

AFRL-AFOSR-VA-TR-2019-0272

Tuning Metal-Insulator Transitions in Ultra-Thin Correlated Materials

Yuri Suzuki LELAND STANFORD JUNIOR UNIVERSITY

09/12/2019 Final Report

DISTRIBUTION A: Distribution approved for public release.

Air Force Research Laboratory AF Office Of Scientific Research (AFOSR)/ RTA1 Arlington, Virginia 22203 Air Force Materiel Command

DISTRIBUTION A: Distribution approved for public release.

Г

REPORT DOCUMENTATION PAGE						Form Approved OMB No. 0704-0188
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. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.						
1. REPORT DA	TE (DD-MM-YYY	Y) 2. R	EPORT TYPE			3. DATES COVERED (From - To)
A. TITLE AND SUBTITLE Tuning Metal-Insulator Transitions in Ultra-Thin Correlated Materials					5a.	CONTRACT NUMBER
					5b.	GRANT NUMBER FA9550-16-1-0235
					5c.	PROGRAM ELEMENT NUMBER 61102F
6. AUTHOR(S) Yuri Suzuki					5d.	PROJECT NUMBER
					5e.	TASK NUMBER
					5f.	WORK UNIT NUMBER
 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) LELAND STANFORD JUNIOR UNIVERSITY 450 SERRA MALL STANFORD, CA 94305-2004 US 					I	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 						10. SPONSOR/MONITOR'S ACRONYM(S) AFRL/AFOSR RTA1
Arlington, VA 22203						11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-AFOSR-VA-TR-2019-0272
12. DISTRIBUTION/AVAILABILITY STATEMENT A DISTRIBUTION UNLIMITED: PB Public Release						
13. SUPPLEMENTARY NOTES						
14. ABSTRACT During the final year of the grant, we have demonstrated reversible tunability of coupled phases transitions, including a perpendicular ferromagnetic transition, a metal insulator transition, an optical transition and a structural phase transition, by electrolytic gating of SrIrO3/(La,Sr)MnO3 superlattices. All of these effects are found to exist at room temperature. In addition, we have combined strongly spin-orbit coupled SrIrO3 with CoFeB to find that we can manipulate the magnetic moments in the ferromagnetic CoFeB layer via microwave charge current in the SrIrO3 layer. The versatility of the SrIrO3 layer for a wide range of functionalities make it a promising material for applications of interest to the Air Force.						
15. SUBJECT TERMS 5d electrons, metal-to-insulator transition, oxide, heterostructure, switch, MBE						
16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF 18. NUMBER 19a. N					19a. NAM	E OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE	ABSTRACT	OF	GORETTA,	KENNETH
Unclassified	Unclassified	Unclassified	UU	PAGES	19b. TELEP 703-696-73	PHONE NUMBER (Include area code) 349
Standard Form 298 (Rev. 8/98)						

Prescribed by ANSI Std. Z39.18

Final Report GHz and THz Electronics and Materials Program Air Force Office of Scientific Research Department of Defense

Grant No: FA9550-16-1-0235

Institution: Stanford University

Title of Award: Tuning Metal-Insulator Transitions in Ultra-Thin Correlated Materials

PI: Yuri Suzuki

Date: August 6, 2018

Reporting Period: August 15, 2018- August 14, 2019

The *main research objective* of the proposed program has been (i) to develop a class of 4d and 5d transition metal oxides on the verge of an MIT and (ii) to determine the extent to which its functional properties can be tuned by an external parameter.

During the *final year* of the grant, we have demonstrated reversible tunability of coupled phases transitions, including a perpendicular ferromagnetic transition, a metal insulator transition, an optical transition and a structural phase transition, by electrolytic gating of SrIrO₃/(La,Sr)MnO₃ superlattices. All of these effects are found to exist at room temperature. In addition, we have combined strongly spin-orbit coupled SrIrO₃ with CoFeB to find that we can manipulate the magnetic moments in the ferromagnetic CoFeB layer via microwave charge current in the SrIrO₃ layer. The versatility of the SrIrO₃ layer for a wide range of functionalities make it a promising material for electronic applications of interest to the Air Force.

Reversible Coupled Phase *Transformations* Room • at Temperature in (La,Sr)MnO₃/SrIrO₃ superlattices. One of the important results of this past year has been the demonstration of *reversibility* in the coupled phase transformations of perpendicular ferromagnetism, electrical transport, optical transparency and structure. Last year we had found that charge transfer from the iridate to the manganite, along with oxygen octahedral rotations at the interface, gives rise to interfacial perpendicular ferromagnetism in our superlattices and that this charge-based mechanism translated into electronic and optical phase transitions. However more recently we have demonstrated reversibility at room temperature and directly correlated it with a reversible structural transition associated with the dual ion transfer of oxygen and hydrogen ions. These superlattice materials with perpendicular magnetic anisotropy (PMA) may enable spin-torque-driven magnetic memory and logic devices.

More specifically we have performed electrolytic gating measurements of superlattices comprised of alternating unit-cells of La_{0.2}Sr_{0.8}MnO₃ and SrIrO₃



Figure 1. (a) Schematic of ionic liquid gating that induces ion transfer between oxides and ionic liquid. We studied manganate ($La_{0.2}Sr_{0.8}MnO_3$ and $La_{0.7}Sr_{0.3}MnO_3$) and iridate (SrIrO₃) films, solid solution (Sr(Mn_{0.5}Ir_{0.5})O_3) films and superlattices ([($La_{0.2}Sr_{0.8}MnO_3$)_1(SrIrO₃)_1]_{20}) on SrTiO₃ substrates. (b) Modulation of out-of-plane lattice constant ($\Delta c/c$) during voltage cycling (with incremental positive voltages to +2.5 V and -3.0 V) for different samples. The lattice constant was extracted from in-situ measurements of the (002) peak position. (c) *In-situ* X-ray diffraction results of the superlattices around the (002) peak during ILG in repeated voltage cycling (sequence of +2.5 V, -3.0 V, +2.5 V, -3.0 V), showing a reversible electric-field-controlled transformation between two phases of the superlattices. (d) Full-range X-ray diffraction of a superlattice in as-grown pristine state, positively gated state and reversibly gated state. (e) Schematic of the reversible phase transformation mediated by dual-ion (both H⁺ and O²⁻) transfer.

 $([(La_{0.2}Sr_{0.8}MnO_3)_1(SrIrO_3)_1]_{20})$, as well as single-phase films of $La_{0.2}Sr_{0.8}MnO_3$, $La_{0.7}Sr_{0.3}MnO_3$ and SrIrO₃. The ILG induces non-volatile reversible changes in the crystal structure from the original phase A to a new phase B. Phase B has up to a 7% lattice expansion along the (001) direction compared to phase A (Figure 1).

Through secondary ion mass spectrometry (SIMS), we confirm the transfer of both hydrogen and oxygen ions. SIMS results of the superlattice in phase B (red) reveal a significantly higher concentration of hydrogen than that of phase A (blue), confirming the incorporation of hydrogen ions in phase B. At the same time, there is evidence for oxygen ion extraction (oxygen vacancy creation) in phase B. By thermally annealing both phase A and B samples in ¹⁸O₂ gas, we find that the phase B sample after thermal annealing in ¹⁸O₂ shows a dramatic increase in ¹⁸O signal throughout the entire sample, while the phase A sample only shows an increase at the surface (Figure 2). The extra incorporation of ¹⁸O indicates that ILG also creates oxygen vacancies in phase B. It is noted that the SIMS results are consistent with polarized neutron reflectivity results, revealing the accumulation of oxygen vacancies and hydrogen ions in phase B.



Figure 2. (a) Depth profiles of H and O signals in the two phases of the superlattices, by using secondaryion mass spectrometry. The H signal was obtained in phase A (red) and B (blue) of the superlattices under ILG. The Ti signal from the substrate indicates the interface position. (b) Depth profiles of ¹⁸O signals in the two phases of the superlattices after thermal annealing in ¹⁸O₂. To measure ¹⁸O signal, the superlattices were first stabilized in phase A and B under ILG, and then thermally annealed in ¹⁸O₂ gas.

The large structural changes induced by ILG should be accompanied by changes in cation valence and oxygen bonding as measured by x-ray absorption spectroscopy at the Mn L-edge, Ir L-edge and O K-edges. Indeed the Mn and Ir absorption peaks show a shift to lower energies corresponding to decreases in Mn and Ir valence respectively.

Although it is challenging to precisely quantify the local concentration of ions, we note that the magnitude of lattice expansion (~7%) and valence change are comparable to the highest reported values in singe-phase perovskite TMOs (e.g. $H_xSrCoO_{3-\delta}$ with large transfer of hydrogen ($x \sim 1$) and oxygen ($\delta \sim 0.5$) ions). Strikingly the large structural and chemical changes are accompanied by a concurrent metal-insulator transition, suppression of perpendicular ferromagnetism and enhancement of optical transparency. These phenomena are not otherwise observed in the individual constituent oxides or their solid solutions. Our findings reveal a hitherto-unexplored strategy to develop complex oxides, in which the electrolyte-based ionic control can provide extensive tunability that is crucial for electronic/spintronic, energy and environmental applications.

• Low Energy Magnetization Switching by Spin Hall Oxide SrIrO₃

We have also recently demonstrated that SrIrO₃ is an effective spin-to-charge conversion material that enables us to control the magnetic moment of a neighboring ferromagnet. More specifically, we have found that SrIrO₃ can exhibit a spin Hall angle (i.e., the ratio of charge to spin current) as high as 1.6. To date, spin Hall angles of about 0.5 and magnetization switching of a neighboring ferromagnetic SrRuO₃ layer have been verified in SrIrO₃-based bilayers. In our study, we have demonstrated much more efficient magnetization switching of an adjacent ferromagnetic CoFeB layer. We also show for the first time in a SrIrO₃-based system that a unidirectional magnetoresistance can be measured and is indicative of a current-induced spin accumulation at the interface that is coupled to

the electrical conductivity. Together these results indicate a route to controlling resistance and detecting magnetization in a two-terminal geometry.

Publications

- M.J. Veit, Di Yi, Y. Suzuki, "Near Room Temperature Quantum Spin Hall Effect in a Perovskite Oxide Heterostructure," under review at *Science* (2019).
- Di Yi, Yujia Wang, Olaf M. J. van't Erve, Hongtao Yuan, Michael J. Veit, Alpha T. N'Diaye, Padraic Shafer, Elke Arenholz, Yongseong Choi, Pu Yu, Berend T. Jonker and Yuri Suzuki, "Electric Field Control of Coincident Magnetic, Electronic and Structural Transition in SrMnO₃/SrIrO₃ Superlattices," under review at *Nature Communications*.

Talks

- "Control of Emergent Magnetic Properties in Layered Superlattices," Di Yi (*invited talk*), 2018 European Materials Research Society Meeting, Warsaw, Poland, September 2018.
- "Controlling emergent magnetic properties in iridate-based superlattices", Di Yi (*invited talk*), NIST Center for Neutron Research, Gaithersburg, MD, October 2018.
- "Emergent Magnetic Phenomena via Oxide Epitaxy," Di Yi (*invited talk*), Physics Colloquium, Department of Physics, University of Arkansas, Fayetteville, AR, February 2019.
- "Electrical control of phase transitions through ion transfer in oxide superlattices", Di Yi, Yujia Wang, Hongtao Yuan, Olaf M. J. van't Erve, Michael J. Veit, Purnima Balakrishnan, Yongseong Choi, Jian Liu, Alpha T. N'Diaye, Padraic Shafer, Elke Arenholz, Berend T. Jonker, Pu Yu and Yuri Suzuki, American Physical Society Meeting, Boston, MA, March 2019.
- "Spintronic Functionality in Complex Oxides: Emergent Magnetic Phenomena and Electric Field Control," Di Yi (*invited talk*), Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC, April 2019.

Significant Department of Defense Collaborations

In the past year, we have collaborated with Drs. Brandon Howe, Michael McConney, Krishnamurthy Mahalingham of AFRL and Michael Osofsky and Berry Jonker of NRL. The AFRL collaboration has focused on structural characterization of our manganite/iridate superlattices by transmission electron microscopy and electron energy loss spectroscopy. In addition, we have also provided ferromagnetic resonance characterization of low loss spinel ferrite thin films synthesized at AFRL for magnetoelastic applications.