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Electronic and Optical Properties of Two-dimensional TiSe₂ and NbSe₂ and Elemental Black Phosphorus

**Theresa Maldonado
UNIVERSITY OF TEXAS AT EL PASO**

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Final Report**

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14. ABSTRACT
 The selenides of the early transition metals, Ti and Nb, are a far less explored material system when compared to the selenides of the other transition metals, such as Mo or W. Besides conducting a systematic investigation of the electronic and optical properties of NbSe2 and TiSe2, we will also examine the properties of black phosphorous, an emerging elemental layered material complementing graphene. Together, these materials exhibit interesting collective behavior at low temperatures. For example, NbSe2 and TiSe2 exhibit charge density waves (CDW) upon cooling, and doped structures show the onset of superconductivity. In a similar vein, black phosphorous also exhibits superconductivity in the bulk at high

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ABSTRACT

Through this AFOSR grant, significant progress has been made in setting up chemical vapor deposition capabilities for the synthesis of crystalline two dimensional layered materials as well as developing a residue-free viscoelastic stamping process for nanodevice fabrication involving black phosphorus, NbSe₂ and other van der Waals solids. These capabilities were nonexistent in Prof. Kaul's group prior to the start of this AFOSR grant. Over the course of the AFOSR grant, the clean viscoelastic stamping process has resulted in suspended membranes of MoS₂, black phosphorus and NbSe₂ to study their light-matter interactions. As an example, mesoscopic multilayer MoS₂ in a metal-semiconductor-metal (MSM) architecture showed an excellent photoresponse where the dominant photocurrent mechanism was determined to arise from the photoconductive effect (PCE), and the external quantum efficiency (EQE) with gating was determined to be $\sim 10^4$. An analysis of the temperature-dependent optoelectronic properties of multilayer black phosphorus (BP) contacted with Mo electrodes unveiled that the Schottky barrier ϕ_{SB} of the Mo-BP interface was low, ~ 44.8 meV, which helped in achieving a high photoresponsivity of $\sim 4.25 \times 10^4$ A/W. The thermally driven photocurrent generation mechanism arising from the photobolometric effect (PBE) dominated the carrier dynamics, particularly for temperatures > 175 K, while below this temperature, the photovoltaic effect (PVE) appeared to be at play. The comparative study on MoS₂ devices yielded the broad dominance of the PVE over the entire thermal range (6 K up to 350 K). Finally, the activation energy E_a and the maximum bolometric coefficient β_{max} were empirically calculated to be ~ 23.5 meV and $- 3.85$ mS/K, respectively. It is notable that this is the highest β reported on multilayer BP at 350 K. Our work generally shows the exceptional potential of 2D layered materials to shape the landscape of future electronic, optoelectronic and quantum scale devices over the coming years.

Final Report

The Kaul Group is extremely grateful to the support received from Dr. Kenneth Goretta's program at the AFOSR to pursue this research, and also to UTEP Engineering Dean, Dr. Theresa Maldonado, whose assistance has been invaluable during the transition process for Dr. Kaul from UTEP to UNT. Provided below are the publications that have appeared or are in the process of being prepared or submitted for peer review, through the support received from this AFOSR grant, along with other activities.

PUBLICATIONS

JOURNAL

1. G. L. Saenz, G. Karapetrov, J. Curtis, and A. B. Kaul, "Ultra-high photoresponsivity in suspended metal-semiconductor-metal mesoscopic multilayer MoS₂ broadband detector from UV-to-IR with low Schottky Barrier contacts," *Nature Sci. Reports* 8, 1276 (2018); DOI:10.1038/s41598-018-19367-1.
2. D. Fadil, R. F. Hossain, G. A. Saenz, and A. B. Kaul, "On the chemically-assisted excitonic enhancement in environmentally-friendly solution dispersions of two-dimensional MoS₂ and WS₂," *Journal of Materials Chemistry C* 5, 5323 (2017); DOI: 10.1039/C7TC01001J; **Article selected for back cover image.**
3. A. S. Bandyopadhyay, C. Biswas, and A. B. Kaul, "Light-matter interactions in two dimensional layered WSe₂ for gauging evolution of phonon dynamics," manuscript submitted, *J. Phys. Chem. C* (in review).
4. S. Chugh, N. Adhikari, J. Lee, D. Berman, L. Echegoyen, and A. B. Kaul, "Dramatic Enhancement of Optoelectronic Properties of Electrophoretically Deposited C60-Graphene Hybrids," manuscript submitted, *ACS Appl. Mat. and Intf.* (in review).
5. S. Chugh, N. Adhikari, M. Min, L. Echegoyen, and A. B. Kaul, "Sc₃N@C80 and La@C82 Doped Graphene for a New Class of Optoelectronic Devices," manuscript submitted, *Adv. Mat.* (in review).
6. A. S. Bandyopadhyay, N. Adhikari, G. A. Saenz, and A. B. Kaul, "Quantum Multi-body Interactions in Halide-assisted Vapor Synthesized Monolayer WSe₂ and Its Integration in a High Responsivity Photodiode with Low Interface Trap Density," manuscript submitted, *Materials Today* (in review).
7. G. A. Saenz, D. Fadil, and A. B. Kaul, "Photocurrent generation mechanism in multilayer black phosphorus and extraction of the bolometric coefficient over multiple thermal regimes," to be submitted, 2019.

8. G. A. Saenz, A. S. Bandyopadhyay, R. Mehta, Z. Liu, W. Zhou, and A. B. Kaul, "Phonon dynamics in NbSe₂ using non-contact confocal Micro-Raman and Photoluminescence Spectroscopy and correlation to electronic transport measurements," to be submitted, June, 2019.
9. A. S. Bandyopadhyay, G. A. Saenz, and A. B. Kaul, "Three-terminal, ambipolar WSe₂ photo-transistors," manuscript in preparation, to be submitted, 2019.
10. C. De Anda, G. L. Saenz, and A. B. Kaul, "Plasmonically-enhanced photodetection in semiconducting MoS₂ membranes with Au nanoparticles," manuscript in preparation, to be submitted, 2019.
11. S. Chugh, A. S. Bandyopadhyay, R. Hossain, N. Adhikari, M. Min, L. Echevoyen, and A. B. Kaul, "Photoinduced Electron Transfer and Exciton-Trion Dynamics in 0D-2D WSe₂ Hybrid System," manuscript in preparation, to be submitted, 2019.
12. S. Chugh, N. Adhikari, R. Hossain, M. Min, L. Echevoyen, and A. B. Kaul, "Probing the Charge Carrier Dynamics in Quantum Dots and Sc₃N@C₈₀ endohedrals integrated with monolayer WSe₂," manuscript in preparation, to be submitted, 2019.

CONFERENCE PUBLICATIONS & PROCEEDINGS ARTICLES

3 abstracts to be submitted to the American Vacuum Society Conference, Fall 2019.

1. N. Adhikari, A. S. Bandyopadhyay, and A. B. Kaul, "Nanoscale characterization of WSe₂ for opto-electronic applications," *MRS Advances*, vol. 2, issue 60 (Electronics and Photonics), pp. 3715-3720, 2017.
2. A. S. Bandyopadhyay, G. A. Saenz, and A. B. Kaul, "Characterization of few layer tungsten diselenide based FET under thermal excitation," *MRS Advances*, vol. 2, issue 60 (Electronics and Photonics), pp. 3721-3726, 2017.
3. G. A. Saenz, C. de Anda Orea, and A. B. Kaul, "Single and few-layer MoS₂: CVD synthesis, transference and photodetection application," *MRS Advances*, vol. 2, issue 60 (Electronics and Photonics), pp. 3709-3714, 2017.
4. M. Min, G. A. Saenz, G. Qiu, A. Charnas, P. Ye, and A. B. Kaul, "Chemical exfoliation of black phosphorus for nanoelectronics applications," *MRS Advances*, vol. 2, issue 60 (Electronics and Photonics), pp. 3697-3702, 2017.
5. G. A. Saenz, D. Fadil, A. B. Kaul, "Analysis of multilayer black phosphorus for photodetector applications," Proc. SPIE 10209, Image Sensing Technologies: Materials, Devices, Systems, and Applications IV, 1020912, April 2017, doi: 10.1117/12.2262854
6. A. S. Bandyopadhyay, G. A. Saenz, C. Biswas, and A. B. Kaul, "Characterization of monolayer tungsten diselenide based devices under optical excitation," SPIE Defense, Security and Sensing Conference, Anaheim, April 2017.

7. S. Chugh, L. Echegoyen, and A. B. Kaul, "Hybrid zero-dimensional C60 clusters with graphene – synthesis, fabrication and transport characteristics," *MRS Advances*, vol. 2, issue 60 (Electronics and Photonics), pp. 3727-3732, 2017.
8. A. S. Bandyopadhyay, et. al and A. B. Kaul, "Enhancement of optical properties by incorporating Au quantum dots in CVD WSe2 based photodetector," to appear in Proc. SPIE Defense, Security and Sensing Conference; Energy Harvesting and Storage: Materials, Devices, and Applications IX, Baltimore, MD, April 2019.
9. G. A. Saenz, C. De Anda Coreia, A. B. Kaul, "Photocurrent enhancement of CVD MoS2 photodetector via nanoplasmonics," to appear in Proc. SPIE Defense and Commercial Sensing Conference; Image Sensing Technologies: Materials, Devices, Systems, and Applications VI, Baltimore, MD, April 2019.
10. G. A. Saenz, C. De Anda Orea, A. B. Kaul, "Synthesis and Characterization of CVD MoO2 Nanosheets for High Hole Injection in Flexible 2D Semiconductors," to appear in Proceedings of Society of Vacuum Coaters 62nd Annual Technical Conference, April 27 - May 2, 2019; Long Beach, CA; to appear in the Special Issue of *Surface & Coatings Technology*
11. A. S. Bandyopadhyay, et. al and A. B. Kaul, "Role of metal contacts and effect of vacuum Annealing in high Performance 2D WSe2 FETs on flexible substrates," to appear in Proceedings of Society of Vacuum Coaters 62nd Annual Technical Conference, April 27 - May 2, 2019; Long Beach, CA; to appear in the Special Issue of *Surface & Coatings Technology*

KEYNOTE, INVITED TALKS & OTHER PRESENTATIONS

1. A. S. Bandyopadhyay, et. al and A. B. Kaul, "Enhancement of optical properties by incorporating Au quantum dots in CVD WSe2 based photodetector," Oral Presentation, SPIE Defense, Security and Sensing Conference; Energy Harvesting and Storage: Materials, Devices, and Applications IX, Baltimore, MD, April 2019.
2. G. A. Saenz, C. De Anda Coreia, A. B. Kaul, "Photocurrent enhancement of CVD MoS2 photodetector via nanoplasmonics," Poster presentation, SPIE Defense and Commercial Sensing Conference; Image Sensing Technologies: Materials, Devices, Systems, and Applications VI, Baltimore, MD, April 2019.
3. G. A. Saenz, C. De Anda Orea, A. B. Kaul, "Synthesis and Characterization of CVD MoO2 Nanosheets for High Hole Injection in Flexible 2D Semiconductors," Poster presentation, Society of Vacuum Coaters 62nd Annual Technical Conference, April 27 - May 2, 2019; Long Beach, CA.
4. A. S. Bandyopadhyay, et. al and A. B. Kaul, "Role of metal contacts and effect of vacuum Annealing in high Performance 2D WSe2 FETs on flexible substrates," Poster presentation, Society of Vacuum Coaters 62nd Annual Technical Conference, April 27 - May 2, 2019; Long Beach, CA.

5. Avra S. Bandyopadhyay, et al., A. B. Kaul, "High Responsivity and Short Response Time in CVD-grown Monolayer WSe₂ based Photodiode," Poster presentation, 2nd Annual Photonics Workshop and Showcase, University of Texas, Dallas, Feb. 2019.
6. G. A. Saenz, et al., A. B. Kaul, "High-performance broadband photodetector based on suspended multilayer MoS₂," Poster presentation, 2nd Annual Photonics Workshop and Showcase, University of Texas, Dallas, Feb. 2019.
7. INVITED: A. B. Kaul, "Black phosphorus ink-jet printing," *Annual American Chemical Society Meeting*, Boston, Aug. 2018.
8. INVITED: A. B. Kaul, "Top-down and Bottom-up Synthesis of 2D Transition Metal Sulphides and Selenides and their Device Applications," *EU US Workshop on 2D Materials, Heterostructures and Devices*, Arlington, VA, Oct. 2017.
9. INVITED: A. B. Kaul, "Solution-cast 2D layered materials for flexible and printed electronics ," Printed and Flexible Electronics Symposium, NanoTech 2017 Conference & Expo (part of Techconnect World Innovation Conference & Expo), National Harbor, MD, May, 2017.
10. N. Adhikari, A. S. Bandyopadhyay, and A. B. Kaul, "Nanoscale characterization of WSe₂ for opto-electronic applications," poster presentation, *The Materials Research Society (AVS) Spring Meeting*, Phoenix, AZ, April 2017.
11. A. S. Bandyopadhyay, G. A. Saenz, and A. B. Kaul, "Characterization of few layer tungsten diselenide based FET under thermal excitation," poster presentation, *The Materials Research Society (AVS) Spring Meeting*, Phoenix, AZ, April 2017.
12. G. A. Saenz, C. de Anda Orea, and A. B. Kaul, "Single and few-layer MoS₂: CVD synthesis, transference and photodetection application," poster presentation, *The Materials Research Society (AVS) Spring Meeting*, Phoenix, AZ, April 2017.
13. S. Chugh, L. Echegoyen, and A. B. Kaul, "Hybrid zero-dimensional C60 clusters with graphene – synthesis, fabrication and transport characteristics," poster presentation, *The Materials Research Society (AVS) Spring Meeting*, Phoenix, AZ, April 2017.
14. M. Min, G. A. Saenz, G. Qiu, A. Charnas, P. Ye, and A. B. Kaul, "Chemical exfoliation of black phosphorus for nanoelectronics applications," poster presentation, *The Materials Research Society (AVS) Spring Meeting*, Phoenix, AZ, April 2017.
15. G. A. Saenz, D. Fadil, A. B. Kaul, "Analysis of multilayer black phosphorus for photodetector applications," poster presentation, SPIE Defense, Security and Sensing Systems Conference (DSSS), Image Sensing Technologies: Materials, Devices, Systems, and Applications IV, Anaheim, CA, April 2017.

STUDENT RECOGNITIONS

Ridwan Hossain (PhD candidate): 2nd place in North Texas Federation Symposium, Texas Women's University, Denton, TX, Spring 2018.

Ridwan Hossain (PhD candidate): 1st place in Graduate Student Expo, University of Texas, El Paso, Fall 2017.

TEACHING

Courses Developed and Taught

University of North Texas, Denton, TX

- ***“Fundamentals of Materials Science and Engineering”*** Spring 2018, 2019
 - Introductory concepts of Materials Science and Engineering geared for upper division undergraduate students (juniors and seniors). Course offered as: MTSE 3000
 - Topics discussed include: Principles of bonding, structure, and structure/property relationships for metals and their alloys, ceramics, polymers and composites. Emphasis on properties and how processes change structure and, consequently, properties.

CONFERENCE ORGANIZING

- Scientific Committee Member, *International Conference on Nanomaterials, Nanodevices, Fabrication and Characterization (CNNFC'16)*, Prague, Czech Republic, April 2017, April 2018.

PROFESSIONAL ACTIVITIES

- Editorial Board Member, *Nature Sci. Reports*, Jan. 2019 – present
- Nucleating research and educational activities under the PACCAR Technology Institute (PTI) for PTI-affiliated faculty and students at the University of North Texas, <https://paccar.unt.edu/home>
- External Advisory Board Members review meetings for Penn State University's 2D Crystal Consortium (2DCC), A National User Facility funded by the NSF Division of Materials Research (DMR), Materials Innovation Platform (MIP) at ~ \$18 Million for 5 years, renewable for an additional 5 years.