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13. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

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a. REPORT	b. ABSTRACT	c. THIS PAGE			Roland Kawakami
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RPPR Final Report
as of 13-Nov-2017

Agency Code:

Proposal Number: 65173MSRIP **Agreement Number: W911NF-14-1-0457**

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Report Date: 31-Jan-2017 Date Received: 09-Nov-2017
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Title: Spin-Polarized Scanning Tunneling Microscope for Atomic-Scale Studies of Spin Transport, Spin Relaxation, and Magnetism in Graphene
Begin Performance Period: 01-Aug-2014 **End Performance Period:** 31-Oct-2016
Report Term: 0-Other

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STEM Degrees: 0 **STEM Participants:** 3

Major Goals: Our ultimate goal is use spin-polarization scanning tunneling microscopy (SP-STM) to measure magnetization at the atomic scale in thin films and in devices. For devices, our goal is to correlate the atomic-scale magnetism and spin density with the macroscopic spin transport properties of 2D materials. This is a long-term effort at the forefront of research. We have made important progress and are approaching the ultimate goals.

Goals:
* Set up the scanning tunneling microscope (STM)
* Achieve atomic resolution in STM
* Measure a magnetic material with STM
* Measure a graphene film with STM
* Measure a device simultaneously by transport and STM
* Develop a bulk Cr tip for spin-polarized STM (SP-STM)
* Measure magnetization with atomic scale resolution
* Measure a spin transport device simultaneously by transport and SP-STM

The progress through these goals is highlighted in the "Accomplishments" document.

Accomplishments: The PDF is uploaded.

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Training Opportunities: Three graduate students and a visiting scholar were trained with the essential skills for performing advanced microscopy studies. The training includes: STM tip preparation, sample surface preparation and characterization, and operation of the scanning tunneling microscope. Furthermore, additional skills related to the project, such as material synthesis with molecular beam epitaxy (MBE), nano-device fabrication with e-beam lithography (EBL) are included in the training. The students gained extended experience with the above skills from the training process, which is valuable for future careers in industrial, government/national lab, and academic settings. Specific training opportunities are listed below.

Specific training opportunities with STM:
* Expertise with ultrahigh vacuum procedures
* Surface preparation by Ar sputtering and annealing
* In situ characterization of surface chemical composition analysis by Auger electron spectroscopy
* In situ characterization of long range atomic ordering on surfaces by low energy electron diffraction
* Electrochemical etching to form sharp STM tips
* In situ tip preparation by field emission and electron beam heating
* Atomic scale imaging of surface topography
* Local density of states measurement by STM spectroscopy
* Use and safe handling of cryogens liquid helium and liquid nitrogen
* Use and proper handling of superconducting magnets

Specific training opportunities with MBE:
* Construction of Knudsen cells for high purity material deposition
* Beam flux characterization for precise atomic scale thickness
* Analysis of high energy electron diffraction patterns for characterizing surface structure
* Ex situ material characterization by atomic force microscopy for characterization of surface morphology
* Ex situ material characterization by x-ray diffraction for characterization of film orientation
* Ex situ material characterization by x-ray reflectivity for characterization of film thickness
* Ex situ material characterization by SQUID magnetometer for characterization of magnetic ordering

Specific training opportunities with EBL:
* Exfoliation of graphene and other 2D materials
* Device design
* Developing electrode patterns in polymer resist by EBL
* Metal deposition onto resist patterns and subsequent removal of resist ("Lift off" process) for creating device electrodes
* Precision alignment of patterns in multi-step lithographic processes
* Electrical measurement of devices

Results Dissemination: Our results will be disseminated through refereed journal publications and conference presentation. We are currently preparing two manuscripts. The first one is on the structural characterization and spectroscopy of FeGe by STM and the second one is hydrogen doped bilayer graphene studied by STM. The data taking part of FeGe project is completed, while the complete data set of bilayer graphene project is currently being taken. In addition, future publications performed on this STM will acknowledge this DURIP grant.

Honors and Awards: 2015 APS Fellow for Roland Kawakami.
2016-17 ASC Diversity Enhancement Faculty Award for Jay Gupta.

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI
Participant: Roland K Kawakami
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:

International Travel:
National Academy Member: N
Other Collaborators:

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Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
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Project Contribution:
International Collaboration:
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International Collaboration:
International Travel:
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Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

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as of 13-Nov-2017

Accomplishments

Our ultimate goal is use spin-polarization scanning tunneling microscopy (SP-STM) to measure magnetization at the atomic scale in thin films and in devices. For devices, our goal is to correlate the atomic-scale magnetism and spin density with the macroscopic spin transport properties of 2D materials. This is a long-term effort at the forefront of research. We have made important progress and are approaching the ultimate goals.

Goals:

- ☒ Set up the scanning tunneling microscope (STM)
- ☒ Achieve atomic resolution in STM
- ☒ Measure a magnetic material with STM
- ☒ Measure a graphene film with STM
- ☒ Measure a device simultaneously by transport and STM
- ☒ (in progress) Develop a bulk Cr tip for spin-polarized STM (SP-STM)
- ☐ Measure magnetization with atomic scale resolution
- ☐ Measure a spin transport device simultaneously by transport and SP-STM

1. Installation of LT-STM/AFM

Our original plan was to home-build a 2-axis magnetic field STM, due to excessive cost of commercial systems with more than 1 axis (Specs JT-system with 1-axis: $1.4M, Omicron Tesla system with 2-axis: $1.1M (discontinued), Unisoku 2-axis system: $1.1M). But later, we learned of an STM system with magnetic field by Createc and discussion led to a $701k quote for a complete system consisting of STM and non-contact qPlus atomic force microscopy (AFM), 2-axis superconducting magnet, 4.2 K base temperature, 7 electrodes for device transport, rf-cabling for microwave resonance experiments at the atomic scale, and additional hardware consisting of UHV chamber, control electronics, preparation/growth chamber, and vibration isolation. Considering the additional capability beyond our original plans including AFM operation, high-speed rf-cabling, and a sample preparation/growth chamber as well as the reliability of a commercially engineered system, we decided it was better overall in terms of capability and pricing to go with this option instead of home-building the STM (this option was made possible by combining DURIP funds with separate funds budgeted for a growth chamber). The system shown in Fig. 1 was installed in August 2016. It has been very stable, operates reliably, and has excellent imaging and spectroscopy characteristics.

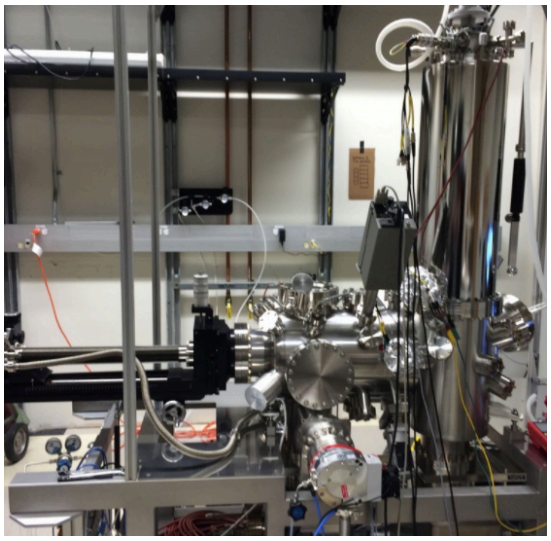

Fig. 1. The LT-STM/AFM system.

2. STM measurements of FeGe/Si(111) magnetic materials

Our first project was to study the atomic structure and electronic property of FeGe(111) thin films grown by our group using molecular beam epitaxy (MBE). FeGe has been shown to carry complex non-collinear spin structure with different magnetic phases, including the skyrmion crystal phase which is interesting for future SP-STM studies. Initial studies were performed on air-exposed samples due to their immediate availability, and later on samples transferred by UHV suitcase. The FeGe is relatively air stable,

but air-exposed samples require gentle sputter/annealing to clean up the surface oxidation and adsorbates. Fig. 2a shows the low energy electron diffraction (LEED) image of the sample after the surface preparation. The sample was then transported into the STM chamber. Fig. 2b shows the atomic structure of the FeGe(111) surface. To study the electronic properties of FeGe(111) under external magnetic field, we performed field dependent spectroscopy on the sample. Fig. 2c shows the summary of dI/dV curves taken for different out-of-plane magnetic field strength, while measuring at the same atomic site. We we able to reliably measure the spectrum under magnetic fields, and interestingly, we didn't observe any significant effect of magnetic field on the local electronic structure of the sample. These results were later confirmed on samples transferred by UHV suitcase to avoid air exposure between MBE growth and STM characterization.

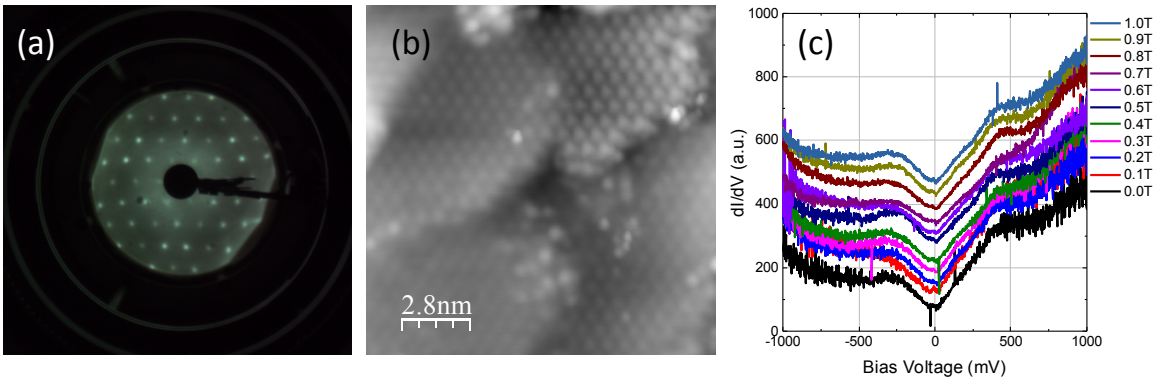

Fig. 2. (a) Low energy electron diffraction (LEED) pattern for FeGe. (b) STM image of FeGe. (c) STM spectroscopy at different magnetic fields. Curves are offset for clarify.

3. Combined STM and transport measurements of graphene devices

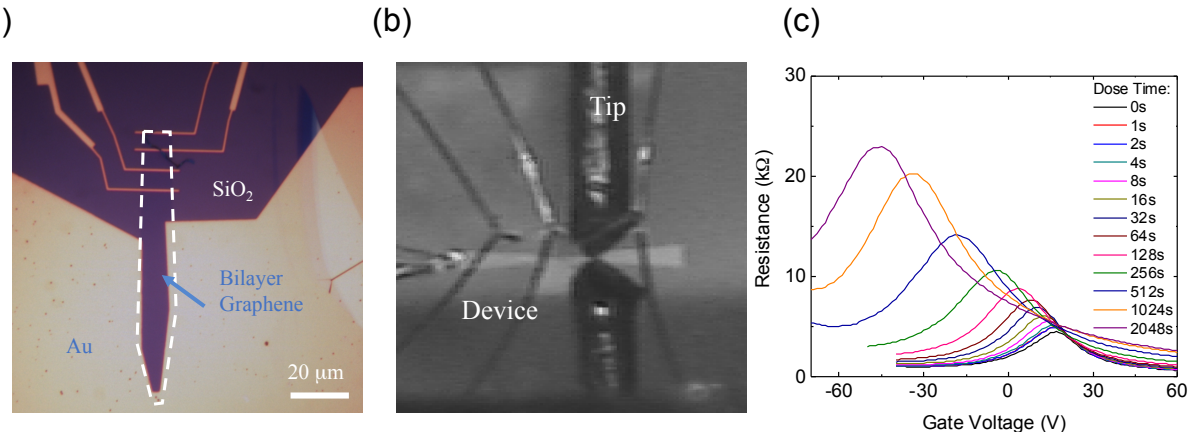

Fig. 3. (a) Optical microscope image of the bilayer graphene device. (b) Picture of the bilayer graphene device under STM tip. (c) Charge transport measurement of graphene gate dependent resistance.

Combining the transport and STM measurement in the same system provides the opportunity for understanding how material structure at the atomic scale can affect its macroscopic properties. We have made significant progress in developing such a technique. Fig. 3a shows an optical microscope image of a bilayer graphene nano-device. After loading the device into the STM system (as shown in Fig. 3b), we perform atomic hydrogenation on the device, and monitor the charge transport *in-situ*. The gate dependent resistance in Fig. 3c shows a negative shift in gate voltage of the charge neutrality point and increase in resistance with successive exposure to atomic hydrogen flux, indicating n-type doping and

additional scattering induced by the hydrogen adatoms. To correlate the change in transport with the atomic structure of hydrogen-doped graphene, we subsequently use the STM to investigate the graphene surface of the same device. Using a capacitive navigation method, we are able to locate the small graphene flake with the STM tip, and perform STM measurements. Fig. 4a shows the atomically resolved bilayer graphene lattice. Within our scanning range, no obvious point defect is observed, which indicates possibly uniform hydrogenation. Furthermore, we perform STM spectroscopy (Fig. 4b) at different gate voltages. The changes in STM spectra with gate voltage reflects the changes in the local density of states relative to the Fermi level, which is expected due to the strong tunability of the Fermi level in 2D materials. We note that the STM can also manipulate adatoms on the graphene surface. Our plan is to use the STM tip to selectively remove atomic hydrogen adsorbates and study the corresponding transport response.

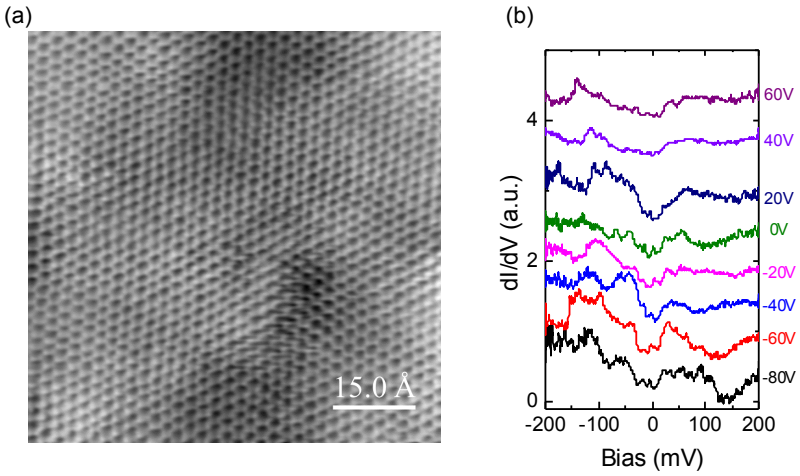

Fig. 4. (a) Atomic resolution image of the graphene lattice. (b) Gate dependent spectroscopy of the graphene surface. Curves are offset for clarity.

4. Developing SP-STM using Fe/Ir(111) skyrmion films and bulk Cr tips

Fe/Ir(111) is a good system to use for testing and calibrating SP-STM because it has variation of magnetization on the few nanometer scale (skyrmion ordering) and is well studied. We begin by preparing the Ir(111) substrate with multiple cycles of Ar sputtering at room temperature and annealing at 1150°C. A large scale image of the clean Ir(111) surface shows numerous atomically flat terraces (Fig. 5a), and a zoom in reveals the atomic structure (Fig. 5b) which demonstrates the success of the surface preparation. This is further confirmed by a typical dI/dV spectrum (Fig. 5c) where the appearance of a 'step' feature at -300mV is indicative of the surface state native to the clean Ir(111) surface. Deposition of submonolayer Fe leads to new features within the terraces, which are highlighted by the contour lines in Fig. 5d.

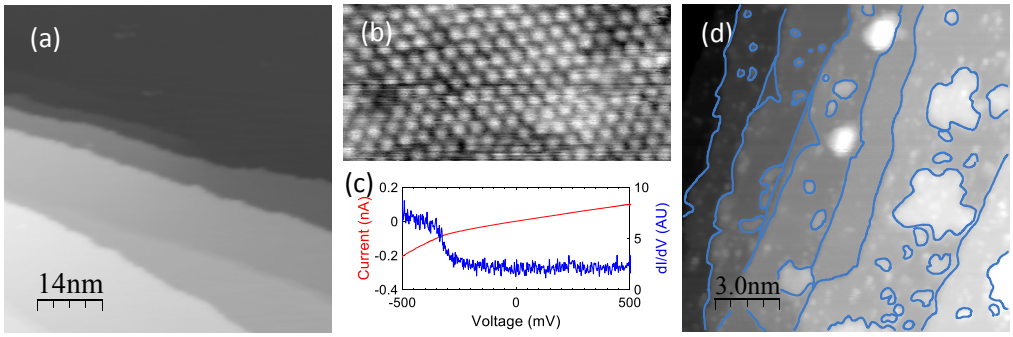

Fig. 5. (a) STM image of terraces on Ir(111), (b) Zoom in showing atomic resolution, (c) STM spectroscopy showing native surface state for clean Ir at -300 mV. (d) STM after submonolayer deposition of Fe.

The next step is to develop the bulk Cr tips needed for spin contrast in the STM measurement. Fig. 6a shows a relatively sharp Cr tip. This is a Cr strip cut from a Cr foil by wire electrical discharge machining (EDM) and subsequently electrochemically etched in KOH. Fig. 6b is a scanning electron microscopy (SEM) image showing radius of curvature of 19 microns. Initial imaging studies show atomic resolution but not yet spin contrast. We are developing tip preparation procedures including e-beam heating and Ar sputtering in UHV to achieve spin sensitivity in the atomic scale imaging.

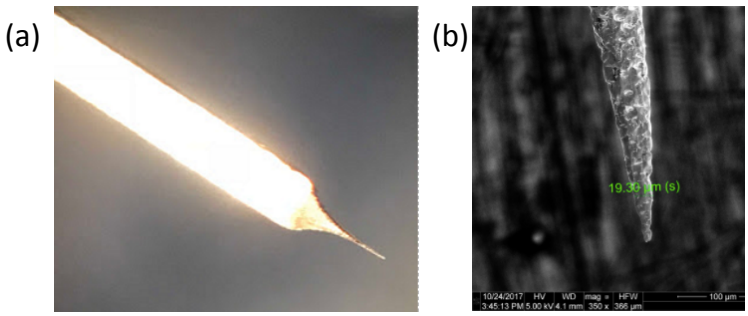

Fig. 6. (a) Optical microscope image of Cr tip. (b) SEM image of Cr tip.

Final Remarks

We have made substantial progress in developing SP-STM for studies on films and devices. Optimization of the Cr tip will be the next important step to establish this technique. We are writing up these early results, but maintain focus toward developing the SP-STM technique. Once we develop spin-sensitive imaging, its integration with MBE growth and device fabrication will make our SP-STM program one of the strongest in the US and highly competitive in the world.