



AFRL-AFOSR-VA-TR-2016-0264

**MICROSCOPIC ELECTRONIC AND MECHANICAL
PROPERTIES OF ULTRA-THIN LAYERED MATERIALS**

**Abhay Pasupathy
THE TRUSTEES OF COLUMBIA UNIVERSITY IN THE CITY OF NEW YORK
116TH AND BDWY
NEW YORK, NY 10027**

**07/25/2016
Final Report**

DISTRIBUTION A: Distribution approved for public release.

Air Force Research Laboratory
AF Office Of Scientific Research (AFOSR)/RTB1

Arlington, Virginia 22203
Air Force Materiel Command

REPORT DOCUMENTATION PAGE		<i>Form Approved</i> OMB No. 0704-0188
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Executive Services, Directorate (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.</p>		
1. REPORT DATE (DD-MM-YYYY) 25-07-2016	2. REPORT TYPE Final Performance	3. DATES COVERED (From - To) 01 Apr 2011 to 31 Mar 2016
4. TITLE AND SUBTITLE MICROSCOPIC ELECTRONIC AND MECHANICAL PROPERTIES OF ULTRA-THIN LAYERED MATERIALS	5a. CONTRACT NUMBER	
	5b. GRANT NUMBER FA9550-11-1-0010	
	5c. PROGRAM ELEMENT NUMBER 61102F	
6. AUTHOR(S) Abhay Pasupathy	5d. PROJECT NUMBER	
	5e. TASK NUMBER	
	5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) THE TRUSTEES OF COLUMBIA UNIVERSITY IN THE CITY OF NEW YORK 116TH AND BDWY NEW YORK, NY 10027 US		8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AF Office of Scientific Research 875 N. Randolph St. Room 3112 Arlington, VA 22203		10. SPONSOR/MONITOR'S ACRONYM(S) AFRL/AFOSR RTB1
		11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-AFOSR-VA-TR-2016-0264
12. DISTRIBUTION/AVAILABILITY STATEMENT A DISTRIBUTION UNLIMITED: PB Public Release		
13. SUPPLEMENTARY NOTES		
<p>14. ABSTRACT</p> <p>The research goals of this project were to characterize the microscopic electronic and structural properties of ultra-thin (few layer) crystalline materials, commonly referred to as 2D materials. The technical approach used was to perform atomic-resolution scanning tunneling microscopy along with nanofabrication and transport measurements. The materials studied under the grant were graphene and transition metal dichalcogenides. In graphene, studies centered on material created by the chemical vapor deposition technique. A number of studies were conducted to determine the optimal conditions to grow graphene under. The doping of graphene with foreign atoms was investigated extensively. Finally, exotic electronic states in graphene that can be induced via substrate and adatom interactions were investigated. In the transition-metal dichalcogenides, studies initially focused on the charge density wave materials. It was discovered that the charge density wave transition is extremely sensitive to disorder. It was then found that the charge density wave is not driven by Fermi surface nesting, but rather by strong electron-phonon coupling. Superconductivity in transition metal dichalcogenides was then investigated, and it was found that in the limit of thin samples, a new Bose metal state emerges in the presence of a magnetic field. Finally, semiconducting transition metal dichalcogenides grown by metal organic chemical vapor deposition were studied and their atomic and electronic quality were measured by scanning tunneling microscopy.</p>		
<p>15. SUBJECT TERMS</p> <p>Scanning Tunneling Microscopy, Graphene</p>		

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON WEINSTOCK, HAROLD
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER <i>(Include area code)</i> 703-696-8572

Abhay Pasupathy Narayan: Final Report

Title: MICROSCOPIC ELECTRONIC AND MECHANICAL PROPERTIES OF ULTRA-THIN LAYERED MATERIALS

Contract No.: FA9550S 11S 1S 0010

Abstract

The research goals of this project were to characterize the microscopic electronic and structural properties of ultra-thin (few layer) crystalline materials, commonly referred to as 2D materials. The technical approach used was to perform atomic-resolution scanning tunneling microscopy along with nanofabrication and transport measurements. The materials studied under the grant were graphene and transition metal dichalcogenides. In graphene, studies centered on material created by the chemical vapor deposition technique. A number of studies were conducted to determine the optimal conditions to grow graphene under. The doping of graphene with foreign atoms was investigated extensively. Finally, exotic electronic states in graphene that can be induced via substrate and adatom interactions were investigated. In the transition-metal dichalcogenides, studies initially focused on the charge density wave materials. It was discovered that the charge density wave transition is extremely sensitive to disorder. It was then found that the charge density wave is not driven by Fermi surface nesting, but rather by strong electron-phonon coupling. Superconductivity in transition metal dichalcogenides was then investigated, and it was found that in the limit of thin samples, a new Bose metal state emerges in the presence of a magnetic field. Finally, semiconducting transition metal dichalcogenides grown by metal organic chemical vapor deposition were studied and their atomic and electronic quality were measured by scanning tunneling microscopy.

Description

The primary goal of this project was to characterize the structural and electronic quality of new two-dimensional (2D) materials that were grown by chemical vapor deposition (CVD) on metal and insulator surfaces. Under this theme, studies were performed on pristine graphene, doped graphene and transition-metal dichalcogenides. Apart from this, studies were also performed on exfoliated samples, primarily focusing on materials beyond graphene to study new electronic functionality at the ultrathin limit. A total of 18 publications and 4 in review/press have resulted from the award – one in Science, four in Nature Physics and two in Phys Rev Letters. Two patents have been filed based on the award. Described below are the summaries of each of these works:

1. Growth of graphene on single crystal copper substrates (reference [1]):

We study the influence of the surface structure of copper single crystals on the growth of large area monolayer graphene by chemical vapor deposition (CVD) in ultra-high vacuum (UHV). Using atomic resolution scanning tunneling microscopy (STM), we find that graphene grows primarily in registry with the underlying copper lattice for both Cu(111) and Cu(100). The graphene has a hexagonal superstructure on Cu(111) with a significant electronic component, whereas it has a linear superstructure on Cu(100). Graphene on Cu(111) forms a microscopically uniform sheet, the quality of which is determined by the presence of grain boundaries where graphene grains with different

orientations meet. Graphene grown on Cu(100) under similar conditions does not form a uniform sheet and instead displays exposed nanoscale edges. Our results indicate the importance of the copper crystal structure on the microstructure of graphene films produced by CVD.

2. Visualizing Individual Nitrogen Dopants in Monolayer Graphene (reference [2])

In monolayer graphene, substitutional doping during growth can be used to alter its electronic properties. We used scanning tunneling microscopy (STM), Raman spectroscopy, x-ray spectroscopy, and first principles calculations to characterize individual nitrogen dopants in monolayer graphene grown on a copper substrate. Individual nitrogen atoms were incorporated as graphitic dopants, and a fraction of the extra electron on each nitrogen atom was delocalized into the graphene lattice. The electronic structure of nitrogen-doped graphene was strongly modified only within a few lattice spacings of the site of the nitrogen dopant. These findings show that chemical doping is a promising route to achieving high-quality graphene films with a large carrier concentration.

3. Large physisorption strain in chemical vapor deposition of graphene on copper substrates (reference [3])

Graphene single layers grown by chemical vapor deposition on single crystal Cu substrates are subject to nonuniform physisorption strains that depend on the orientation of the Cu surface. The strains are revealed in Raman spectra and quantitatively interpreted by molecular dynamics (MD) simulations. An average compressive strain on the order of 0.5% is determined in graphene on Cu (111). In graphene on Cu (100), MD simulations interpret the observed highly nonuniform strains.

4. Connecting dopant bond type with electronic structure in N-doped graphene (reference [4])

Robust methods to tune the unique electronic properties of graphene by chemical modification are in great demand due to the potential of the two dimensional material to impact a range of device applications. Here we show that carbon and nitrogen core-level resonant X-ray spectroscopy is a sensitive probe of chemical bonding and electronic structure of chemical dopants introduced in single-sheet graphene films. In conjunction with density functional theory based calculations, we are able to obtain a detailed picture of bond types and electronic structure in graphene doped with nitrogen at the sub-percent level. We show that different N-bond types, including graphitic, pyridinic, and nitrilic, can exist in a single, dilutely N-doped graphene sheet. We show that these various bond types have profoundly different effects on the carrier concentration, indicating that control over the dopant bond type is a crucial requirement in advancing graphene electronics.

5. Molecular beam growth of graphene nanocrystals on dielectric substrates (reference [5])

We demonstrate the growth of graphene nanocrystals by molecular beam methods that employ a solid carbon source, and that can be used on a diverse class of large area dielectric substrates. Characterization by Raman and Near Edge X-ray Absorption Fine

Structure spectroscopies reveal a sp² hybridized hexagonal carbon lattice in the nanocrystals. Lower growth rates favor the formation of higher quality, larger size multi-layer graphene crystallites on all investigated substrates. The surface morphology is determined by the roughness of the underlying substrate and graphitic monolayer steps are observed by ambient scanning tunneling microscopy.

6. Substrate level control of the local doping in graphene (reference [6])

Graphene exfoliated onto muscovite mica is studied using ultrahigh vacuum scanning tunneling microscopy (UHV-STM) techniques. Mica provides an interesting dielectric substrate interface to measure the properties of graphene due to the ultraflat nature of a cleaved mica surface and the surface electric dipoles it possesses. Flat regions of the mica surface show some surface modulation of the graphene topography (24 pm) due to topographic modulation of the mica surface and full conformation of the graphene to that surface. In addition to these ultraflat regions, plateaus of varying size having been found. A comparison of topographic images and STS measurements show that these plateaus are of two types: one with characteristics of water monolayer formation between the graphene and mica, and the other arising from potassium ions trapped at the interfacial region. Immediately above the water induced plateaus, graphene is insulated from charge doping, while p-type doping is observed in areas adjacent to these water nucleation points. However, above and in the neighborhood of interfacial potassium ions, only n-type doping is observed. Graphene regions above the potassium ions are more strongly n-doped than regions adjacent to these alkali atom plateaus. Furthermore, a direct correlation of these Fermi level shifts with topographic features is seen without the random charge carrier density modulation observed in other dielectric substrates. This suggests a possible route to nanoscopic control of the local electron and hole doping in graphene via specific substrate architecture.

7. Visualizing the Charge Density Wave Transition in 2H-NbSe₂ in Real Space (reference [7])

We report the direct observation in real space of the charge density wave (CDW) phase transition in pristine 2H-NbSe₂ using atomic-resolution scanning tunneling microscopy. We find that static CDW order is established in nanoscale regions in the vicinity of defects at temperatures that are several times the bulk transition temperature T_{CDW}. On lowering the temperature, the correlation length of these patches increases steadily until CDW order is established in all of space, demonstrating the crucial role played by defects in the physics of the transition region. The nanoscale CDW order has an energy- and temperature-independent wavelength. Spectroscopic imaging measurements of the real-space phase of the CDW provide indirect evidence that an energy gap in NbSe₂ occurs at 0.7 eV below the Fermi energy in the CDW phase, suggesting that strong electron-lattice interactions, and not Fermi surface physics, are the dominant cause for CDW formation in NbSe₂.

8. Local atomic and electronic structure of boron chemical doping in monolayer graphene (reference [8])

We use scanning tunneling microscopy and X-ray spectroscopy to characterize the atomic and electronic structure of boron-doped and nitrogen-doped graphene created by

chemical vapor deposition on copper substrates. Microscopic measurements show that boron, like nitrogen, incorporates into the carbon lattice primarily in the graphitic form and contributes ~ 0.5 carriers into the graphene sheet per dopant. Density functional theory calculations indicate that boron dopants interact strongly with the underlying copper substrate while nitrogen dopants do not. The local bonding differences between graphitic boron and nitrogen dopants lead to large scale differences in dopant distribution. The distribution of dopants is observed to be completely random in the case of boron, while nitrogen displays strong sublattice clustering. Structurally, nitrogen-doped graphene is relatively defect-free while boron-doped graphene films show a large number of Stone-Wales defects. These defects create local electronic resonances and cause electronic scattering, but do not electronically dope the graphene film.

9. Visualization of electron nematicity and unidirectional antiferroic fluctuations at high temperatures in NaFeAs (reference [9])

The driving forces behind electronic nematicity in the iron pnictides remain hotly debated. We use atomic-resolution variable-temperature scanning tunneling spectroscopy to provide the first direct visual evidence that local electronic nematicity and unidirectional antiferroic (stripe) fluctuations persist to temperatures almost twice the nominal structural ordering temperature in the parent pnictide NaFeAs. Low-temperature spectroscopic imaging of nematically-ordered NaFeAs shows anisotropic electronic features that are not observed for isostructural, non-nematic LiFeAs. The local electronic features are shown to arise from scattering interference around crystalline defects in NaFeAs, and their spatial anisotropy is a direct consequence of the structural and stripe-magnetic order present at low temperature. We show that the anisotropic features persist up to high temperatures in the nominally tetragonal phase of the crystal. The spatial distribution and energy dependence of the anisotropy at high temperatures is explained by the persistence of large amplitude, short-range, unidirectional, antiferroic (stripe) fluctuations, indicating that strong density wave fluctuations exist and couple to near-Fermi surface electrons even far from the structural and density wave phase boundaries.

10. Segregation of sublattice domains in nitrogen-doped graphene (reference [10])

Atomic-level details of dopant distributions can significantly influence the material properties. Using scanning tunneling microscopy, we investigate the distribution of substitutional dopants in nitrogen-doped graphene with regard to sublattice occupancy within the honeycomb structure. Samples prepared by chemical vapor deposition (CVD) using pyridine on copper exhibit well-segregated domains of nitrogen dopants in the same sublattice, extending beyond 100 nm. On the other hand, samples prepared by postsynthesis doping of pristine graphene exhibit a random distribution between sublattices. On the basis of theoretical calculations, we attribute the formation of sublattice domains to the preferential attachment of nitrogen to the edge sites of graphene during the CVD growth process. The breaking of sublattice symmetry in doped graphene can have important implications in its electronic applications, such as the opening of a tunable band gap in the material.

11. Experimental evidence for a Bragg glass density wave phase in a transition-metal dichalcogenide (reference [11])

Analysis of the spatial dependence of current-voltage characteristics obtained from scanning tunneling microscopy experiments indicates that the charge density wave (CDW) occurring in NbSe₂ is subject to locally strong pinning by a non-negligible density of defects, but that on the length scales accessible in this experiment the material is in a “Bragg glass” phase where dislocations and antidislocations occur in bound pairs and free dislocations are not observed. An analysis based on a Landau theory is presented showing how a strong local modulation may produce only a weak long range effect on the CDW phase.

12. Quasiparticle Interference, Quasiparticle Interactions, and the Origin of the Charge Density Wave in 2H-NbSe₂ (reference [12])

We show that a small number of intentionally introduced defects can be used as a spectroscopic tool to amplify quasiparticle interference in 2H-NbSe₂ that we measure by scanning tunneling spectroscopic imaging. We show, from the momentum and energy dependence of the quasiparticle interference, that Fermi surface nesting is inconsequential to charge density wave formation in 2H-NbSe₂. We demonstrate that, by combining quasiparticle interference data with additional knowledge of the quasiparticle band structure from angle resolved photoemission measurements, one can extract the wave vector and energy dependence of the important electronic scattering processes thereby obtaining direct information both about the fermiology and the interactions. In 2H-NbSe₂, we use this combination to confirm that the important near-Fermi-surface electronic physics is dominated by the coupling of the quasiparticles to soft mode phonons at a wave vector different from the charge density wave ordering wave vector.

13. Nature of the quantum metal in a two-dimensional crystalline superconductor (reference [13])

Two-dimensional (2D) materials are not expected to be metals at low temperature owing to electron localization. Consistent with this, pioneering studies on thin films reported only superconducting and insulating ground states, with a direct transition between the two as a function of disorder or magnetic field. However, more recent works have revealed the presence of an intermediate quantum metallic state occupying a substantial region of the phase diagram, whose nature is intensely debated. Here, we observe such a state in the disorder-free limit of a crystalline 2D superconductor, produced by mechanical co-lamination of NbSe₂ in an inert atmosphere. Under a small perpendicular magnetic field, we induce a transition from superconductor to the quantum metal. We find a unique power-law scaling with field in this phase, which is consistent with the Bose-metal model where metallic behaviour arises from strong phase fluctuations caused by the magnetic field

14. Structure and control of charge density waves in two-dimensional 1T-TaS₂ (reference [14])

The layered transition metal dichalcogenides host a rich collection of charge density wave phases in which both the conduction electrons and the atomic structure display translational symmetry breaking. Manipulating these complex states by purely electronic methods has been a long-sought scientific and technological goal. Here, we show how this can be achieved in 1T-TaS₂ in the 2D limit. We first demonstrate that the intrinsic

properties of atomically thin flakes are preserved by encapsulation with hexagonal boron nitride in inert atmosphere. We use this facile assembly method together with transmission electron microscopy and transport measurements to probe the nature of the 2D state and show that its conductance is dominated by discommensurations. The discommensuration structure can be precisely tuned in few-layer samples by an in-plane electric current, allowing continuous electrical control over the discommensuration-melting transition in 2D.

15. Modification of the G-phonon mode of graphene by nitrogen doping (reference [15])

The effect of nitrogen doping on the phonon spectra of graphene is analyzed. In particular, we employ first-principles calculations and scanning Raman analysis to investigate the dependence of phonon frequencies in graphene on the concentration of nitrogen dopants. We demonstrate that the G phonon frequency shows oscillatory behavior as a function of nitrogen concentration. We analyze different mechanisms which could potentially be responsible for this behavior, such as Friedel charge oscillations around the localized nitrogen impurity atom, the bond length change between nitrogen impurity and its nearest neighbor carbon atoms, and the long-range interactions of the nitrogen point defects. We show that the bond length change and the long range interaction of point defects are possible mechanisms responsible for the oscillatory behavior of the G frequency as a function of nitrogen concentration. At the same time, Friedel charge oscillations are unlikely to contribute to this behavior.

16. Klein tunneling and electron trapping in nanometre-scale graphene quantum dots (reference [16])

Relativistic fermions that are incident on a high potential barrier can pass through unimpeded, a striking phenomenon termed the “Klein paradox” in quantum electrodynamics. Electrostatic potential barriers in graphene provide a solid-state analog to realize this phenomenon. Here, we use scanning tunneling microscopy to directly probe the transmission of electrons through sharp circular potential wells in graphene created by substrate engineering. We find that electrons in this geometry display quasi-bound states where the electron is trapped for a finite time before escaping via Klein tunneling. We show that the continuum Dirac equation can be successfully used to model the energies and wavefunctions of these quasi-bound states down to atomic dimensions. We demonstrate that by tuning the geometry of the barrier it is possible to trap particular energies and angular momentum states with increased efficiency, showing that atomic-scale electrostatic potentials can be used to engineer quantum transport through graphene.

17. Imaging chiral symmetry breaking from Kekulé bond order in graphene (reference [17])

Chirality — or “handedness” — is a symmetry property crucial to fields as diverse as biology, chemistry, and high-energy physics. In graphene, chiral symmetry emerges naturally as a consequence of the carbon honeycomb lattice. This symmetry can be broken by interactions that couple electrons with opposite momenta in graphene. Here we directly visualize the formation of Kekulé bond order, one such phase of broken chiral symmetry, in an ultraflat graphene sheet grown epitaxially on a copper substrate. We show that its origin lies in the interactions between individual vacancies in the copper

substrate that are mediated electronically by the graphene. We show that this interaction causes the bonds in graphene to distort, creating a phase with broken chiral symmetry. The Kekulé ordering is robust at ambient temperature and atmospheric conditions, indicating that intercalated atoms may be harnessed to drive graphene and other two-dimensional (2D) materials towards electronically desirable and exotic collective phases.

18. Atomic-Scale Spectroscopy of Gated Monolayer MoS₂ (reference [18])

The electronic properties of semiconducting monolayer transition-metal dichalcogenides can be tuned by electrostatic gate potentials. Here we report gate tunable imaging and spectroscopy of monolayer MoS₂ by atomic-resolution scanning tunneling microscopy/spectroscopy (STM/STS). Our measurements are performed on large-area samples grown by metal-organic chemical vapor deposition (MOCVD) techniques on a silicon oxide substrate. Topographic measurements of defect density indicate a sample quality comparable to single crystal MoS₂. From gate voltage dependent spectroscopic measurements, we determine that in-gap states exist in or near the MoS₂ film at a density of $1.3 \times 10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$. By combining the single-particle band gap measured by STS with optical measurements, we estimate an exciton binding energy of 230 meV on this substrate, in qualitative agreement with numerical simulation. Grain boundaries are observed in these polycrystalline samples, which are seen to not have strong electronic signatures in STM imaging.

References (published under the grant):

- 1 Zhao, L., Rim, K. T., Zhou, H., He, R., Heinz, T. F., Pinczuk, A., Flynn, G. W. & Pasupathy, A. N. Influence of copper crystal surface on the CVD growth of large area monolayer graphene. *Solid State Communications* **151**, p. 509-513, (2011).
- 2 Zhao, L. Y. *et al.* Visualizing Individual Nitrogen Dopants in Monolayer Graphene. *Science* **333**, p. 999-1003, (2011).
- 3 He, R., Zhao, L. Y., Petrone, N., Kim, K. S., Roth, M., Hone, J., Kim, P., Pasupathy, A. & Pinczuk, A. Large Physisorption Strain in Chemical Vapor Deposition of Graphene on Copper Substrates. *Nano Letters* **12**, p. 2408-2413, (2012).
- 4 Schiros, T. *et al.* Connecting Dopant Bond Type with Electronic Structure in N-Doped Graphene. *Nano Lett* **12**, p. 4025-4031, (2012).
- 5 Wurstbauer, U. *et al.* Molecular beam growth of graphene nanocrystals on dielectric substrates. *Carbon* **50**, p. 4822-4829, (2012).
- 6 Goncher, S. J., Zhao, L. Y., Pasupathy, A. N. & Flynn, G. W. Substrate Level Control of the Local Doping in Graphene. *Nano Letters* **13**, p. 1386-1392, (2013).
- 7 Arguello, C. J. *et al.* Visualizing the charge density wave transition in 2H-NbSe_2 in real space. *Physical Review B* **89**, p. 235115, (2014).
- 8 Zhao, L. *et al.* Local Atomic and Electronic Structure of Boron Chemical Doping in Monolayer Graphene. *Nano Letters* **13**, p. 4659-4665, (2013).
- 9 Rosenthal, E. P., Andrade, E. F., Arguello, C. J., Fernandes, R. M., Xing, L. Y., Wang, X. C., Jin, C. Q., Millis, A. J. & Pasupathy, A. N. Visualization of electron

- nematicity and unidirectional antiferroic fluctuations at high temperatures in NaFeAs. *Nature Physics* **10**, p. 225-232, (2014).
- 10 Zabet-Khosousi, A., Zhao, L., Pálová, L., Hybertsen, M. S., Reichman, D. R., Pasupathy, A. N. & Flynn, G. W. Segregation of Sublattice Domains in Nitrogen-Doped Graphene. *Journal of the American Chemical Society* **136**, p. 1391-1397, (2014).
- 11 Okamoto, J.-i., Arguello, C. J., Rosenthal, E. P., Pasupathy, A. N. & Millis, A. J. Experimental Evidence for a Bragg Glass Density Wave Phase in a Transition-Metal Dichalcogenide. *Physical Review Letters* **114**, p. 026802, (2015).
- 12 Arguello, C. J. *et al.* Quasiparticle Interference, Quasiparticle Interactions, and the Origin of the Charge Density Wave in 2H-NbSe₂. *Physical Review Letters* **114**, p. 037001, (2015).
- 13 Tsen, A. W. *et al.* Nature of the Quantum Metal in a crystalline 2D superconductor. *Nat Phys*, (2016).
- 14 Tsen, A. W. *et al.* Structure and control of charge density waves in two-dimensional 1T-TaS₂. *Proceedings of the National Academy of Sciences* **112**, p. 15054-15059, (2015).
- 15 Lukashev, P. V., Zhao, L., Paudel, T. R., Schiros, T., Hurley, N., Tsymbal, E. Y., Pinczuk, A., Pasupathy, A. & He, R. Modification of the G-phonon mode of graphene by nitrogen doping. *Applied Physics Letters* **108**, p. 041907, (2016).
- 16 C Gutiérrez, L. B., CJ Kim, J Park, AN Pasupathy. Klein tunnelling and electron trapping in nanometre-scale graphene quantum dots. *Nature Physics (advanced online publication)*, (2016).
- 17 Christopher Gutiérrez, C.-J. K., Lola Brown, Theanne Schiros, Dennis Nordlund, Edward B Lochocki, Kyle M Shen, Jiwoong Park, Abhay N Pasupathy. Imaging chiral symmetry breaking from Kekule bond order in graphene. *Nature Physics (advanced online publication)*, (2016).
- 18 Zhou, X., Kang, K., Xie, S., Dadgar, A., Monahan, N. R., Zhu, X. Y., Park, J. & Pasupathy, A. N. Atomic-Scale Spectroscopy of Gated Monolayer MoS₂. *Nano Letters* **16**, p. 3148-3154, (2016).

AFOSR Deliverables Submission Survey

Response ID:6582 Data

1.

1. Report Type

Final Report

Primary Contact E-mail

Contact email if there is a problem with the report.

apn2108@columbia.edu

Primary Contact Phone Number

Contact phone number if there is a problem with the report

2128546335

Organization / Institution name

Columbia University

Grant/Contract Title

The full title of the funded effort.

MICROSCOPIC ELECTRONIC AND MECHANICAL PROPERTIES OF ULTRA-THIN LAYERED MATERIALS

Grant/Contract Number

AFOSR assigned control number. It must begin with "FA9550" or "F49620" or "FA2386".

FA9550-11-1-0010

Principal Investigator Name

The full name of the principal investigator on the grant or contract.

Abhay Pasupathy Narayan

Program Manager

The AFOSR Program Manager currently assigned to the award

Harold Weinstock

Reporting Period Start Date

04/01/2011

Reporting Period End Date

03/31/2016

Abstract

The research goals of this project were to characterize the microscopic electronic and structural properties of ultra-thin (few layer) crystalline materials, commonly referred to as 2D materials. The technical approach used was to perform atomic-resolution scanning tunneling microscopy along with nanofabrication and transport measurements. The materials studied under the grant were graphene and transition metal dichalcogenides. In graphene, studies centered on material created by the chemical vapor deposition technique. A number of studies were conducted to determine the optimal conditions to grow graphene under. The doping of graphene with foreign atoms was investigated extensively. Finally, exotic electronic states in graphene that can be induced via substrate and adatom interactions were investigated. In the transition-metal dichalcogenides, studies initially focused on the charge density wave materials. It was discovered that the charge density wave transition is extremely sensitive to disorder. It was then found that the charge density wave is not driven by Fermi surface nesting, but rather by strong electron-phonon coupling. Superconductivity in transition metal dichalcogenides was then investigated, and it was found that in the limit of thin samples, a new Bose metal state emerges in the presence of a magnetic field.

DISTRIBUTION A: Distribution approved for public release.

Finally, semiconducting transition metal dichalcogenides grown by metal organic chemical vapor deposition were studied and their atomic and electronic quality were measured by scanning tunneling microscopy.

Distribution Statement

This is block 12 on the SF298 form.

Distribution A - Approved for Public Release

Explanation for Distribution Statement

If this is not approved for public release, please provide a short explanation. E.g., contains proprietary information.

SF298 Form

Please attach your SF298 form. A blank SF298 can be found [here](#). Please do not password protect or secure the PDF. The maximum file size for an SF298 is 50MB.

[SF298.pdf](#)

Upload the Report Document. File must be a PDF. Please do not password protect or secure the PDF. The maximum file size for the Report Document is 50MB.

[Report.pdf](#)

Upload a Report Document, if any. The maximum file size for the Report Document is 50MB.

Archival Publications (published) during reporting period:

Total of 18, as described in the report.

2. New discoveries, inventions, or patent disclosures:

Do you have any discoveries, inventions, or patent disclosures to report for this period?

No

Please describe and include any notable dates

Do you plan to pursue a claim for personal or organizational intellectual property?

Changes in research objectives (if any):

None

Change in AFOSR Program Manager, if any:

None

Extensions granted or milestones slipped, if any:

None

AFOSR LRIR Number

LRIR Title

Reporting Period

Laboratory Task Manager

Program Officer

Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, \$K)

	Starting FY	FY+1	FY+2
Salary			
Equipment/Facilities			
Supplies			
Total			

Report Document

Report Document - Text Analysis

Report Document - Text Analysis

Appendix Documents

2. Thank You

E-mail user

Jul 24, 2016 19:18:35 Success: Email Sent to: apn2108@columbia.edu