DOE Final Technical Report

Cover Page

Title:	Investigation of spin and magnetism in two dimensional materials with atomic-scale spatial resolution
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1. Summary of Research Publications

Papers attributed to this grant (DE-SC0018172):

1. * O'Hara, D. J., Zhu, T., Trout, A. H., Ahmed, A. S., Luo, Y. K., Lee, C. H., Brenner, M. R., Rajan, S., Gupta, J. A., McComb, D. W. & Kawakami, R. K. Room Temperature Intrinsic Ferromagnetism in Epitaxial Manganese Selenide Films in the Monolayer Limit. *Nano Letters* **18,** 3125–3131 (2018).
2. * O'Hara, D. J., Zhu, T. & Kawakami, R. K. Importance of Paramagnetic Background Subtraction for Determining the Magnetic Moment in Epitaxially Grown Ultrathin van der Waals Magnets. *IEEE Magnetics Letters* **9,** 1–5 (2018).
3. * Katoch, J., Zhu, T., Kochan, D., Singh, S., Fabian, J. & Kawakami, R. K. Transport Spectroscopy of Sublattice-Resolved Resonant Scattering in Hydrogen-Doped Bilayer Graphene. *Phys. Rev. Lett.* **121,** 136801 (2018).
4. * Zhu, T., Singh, S., Katoch, J., Wen, H., Belashchenko, K., Žutić, I. & Kawakami, R. K. Probing tunneling spin injection into graphene via bias dependence. *Phys. Rev. B* **98,** 054412 (2018).
5. * Zhu, T. & Kawakami, R. K. Modeling the oblique spin precession in lateral spin valves for accurate determination of the spin lifetime anisotropy: Effect of finite contact resistance and channel length. *Phys. Rev. B* **97,** 144413 (2018).

Work started on this grant and attributed to the renewal (DE-SC0016379):

6. ** Noesges, B. A., Zhu, T., Repicky, J. J., Yu, S., Yang, F., Gupta, J. A., Kawakami, R. K. & Brillson, L. J. Chemical Migration and Dipole Formation at van der Waals Interfaces between Magnetic Transition Metal Chalcogenides and Topological Insulators. *Phys. Rev. Materials,* in press (2020). (arXiv:2004.05748)
7. * Zhu, T., Bishop, A. J., Zhou, T., Zhu, M., O'Hara, D. J., Baker, A. A., Cheng, S., Walko, R. C., Repicky, J. J., Gupta, J. A., Jozwiak, C. M., Rotenberg, E., Hwang, J., Žutić, I. & Kawakami, R. K. Magnetic Properties and Electronic Structure of Magnetic Topological Insulator $MnBi_2Se_4$. arXiv:2003.07938 (2020).
8. * Zhu, T., O'Hara, D. J., Noesges, B. A., Zhu, M., Repicky, J. J., Brenner, M. R., Brillson, L. J., Hwang, J., Gupta, J. A. & Kawakami, R. K. Coherent Growth and Characterization of van der Waals 1T-VSe_2 Layers on GaAs(111)B Using Molecular Beam Epitaxy. arXiv:2004.05506 (2020).

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2. Technical Description

2.1 Overview

Spintronics is an approach to energy-efficient electronics beyond silicon CMOS that utilizes the electron's spin degree of freedom for memory and logic. The record spin diffusion length in graphene has generated considerable interest in two dimensional (2D) materials (i.e. graphene and beyond) as a platform for spintronics. Magnetism in 2D van der Waals materials may offer additional opportunities for tunability via strain, external fields, and layer-dependent quantum effects. The inherently atomic-scale nature of exchange interactions and the inherently all-surface nature of 2D sheets motivate an integrated approach combining atomic-scale magnetic characterization, epitaxial growth, and nanodevice fabrication.

The mission of the research is to develop and utilize atomic-scale imaging of spin and magnetism via spin-polarized scanning tunneling microscopy (STM) in conjunction with atom-by-atom materials growth via molecular beam epitaxy (MBE) and nanoscale device fabrication to explore new frontiers of spintronics and quantum science in 2D materials. The PIs are particularly motivated by understanding how the magnetic and spin-dependent properties at the atomic scale lead to interesting and potentially useful phenomena in spintronic devices at the macroscopic scale.

2.2 Accomplishments

- Room temperature ferromagnetism in $MnSe_2$, an epitaxial 2D magnet

We have developed MBE growth of monolayer $MnSe_2$, which is among the first monolayer magnets to exhibit ferromagnetism at room temperature (paper #1, O'Hara et al. *Nano Letters* 2018). Magnetic and structural characterization provides strong evidence that in the monolayer limit, ferromagnetism originates from a vdW manganese diselenide ($MnSe_2$) monolayer, while for thicker films it could originate from a combination of vdW $MnSe_2$ and/or interfacial magnetism of α-MnSe(111). Magnetization measurements of monolayer $MnSe_2$ films on GaSe and $SnSe_2$ epilayers show ferromagnetic ordering with a large saturation magnetization of ~ 4 Bohr magnetons per Mn, which is consistent with density functional theory calculations predicting ferromagnetism in monolayer 1T-$MnSe_2$. The proper determination of the magnetization required the subtraction of a paramagnetic background from Mn ions (paper #2, O'Hara et al., *IEEE Magnetics Letters* 2018). Growing Mn-Se films on GaSe up to high thickness (~ 40 nm) produces α-MnSe(111), and an enhanced magnetic moment (~ 2x) compared to the monolayer $MnSe_2$ samples. Detailed structural characterization by scanning transmission electron microscopy (STEM), scanning tunneling microscopy (STM), and reflection high energy electron diffraction (RHEED) reveal an abrupt and clean interface between GaSe(0001) and α-MnSe(111). In particular, the structure measured by STEM is consistent with the presence of a $MnSe_2$ monolayer at the interface. The results are summarized in Figure 1. Here, Figure 1a shows a model of the lattice and Figure 1s shows the room temperature ferromagnetic hysteresis loop. STM images of the GaSe substrate are shown in Figure 1c, while a three-layer MnSe film is shown in Figure 1d. These images show atomic resolution and the corresponding spectroscopy shows a band gap that is consistent with the literature for both GaSe and α-MnSe.

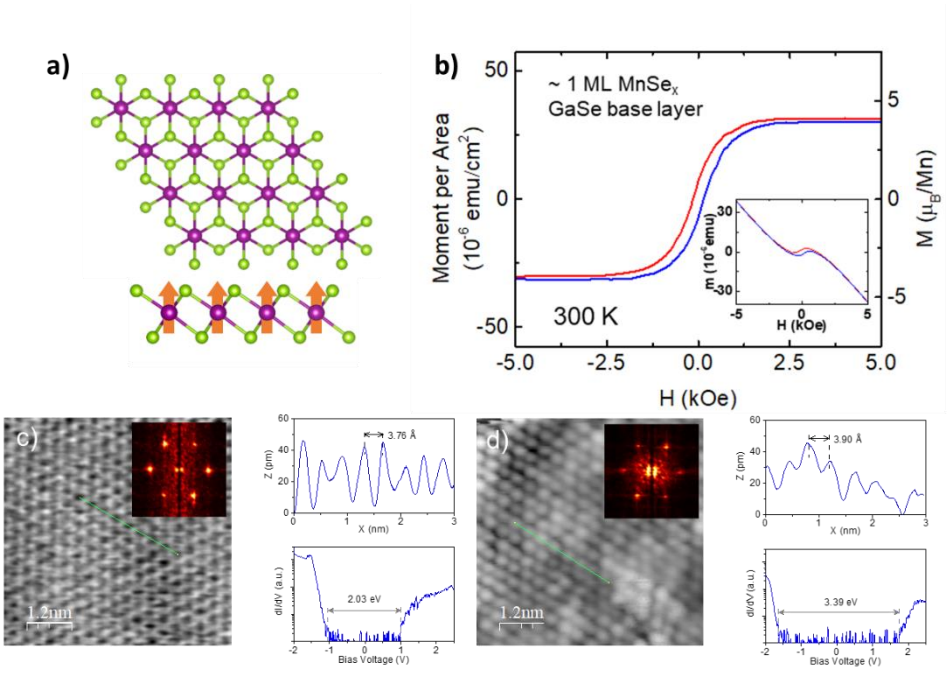

Figure 1. a) Schematic of the $MnSe_2$ lattice structure. **b)** Magnetic hysteresis loop of ~ 1ML $MnSe_x$ on GaSe base layer showing ferromagnetic behavior. Inset: the unprocessed SQUID data before background subtraction. **c)** STM topography image and dI/dV spectroscopy of the GaSe substrate and **d)** STM topography and dI/dV spectroscopy of ~3 layers of Mn-Se show a quick structural transition of the deposited material into α-MnSe(111).

- <u>Development of spin-polarized STM measurement capability</u>

We have developed spin-polarized STM (SPSTM) measurement capability to characterize magnetism at the atomic scale. We created spin-polarized tips by etching Cr wire (Figure 2a), which is antiferromagnetic with a spin-polarized surface to produce spin-contrast without generating magnetic fringe fields. The SPSTM method was tested on Cr(001) surfaces which possess layered antiferromagnetic order. When the surface of Cr(001) was imaged using the etched Cr tip, we observed spin contrast showing alternating magnetizations with each atomic terrace (Figure 2b-2d), as one would expect for a layered antiferromagnetic surface. Our ongoing work will be to use SPSTM to image magnetization at the atomic-scale in 2D magnets.

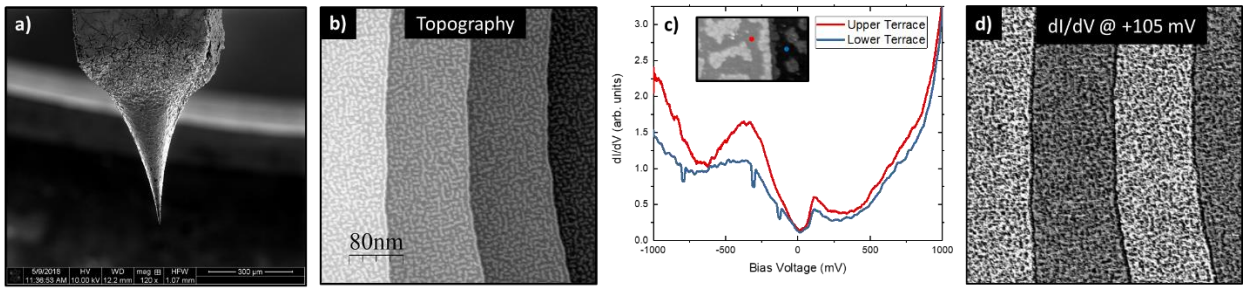

Figure 2. (a) SEM image of an etched Cr tip. (b) Topography of Cr(001) surface. (c) dI/dV spectra measured on adjacent terraces, where differences are due to the magnetization of the layers. (d) dI/dV mapping at +105 mV bias voltage reveals the layered antiferromagnetic order (alternating bright and dark contrast) of Cr(001).

- <u>Transport spectroscopy of hydrogen-doped bilayer graphene: Sublattice recognition through macroscopic electrical measurements</u>

Graphene with hydrogen adatom doping is an interesting system for the study of magnetism because the hydrogen generates localized magnetic moments within the graphene lattice. In this study, we report the groundbreaking experimental observation of sublattice-resolved resonant scattering in bilayer graphene (paper #3, Katoch et al., *Phys. Rev. Lett.* 2018). By performing simultaneous cryogenic atomic hydrogen doping and electron transport measurements on bilayer graphene nano-devices under ultrahigh vacuum, we detect two well-defined resonant scattering peaks in the gate-dependent resistance. Theoretical analysis shows they originate from hydrogen adatoms on the two inequivalent sublattices. These results allow us to monitor the atomic hydrogen adsorption on different sublattices of bilayer graphene without atomic-scale microscopy. Based on this new capability, we realize hydrogen doping with adatoms primarily on a single sublattice, which is highly desired for generating ferromagnetism. The results are summarized in Figure 2.

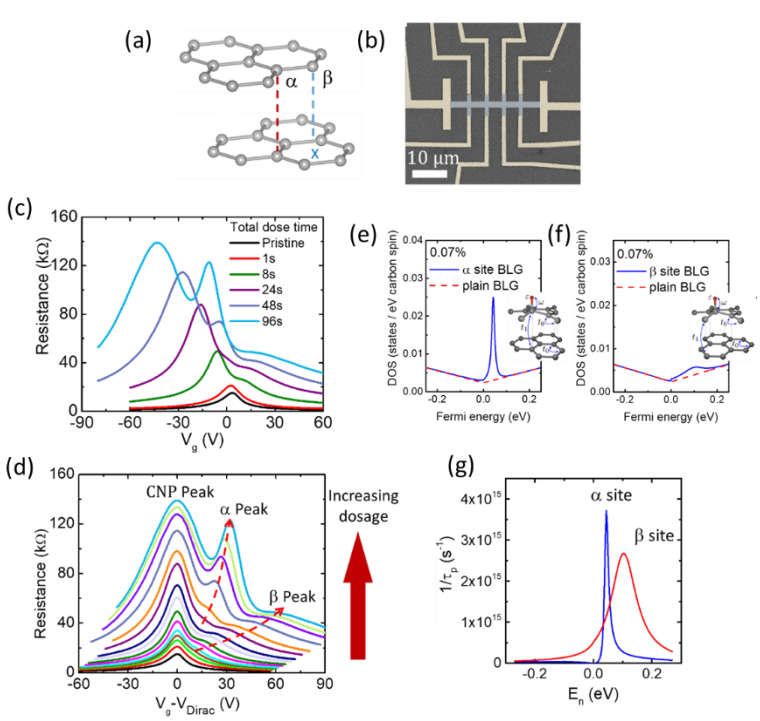

Figure 3. (a) Schematic of bilayer graphene, depicting α and β sites. (b) SEM picture of the typical device used for *in situ* hydrogenation and transport measurements in this study. (c) Gate dependent resistance at 21 K of undoped (black color curve) bilayer graphene and after hydrogen exposure. (d) With increasing hydrogen dosage the evolution of bilayer graphene resistance as a function of $V_g - V_{CNP}$. The dashed arrow lines show the progression of the two peaks labeled as α peak and β peak in resistance with increasing hydrogen dosage. (e, f, g) Tight-binding model calculation of the density of states (DOS), respectively, for 0.07% hydrogen doping of the α-sublattice (dimer site) and β-sublattice (non-dimer site) and corresponding momentum relaxation-rates.

Here, Figure 3a shows the two inequivalent sublattices of bilayer graphene, labeled α and β. On a device with backgate (Figure 3b), the deposition of hydrogen at cryogenic temperatures in UHV causes the charge neutrality point in the gate-dependent resistance to shift left, indicating electron doping (Figure 3c). As more hydrogen is deposited, two side peaks emerge (Figure 3d) which correspond to resonant scattering by hydrogen adatoms on either the α-sublattice or the β-sublattice. This assignment is confirmed through density functional theory calculations (Figures 3e, 3f), and the corresponding momentum scattering rate (Figure 3g) models the transport data.

- Development of *in operando* STM measurements on 2D nanoscale devices

To correlate the transport properties of hydrogen-doped bilayer graphene devices with the atomic-scale structure of the hydrogen dopants, we developed the capability for *in operando* STM measurements on 2D nanoscale devices. The process is shown in Figure 4. Samples were prepared by exfoliation of bilayer graphene onto SiO_2 on a Si substrate which was used as a backgate. As shown in Figure 4a, gold electrodes were patterned onto the sample by e-beam lithography, and a large gold "landing pad" adjacent to the device was fabricated to enable the STM tip approach. An argon/hydrogen gas anneal was sufficient to clean away polymer residue. Optical alignment of the tip approach was sufficient for landing onto the gold pad (Figure 4b). To move from the pad to the device, we utilized a capacitive navigation method, where the capacitance between the tip and conducting regions of the sample produce a mapping of the device with the tip safely retracted from the surface. Approaching the bilayer graphene surface led to the observation of atomic-resolution images. We obtained STM images before and after atomic hydrogen exposure in UHV at 5 K. Figure 4c shows the surface after hydrogen exposure. Figure 4d shows the dI/dV spectroscopy of the hydrogen-doped surface for various backgate voltages. We intend to apply these techniques for investigating small exfoliated 2D magnet samples by SPSTM.

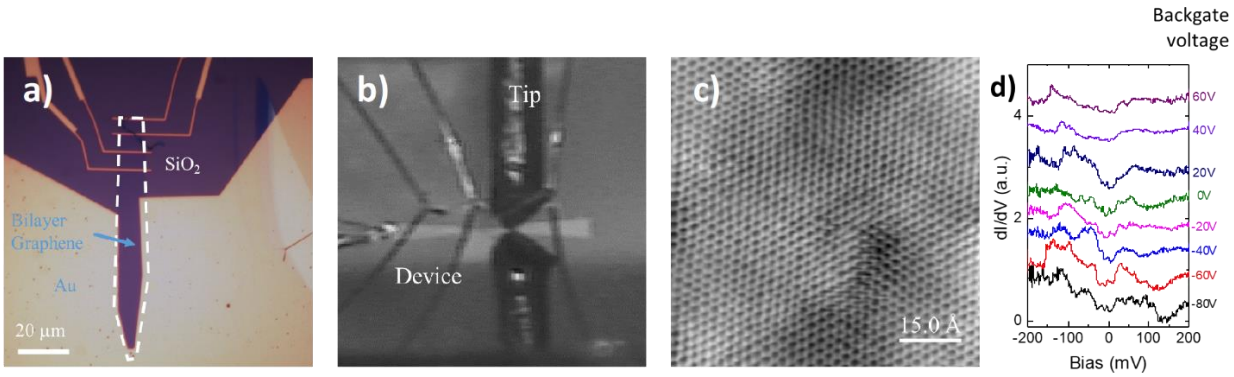

Figure 4. (a) Optical micrograph of a bilayer graphene device that is adjacent to a large gold landing pad in the lower half of the image. (b) Photograph of STM time approaching the gold landing pad. (c) Atomic-resolution STM image of a bilayer graphene surface of the device, after exposure to hydrogen. (d) STM spectroscopy dI/dV curves for different backgate voltages.

- Experimental and theoretical studies of spin transport and spin precession in graphene

Connected to our initial goals of investigating spin accumulation in graphene by scanning probe methods, we performed some experimental and theoretical studies of spin transport in

graphene. For the experiments, we investigated the bias dependence of spin injection into graphene through non-local spin transport measurements (paper #4, T. Zhu et al., *Phys. Rev. B* 2018). We observed a nonlinear dependence of the spin transport signal as a function of current bias. Similarities were observed for different ferromagnetic injector materials, specifically Co and Fe. Moreover, a correlation of spin signal on bias voltage as opposed to bias current, suggested the importance of the tunnel barrier materials rather than the specific ferromagnetic material in determining the bias dependence of spin injection into graphene.

For the theoretical work, we developed analysis for the investigation of spin relaxation in graphene through measurement of the spin lifetime anisotropy (paper #5, T. Zhu and R. K. Kawakami, *Phys. Rev. B* 2018) The spin lifetime anisotropy is the ratio of the lifetime for out-of-plane spins to the lifetime for in-plane spins, and it provides a measure of the spin-orbit coupling in graphene. Experiments measure the spin lifetime anisotropy of graphene through spin transport and spin precession measurements in graphene spin valves. The specific advance of this work is to include the effects of spin absorption into the contacts, which allows for a more accurate determination of the spin lifetime anisotropy from the experimental data. This is relevant for experimental studies that probe for the origin of spin relaxation in graphene, which is of interest for this project.

- Ongoing work

Several projects related to the MBE growth and characterization of vdW magnetic materials were initiated in this grant and completed in the renewal (DE-SC0016379). Continuing the study of monolayer $MnSe_2$ (Figure 1), we grew $MnSe_2$ on top of topological insulator Bi_2Se_3. Studies by x-ray photoelectron spectroscopy (XPS) and STM showed the presence of chemical migration, interface electric dipole formation, and the stabilization of both vdW-bonded $MnSe_2$ layers and covalently-bonded MnSe on the Bi_2Se_3 surface (paper #6, Noesges et al., *Phys. Rev. Materials* 2020). The presence of the covalent-bonded MnSe motivated further study and we found that suitable modification of the growth conditions produces septuple layers of $MnBi_2Se_4$, leading to the first synthesis of multilayer trigonal $MnBi_2Se_4$ (paper #7, Zhu et al., arXiv:2003.07938, 2020). The magnetic characterization is consistent with antiferromagnetic order, while ARPES studies above the ordering temperature show the presence of a Dirac surface state. Finally, we investigated the growth of 2D magnet VSe_2 on GaAs(111)B and demonstrated epitaxial growth up to 30 monolayers (paper #8, Zhu et al., arXiv:2004.05506, 2020). The growth and study of 2D/III-V hybrid structures are among the goals of the renewal project.