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Smart Core-Shell Nanowire Architectures for Multifunctional Nanoscale Devices

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Jonathan E Spanier

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Drexel University
Office of Research Admin
3201 Arch St, Suite 100
Philadelphia, PA 19104 -2760

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14. ABSTRACT

We report on discovery of and strategies for designing new complex oxide materials in which two normally contradictory properties coexist, and its publication. In one example, switchable polar character (ferroelectricity) arising from non-centrosymmetric structure is achieved in a narrow-gap material through design and synthesis of cation and oxygen vacancy-driven tuning of band gap without loss of polar character. Shown for a single phase solid solution ferroelectric oxide perovskite (K,Ba),(Ni,Nb)O_(3-delta), this material exhibits a compositionally tunable and direct band gap in the range of 1.1 – 3.8 eV, with potential for novel nonlinear light-matter applications in addition to high-efficiency photovoltaic solar energy conversion. In a second example we report, with collaborators, on the discovery, synthesis and properties of a completely new family of non-perovskite complex oxide that exhibits ferroelectric and antiferromagnetic order. We report on publication of a new thin film synthesis strategy that enables, through epitaxial stabilization, low-energy and highly scalable growth of single-crystal heteroepitaxial complex oxide thin films featuring low-temperature deposition and a brief annealing under wellcontrolled conditions. Finally, we describe progress in using inelastic light scattering, in conjunction with other techniques, to characterize and quantify oxygen vacancy concentrations, including their effects on structure and electronic phase transitions.

15. SUBJECT TERMS

ferroelectric semiconductors, complex oxides, multiferroics, atomic layer deposition, multiferroics

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Report Title

Final Report for ARO W911NF-08-1-0067 for period ending 8/31/2013

ABSTRACT

We report on discovery of and strategies for designing new complex oxide materials in which two normally contradictory properties co-exist, and its publication. In one example, switchable polar character (ferroelectricity) arising from non-centrosymmetric structure is achieved in a narrow-gap material through design and synthesis of cation and oxygen vacancy-driven tuning of band gap without loss of polar character. Shown for a single phase solid solution ferroelectric oxide perovskite (K,Ba),(Ni,Nb)O_(3-delta), this material exhibits a compositionally tunable and direct band gap in the range of 1.1 – 3.8 eV, with potential for novel nonlinear light-matter applications in addition to high-efficiency photovoltaic solar energy conversion. In a second example we report, with collaborators, on the discovery, synthesis and properties of a completely new family of non-perovskite complex oxide that exhibits ferroelectric and antiferromagnetic order. We report on publication of a new thin film synthesis strategy that enables, through epitaxial stabilization, low-energy and highly scalable growth of single-crystal heteroepitaxial complex oxide thin films featuring low-temperature deposition and a brief annealing under well-controlled conditions. Finally, we describe progress in using inelastic light scattering, in conjunction with other techniques, to characterize and quantify oxygen vacancy concentrations, including their effects on structure and electronic phase transitions.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received	Paper
02/15/2014 21.00	Ilya Grinberg, D. Vincent West, Maria Torres, Gaoyang Gou, David M. Stein, Liyan Wu, Guannan Chen, Eric M. Gallo, Andrew R. Akbashev, Peter K. Davies, Jonathan E. Spanier, Andrew M. Rappe. Perovskite oxides for visible-light-absorbing ferroelectric and photovoltaic materials, Nature, (11 2013): 0. doi: 10.1038/nature12622
02/15/2014 22.00	Andrew R. Akbashev, Guannan Chen, Jonathan E. Spanier. A Facile Route for Producing Single-Crystalline Epitaxial Perovskite Oxide Thin Films, Nano Letters, (01 2014): 0. doi: 10.1021/nl4030038
02/15/2014 23.00	Feng Yan, Guannan Chen, Li Lu, Peter Finkel, Jonathan E. Spanier. Local probing of magnetoelectric coupling and magnetoelastic control of switching in BiFeO3-CoFe2O4 thin-film nanocomposite, Applied Physics Letters, (2013): 0. doi: 10.1063/1.4816793
02/15/2014 24.00	Guannan Chen, Guan Sun, Yujie J. Ding, Paola Prete, Ilio Miccoli, Nico Lovergine, Hadas Shtrikman, Patrick Kung, Tsachi Livneh, Jonathan E. Spanier. Direct Measurement of Band Edge Discontinuity in Individual Core–Shell Nanowires by Photocurrent Spectroscopy, Nano Letters, (09 2013): 0. doi: 10.1021/nl401737u
02/15/2014 25.00	Eric M. Gallo, Adriano Cola, Fabio Quaranta, Jonathan E. Spanier. High speed photodetectors based on a two-dimensional electron/hole gas heterostructure, Applied Physics Letters, (04 2013): 0. doi: 10.1063/1.4802595
02/15/2014 26.00	Mohammad A Islam, James M Rondinelli, Jonathan E Spanier. Normal mode determination of perovskite crystal structures with octahedral rotations: theory and applications, Journal of Physics: Condensed Matter, (05 2013): 0. doi: 10.1088/0953-8984/25/17/175902
02/16/2014 27.00	M D. Scafetta, Y. J. Xie, M. Torres, J. E. Spanier, S. J. May. Optical absorption in epitaxial La[sub 1?x]Sr[sub x]FeO[sub 3] thin films, Applied Physics Letters, (02 2013): 0. doi: 10.1063/1.4794145
03/21/2013 19.00	Christopher J. Hawley, Terrence McGuckin, Jonathan E. Spanier. Selective Epitaxial Growth on Germanium Nanowires via Hybrid Oxide-Stabilized/Vapor–Liquid–Solid Growth, Crystal Growth & Design, (02 2013): 0. doi: 10.1021/cg3016595
09/15/2012 15.00	Feng Yan, Guannan Chen, Li Lu, Jonathan E. Spanier. Dynamics of Photogenerated Surface Charge on BiFeO, ACS Nano, (03 2012): 0. doi: 10.1021/nn204604m
09/15/2012 18.00	Brian R. Beatty, Guannan Chen, Jonathan E. Spanier, Christopher J. Hawley. Shape-Controlled Vapor-Transport Growth of Tellurium Nanowires, Crystal Growth & Design, (06 2012): 0. doi: 10.1021/cg2014368
09/15/2012 17.00	Stephen S. Nonnenmann, Mohammad A. Islam, Brian R. Beatty, Eric M. Gallo, Terrence McGuckin, Jonathan E. Spanier. The Ferroelectric Field Effect within an Integrated Core/Shell Nanowire, Advanced Functional Materials, (07 2012): 0. doi: 10.1002/adfm.201200865
09/15/2012 16.00	Nick M. Sbrockey, Michael Luong, Eric M. Gallo, Jennifer D. Sloppy, Guannan Chen, Christopher R. Winkler, Stephanie H. Johnson, Mitra L. Taheri, Gary S. Tompa, Jonathan E. Spanier. LaAlO3/SrTiO3 Epitaxial Heterostructures by Atomic Layer Deposition, Journal of Electronic Materials, (02 2012): 0. doi: 10.1007/s11664-012-1960-6

11/07/2011 3.00 Eric M. Gallo, Guannan Chen, Marc Currie, Terrence McGuckin, Paola Prete, Nico Lovergine, Bahram Nabet, Jonathan E. Spanier. Picosecond response times in GaAs/AlGaAs core/shell nanowire-based photodetectors,
Applied Physics Letters, (06 2011): 241113. doi: 10.1063/1.3600061

11/07/2011 1.00 Guannan Chen, Eric Gallo, Oren Leaffer, Terrence McGuckin, Paola Prete, Nico Lovergine, Jonathan Spanier. Tunable Hot-Electron Transfer Within a Single Core-Shell Nanowire,
Physical Review Letters, (10 2011): 156802. doi: 10.1103/PhysRevLett.107.156802

11/07/2011 2.00 Peter Finkel, Stephanie H. Johnson, Oren D. Leaffer, Stephen S. Nonnenmann, Konrad Bussmann, Jonathan E. Spanier. Magneto-elastic tuning of ferroelectricity within a magnetoelectric nanowire,
Applied Physics Letters, (10 2011): 182901. doi: 10.1063/1.3657152

11/07/2011 5.00 Bora Garipcan, Sedat Odabas, Gokhan Demirel, Joan Burger, Stephen S. Nonnenmann, Michael T. Coster, Eric M. Gallo, Bahram Nabet, Jonathan E. Spanier, Erhan Piskin. In Vitro Biocompatibility of n-Type and Undoped Silicon Nanowires,
Advanced Engineering Materials, (02 2011): 0. doi: 10.1002/adem.200980045

11/07/2011 6.00 Stephen S. Nonnenmann, Eric M. Gallo, Jonathan E. Spanier. Redox-based resistive switching in ferroelectric perovskite nanotubes,
Applied Physics Letters, (09 2010): 102904. doi: 10.1063/1.3486224

11/07/2011 7.00 Guannan Chen, Eric M. Gallo, Joan Burger, Bahram Nabet, Adriano Cola, Paola Prete, Nico Lovergine, Jonathan E. Spanier. On direct-writing methods for electrically contacting GaAs and Ge nanowire devices,
Applied Physics Letters, (06 2010): 223107. doi: 10.1063/1.3441404

11/07/2011 8.00 Stephen S. Nonnenmann, Oren D. Leaffer, Eric M. Gallo, Michael T. Coster, Jonathan E. Spanier. Finite Curvature-Mediated Ferroelectricity,
Nano Letters, (02 2010): 542. doi: 10.1021/nl903384p

11/07/2011 9.00 Stephanie H. Johnson, Craig L. Johnson, Steven J. May, Samuel Hirsch, M. W. Cole, Jonathan E. Spanier. Co@CoO@Au core-multi-shell nanocrystals,
Journal of Materials Chemistry, (11 2009): 439. doi: 10.1039/b919610b

11/07/2011 10.00 Stephen S. Nonnenmann, Eric M. Gallo, Michael T. Coster, Gregory R. Soja, Craig L. Johnson, Rahul S. Joseph, Jonathan E. Spanier. Piezoresponse through a ferroelectric nanotube wall,
Applied Physics Letters, (12 2009): 232903. doi: 10.1063/1.3263714

11/07/2011 11.00 Stephen S. Nonnenmann, Jonathan E. Spanier. Ferroelectricity in chemical nanostructures: proximal probe characterization and the surface chemical environment,
Journal of Materials Science, (7 2009): 5205. doi: 10.1007/s10853-009-3680-8

11/07/2011 12.00 Valerie R. Binetti, Jessica D. Schiffman, Oren D. Leaffer, Jonathan E. Spanier, Caroline L. Schauer. The natural transparency and piezoelectric response of the Greta oto butterfly wing,
Integrative Biology, (02 2009): 324. doi: 10.1039/b820205b

11/07/2011 13.00 James A. Shackleford, Richard Grote, Marc Currie, Jonathan E. Spanier, Bahram Nabet. Integrated plasmonic lens photodetector,
Applied Physics Letters, (02 2009): 83501. doi: 10.1063/1.3086898

TOTAL: 24

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

"A facile route for single-crystal heteroepitaxial ferroic perovskite oxide thin films", Symposium on Multiferroic Materials and Multilayer Ferroic Heterostructures: Properties and Applications, in Electronic Materials and Applications 2014 (ACerS), Jan. 2014 in Orlando, FL USA.

"Electronic landscapes near semiconductor nanowire heterostructures", Department of Chemistry, Washington University of St Louis, Oct. 2013.

"Ferroelectric oxides: pathways and properties, Dept. of Materials Science & Engineering, University of Texas at Dallas, 1 Aug, 2013.

"A facile route for producing single-crystalline oxide perovskite thin films, International Conference on Integrated Functionalities, Dallas, TX 29 July 2013.

"A facile route for heteroepitaxial perovskite oxide thin films, ENEA: Italian National Agency for New Technologies, Energy and Sustainable Economic Development, Brindisi, Italy, 26 June, 2013.

"Electronic landscapes near semiconductor nanowire heterostructures, CNR-Lecce, 24 June, 2013.

"A facile route for heteroepitaxial perovskite oxide thin films, Oak Ridge National Laboratory, Center for Nanoscale Materials Science, TN, 6 June, 2013.

"The ferroelectric phase at the nanoscale, Asylum Research Corporation, Santa Barbara, CA, April 4, 2013.

Number of Presentations: 8.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received	Paper
03/21/2013 20.00	Y. J. Xie, M. Torres, J. E. Spanier, S. J. May, M D. Scafetta. Optical absorption in epitaxial La[sub 1?x]Sr [sub x]FeO[sub 3] thin films, Applied Physics Letters (03 2013)

TOTAL: **1**

Number of Manuscripts:

Books

Received	Paper

TOTAL:

Patents Submitted

Tunable Hot-Electron Transfer within a Nanostructure
United States Patent Application No. 13/626,934

SEMICONDUCTOR FERROELECTRIC COMPOSITIONS AND THEIR USE IN PHOTOVOLTAIC DEVICES
U.S. patent application 61/545,932

Patents Awarded

Awards

1. 2014 Japan Trust Foundation Fellow, Fujitsu Labs & Toyko Inst. of Tech.
2. 2013 Louis and Bessie Stein Family Fellowship (Israel), Drexel University
3. 2013 Distinguished Service Award, Louis R Stokes Alliance for Minority Participation

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Guannan Chen	0.50	
Andrew Akbashev	0.50	
Stephanie H Johnson	0.10	
FTE Equivalent:	**1.10**	
Total Number:	**3**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Alessia Polemi	0.50
FTE Equivalent:	**0.50**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Jonathan E Spanier	0.11	No
FTE Equivalent:	**0.11**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Brittany Pattinson	0.20	Materials Science & Engineering
FTE Equivalent:	**0.20**	
Total Number:	**1**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 1.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 1.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 1.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 1.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME
Stephanie H Johnson
Total Number: **1**

Names of other research staff

NAME PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

5 **Co-axial ferroic nanostructures for tunable broadband contactless magnetic sensing and energy harvesting**

Patent Filed in US? (5d-1) N

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: Jonathan E Spanier

5f-1a: Drexel University

5f-c:

5a: Peter Finkel

5f-1a: Naval Undersea Warfare Center

5f-c:

5 **Ferroelectric Nanoshell Devices**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) Y

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2): International

5a: Oren D Leaffer

5f-1a: Drexel University

5f-c:

5a: Stephen S Nonnenmann

5f-1a: Drexel University

5f-c:

5a: Jonathan E Spanier

5f-1a: Drexel University

5f-c:

5 **Integrated Plasmonic Lens Photodetector**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: Richard Grote

5f-1a: Drexel University

5f-c:

5a: Bahram Nabet

5f-1a: Drexel University

5f-c:

5a: Jonathan E Spanier

5f-1a: Drexel University

5f-c:

5 **Process for producing compositionally tunable semiconducting ferroelectric thin film materials**

Patent Filed in US? (5d-1) N

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: Andrew Akbashev

5f-1a: Drexel University

5f-c:

Philadelphia PA 19104

5a: Liyan Wu

5f-1a: University of Pennsylvania

5f-c:

Philadelphia PA

5a: Peter K Davies

5f-1a: University of Pennsylvania

5f-c: Materials Science & Engineering

Philadelphia PA 19104

5a: Jonathan E Spanier

5f-1a: Drexel University

5f-c: 3141 Chestnut Street

Philadelphia PA 19104

5a: Andrew M Rappe

5f-1a: University of Pennsylvania

5f-c: Chemistry

Philadelphia PA 19104

5 **Pulsed Precursor Deposition of 2DEG film Devices**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: Nick Sbrockey

5f-1a: Structured Materials Industries

5f-c:

5a: Jonathan E Spanier

5f-1a: Drexel University

5f-c:

5a: Gary S Tompa

5f-1a: Structured Materials Industries

5f-c:

5 **Tunable Hot-Electron Transfer within a Nanostructure**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) Y

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2): International

5a: Baris Taskin

5f-1a: Drexel University

5f-c:

5a: Eric M Gallo

5f-1a: Drexel University

5f-c:

5a: Guannan Chen

5f-1a: Drexel University

5f-c:

5a: Jonathan E Spanier

5f-1a: Drexel University

5f-c:

Scientific Progress

Scientific Progress and Acomplishments for ARO W911NF-08-1-0067 for period ending 8/31/2013.

Semiconducting Ferroelectrics and Vacancy-Induced Composition Tuning of Bandgap.
We report on discovery of and strategies for designing new complex oxide materials in which two normally contradictory properties co-exist, and its publication as a cover story in the Nov 28, 2013 issue of Nature. In one example, switchable polar character (ferroelectricity) arising from non-centrosymmetric structure is achieved in a narrow-gap material through design and synthesis of cation and oxygen vacancy-driven tuning of band gap without loss of polar character. Shown for a single phase solid solution ferroelectric oxide perovskite (K,Ba),(Ni,Nb)O_(3-delta), this material exhibits a compositionally tunable and direct band gap in the range of 1.1 – 3.8 eV, with potential for novel nonlinear light-matter applications in addition to high-efficiency photovoltaic solar energy conversion.

New Complex Oxide Multiferroic.
In a second example we report, with collaborators, on the discovery, synthesis and properties of a completely new family of non-perovskite complex oxide that exhibits ferroelectric and antiferromagnetic order. Pursuing single phase multiferroics is challenging due to the almost intrinsic paradox of combining more than one ferroic order parameter in a crystal system. Discovery of new complex oxides that exhibit both magnetic and ferroelectric properties is therefore of great interest in the design of functional magnetoelectric films, in which research is driven by the technologically exciting prospect of controlling charges by magnetic fields and spins by voltages, for sensors, transducers, 4-state logic, and spintronics. Motivated by the notion of a tool-kit for complex oxide design, our collaborators have developed a chemical processing technique that allows for selective stoichiometric combination of transition metals, to generate a single phase multifunctional lattice in nanocrystalline form. We introduce a new class of multiferroic Ba-Mn-Ti oxides not apparent in nature, based on the hollandite structure, and show that substitution with Fe and Ni is also possible. The chemical method, first produces gels of Ba-Mn-Ti-O, or variations, that can be transformed at ~700C to fully crystallized discrete nanoparticles with sizes of ~ 20 nm. The nanocrystal compound BMnT-134, was studied by HRTEM and PDF in order to fully characterize and deduce the structure. PDF was found to be an ideal characterization tool due its ability to discern order at short range. Magnetic characterization, consistent with structural analysis, indicates the presence of Mn4+ and Mn3+ ions only, and an antiferromagnetic phase transition, TN ~42 K. BMnT-134 possesses a giant dielectric constant at low frequency and a very stable and high (instrinsic) dielectric constant of 200 up to 100 MHz. BMnT shows evidence of ferroelectric switching over a range of temperatures correlated with magnetic ordering temperatures. Nanocomposite capacitors of BMnT-134/PVDF were prepared, showing potential for very high energy densities. A manuscript “A New Class of Synthetic Hollandite Multiferroics: Nanocrystals and Nanocomposite Films,” is in preparation/revision and will be submitted soon.

ALD and Epitaxial Stabilization of Heteroepitaxial Oxide Perovskite Films.
We published a new thin film synthesis strategy that enables, through epitaxial stabilization, low-energy and highly scalable growth of single-crystal heteroepitaxial complex oxide thin films featuring low-temperature deposition and a brief annealing under well-controlled conditions. This was reported in a publication in Nano Lett.

Raman scattering as a probe of oxygen stoichiometry and electronic properties in complex oxide thin films.
ABO_3 type perovskites are endowed with the unique combination of strong electronic polarization of the transition metal - oxygen bond and highly sensitive electronic correlation properties of the d band electrons in the B atoms. As a result, ABO_3 type perovskites exhibit multifunctional properties that show enhanced susceptibilities to many external stimuli, including electric field, external polarization, temperature and the presence of reactive species on their surface.

A unique property of ABO_(3-delta) perovskites is the ability of these materials to accommodate oxygen vacancies in the range of delta = 0 - 0.5. Since the oxidation states of the cations in these materials are intimately related to the quantity of oxygens in crystal lattice, many critical material properties of ABO_3-delta perovskites depend on and in turn can be tuned by controlling the oxygen vacancy fractions. Accordingly, the ability to control the oxygen vacancies in ABO3 perovskite systems may provide additional flexibility and functionality in their application in switching and electrostatic gating. In bulk oxides the effects of temperature, electric field and environmental conditions on the oxygen content have been studied extensively. However, studies of oxygen content become significantly more complicated in epitaxial films of ABO3 type perovskite heterostructures for practical reasons. Very often few monolayers of one type of ABO3 system is grown on a thick perovskite A'B'O3 of different chemistry and the propensity of oxygen loss of each system could markedly differ. As a result the methods used for bulk system, e.g., thermogravimetric analysis used to demonstrate large changes in sample weight due to reduction and oxidation, is hardly applicable for these thin film systems.

Recently, Xie et al. studied reversible oxygen loss in La_(1-x)SrxFeO3 (LSFO) films through a combination of transport measurements, ellipsometry and X-rays diffration studies. Their results reveal that reversible control of oxygen content at temperatures as low as 200C can induce dramatic changes in electronic resistivity, optical absorption and lattice size in LSFO films of thickness of few tens of nm. Xie et al. argued that the orders of magnitude increase in resistivity upon annealing of the samples at 200C is due to the escape of oxygen atoms from the lattice and subsequent trapping of polarons at the oxygen vacancies. Partly encouraged by these results and partly in an effort to determine the limits of scattering studies from ultrathin films of ABO3 perovskites that may or may not be polar in nature, we undertook the current study to determine the effect of oxygen content on the Raman spectrum of LSFO films. Raman scattering is an established and nonperturbing method for

identifying structural phases in solid, thin film and nanostructured semiconductor and oxide materials, since vibrational modes provide a unique signature of the crystal structure. Previous studies have provided useful information about impurities, internal stress, and crystal symmetry in various thin and ultrathin films. Studying lattice dynamics using Raman spectroscopy using visible laser line excitation in epitaxial films of ABO3 perovskites systems is challenging, due to a combination of several factors. Most of these materials are wide bandgap and absorb weakly in the visible, and visible light penetrates deep into the sample and into the substrate. While the former results in weak Raman signal from the films the latter generates overwhelming Raman signal from the substrate, making the characterization of the film a rather difficult task. The challenge gets accentuated on Raman spectroscopy of a ABO3 perovskite systems with cubic substrates and quasi cubic films with weak first-order Raman-allowed peaks. Attempts to study LSFO ultrathin films grown on cubic SrTiO3 substrates are challenging due to the quasi cubic nature of LSFO with very little rhombohedral distortions. To the best of our knowledge studies of quasi cubic ABO3 films grown on cubic A'B'O3 substrate has not been done. Accordingly, we choose to study LSFO ultrathin films on MgO substrates (LSFO-MgO) due to the substrates low Raman activity in the frequency of interest (200 - 700 cm-1) for LSFO. Our simultaneous Raman spectroscopy and transport measurements indicate that such combination can be a powerful tool to investigate properties of these systems with relative ease.

We have been using inelastic light scattering, in conjunction with other techniques, to characterize and quantify oxygen vacancy concentrations, including their effects on structure and electronic phase transitions. We conducted a series of simultaneous Raman and transport measurements of La1-xSrxFeO_(3-delta) epitaxial films grown on MgO single crystals as a function of air annealing at different temperatures and time. Carrier transport measurements show that loss of oxygen results in orders of magnitude increase in the resistivity of the films with air annealing. Raman results corroborate the transport measurements by showing the oxygen vacancy induced disorder and the associated activation of IR modes in the Raman spectra. The results also show Fano asymmetry in higher energy J-T activated modes and points toward polarization fluctuations in oxygen vacancy induced nanopolar regions in LSFO. A manuscript is in preparation and will be submitted for publication by the end of March 2014.

Technology Transfer