ISEN Fall 2013 Booster Award Final Report

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Project Title:
Probing Thermoelectricity in Large-area, Atomically-Thin Nanomaterials

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Objectives and Background

Nanomaterials such as graphene have been seen as intriguing thermoelectrics because of their low heat transfer and high mechanical strength. The objective of this ISEN Booster award is to explore thermoelectric transport in large-area single-layer molybdenum disulphide (MoS$_2$), a two-dimensional (2D) direct band gap semiconductor. The gate tunability of 2D semiconductors and the reduced thermal phonon transport in low dimensions makes monolayer (1L) materials promising for nano-scale thermoelectric devices with new functionality.

Under illumination above the optical bandgap, 1L transition metal dichalcogenides (TMDCs) such as MoS$_2$ exhibit a fast photoresponse that has been attributed to several mechanisms including photoconductive [1, 2] and photothermal [3] effects. Disentangling these phenomena in a large-area system requires control over the electronic contacts, photo-excitation, electronic transport, and geometry of a thermoelectric device. Accomplishing these interrelated goals prompted us to undertake three research tasks:

- Investigation of suitable procedures for vapor deposition of large-area monolayers of TMDCs.
- Fabrication of and photo-excitation measurements of monolayer devices, metal contacts, and carrier generation for electronic transport measurements, including thermal transport.
- Exploring models of transport in monolayer TMDCs under illumination to reveal carrier transport dynamics in two-dimensional devices.

During this ISEN Booster project, we made progress in each of these tasks, achieving publishable results related to photoexcitation, device fabrication, and modeling.

Research Approach

We followed a multi-pronged to achieve suitable large-area 1L devices. We explored synthesis of large-area monolayer MoS$_2$ by chemical vapor deposition. We simultaneously studied photo-excitation and carrier conduction relevant for thermal transport using both experimental and simulation approaches. This ISEN project primarily supported the activities of one graduate student (Erik Lenferink) in fabrication, measurement, and modeling of electronic transport in 2D nanomaterial devices. Additional supplies provided by ISEN were utilized by another student (Teodor Stanev) and a postdoctoral researcher (Ying Jia) for CVD material preparation.
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FIG. 1. (a) Schematic of our two-step growth process. (b) Image of the CVD MoS$_2$ film. Blue indicates the number of layers is less than 5. (c) Image of large-area CVD-grown MoS$_2$ obtained from collaborator Dravid. (d) Raman spectra of layered MoS$_2$ films. (e) Verification of layer-by-layer Ar plasma etching.

Research Accomplishments

Chemical synthesis of large-area MoS$_2$: Building on recent progress in synthesis methods [4, 5], we implemented vapor deposition to achieve high-quality large-area MoS$_2$ monolayers. We explored both a combined synthesis-etch process [4] and a rate-limited vapor transport process (Fig. 1a) [5]. Monolayer MoS$_2$ was successfully deposited and characterized by atomic force microscopy (AFM), Raman spectroscopy, and photoluminescence (Fig. 1b-d). We have confirmed with AFM that Ar etching can thin MoS$_2$ one layer at a time (Fig. 1e).

Several issues with the growth system were identified, including poor o-ring seals and oxygen leaks. Although these technical issues were fixed, the quality of as-grown large-area CVD materials did not compare favorably with that of monolayers obtained by micromechanical exfoliation, as measured by polarized photoluminescence. We are recruiting a postdoctoral scholar to move to the next phase of this work to begin assembling 2D heterostructures for transport. In the meantime, progress with sample synthesis and fabrication made evident the importance of 1L transfer techniques for assembly of non-trivial devices; dry transfer techniques were implemented [6] and improved in-house for transfer of MoS$_2$ flakes up to several hundred microns in length scale.

Photo-excitation in novel monolayer devices: Nano-electronic devices made from monolayer MoS$_2$ were explored to understand thermal and electrical transport. Spatially-resolved photocurrent microscopy reveals photocurrents generated at the edges between material and metal contacts (Fig. 2a). From the spatially-resolved measurements, it is clear that field-assisted exciton dissociation at contact edges (Fig. 2b-e) plays a crucial role in the photoreponse of 1L-TMDC devices. Due to the reduced screening in 2D, exciton binding energies are large ($\sim 0.5$ eV) and thermal dissociation into free carriers is inefficient. This presents a key challenge for future electronic and thermal transport applications with TMDCs: carrier dissociation is local. Through comparison between predictions of a drift-diffusion model and experimental results, we show that the exciton dissociation model effectively describes photoresponse processes in monolayer MoS$_2$ for moderate electrical biases.

We leveraged our photo-excitation capabilities to study enhanced transport along 1D interfaces in homojunctions of layered materials. Our progress in device processing enabled us to identify and to...
contact interfaces between monolayers and multilayers of MoS$_2$. Photoexcitation measurements of monolayer/multilayer flakes reveal that the interface has significant band-bending, which leads to enhanced photocurrents. Electrical characterization of the junction reveals increased conductivity and mobility of the interface electrons of up to $\sim 1000$ cm$^2$/Vs [7].

**Modeling coupled spin and charge carrier dynamics in photo-excited 2D TMDCs:** Essential to the understanding of transport phenomena in is a model of carrier transport. Spatial transport of the coupled valley and spin degrees of freedom in 1L-TMDCs under polarized illumination has not yet been modeled. Building on my numerical approach to spin Hall effect transport [8], we implemented a drift-diffusion model incorporating valley dynamics as a separate degree of freedom. Using numerical finite-element techniques, we studied influence of geometry and optical excitation on valley and spin accumulation in TMDCs [9]. Fundamental to this model is a deeper understanding of the role of contact and edge geometry in free carrier generation, which is built into the simulation. We measured photoresonse as a function of distance from the edge and compared with simulation results, finding good agreement (Fig. 3). This modeling will be critical for interpreting electrical conduction, thermal transport, and optical responses in 1L TMDC devices.

**Cultivating collaborations:** ISEN funding of our optical and transport experiments has promoted diverse collaborations with my group. We continued on-campus collaborations with Ketterson (Physics), Poeppelmeier (Chemistry) and Dravid (Material Science); we strengthened our ties with staff at Argonne National Laboratory for fabricating more complex devices.

**Impact of the Research on Energy and Sustainability**

This research project advanced our efforts to understand transport in low-dimensional materials. Although prospects for significant thermal transport are questionable, the research activities supported by ISEN funding have resulted in several promising avenues of inquiry. Our ISEN-funded work also contributed to selection for the ISEN NU-Argonne Early Career Investigator for Energy Research, leading to increased interactions with Department of Energy research staff and facilities.

**Impact of ISEN funding on the PI’s Research Program**

ISEN funding made possible an effort toward understanding electron transport in atomically-thin monolayers. Although our exciton dissociation results suggest that thermoelectricity in *monolayer* MoS$_2$ may not play a significant role in practical devices, the ISEN-supported research continued to impact our study of novel nano-electronic phenomena in monolayer materials. This research has led to several accomplishments for the PI’s broader research program arising from ISEN support:

- Development and testing of new procedures, tools, and in-house experience for **large-area CVD synthesis** of atomically-thin transition metal dichalcogenides. Additional progress in CVD will be pursued when a new postdoc joins our group in Summer 2015.
- Derivation and numerical solution of a **comprehensive 2D transport model** for carriers in

![FIG. 3. Experimental data and predictions from an exciton-dissociation model of spatial dependence of photocurrent generation near a metal/semiconductor edge of MoS$_2$.](image)
monolayer semiconductors. This model is now being used to quantitatively understand the observations of the newly-discovered valley Hall effect in MoS$_2$ [9, 10].

- Refinement and optimization of **fabrication and measurement schemes** for nano-electronic device of only a single monolayer in thickness. This experience is being leveraged for transport experiments investigating the valley Hall effect [9] and low-dimensional interface conduction [7] in nano-electronic devices made from atomically-thin materials.

**Research products:**

*Manuscript under review:*


*Manuscript published:*


*Manuscript in preparation:*


**References**