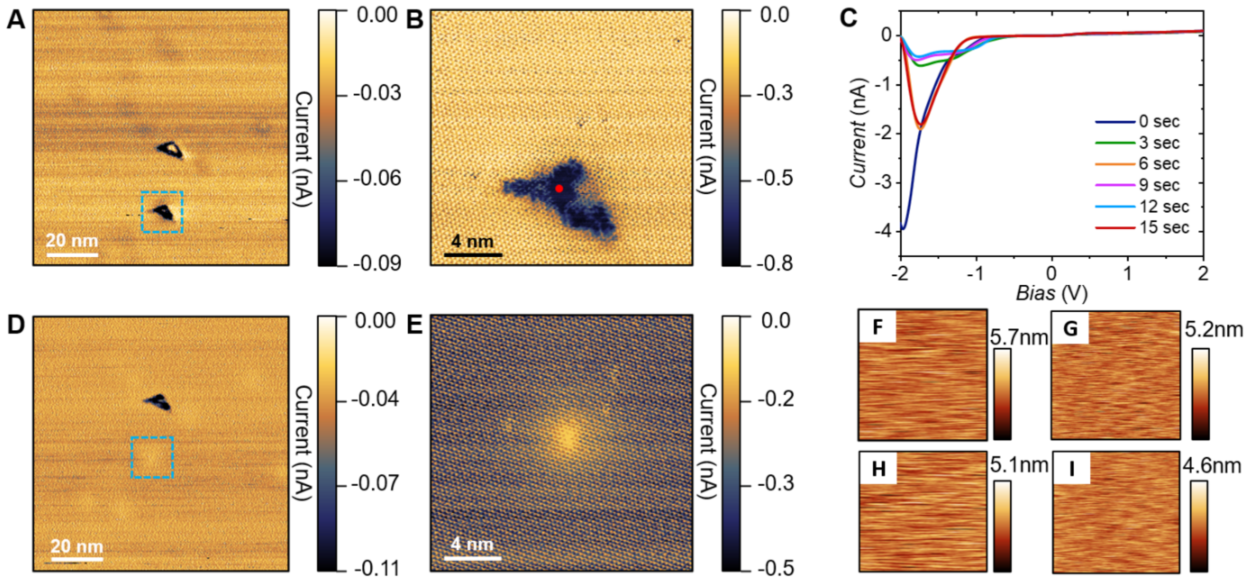

Figure 1. Electronic manipulation of a defect on MoS_2 via C-AFM under ambient conditions. (A) A large-scale current image showing two defects. **(B)** Zoom-in current image on the defect highlighted by the blue dashed square in (**A**). The defect features enhanced conductivity compared to its surroundings. **(C)** *I-V* curves recorded on top of the defect location marked with the red dot in **(B)**. **(D)** Current image of area **(A)** after the *I-V* sweeps. **(E)** Current image capturing the same defect in **(B)** after the *I-V* sweeps. The defect now features a slightly lower conductivity compared to its surroundings, with the uninterrupted atomic lattice overlaid on top of it. **(F-I)** Corresponding topographic images for **(A)**, **(B)**, **(D)**, and **(E)**, respectively. All images were obtained with an applied normal load of 0.0 nN, and at a scanning speed 15.62 Hz. Bias voltages: **(A)** -1.0 V, **(B)** -1.3 V, **(D)** -0.8 V, **(E)** -0.8 V.

4.2 Room-temperature charge ordering on Mo_2C

We employed our methodology to explore the surface electronic properties of thin Mo_2C crystals. In particular, C-AFM measurements revealed a periodic modulation (i.e., ordering) of charge, superimposed on the atomic lattice structure of Mo_2C (Figure 2A), in an area that includes two extended defects. The corresponding Fourier Transform (FT) shown in Figure 2B corroborates this observation, whereby the bright spots highlighted by red circles (with a periodicity of ~2.2 Å) represent the atomic structure of the Mo_2C surface, and the bright spots highlighted by green circles represent the periodic charge modulation with a periodicity of ~11.4 Å. Even more interestingly, the FT clearly shows the broken rotational symmetry between these two periodicities with an angular difference of ~13°. These results are supported by additional measurements on the material surface that show charge ordering (Figures 2C, E), with the corresponding FT again showing two periodicities corresponding to the lattice structure (~2.2 Å) and charge modulation (~11.1 Å), respectively, with an angular difference of ~12° between the two (Figure 2D). This discovery (which would need to be independently confirmed by angle-resolved photoemission spectroscopy (ARPES) measurements) has the potential to be important not only from a fundamental point of view) but also from a technological perspective as it may lead to the possibility of exciting electronic device applications at room temperature.

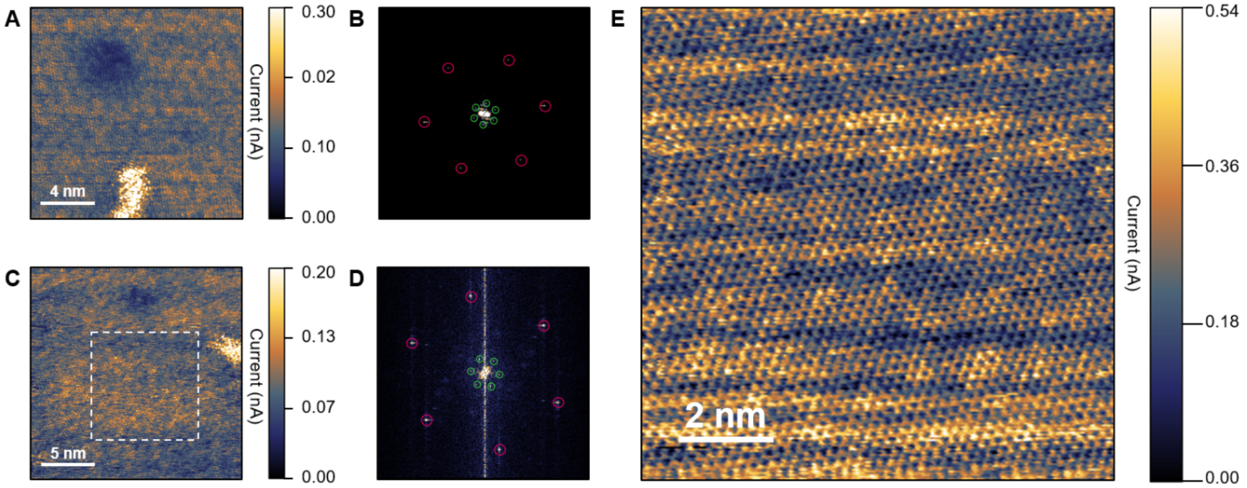

Figure 2. Observation of room-temperature charge ordering on Mo_2C via C-AFM. **(A)** Current image recorded on Mo_2C, showing periodic modulation of charge, along with two defects. **(B)** The corresponding FT of the image shown in **(A)**. The bright spots highlighted by red circles represent the lattice structure of α-Mo_2C with a periodicity of ~ 2.2 Å while the bright spots highlighted by green circles represent the charge modulation with a periodicity of ~11.4 Å. **(C)** Another current image recorded on α-Mo_2C exhibiting charge ordering. **(D)** The corresponding FT of the image shown in **(C)**. The bright spots highlighted by red and green circles represent lattice structure of α-Mo_2C (periodicity ~2.2 Å) and periodic modulation of charge (periodicity ~11.1 Å), respectively. **(E)** Zoom-in current image of the area highlighted by the white dotted rectangle in **(C)**, showing an ordering of charge superimposed on the atomic surface lattice. All images were obtained with an applied normal load of 0.0 nN, and at a scanning frequency of 15.62 Hz. Bias voltages: **(A)** 100 mV, **(C)** 1.3 V, **(E)** 1.3 V.

Award Number: FA9550-19-1-0035

Report Type: Final Performance Report

Reporting Period: 12/15/2018 – 12/14/2022

Distribution Statement: *A – Approved for Public Release*

Program Officer Name: Dr. Ali Sayir

Principle Investigator Name: Mehmet Z. Baykara & Ashlie Martini

Project Title: Investigating the Mechanisms of Electrical Contact Resistance between the Diffusive and Ballistic Limits

Abstract:

The original goal of this project was to investigate the mechanisms of electrical contact resistance (ECR) on small length scales through an interplay of conductive atomic force microscopy (C-AFM) experiments and atomistic simulations. This goal has been pursued, in the first half of the project period, by the following activities and accomplishments: (i) measuring ECR values between gold nano islands and graphite substrates, (ii) improving the C-AFM methodology in order to achieve more reliable and reproducible results, and (iii) understanding the physical mechanisms of the phenomenon of "conduction aging" we often observe in the experiments. In the second half of the project, our work evolved into the use of C-AFM as a powerful atomic-resolution imaging tool under ambient conditions, with exemplary results reported on various 2D materials as well as thin crystals of Mo_2C, in collaboration with the TOBB University of Economics and Technology as well as Eskisehir Technical University (ETU). The results of the project have been shared with the scientific community by way of five journal publications and multiple invited as well as contributed presentations at conferences and research institutions.

1. Accomplishments

1.1 Research Objectives

The main research objectives of this project can be considered under two broad headings, separated into the first and second half of the project period.

(1) During the first half of the project period, the main research objective has been to investigate physical mechanisms of ECR at small length scales, and study the transition from the diffusive to the ballistic conduction regimes.

(2) During the second half of the project, the main research objective has been to utilize C-AFM as an atomic-resolution imaging tool under ambient conditions, to study the structure and electronic properties of defects on various 2D materials as well as thin crystals of Mo_2C grown via chemical vapor deposition (grown by Dr. Goknur Buke's group at TOBB University), a prominent member of the emerging material class of thin TMCs.

1.2 Research Accomplishments

We have been partially successful in meeting the goals associated with Research Objective (1) listed above. In particular:

(i) We have performed C-AFM-based ECR measurements on a sample system comprising atomically flat interfaces (up to several hundreds of nanometers in lateral size) formed between gold islands and a highly oriented pyrolytic graphite (HOPG) substrate. Proof-of-principle experiments performed on gold islands of varying size pointed toward an increasing contribution of the island-HOPG junction to the measured total resistance with decreasing island size. Atomistic simulations complemented and elucidated experimental results, revealing the maximum island sizes below which the electrical contact resistance at the island-HOPG junction can be feasibly extracted from the measured total resistance.

Publication: Vazirisereshk, M.R., Sumaiya, S.A., Martini, A., Baykara, M.Z., *Measurement of Electrical Contact Resistance at Nanoscale Gold-Graphite Interfaces*, Applied Physics Letters **115**, 091602 (2019).

(ii) We have improved our C-AFM methodology in order to achieve more reliable and reproducible results. In particular, we presented an approach aimed at improving the reliability of C-AFM measurements by addressing multiple sources of variability. Specifically, we performed current-voltage (*I-V*) spectroscopy on atomically flat terraces HOPG under an inert nitrogen atmosphere and at controlled temperatures. The sample was annealed before the measurements to desorb adsorbates, and conductive diamond tips are used to limit tip apex deformation. These precautions lead to measured ECR values that follow a Gaussian distribution with significantly smaller standard deviation than those obtained under conventional measurement conditions. The key factor leading

to this improvement was identified as the switch from ambient conditions to a dry nitrogen atmosphere.

Publication: Sumaiya, S.A., Martini, A., Baykara, M.Z., *Improving the Reliability of Conductive Atomic Force Microscopy-Based Electrical Contact Resistance Measurements*, Nano Express **1**, 030023 (2020).

(iii) We employed a combined experimental and computational approach to understand the physical mechanisms of the phenomenon of "electrical conduction aging" we often observe in the experiments. In particular, ECR was shown to decrease over time as measured using C-AFM and estimated using two approaches from MD simulations. The simulations show that time dependence of ECR is attributable to an increase in real contact area due to atoms diffusing into the contact. This diffusion-based aging was found to be a thermally activated process that depends on the local contact pressure.

Publication: Vazirisereshk, M.R., Sumaiya, S.A., Chen, R., Baykara, M.Z., Martini, A., *Time-Dependent Electrical Contact Resistance at the Nanoscale*, Tribology Letters **69**, 50 (2021).

Despite the accomplishments listed above, the superlubric (i.e., ultra-low friction) character of the gold-graphite sample we investigated in the project has prevented us from establishing robust and stable electrical contacts over small gold nano islands, which ultimately prevented us from studying the ballistic transport regime that would only be observable at miniscule contact areas.

On the other hand, the extensive experience we developed with the use of C-AFM throughout the first part of the project fueled an exciting, alternative research direction in the second half of the project, which culminated in the following accomplishment:

(iv) We showed the use of C-AFM as a powerful atomic-resolution imaging tool under ambient conditions, with proof-of-principle measurements performed on a variety of 2D materials (MoS_2, $PtSe_2$, WS_2), as well as CVD-grown thin crystals of Mo_2C. Our method delivered images of defects down to the single vacancy level. Using our method, we additionally reported the capability of in situ charge state manipulation of defects on MoS_2 and the observation of charge ordering on Mo_2C.

Publication: Sumaiya, S.A., Liu, J., Baykara, M.Z., *True Atomic-Resolution Surface Imaging and Manipulation under Ambient Conditions via Conductive Atomic Force Microscopy*, ACS Nano **16**, 20086 (2022).

1.3 Dissemination Activities

As already indicated in the previous sections, the results of our work have been shared with the scientific community by way of multiple journal articles in well-respected outlets, as well as invited and contributed talks at conferences and research institutions.

A list of **all invited talks** associated with this project is provided below:

1. Baykara, M.Z, *Atomic-Resolution Surface Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, Turkish Society of Electron Microscopy Webinar, Stanford Virtual, December 7, 2022.

2. Baykara, M.Z, *Make Measurable What is Not So: Atomic-Resolution Surface Imaging and Manipulation under Ambient Conditions*, Geballe Laboratory for Advanced Materials (GLAM) Special Seminar, Stanford University, Palo Alto, USA, November 2, 2022.

3. Baykara, M.Z., *Where Flatlands Meet: Mechanics and Electronics at Atomically Flat Interfaces*, UCLA, Department of Materials Science & Engineering Seminar, Los Angeles, USA, January 17, 2020.

4. Baykara, M.Z., *Measurement of Electrical Contact Resistance at Nanoscale Gold-Graphite Interfaces*, 15th Nanoscience and Nanotechnology Conference, Antalya, Turkey, November 6, 2019.

A list of **all contributed talks** associated with this project is provided below:

1. Vaziriseresk, M. *et al.*, *Insight into Dynamic Sliding Contacts from Conductive Atomic Force Microscopy*, STLE Virtual Student Conference, May 2020.

2. Vazirisereshk, M. *et al.*, *Electrical Contact Resistance at Gold/Graphene Interfaces,* Tribology Frontiers Conference, Chicago IL, October 2019.

3. Sumaiya, S.A. *et al.*, *True Atomic-Resolution Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, AVS 68th International Symposium & Exhibition, Pittsburgh, USA, November 2022.

4. Sumaiya, S.A. *et al.*, *True Atomic-Resolution Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, 2022 MRS Spring Meeting & Exhibit, Honolulu, USA, May 2022.

5. Sumaiya, S.A. *et al.*, *Atomically Resolved Imaging of Electronic Defects in a CVD Grown Transition Metal Carbide: α–Mo_2C*, 2021 MRS Fall Meeting & Exhibit, Boston, USA, November 2021.
6. Sumaiya, S.A. *et al.*, *Temporal Evolution of Electrical Contact Resistance Observed via Improved Conductive Atomic Force Microscopy*, AVS 67th International Symposium & Exhibition (*Virtual*), October 2021.

Both PIs have been active in general outreach activities throughout the duration of the project, whereby the main tools used during the course of the project (AFM and MD simulations) have been introduced to students from the elementary to the high school level via various events.

2. Impacts

2.1 Impact on the development of the principal discipline(s) of the project

The field of atomic-resolution surface imaging has been essentially confined to the pristine yet impractical conditions of ultra-high vacuum (UHV) and low temperatures. With our new C-AFM method being able to provide true atomic-resolution maps of surfaces under ambient conditions, without the need for expensive and hard-to-maintain UHV equipment, we expect the results of our project to have significant impact on the principal discipline of scanning probe microscopy (SPM). Perhaps equally importantly, having access to the structure and electronic properties of material surfaces under ambient conditions is projected to have important contributions for potential device applications based on emerging materials, which will, most of the time, operate under ambient conditions, as opposed to the pristine UHV environment.

2.2 Impact on the development of human resources

Three PhD students have been funded by the project throughout its existence as Graduate Student Researchers (GSRs), which provided significant opportunities for academic and professional growth. **Saima A. Sumaiya**, the GSR who worked on the project from the first day and performed all associated experiments, graduated recently with flying colors and has started a position as **Postdoctoral Fellow at Columbia University**. Saima won multiple awards during his time at UC Merced thanks to the AFOSR project, which include the *STLE Northern California Section Research Scholarship* as well as the *Graduate Dean's Dissertation Fellowship* at UC Merced. **Mohammad Vazirisereshk**, the first computational GSR to work on this project, obtained his PhD in May 2021 and then obtained a research position at Lam Research. **Karen Mohammadtabar**, who worked on the second half of the project, just successfully defended his PhD in December 2022. Both Mohammad and Karen won the *STLE Northern California Section Research Scholarship*, in 2019 and 2020, respectively. Also, Karen was among the ten finalists at UC Merced's GradSlam competition in 2022, where students present their research via three slides in three minutes.

3. Changes

3.1 Changes in approach

As explained in Section 1.2, the scope and goals of the project changed after about 2 years from its start. Specifically, instead of performing a detailed study of the transition between the electronic and ballistic electron transport regimes (which have been hampered by the superlubricity of the gold-graphite sample which prevented the formation of robust and stable electrical contacts on small gold islands), our efforts have been re-directed at the use of C-AFM for the atomic-resolution study of defects on 2D materials as well as thin, chemical-vapor-deposition-grown Mo_2C crystals (provided by Prof. Goknur Buke and her research group at TOBB University). This change in direction has been extensively discussed with and approved by the program officer.

4. Technical Updates

The progress associated with the 3-year reporting period between 12/2018 and 12/2021 has been covered in detail in prior progress reports. Here, we report on technical updates that have been realized in the last period of the project, from 12/2021 to 12/2022.

4.1 Electronic manipulation of defects via C-AFM

Going beyond imaging, we also investigated the capability of our method to electronically manipulate defects under ambient conditions. In particular, Figure 1A shows a current image on MoS_2 with two extended defects that exhibit higher conductivity than their surroundings. Magnified images on the defects allow their study with high spatial resolution (Figure 1B). By performing *I-V* sweeps for multiple cycles (Figure 1C), we found an emerging peak in the *I-V* curves at a bias voltage of about -1.7 V, which is first attenuated and then re-emerges during the *I-V* cycles. This is accompanied by a side peak appearing between -1.1 and -1.3 V. After the *I-V* sweeps, the high conductivity region associated with the defect disappears (see Figures 1D, E, to be compared with Figures1A, B). The possibility of surface contamination can be ruled out as roughness fluctuations are not observed in the corresponding topography images (Figures 1F-I). The negative differential resistance in Figure 1C, characterized by a decrease in current with increasing voltage, may be related to localized surface charging/discharging behavior. According to the passive sign convention, more electrons may flow out of the defect location, indicating a pre-existing negatively charged region. After *I-V* sweeping, more positive charge will accumulate in the region to compensate the non-uniform charge states, which may explain the slightly lower current detected on the defect location after the *I-V* sweeps (Figure 1E). These experiments demonstrate that our C-AFM method may provide a feasible strategy for localized manipulation/elimination of electrical surface defects on 2D materials under ambient conditions.

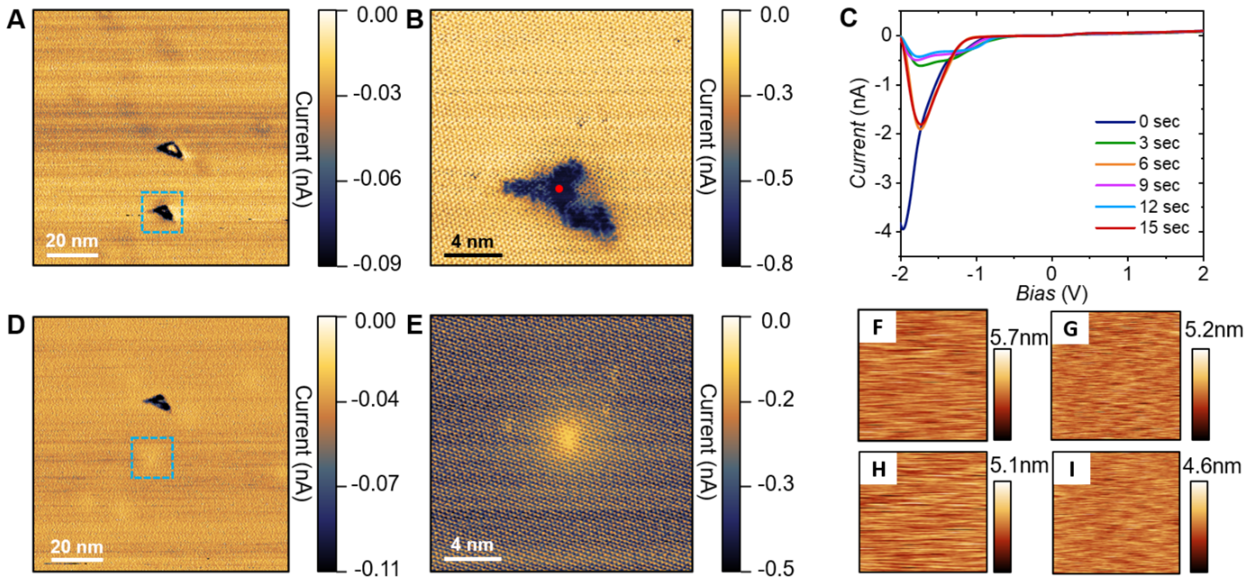

Figure 1. Electronic manipulation of a defect on MoS_2 via C-AFM under ambient conditions. (A) A large-scale current image showing two defects. **(B)** Zoom-in current image on the defect highlighted by the blue dashed square in (**A**). The defect features enhanced conductivity compared to its surroundings. **(C)** *I*-*V* curves recorded on top of the defect location marked with the red dot in **(B)**. **(D)** Current image of area **(A)** after the *I*-*V* sweeps. **(E)** Current image capturing the same defect in **(B)** after the *I*-*V* sweeps. The defect now features a slightly lower conductivity compared to its surroundings, with the uninterrupted atomic lattice overlaid on top of it. **(F-I)** Corresponding topographic images for **(A)**, **(B)**, **(D)**, and **(E)**, respectively. All images were obtained with an applied normal load of 0.0 nN, and at a scanning speed 15.62 Hz. Bias voltages: **(A)** -1.0 V, **(B)** -1.3 V, **(D)** -0.8 V, **(E)** -0.8 V.

4.2 Room-temperature charge ordering on Mo_2C

We employed our methodology to explore the surface electronic properties of thin Mo_2C crystals. In particular, C-AFM measurements revealed a periodic modulation (i.e., ordering) of charge, superimposed on the atomic lattice structure of Mo_2C (Figure 2A), in an area that includes two extended defects. The corresponding Fourier Transform (FT) shown in Figure 2B corroborates this observation, whereby the bright spots highlighted by red circles (with a periodicity of ~2.2 Å) represent the atomic structure of the Mo_2C surface, and the bright spots highlighted by green circles represent the periodic charge modulation with a periodicity of ~11.4 Å. Even more interestingly, the FT clearly shows the broken rotational symmetry between these two periodicities with an angular difference of ~13°. These results are supported by additional measurements on the material surface that show charge ordering (Figures 2C, E), with the corresponding FT again showing two periodicities corresponding to the lattice structure (~2.2 Å) and charge modulation (~11.1 Å), respectively, with an angular difference of ~12° between the two (Figure 2D). This discovery (which would need to be independently confirmed by angle-resolved photoemission spectroscopy (ARPES) measurements) has the potential to be important not only from a fundamental point of view) but also from a technological perspective as it may lead to the possibility of exciting electronic device applications at room temperature.

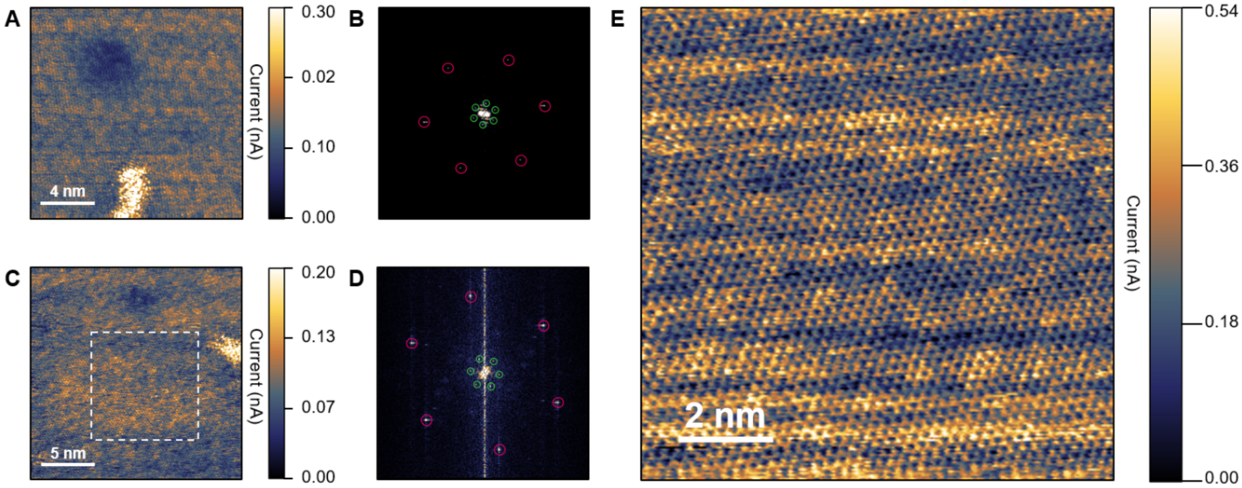

Figure 2. Observation of room-temperature charge ordering on Mo_2C via C-AFM. **(A)** Current image recorded on Mo_2C, showing periodic modulation of charge, along with two defects. **(B)** The corresponding FT of the image shown in **(A)**. The bright spots highlighted by red circles represent the lattice structure of α-Mo_2C with a periodicity of ~ 2.2 Å while the bright spots highlighted by green circles represent the charge modulation with a periodicity of ~11.4 Å. **(C)** Another current image recorded on α-Mo_2C exhibiting charge ordering. **(D)** The corresponding FT of the image shown in **(C)**. The bright spots highlighted by red and green circles represent lattice structure of α-Mo_2C (periodicity ~2.2 Å) and periodic modulation of charge (periodicity ~11.1 Å), respectively. **(E)** Zoom-in current image of the area highlighted by the white dotted rectangle in **(C)**, showing an ordering of charge superimposed on the atomic surface lattice. All images were obtained with an applied normal load of 0.0 nN, and at a scanning frequency of 15.62 Hz. Bias voltages: **(A)** 100 mV, **(C)** 1.3 V, **(E)** 1.3 V.

Award Number: FA9550-19-1-0035

Report Type: Final Performance Report

Reporting Period: 12/15/2018 – 12/14/2022

Distribution Statement: *A – Approved for Public Release*

Program Officer Name: Dr. Ali Sayir

Principle Investigator Name: Mehmet Z. Baykara & Ashlie Martini

Project Title: Investigating the Mechanisms of Electrical Contact Resistance between the Diffusive and Ballistic Limits

Abstract:

The original goal of this project was to investigate the mechanisms of electrical contact resistance (ECR) on small length scales through an interplay of conductive atomic force microscopy (C-AFM) experiments and atomistic simulations. This goal has been pursued, in the first half of the project period, by the following activities and accomplishments: (i) measuring ECR values between gold nano islands and graphite substrates, (ii) improving the C-AFM methodology in order to achieve more reliable and reproducible results, and (iii) understanding the physical mechanisms of the phenomenon of "conduction aging" we often observe in the experiments. In the second half of the project, our work evolved into the use of C-AFM as a powerful atomic-resolution imaging tool under ambient conditions, with exemplary results reported on various 2D materials as well as thin crystals of Mo_2C, in collaboration with the TOBB University of Economics and Technology as well as Eskisehir Technical University (ETU). The results of the project have been shared with the scientific community by way of five journal publications and multiple invited as well as contributed presentations at conferences and research institutions.

1. Accomplishments

1.1 Research Objectives

The main research objectives of this project can be considered under two broad headings, separated into the first and second half of the project period.

- **(1)** During the first half of the project period, the main research objective has been to investigate physical mechanisms of ECR at small length scales, and study the transition from the diffusive to the ballistic conduction regimes.

- **(2)** During the second half of the project, the main research objective has been to utilize C-AFM as an atomic-resolution imaging tool under ambient conditions, to study the structure and electronic properties of defects on various 2D materials as well as thin crystals of Mo_2C grown via chemical vapor deposition (grown by Dr. Goknur Buke's group at TOBB University), a prominent member of the emerging material class of thin TMCs.

1.2 Research Accomplishments

We have been partially successful in meeting the goals associated with Research Objective (1) listed above. In particular:

- **(i)** We have performed C-AFM-based ECR measurements on a sample system comprising atomically flat interfaces (up to several hundreds of nanometers in lateral size) formed between gold islands and a highly oriented pyrolytic graphite (HOPG) substrate. Proof-of-principle experiments performed on gold islands of varying size pointed toward an increasing contribution of the island-HOPG junction to the measured total resistance with decreasing island size. Atomistic simulations complemented and elucidated experimental results, revealing the maximum island sizes below which the electrical contact resistance at the island-HOPG junction can be feasibly extracted from the measured total resistance.

  Publication: Vazirisereshk, M.R., Sumaiya, S.A., Martini, A., Baykara, M.Z., *Measurement of Electrical Contact Resistance at Nanoscale Gold-Graphite Interfaces*, Applied Physics Letters **115**, 091602 (2019).

- **(ii)** We have improved our C-AFM methodology in order to achieve more reliable and reproducible results. In particular, we presented an approach aimed at improving the reliability of C-AFM measurements by addressing multiple sources of variability. Specifically, we performed current-voltage (*I-V*) spectroscopy on atomically flat terraces HOPG under an inert nitrogen atmosphere and at controlled temperatures. The sample was annealed before the measurements to desorb adsorbates, and conductive diamond tips are used to limit tip apex deformation. These precautions lead to measured ECR values that follow a Gaussian distribution with significantly smaller standard deviation than those obtained under conventional measurement conditions. The key factor leading

to this improvement was identified as the switch from ambient conditions to a dry nitrogen atmosphere.

Publication: Sumaiya, S.A., Martini, A., Baykara, M.Z., *Improving the Reliability of Conductive Atomic Force Microscopy-Based Electrical Contact Resistance Measurements*, Nano Express **1**, 030023 (2020).

(iii) We employed a combined experimental and computational approach to understand the physical mechanisms of the phenomenon of "electrical conduction aging" we often observe in the experiments. In particular, ECR was shown to decrease over time as measured using C-AFM and estimated using two approaches from MD simulations. The simulations show that time dependence of ECR is attributable to an increase in real contact area due to atoms diffusing into the contact. This diffusion-based aging was found to be a thermally activated process that depends on the local contact pressure.

Publication: Vazirisereshk, M.R., Sumaiya, S.A., Chen, R., Baykara, M.Z., Martini, A., *Time-Dependent Electrical Contact Resistance at the Nanoscale*, Tribology Letters **69**, 50 (2021).

Despite the accomplishments listed above, the superlubric (i.e., ultra-low friction) character of the gold-graphite sample we investigated in the project has prevented us from establishing robust and stable electrical contacts over small gold nano islands, which ultimately prevented us from studying the ballistic transport regime that would only be observable at miniscule contact areas.

On the other hand, the extensive experience we developed with the use of C-AFM throughout the first part of the project fueled an exciting, alternative research direction in the second half of the project, which culminated in the following accomplishment:

(iv) We showed the use of C-AFM as a powerful atomic-resolution imaging tool under ambient conditions, with proof-of-principle measurements performed on a variety of 2D materials (MoS_2, $PtSe_2$, WS_2), as well as CVD-grown thin crystals of Mo_2C. Our method delivered images of defects down to the single vacancy level. Using our method, we additionally reported the capability of in situ charge state manipulation of defects on MoS_2 and the observation of charge ordering on Mo_2C.

Publication: Sumaiya, S.A., Liu, J., Baykara, M.Z., *True Atomic-Resolution Surface Imaging and Manipulation under Ambient Conditions via Conductive Atomic Force Microscopy*, ACS Nano **16**, 20086 (2022).

1.3 Dissemination Activities

As already indicated in the previous sections, the results of our work have been shared with the scientific community by way of multiple journal articles in well-respected outlets, as well as invited and contributed talks at conferences and research institutions.

A list of **all invited talks** associated with this project is provided below:

1. Baykara, M.Z, *Atomic-Resolution Surface Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, Turkish Society of Electron Microscopy Webinar, Stanford Virtual, December 7, 2022.

2. Baykara, M.Z, *Make Measurable What is Not So: Atomic-Resolution Surface Imaging and Manipulation under Ambient Conditions*, Geballe Laboratory for Advanced Materials (GLAM) Special Seminar, Stanford University, Palo Alto, USA, November 2, 2022.

3. Baykara, M.Z., *Where Flatlands Meet: Mechanics and Electronics at Atomically Flat Interfaces*, UCLA, Department of Materials Science & Engineering Seminar, Los Angeles, USA, January 17, 2020.

4. Baykara, M.Z., *Measurement of Electrical Contact Resistance at Nanoscale Gold-Graphite Interfaces*, 15th Nanoscience and Nanotechnology Conference, Antalya, Turkey, November 6, 2019.

A list of **all contributed talks** associated with this project is provided below:

1. Vaziriseresk, M. *et al.*, *Insight into Dynamic Sliding Contacts from Conductive Atomic Force Microscopy*, STLE Virtual Student Conference, May 2020.

2. Vazirisereshk, M. *et al.*, *Electrical Contact Resistance at Gold/Graphene Interfaces,* Tribology Frontiers Conference, Chicago IL, October 2019.

3. Sumaiya, S.A. *et al.*, *True Atomic-Resolution Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, AVS 68th International Symposium & Exhibition, Pittsburgh, USA, November 2022.

4. Sumaiya, S.A. *et al.*, *True Atomic-Resolution Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, 2022 MRS Spring Meeting & Exhibit, Honolulu, USA, May 2022.

5. Sumaiya, S.A. *et al.*, *Atomically Resolved Imaging of Electronic Defects in a CVD Grown Transition Metal Carbide: α–Mo_2C*, 2021 MRS Fall Meeting & Exhibit, Boston, USA, November 2021.
6. Sumaiya, S.A. *et al.*, *Temporal Evolution of Electrical Contact Resistance Observed via Improved Conductive Atomic Force Microscopy*, AVS 67th International Symposium & Exhibition (*Virtual*), October 2021.

Both PIs have been active in general outreach activities throughout the duration of the project, whereby the main tools used during the course of the project (AFM and MD simulations) have been introduced to students from the elementary to the high school level via various events.

2. Impacts

2.1 Impact on the development of the principal discipline(s) of the project

The field of atomic-resolution surface imaging has been essentially confined to the pristine yet impractical conditions of ultra-high vacuum (UHV) and low temperatures. With our new C-AFM method being able to provide true atomic-resolution maps of surfaces under ambient conditions, without the need for expensive and hard-to-maintain UHV equipment, we expect the results of our project to have significant impact on the principal discipline of scanning probe microscopy (SPM). Perhaps equally importantly, having access to the structure and electronic properties of material surfaces under ambient conditions is projected to have important contributions for potential device applications based on emerging materials, which will, most of the time, operate under ambient conditions, as opposed to the pristine UHV environment.

2.2 Impact on the development of human resources

Three PhD students have been funded by the project throughout its existence as Graduate Student Researchers (GSRs), which provided significant opportunities for academic and professional growth. **Saima A. Sumaiya**, the GSR who worked on the project from the first day and performed all associated experiments, graduated recently with flying colors and has started a position as **Postdoctoral Fellow at Columbia University**. Saima won multiple awards during his time at UC Merced thanks to the AFOSR project, which include the *STLE Northern California Section Research Scholarship* as well as the *Graduate Dean's Dissertation Fellowship* at UC Merced. **Mohammad Vazirisereshk**, the first computational GSR to work on this project, obtained his PhD in May 2021 and then obtained a research position at Lam Research. **Karen Mohammadtabar**, who worked on the second half of the project, just successfully defended his PhD in December 2022. Both Mohammad and Karen won the *STLE Northern California Section Research Scholarship*, in 2019 and 2020, respectively. Also, Karen was among the ten finalists at UC Merced's GradSlam competition in 2022, where students present their research via three slides in three minutes.

3. Changes

3.1 Changes in approach

As explained in Section 1.2, the scope and goals of the project changed after about 2 years from its start. Specifically, instead of performing a detailed study of the transition between the electronic and ballistic electron transport regimes (which have been hampered by the superlubricity of the gold-graphite sample which prevented the formation of robust and stable electrical contacts on small gold islands), our efforts have been re-directed at the use of C-AFM for the atomic-resolution study of defects on 2D materials as well as thin, chemical-vapor-deposition-grown Mo_2C crystals (provided by Prof. Goknur Buke and her research group at TOBB University). This change in direction has been extensively discussed with and approved by the program officer.

4. Technical Updates

The progress associated with the 3-year reporting period between 12/2018 and 12/2021 has been covered in detail in prior progress reports. Here, we report on technical updates that have been realized in the last period of the project, from 12/2021 to 12/2022.

4.1 Electronic manipulation of defects via C-AFM

Going beyond imaging, we also investigated the capability of our method to electronically manipulate defects under ambient conditions. In particular, Figure 1A shows a current image on MoS_2 with two extended defects that exhibit higher conductivity than their surroundings. Magnified images on the defects allow their study with high spatial resolution (Figure 1B). By performing *I-V* sweeps for multiple cycles (Figure 1C), we found an emerging peak in the *I-V* curves at a bias voltage of about -1.7 V, which is first attenuated and then re-emerges during the *I-V* cycles. This is accompanied by a side peak appearing between -1.1 and -1.3 V. After the *I-V* sweeps, the high conductivity region associated with the defect disappears (see Figures 1D, E, to be compared with Figures1A, B). The possibility of surface contamination can be ruled out as roughness fluctuations are not observed in the corresponding topography images (Figures 1F-I). The negative differential resistance in Figure 1C, characterized by a decrease in current with increasing voltage, may be related to localized surface charging/discharging behavior. According to the passive sign convention, more electrons may flow out of the defect location, indicating a pre-existing negatively charged region. After *I-V* sweeping, more positive charge will accumulate in the region to compensate the non-uniform charge states, which may explain the slightly lower current detected on the defect location after the *I-V* sweeps (Figure 1E). These experiments demonstrate that our C-AFM method may provide a feasible strategy for localized manipulation/elimination of electrical surface defects on 2D materials under ambient conditions.

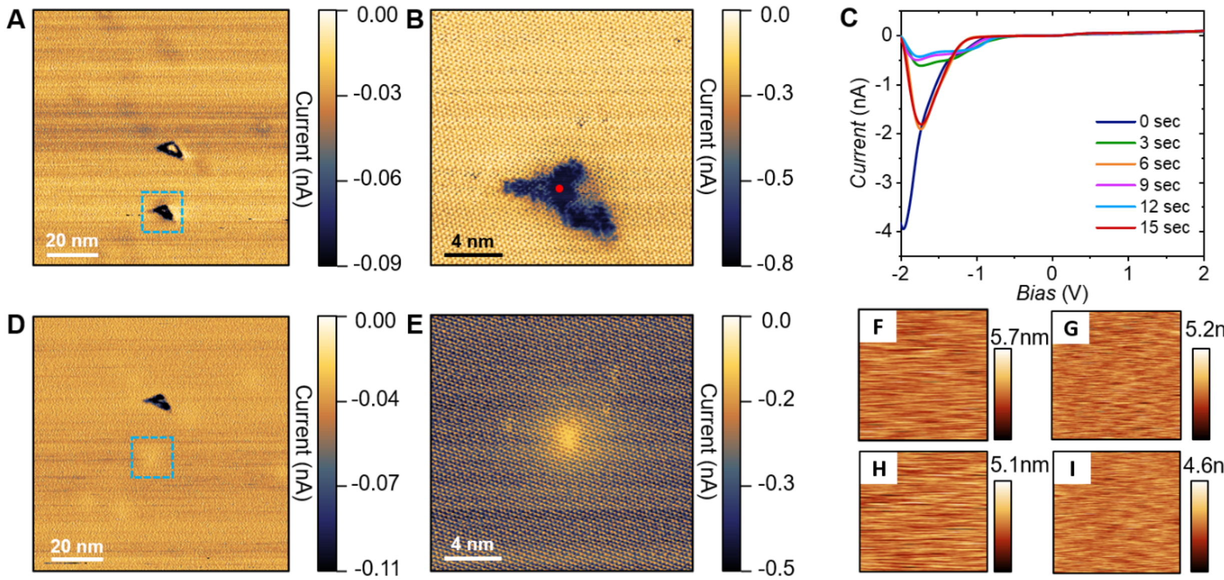

Figure 1. Electronic manipulation of a defect on MoS_2 via C-AFM under ambient conditions. (A) A large-scale current image showing two defects. **(B)** Zoom-in current image on the defect highlighted by the blue dashed square in (**A**). The defect features enhanced conductivity compared to its surroundings. **(C)** *I-V* curves recorded on top of the defect location marked with the red dot in **(B)**. **(D)** Current image of area **(A)** after the *I-V* sweeps. **(E)** Current image capturing the same defect in **(B)** after the *I-V* sweeps. The defect now features a slightly lower conductivity compared to its surroundings, with the uninterrupted atomic lattice overlaid on top of it. **(F-I)** Corresponding topographic images for **(A)**, **(B)**, **(D)**, and **(E)**, respectively. All images were obtained with an applied normal load of 0.0 nN, and at a scanning speed 15.62 Hz. Bias voltages: **(A)** -1.0 V, **(B)** -1.3 V, **(D)** -0.8 V, **(E)** -0.8 V.

4.2 Room-temperature charge ordering on Mo_2C

We employed our methodology to explore the surface electronic properties of thin Mo_2C crystals. In particular, C-AFM measurements revealed a periodic modulation (i.e., ordering) of charge, superimposed on the atomic lattice structure of Mo_2C (Figure 2A), in an area that includes two extended defects. The corresponding Fourier Transform (FT) shown in Figure 2B corroborates this observation, whereby the bright spots highlighted by red circles (with a periodicity of ~2.2 Å) represent the atomic structure of the Mo_2C surface, and the bright spots highlighted by green circles represent the periodic charge modulation with a periodicity of ~11.4 Å. Even more interestingly, the FT clearly shows the broken rotational symmetry between these two periodicities with an angular difference of ~13°. These results are supported by additional measurements on the material surface that show charge ordering (Figures 2C, E), with the corresponding FT again showing two periodicities corresponding to the lattice structure (~2.2 Å) and charge modulation (~11.1 Å), respectively, with an angular difference of ~12° between the two (Figure 2D). This discovery (which would need to be independently confirmed by angle-resolved photoemission spectroscopy (ARPES) measurements) has the potential to be important not only from a fundamental point of view) but also from a technological perspective as it may lead to the possibility of exciting electronic device applications at room temperature.

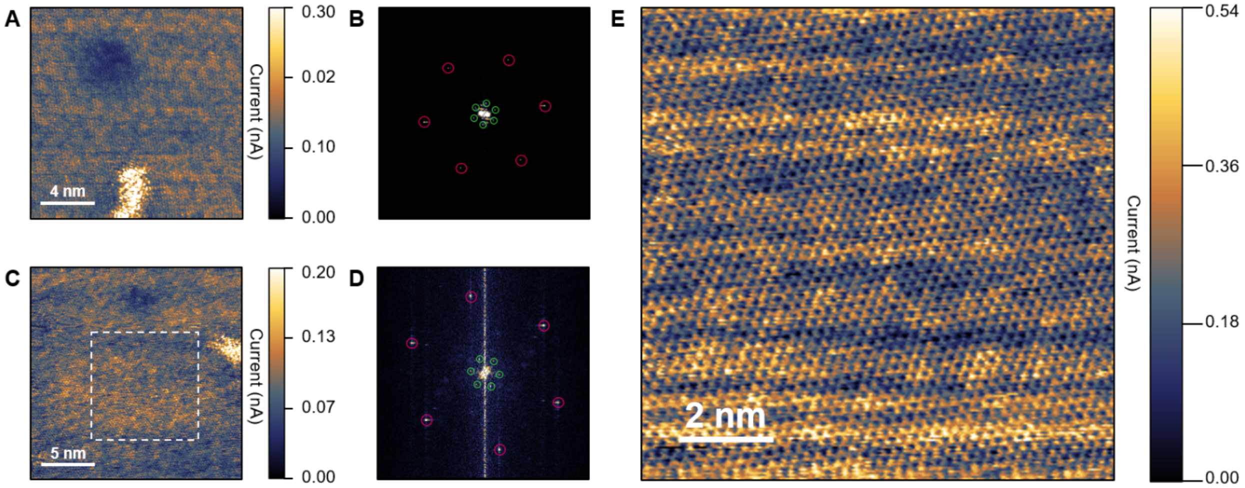

Figure 2. Observation of room-temperature charge ordering on Mo_2C via C-AFM. **(A)** Current image recorded on Mo_2C, showing periodic modulation of charge, along with two defects. **(B)** The corresponding FT of the image shown in **(A)**. The bright spots highlighted by red circles represent the lattice structure of α-Mo_2C with a periodicity of ~ 2.2 Å while the bright spots highlighted by green circles represent the charge modulation with a periodicity of ~11.4 Å. **(C)** Another current image recorded on α-Mo_2C exhibiting charge ordering. **(D)** The corresponding FT of the image shown in **(C)**. The bright spots highlighted by red and green circles represent lattice structure of α-Mo_2C (periodicity ~2.2 Å) and periodic modulation of charge (periodicity ~11.1 Å), respectively. **(E)** Zoom-in current image of the area highlighted by the white dotted rectangle in **(C)**, showing an ordering of charge superimposed on the atomic surface lattice. All images were obtained with an applied normal load of 0.0 nN, and at a scanning frequency of 15.62 Hz. Bias voltages: **(A)** 100 mV, **(C)** 1.3 V, **(E)** 1.3 V.

Award Number: FA9550-19-1-0035

Report Type: Final Performance Report

Reporting Period: 12/15/2018 – 12/14/2022

Distribution Statement: *A – Approved for Public Release*

Program Officer Name: Dr. Ali Sayir

Principle Investigator Name: Mehmet Z. Baykara & Ashlie Martini

Project Title: Investigating the Mechanisms of Electrical Contact Resistance between the Diffusive and Ballistic Limits

Abstract:

The original goal of this project was to investigate the mechanisms of electrical contact resistance (ECR) on small length scales through an interplay of conductive atomic force microscopy (C-AFM) experiments and atomistic simulations. This goal has been pursued, in the first half of the project period, by the following activities and accomplishments: (i) measuring ECR values between gold nano islands and graphite substrates, (ii) improving the C-AFM methodology in order to achieve more reliable and reproducible results, and (iii) understanding the physical mechanisms of the phenomenon of "conduction aging" we often observe in the experiments. In the second half of the project, our work evolved into the use of C-AFM as a powerful atomic-resolution imaging tool under ambient conditions, with exemplary results reported on various 2D materials as well as thin crystals of Mo_2C, in collaboration with the TOBB University of Economics and Technology as well as Eskisehir Technical University (ETU). The results of the project have been shared with the scientific community by way of five journal publications and multiple invited as well as contributed presentations at conferences and research institutions.

1. Accomplishments

1.1 Research Objectives

The main research objectives of this project can be considered under two broad headings, separated into the first and second half of the project period.

(1) During the first half of the project period, the main research objective has been to investigate physical mechanisms of ECR at small length scales, and study the transition from the diffusive to the ballistic conduction regimes.

(2) During the second half of the project, the main research objective has been to utilize C-AFM as an atomic-resolution imaging tool under ambient conditions, to study the structure and electronic properties of defects on various 2D materials as well as thin crystals of Mo_2C grown via chemical vapor deposition (grown by Dr. Goknur Buke's group at TOBB University), a prominent member of the emerging material class of thin TMCs.

1.2 Research Accomplishments

We have been partially successful in meeting the goals associated with Research Objective (1) listed above. In particular:

(i) We have performed C-AFM-based ECR measurements on a sample system comprising atomically flat interfaces (up to several hundreds of nanometers in lateral size) formed between gold islands and a highly oriented pyrolytic graphite (HOPG) substrate. Proof-of-principle experiments performed on gold islands of varying size pointed toward an increasing contribution of the island-HOPG junction to the measured total resistance with decreasing island size. Atomistic simulations complemented and elucidated experimental results, revealing the maximum island sizes below which the electrical contact resistance at the island-HOPG junction can be feasibly extracted from the measured total resistance.

Publication: Vazirisereshk, M.R., Sumaiya, S.A., Martini, A., Baykara, M.Z., *Measurement of Electrical Contact Resistance at Nanoscale Gold-Graphite Interfaces*, Applied Physics Letters **115**, 091602 (2019).

(ii) We have improved our C-AFM methodology in order to achieve more reliable and reproducible results. In particular, we presented an approach aimed at improving the reliability of C-AFM measurements by addressing multiple sources of variability. Specifically, we performed current-voltage (*I-V*) spectroscopy on atomically flat terraces HOPG under an inert nitrogen atmosphere and at controlled temperatures. The sample was annealed before the measurements to desorb adsorbates, and conductive diamond tips are used to limit tip apex deformation. These precautions lead to measured ECR values that follow a Gaussian distribution with significantly smaller standard deviation than those obtained under conventional measurement conditions. The key factor leading

to this improvement was identified as the switch from ambient conditions to a dry nitrogen atmosphere.

Publication: Sumaiya, S.A., Martini, A., Baykara, M.Z., *Improving the Reliability of Conductive Atomic Force Microscopy-Based Electrical Contact Resistance Measurements*, Nano Express **1**, 030023 (2020).

(iii) We employed a combined experimental and computational approach to understand the physical mechanisms of the phenomenon of "electrical conduction aging" we often observe in the experiments. In particular, ECR was shown to decrease over time as measured using C-AFM and estimated using two approaches from MD simulations. The simulations show that time dependence of ECR is attributable to an increase in real contact area due to atoms diffusing into the contact. This diffusion-based aging was found to be a thermally activated process that depends on the local contact pressure.

Publication: Vazirisereshk, M.R., Sumaiya, S.A., Chen, R., Baykara, M.Z., Martini, A., *Time-Dependent Electrical Contact Resistance at the Nanoscale*, Tribology Letters **69**, 50 (2021).

Despite the accomplishments listed above, the superlubric (i.e., ultra-low friction) character of the gold-graphite sample we investigated in the project has prevented us from establishing robust and stable electrical contacts over small gold nano islands, which ultimately prevented us from studying the ballistic transport regime that would only be observable at miniscule contact areas.

On the other hand, the extensive experience we developed with the use of C-AFM throughout the first part of the project fueled an exciting, alternative research direction in the second half of the project, which culminated in the following accomplishment:

(iv) We showed the use of C-AFM as a powerful atomic-resolution imaging tool under ambient conditions, with proof-of-principle measurements performed on a variety of 2D materials (MoS_2, $PtSe_2$, WS_2), as well as CVD-grown thin crystals of Mo_2C. Our method delivered images of defects down to the single vacancy level. Using our method, we additionally reported the capability of in situ charge state manipulation of defects on MoS_2 and the observation of charge ordering on Mo_2C.

Publication: Sumaiya, S.A., Liu, J., Baykara, M.Z., *True Atomic-Resolution Surface Imaging and Manipulation under Ambient Conditions via Conductive Atomic Force Microscopy*, ACS Nano **16**, 20086 (2022).

1.3 Dissemination Activities

As already indicated in the previous sections, the results of our work have been shared with the scientific community by way of multiple journal articles in well-respected outlets, as well as invited and contributed talks at conferences and research institutions.

A list of **all invited talks** associated with this project is provided below:

1. Baykara, M.Z, *Atomic-Resolution Surface Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, Turkish Society of Electron Microscopy Webinar, Stanford Virtual, December 7, 2022.

2. Baykara, M.Z, *Make Measurable What is Not So: Atomic-Resolution Surface Imaging and Manipulation under Ambient Conditions*, Geballe Laboratory for Advanced Materials (GLAM) Special Seminar, Stanford University, Palo Alto, USA, November 2, 2022.

3. Baykara, M.Z., *Where Flatlands Meet: Mechanics and Electronics at Atomically Flat Interfaces*, UCLA, Department of Materials Science & Engineering Seminar, Los Angeles, USA, January 17, 2020.

4. Baykara, M.Z., *Measurement of Electrical Contact Resistance at Nanoscale Gold-Graphite Interfaces*, 15th Nanoscience and Nanotechnology Conference, Antalya, Turkey, November 6, 2019.

A list of **all contributed talks** associated with this project is provided below:

1. Vaziriseresk, M. *et al.*, *Insight into Dynamic Sliding Contacts from Conductive Atomic Force Microscopy*, STLE Virtual Student Conference, May 2020.

2. Vazirisereshk, M. *et al.*, *Electrical Contact Resistance at Gold/Graphene Interfaces,* Tribology Frontiers Conference, Chicago IL, October 2019.

3. Sumaiya, S.A. *et al.*, *True Atomic-Resolution Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, AVS 68th International Symposium & Exhibition, Pittsburgh, USA, November 2022.

4. Sumaiya, S.A. *et al.*, *True Atomic-Resolution Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, 2022 MRS Spring Meeting & Exhibit, Honolulu, USA, May 2022.

5. Sumaiya, S.A. *et al.*, *Atomically Resolved Imaging of Electronic Defects in a CVD Grown Transition Metal Carbide: α–Mo_2C*, 2021 MRS Fall Meeting & Exhibit, Boston, USA, November 2021.
6. Sumaiya, S.A. *et al.*, *Temporal Evolution of Electrical Contact Resistance Observed via Improved Conductive Atomic Force Microscopy*, AVS 67th International Symposium & Exhibition (*Virtual*), October 2021.

Both PIs have been active in general outreach activities throughout the duration of the project, whereby the main tools used during the course of the project (AFM and MD simulations) have been introduced to students from the elementary to the high school level via various events.

2. Impacts

2.1 Impact on the development of the principal discipline(s) of the project

The field of atomic-resolution surface imaging has been essentially confined to the pristine yet impractical conditions of ultra-high vacuum (UHV) and low temperatures. With our new C-AFM method being able to provide true atomic-resolution maps of surfaces under ambient conditions, without the need for expensive and hard-to-maintain UHV equipment, we expect the results of our project to have significant impact on the principal discipline of scanning probe microscopy (SPM). Perhaps equally importantly, having access to the structure and electronic properties of material surfaces under ambient conditions is projected to have important contributions for potential device applications based on emerging materials, which will, most of the time, operate under ambient conditions, as opposed to the pristine UHV environment.

2.2 Impact on the development of human resources

Three PhD students have been funded by the project throughout its existence as Graduate Student Researchers (GSRs), which provided significant opportunities for academic and professional growth. **Saima A. Sumaiya**, the GSR who worked on the project from the first day and performed all associated experiments, graduated recently with flying colors and has started a position as **Postdoctoral Fellow at Columbia University**. Saima won multiple awards during his time at UC Merced thanks to the AFOSR project, which include the *STLE Northern California Section Research Scholarship* as well as the *Graduate Dean's Dissertation Fellowship* at UC Merced. **Mohammad Vazirisereshk**, the first computational GSR to work on this project, obtained his PhD in May 2021 and then obtained a research position at Lam Research. **Karen Mohammadtabar**, who worked on the second half of the project, just successfully defended his PhD in December 2022. Both Mohammad and Karen won the *STLE Northern California Section Research Scholarship*, in 2019 and 2020, respectively. Also, Karen was among the ten finalists at UC Merced's GradSlam competition in 2022, where students present their research via three slides in three minutes.

3. Changes

3.1 Changes in approach

As explained in Section 1.2, the scope and goals of the project changed after about 2 years from its start. Specifically, instead of performing a detailed study of the transition between the electronic and ballistic electron transport regimes (which have been hampered by the superlubricity of the gold-graphite sample which prevented the formation of robust and stable electrical contacts on small gold islands), our efforts have been re-directed at the use of C-AFM for the atomic-resolution study of defects on 2D materials as well as thin, chemical-vapor-deposition-grown Mo_2C crystals (provided by Prof. Goknur Buke and her research group at TOBB University). This change in direction has been extensively discussed with and approved by the program officer.

4. Technical Updates

The progress associated with the 3-year reporting period between 12/2018 and 12/2021 has been covered in detail in prior progress reports. Here, we report on technical updates that have been realized in the last period of the project, from 12/2021 to 12/2022.

4.1 Electronic manipulation of defects via C-AFM

Going beyond imaging, we also investigated the capability of our method to electronically manipulate defects under ambient conditions. In particular, Figure 1A shows a current image on MoS_2 with two extended defects that exhibit higher conductivity than their surroundings. Magnified images on the defects allow their study with high spatial resolution (Figure 1B). By performing *I-V* sweeps for multiple cycles (Figure 1C), we found an emerging peak in the *I-V* curves at a bias voltage of about -1.7 V, which is first attenuated and then re-emerges during the *I-V* cycles. This is accompanied by a side peak appearing between -1.1 and -1.3 V. After the *I-V* sweeps, the high conductivity region associated with the defect disappears (see Figures 1D, E, to be compared with Figures1A, B). The possibility of surface contamination can be ruled out as roughness fluctuations are not observed in the corresponding topography images (Figures 1F-I). The negative differential resistance in Figure 1C, characterized by a decrease in current with increasing voltage, may be related to localized surface charging/discharging behavior. According to the passive sign convention, more electrons may flow out of the defect location, indicating a pre-existing negatively charged region. After *I-V* sweeping, more positive charge will accumulate in the region to compensate the non-uniform charge states, which may explain the slightly lower current detected on the defect location after the *I-V* sweeps (Figure 1E). These experiments demonstrate that our C-AFM method may provide a feasible strategy for localized manipulation/elimination of electrical surface defects on 2D materials under ambient conditions.

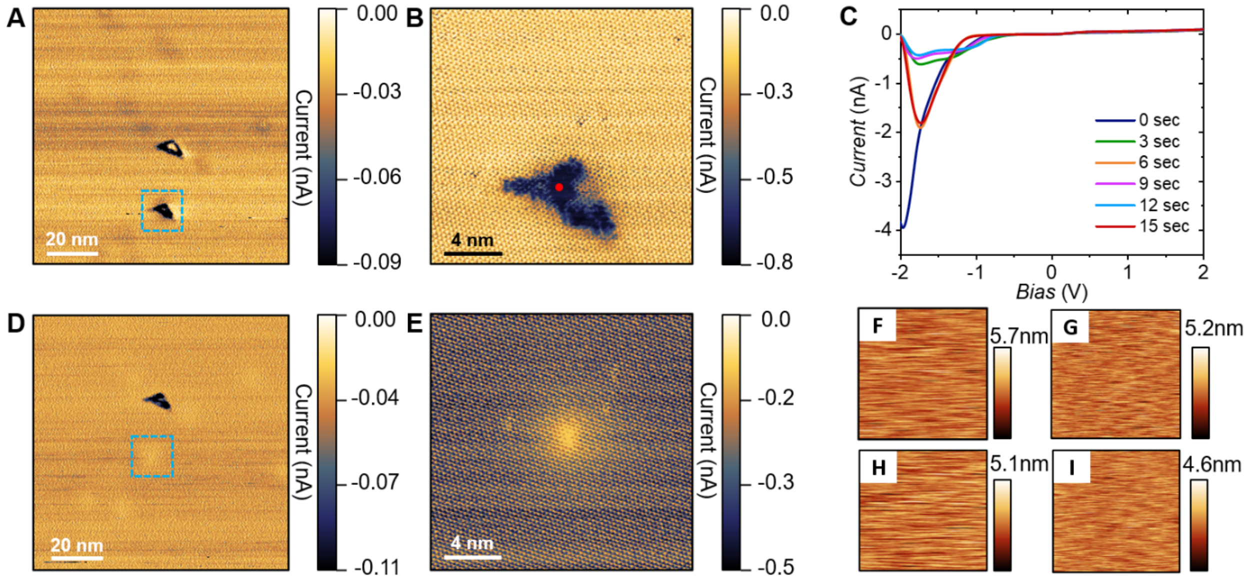

Figure 1. Electronic manipulation of a defect on MoS_2 via C-AFM under ambient conditions. (A) A large-scale current image showing two defects. **(B)** Zoom-in current image on the defect highlighted by the blue dashed square in (**A**). The defect features enhanced conductivity compared to its surroundings. **(C)** *I*-*V* curves recorded on top of the defect location marked with the red dot in **(B)**. **(D)** Current image of area **(A)** after the *I*-*V* sweeps. **(E)** Current image capturing the same defect in **(B)** after the *I*-*V* sweeps. The defect now features a slightly lower conductivity compared to its surroundings, with the uninterrupted atomic lattice overlaid on top of it. **(F-I)** Corresponding topographic images for **(A)**, **(B)**, **(D)**, and **(E)**, respectively. All images were obtained with an applied normal load of 0.0 nN, and at a scanning speed 15.62 Hz. Bias voltages: **(A)** -1.0 V, **(B)** -1.3 V, **(D)** -0.8 V, **(E)** -0.8 V.

4.2 Room-temperature charge ordering on Mo_2C

We employed our methodology to explore the surface electronic properties of thin Mo_2C crystals. In particular, C-AFM measurements revealed a periodic modulation (i.e., ordering) of charge, superimposed on the atomic lattice structure of Mo_2C (Figure 2A), in an area that includes two extended defects. The corresponding Fourier Transform (FT) shown in Figure 2B corroborates this observation, whereby the bright spots highlighted by red circles (with a periodicity of ~2.2 Å) represent the atomic structure of the Mo_2C surface, and the bright spots highlighted by green circles represent the periodic charge modulation with a periodicity of ~11.4 Å. Even more interestingly, the FT clearly shows the broken rotational symmetry between these two periodicities with an angular difference of ~13°. These results are supported by additional measurements on the material surface that show charge ordering (Figures 2C, E), with the corresponding FT again showing two periodicities corresponding to the lattice structure (~2.2 Å) and charge modulation (~11.1 Å), respectively, with an angular difference of ~12° between the two (Figure 2D). This discovery (which would need to be independently confirmed by angle-resolved photoemission spectroscopy (ARPES) measurements) has the potential to be important not only from a fundamental point of view) but also from a technological perspective as it may lead to the possibility of exciting electronic device applications at room temperature.

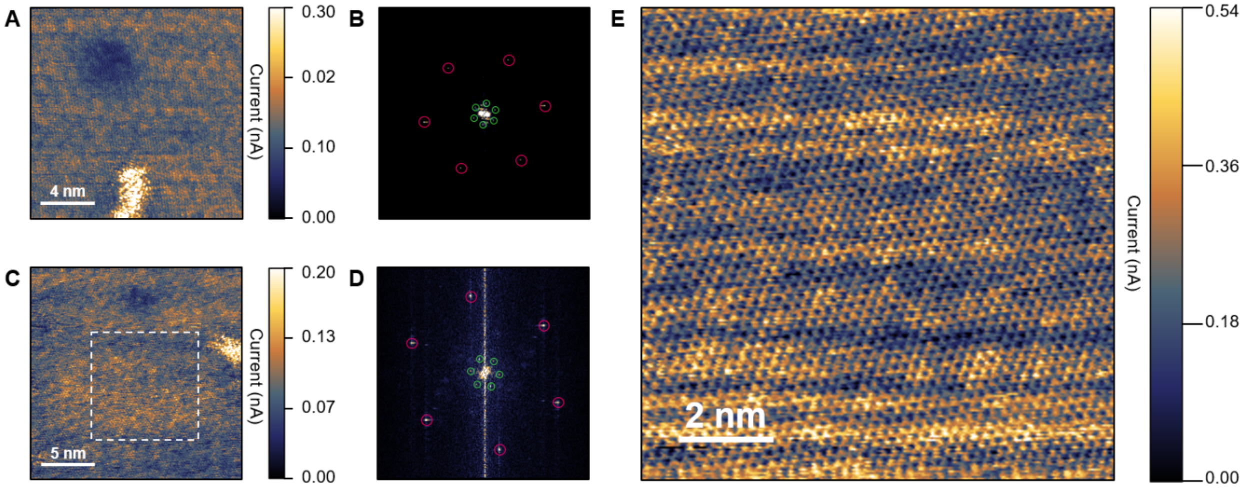

Figure 2. Observation of room-temperature charge ordering on Mo_2C via C-AFM. **(A)** Current image recorded on Mo_2C, showing periodic modulation of charge, along with two defects. **(B)** The corresponding FT of the image shown in **(A)**. The bright spots highlighted by red circles represent the lattice structure of α-Mo_2C with a periodicity of ~ 2.2 Å while the bright spots highlighted by green circles represent the charge modulation with a periodicity of ~11.4 Å. **(C)** Another current image recorded on α-Mo_2C exhibiting charge ordering. **(D)** The corresponding FT of the image shown in **(C)**. The bright spots highlighted by red and green circles represent lattice structure of α-Mo_2C (periodicity ~2.2 Å) and periodic modulation of charge (periodicity ~11.1 Å), respectively. **(E)** Zoom-in current image of the area highlighted by the white dotted rectangle in **(C)**, showing an ordering of charge superimposed on the atomic surface lattice. All images were obtained with an applied normal load of 0.0 nN, and at a scanning frequency of 15.62 Hz. Bias voltages: **(A)** 100 mV, **(C)** 1.3 V, **(E)** 1.3 V.

Award Number: FA9550-19-1-0035

Report Type: Final Performance Report

Reporting Period: 12/15/2018 – 12/14/2022

Distribution Statement: *A – Approved for Public Release*

Program Officer Name: Dr. Ali Sayir

Principle Investigator Name: Mehmet Z. Baykara & Ashlie Martini

Project Title: Investigating the Mechanisms of Electrical Contact Resistance between the Diffusive and Ballistic Limits

Abstract:

The original goal of this project was to investigate the mechanisms of electrical contact resistance (ECR) on small length scales through an interplay of conductive atomic force microscopy (C-AFM) experiments and atomistic simulations. This goal has been pursued, in the first half of the project period, by the following activities and accomplishments: (i) measuring ECR values between gold nano islands and graphite substrates, (ii) improving the C-AFM methodology in order to achieve more reliable and reproducible results, and (iii) understanding the physical mechanisms of the phenomenon of "conduction aging" we often observe in the experiments. In the second half of the project, our work evolved into the use of C-AFM as a powerful atomic-resolution imaging tool under ambient conditions, with exemplary results reported on various 2D materials as well as thin crystals of Mo_2C, in collaboration with the TOBB University of Economics and Technology as well as Eskisehir Technical University (ETU). The results of the project have been shared with the scientific community by way of five journal publications and multiple invited as well as contributed presentations at conferences and research institutions.

1. Accomplishments

1.1 Research Objectives

The main research objectives of this project can be considered under two broad headings, separated into the first and second half of the project period.

(1) During the first half of the project period, the main research objective has been to investigate physical mechanisms of ECR at small length scales, and study the transition from the diffusive to the ballistic conduction regimes.

(2) During the second half of the project, the main research objective has been to utilize C-AFM as an atomic-resolution imaging tool under ambient conditions, to study the structure and electronic properties of defects on various 2D materials as well as thin crystals of Mo_2C grown via chemical vapor deposition (grown by Dr. Goknur Buke's group at TOBB University), a prominent member of the emerging material class of thin TMCs.

1.2 Research Accomplishments

We have been partially successful in meeting the goals associated with Research Objective (1) listed above. In particular:

(i) We have performed C-AFM-based ECR measurements on a sample system comprising atomically flat interfaces (up to several hundreds of nanometers in lateral size) formed between gold islands and a highly oriented pyrolytic graphite (HOPG) substrate. Proof-of-principle experiments performed on gold islands of varying size pointed toward an increasing contribution of the island-HOPG junction to the measured total resistance with decreasing island size. Atomistic simulations complemented and elucidated experimental results, revealing the maximum island sizes below which the electrical contact resistance at the island-HOPG junction can be feasibly extracted from the measured total resistance.

Publication: Vazirisereshk, M.R., Sumaiya, S.A., Martini, A., Baykara, M.Z., *Measurement of Electrical Contact Resistance at Nanoscale Gold-Graphite Interfaces*, Applied Physics Letters **115**, 091602 (2019).

(ii) We have improved our C-AFM methodology in order to achieve more reliable and reproducible results. In particular, we presented an approach aimed at improving the reliability of C-AFM measurements by addressing multiple sources of variability. Specifically, we performed current-voltage (*I-V*) spectroscopy on atomically flat terraces HOPG under an inert nitrogen atmosphere and at controlled temperatures. The sample was annealed before the measurements to desorb adsorbates, and conductive diamond tips are used to limit tip apex deformation. These precautions lead to measured ECR values that follow a Gaussian distribution with significantly smaller standard deviation than those obtained under conventional measurement conditions. The key factor leading

to this improvement was identified as the switch from ambient conditions to a dry nitrogen atmosphere.

Publication: Sumaiya, S.A., Martini, A., Baykara, M.Z., *Improving the Reliability of Conductive Atomic Force Microscopy-Based Electrical Contact Resistance Measurements*, Nano Express **1**, 030023 (2020).

(iii) We employed a combined experimental and computational approach to understand the physical mechanisms of the phenomenon of "electrical conduction aging" we often observe in the experiments. In particular, ECR was shown to decrease over time as measured using C-AFM and estimated using two approaches from MD simulations. The simulations show that time dependence of ECR is attributable to an increase in real contact area due to atoms diffusing into the contact. This diffusion-based aging was found to be a thermally activated process that depends on the local contact pressure.

Publication: Vazirisereshk, M.R., Sumaiya, S.A., Chen, R., Baykara, M.Z., Martini, A., *Time-Dependent Electrical Contact Resistance at the Nanoscale*, Tribology Letters **69**, 50 (2021).

Despite the accomplishments listed above, the superlubric (i.e., ultra-low friction) character of the gold-graphite sample we investigated in the project has prevented us from establishing robust and stable electrical contacts over small gold nano islands, which ultimately prevented us from studying the ballistic transport regime that would only be observable at miniscule contact areas.

On the other hand, the extensive experience we developed with the use of C-AFM throughout the first part of the project fueled an exciting, alternative research direction in the second half of the project, which culminated in the following accomplishment:

(iv) We showed the use of C-AFM as a powerful atomic-resolution imaging tool under ambient conditions, with proof-of-principle measurements performed on a variety of 2D materials (MoS_2, $PtSe_2$, WS_2), as well as CVD-grown thin crystals of Mo_2C. Our method delivered images of defects down to the single vacancy level. Using our method, we additionally reported the capability of in situ charge state manipulation of defects on MoS_2 and the observation of charge ordering on Mo_2C.

Publication: Sumaiya, S.A., Liu, J., Baykara, M.Z., *True Atomic-Resolution Surface Imaging and Manipulation under Ambient Conditions via Conductive Atomic Force Microscopy*, ACS Nano **16**, 20086 (2022).

1.3 Dissemination Activities

As already indicated in the previous sections, the results of our work have been shared with the scientific community by way of multiple journal articles in well-respected outlets, as well as invited and contributed talks at conferences and research institutions.

A list of **all invited talks** associated with this project is provided below:

1. Baykara, M.Z, *Atomic-Resolution Surface Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, Turkish Society of Electron Microscopy Webinar, Stanford Virtual, December 7, 2022.

2. Baykara, M.Z, *Make Measurable What is Not So: Atomic-Resolution Surface Imaging and Manipulation under Ambient Conditions*, Geballe Laboratory for Advanced Materials (GLAM) Special Seminar, Stanford University, Palo Alto, USA, November 2, 2022.

3. Baykara, M.Z., *Where Flatlands Meet: Mechanics and Electronics at Atomically Flat Interfaces*, UCLA, Department of Materials Science & Engineering Seminar, Los Angeles, USA, January 17, 2020.

4. Baykara, M.Z., *Measurement of Electrical Contact Resistance at Nanoscale Gold-Graphite Interfaces*, 15th Nanoscience and Nanotechnology Conference, Antalya, Turkey, November 6, 2019.

A list of **all contributed talks** associated with this project is provided below:

1. Vaziriseresk, M. *et al.*, *Insight into Dynamic Sliding Contacts from Conductive Atomic Force Microscopy*, STLE Virtual Student Conference, May 2020.

2. Vazirisereshk, M. *et al.*, *Electrical Contact Resistance at Gold/Graphene Interfaces,* Tribology Frontiers Conference, Chicago IL, October 2019.

3. Sumaiya, S.A. *et al.*, *True Atomic-Resolution Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, AVS 68th International Symposium & Exhibition, Pittsburgh, USA, November 2022.

4. Sumaiya, S.A. *et al.*, *True Atomic-Resolution Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, 2022 MRS Spring Meeting & Exhibit, Honolulu, USA, May 2022.

5. Sumaiya, S.A. *et al.*, *Atomically Resolved Imaging of Electronic Defects in a CVD Grown Transition Metal Carbide: α–Mo_2C*, 2021 MRS Fall Meeting & Exhibit, Boston, USA, November 2021.
6. Sumaiya, S.A. *et al.*, *Temporal Evolution of Electrical Contact Resistance Observed via Improved Conductive Atomic Force Microscopy*, AVS 67th International Symposium & Exhibition (*Virtual*), October 2021.

Both PIs have been active in general outreach activities throughout the duration of the project, whereby the main tools used during the course of the project (AFM and MD simulations) have been introduced to students from the elementary to the high school level via various events.

2. Impacts

2.1 Impact on the development of the principal discipline(s) of the project

The field of atomic-resolution surface imaging has been essentially confined to the pristine yet impractical conditions of ultra-high vacuum (UHV) and low temperatures. With our new C-AFM method being able to provide true atomic-resolution maps of surfaces under ambient conditions, without the need for expensive and hard-to-maintain UHV equipment, we expect the results of our project to have significant impact on the principal discipline of scanning probe microscopy (SPM). Perhaps equally importantly, having access to the structure and electronic properties of material surfaces under ambient conditions is projected to have important contributions for potential device applications based on emerging materials, which will, most of the time, operate under ambient conditions, as opposed to the pristine UHV environment.

2.2 Impact on the development of human resources

Three PhD students have been funded by the project throughout its existence as Graduate Student Researchers (GSRs), which provided significant opportunities for academic and professional growth. **Saima A. Sumaiya**, the GSR who worked on the project from the first day and performed all associated experiments, graduated recently with flying colors and has started a position as **Postdoctoral Fellow at Columbia University**. Saima won multiple awards during his time at UC Merced thanks to the AFOSR project, which include the *STLE Northern California Section Research Scholarship* as well as the *Graduate Dean's Dissertation Fellowship* at UC Merced. **Mohammad Vazirisereshk**, the first computational GSR to work on this project, obtained his PhD in May 2021 and then obtained a research position at Lam Research. **Karen Mohammadtabar**, who worked on the second half of the project, just successfully defended his PhD in December 2022. Both Mohammad and Karen won the *STLE Northern California Section Research Scholarship*, in 2019 and 2020, respectively. Also, Karen was among the ten finalists at UC Merced's GradSlam competition in 2022, where students present their research via three slides in three minutes.

3. Changes

3.1 Changes in approach

As explained in Section 1.2, the scope and goals of the project changed after about 2 years from its start. Specifically, instead of performing a detailed study of the transition between the electronic and ballistic electron transport regimes (which have been hampered by the superlubricity of the gold-graphite sample which prevented the formation of robust and stable electrical contacts on small gold islands), our efforts have been re-directed at the use of C-AFM for the atomic-resolution study of defects on 2D materials as well as thin, chemical-vapor-deposition-grown Mo_2C crystals (provided by Prof. Goknur Buke and her research group at TOBB University). This change in direction has been extensively discussed with and approved by the program officer.

4. Technical Updates

The progress associated with the 3-year reporting period between 12/2018 and 12/2021 has been covered in detail in prior progress reports. Here, we report on technical updates that have been realized in the last period of the project, from 12/2021 to 12/2022.

4.1 Electronic manipulation of defects via C-AFM

Going beyond imaging, we also investigated the capability of our method to electronically manipulate defects under ambient conditions. In particular, Figure 1A shows a current image on MoS_2 with two extended defects that exhibit higher conductivity than their surroundings. Magnified images on the defects allow their study with high spatial resolution (Figure 1B). By performing *I-V* sweeps for multiple cycles (Figure 1C), we found an emerging peak in the *I-V* curves at a bias voltage of about -1.7 V, which is first attenuated and then re-emerges during the *I-V* cycles. This is accompanied by a side peak appearing between -1.1 and -1.3 V. After the *I-V* sweeps, the high conductivity region associated with the defect disappears (see Figures 1D, E, to be compared with Figures1A, B). The possibility of surface contamination can be ruled out as roughness fluctuations are not observed in the corresponding topography images (Figures 1F-I). The negative differential resistance in Figure 1C, characterized by a decrease in current with increasing voltage, may be related to localized surface charging/discharging behavior. According to the passive sign convention, more electrons may flow out of the defect location, indicating a pre-existing negatively charged region. After *I-V* sweeping, more positive charge will accumulate in the region to compensate the non-uniform charge states, which may explain the slightly lower current detected on the defect location after the *I-V* sweeps (Figure 1E). These experiments demonstrate that our C-AFM method may provide a feasible strategy for localized manipulation/elimination of electrical surface defects on 2D materials under ambient conditions.

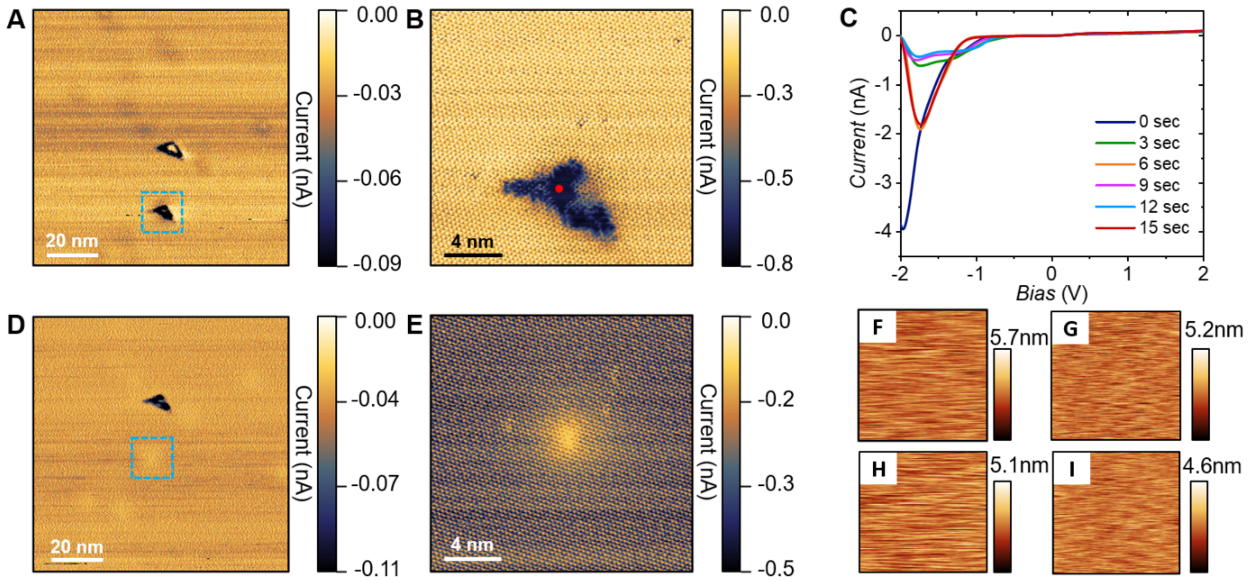

Figure 1. Electronic manipulation of a defect on MoS$_2$ via C-AFM under ambient conditions. (A) A large-scale current image showing two defects. **(B)** Zoom-in current image on the defect highlighted by the blue dashed square in (**A**). The defect features enhanced conductivity compared to its surroundings. **(C)** *I-V* curves recorded on top of the defect location marked with the red dot in **(B)**. **(D)** Current image of area **(A)** after the *I-V* sweeps. **(E)** Current image capturing the same defect in **(B)** after the *I-V* sweeps. The defect now features a slightly lower conductivity compared to its surroundings, with the uninterrupted atomic lattice overlaid on top of it. **(F-I)** Corresponding topographic images for **(A)**, **(B)**, **(D)**, and **(E)**, respectively. All images were obtained with an applied normal load of 0.0 nN, and at a scanning speed 15.62 Hz. Bias voltages: **(A)** -1.0 V, **(B)** -1.3 V, **(D)** -0.8 V, **(E)** -0.8 V.

4.2 Room-temperature charge ordering on Mo$_2$C

We employed our methodology to explore the surface electronic properties of thin Mo$_2$C crystals. In particular, C-AFM measurements revealed a periodic modulation (i.e., ordering) of charge, superimposed on the atomic lattice structure of Mo$_2$C (Figure 2A), in an area that includes two extended defects. The corresponding Fourier Transform (FT) shown in Figure 2B corroborates this observation, whereby the bright spots highlighted by red circles (with a periodicity of ~2.2 Å) represent the atomic structure of the Mo$_2$C surface, and the bright spots highlighted by green circles represent the periodic charge modulation with a periodicity of ~11.4 Å. Even more interestingly, the FT clearly shows the broken rotational symmetry between these two periodicities with an angular difference of ~13°. These results are supported by additional measurements on the material surface that show charge ordering (Figures 2C, E), with the corresponding FT again showing two periodicities corresponding to the lattice structure (~2.2 Å) and charge modulation (~11.1 Å), respectively, with an angular difference of ~12° between the two (Figure 2D). This discovery (which would need to be independently confirmed by angle-resolved photoemission spectroscopy (ARPES) measurements) has the potential to be important not only from a fundamental point of view) but also from a technological perspective as it may lead to the possibility of exciting electronic device applications at room temperature.

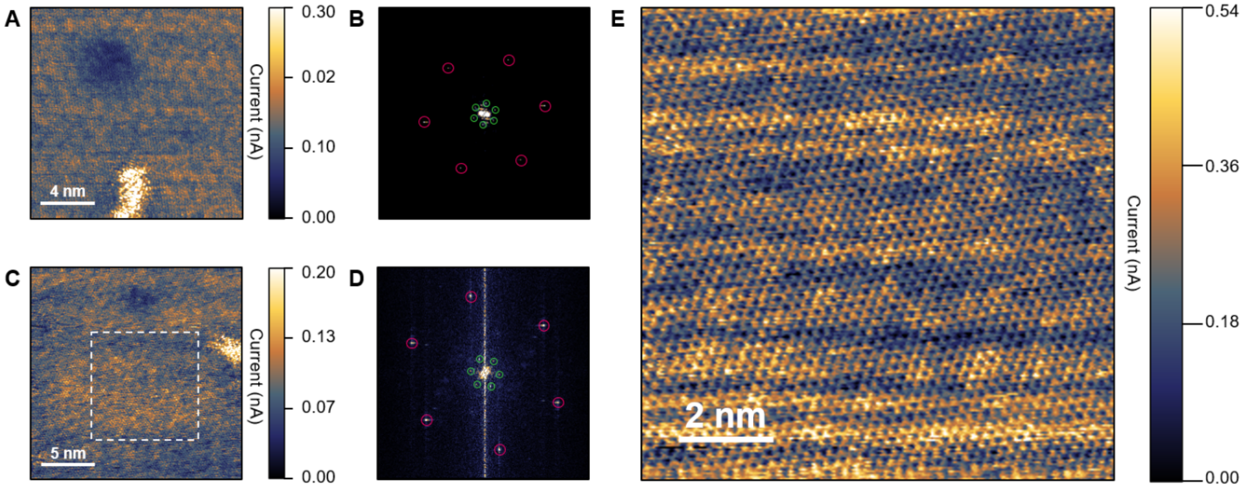

Figure 2. Observation of room-temperature charge ordering on Mo_2C via C-AFM. **(A)** Current image recorded on Mo_2C, showing periodic modulation of charge, along with two defects. **(B)** The corresponding FT of the image shown in **(A)**. The bright spots highlighted by red circles represent the lattice structure of α-Mo_2C with a periodicity of ~ 2.2 Å while the bright spots highlighted by green circles represent the charge modulation with a periodicity of ~11.4 Å. **(C)** Another current image recorded on α-Mo_2C exhibiting charge ordering. **(D)** The corresponding FT of the image shown in **(C)**. The bright spots highlighted by red and green circles represent lattice structure of α-Mo_2C (periodicity ~2.2 Å) and periodic modulation of charge (periodicity ~11.1 Å), respectively. **(E)** Zoom-in current image of the area highlighted by the white dotted rectangle in **(C)**, showing an ordering of charge superimposed on the atomic surface lattice. All images were obtained with an applied normal load of 0.0 nN, and at a scanning frequency of 15.62 Hz. Bias voltages: **(A)** 100 mV, **(C)** 1.3 V, **(E)** 1.3 V.