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14. ABSTRACT

The miniaturization and integration of frequency-agile microwave circuits—electronically tunable filters, resonators, phase shifters and more—with microelectronics offers tantalizing device possibilities, yet requires thin films whose dielectric constant at GHz frequencies can be tuned by applying a quasi-static electric field. We have achieved a new type of tunable microwave dielectric with a figure of merit at room temperature that rivals all known tunable microwave dielectrics. This was achieved in biaxially strained Srn+1TinO3n+1 phases with n ? 3 at frequencies up to 125 GHz. We have also understood the growth mechanism of these new materials. For the

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Final Report: Synthesis of Defect-Mitigating Tunable Dielectric Materials with Atomic-Layer Control

ABSTRACT

The miniaturization and integration of frequency-agile microwave circuits—electronically tunable filters, resonators, phase shifters and more—with microelectronics offers tantalizing device possibilities, yet requires thin films whose dielectric constant at GHz frequencies can be tuned by applying a quasi-static electric field. We have achieved a new type of tunable microwave dielectric with a figure of merit at room temperature that rivals all known tunable microwave dielectrics. This was achieved in biaxially strained Srn+1TinO3n+1 phases with n ? 3 at frequencies up to 125 GHz. We have also understood the growth mechanism of these new materials. For the precise growth of Srn+1TinO3n+1 Ruddlesden–Popper (RP) phases, stoichiometric deposition leads to the loss of the first RP rock-salt double layer, but growing with a strontium-rich surface layer restores the bulk stoichiometry and ordering of the subsurface RP structure. Our results dramatically expand the materials that can be prepared in epitaxial heterostructures with precise interface control—from just the n=? end members (perovskites) to the entire RP homologous series—enabling the exploration of novel quantum phenomena at a richer variety of oxide interfaces.

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
09/06/2016	1	Y.F. Nie, Y. Zhu, C.-H. Lee, L.F. Kourkoutis, J.A. Mundy, J. Junquera, P. Ghosez, D.J. Baek, S. Sung, X. X. Xi, K.M. Shen, D.A. Muller, D.G. Schlom. Atomically precise interfaces from non-stoichiometric deposition, Nature Communications, (08 2014): 0. doi: 10.1038/ncomms5530
09/06/2016	2	C.H. Lee, N.D. Orloff, T. Birol, Y. Zhu, V. Goian, E. Rocas, R. Haislmaier, E. Vlahos, J.A. Mundy, L.F. Kourkoutis, Y. Nie, M.D. Biegalski, J. Zhang, M. Bernhagen, N.A. Benedek, Y. Kim, J.D. Brock, R. Uecker, X.X. Xi, V. Gopalan, D. Nuzhnyy, S. Kamba, D.A. Muller, I. Takeuchi, J.C. Booth, C.J. Fennie, D.G. Schlom. Exploiting dimensionality and defect mitigation to create tunable microwave dielectrics, Nature, (10 2013): 0. doi: 10.1038/nature12582
09/06/2016	3	Veronica Goian, Stanislav Kamba, Nathan Orloff, Turan Birol, Che Hui Lee, Dmitry Nuzhnyy, James C. Booth, Margitta Bernhagen, Reinhard Uecker, Darrell G. Schlom. Influence of the central mode and soft phonon on the microwave dielectric loss near the strain-induced ferroelectric phase transitions in, Physical Review B, ( ): . doi:
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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

C.H. Lee, N.D. Orloff, T. Birol, Y. Zhu, Y. Nie, V. Goian, E. Rocas, R. Haislmaier, E. Vlahos, J.A. Mundy, M.D. Biegalski, D.J. Baek, S. Sung, J. Zhang, M. Bernhagen, N.A. Benedek, Y. Kim, J.D. Brock, J. Junquera, P. Ghosez, R. Uecker, X. X. Xi, V. Gopalan, D. Nuzhnyy, S. Kamba, L.F. Kourkoutis, K.M. Shen, D.A. Muller, I. Takeuchi, J.C. Booth, C.J. Fennie, and D.G. Schlom*, “World Record Tunable Microwave Dielectrics,” presented at the AVS 62nd International Symposium & Exhibition in San Jose, California (2015). (invited)

D.G. Schlom, “Thin-Film Alchemy,” presented at NanoCity 2015 in Amersfoort, Netherlands (2015). (Keynote Lecture)

D.G. Schlom, “Wacky Oxides: Rich Properties in Search of Devices,” presented at the 73rd Device Research Conference in Columbus, Ohio (2015). (invited)

D.G. Schlom, “Thin-Film Alchemy: Creating Astonishing Properties in Oxide Nanosandwiches,” presented at the MESA+ Meeting in Enschede, Netherlands (2014). (Plenary Lecture)

Number of Presentations: 4.00

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

TOTAL:

Number of Manuscripts:

Books

Received	Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

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FTE Equivalent:
Total Number:

Names of Post Doctorates

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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:	0.00
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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:......	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):......	0.00
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The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
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Names of Personnel receiving masters degrees

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Total Number:

Names of personnel receiving PHDs

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Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:

Total Number:

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Scientific Progress

The miniaturization and integration of frequency-agile microwave circuits—relevant to electronically tunable filters, antennas, resonators and phase shifters—with microelectronics offers tantalizing device possibilities, yet requires thin films whose dielectric constant at gigahertz frequencies can be tuned by applying a quasi-static electric field. Appropriate systems such as BaxSr1-xTiO3 have a paraelectric–ferroelectric transition just below ambient temperature, providing high tunability. Unfortunately, such films suffer significant losses arising from defects. Recognizing that progress is stymied by dielectric loss, we start with a system with exceptionally low loss—Srn+1TinO3n+1 phases—in which (SrO)2 crystallographic shear planes provide an alternative to the formation of point defects for accommodating non-stoichiometry. We report the experimental realization of a highly tunable ground state arising from the emergence of a local ferroelectric instability in biaxially strained Srn+1TinO3n+1 phases with n?3 at frequencies up to 125 GHz. In contrast to traditional methods of modifying ferroelectrics—doping or strain—in this unique system an increase in the separation between the (SrO)2 planes, which can be achieved by changing n, bolsters the local ferroelectric instability. This new control parameter, n, can be exploited to achieve a figure of merit at room temperature that rivals all known tunable microwave dielectrics.

Complex oxide heterostructures display some of the most chemically abrupt, atomically precise interfaces, which is advantageous when constructing new interface phases with emergent properties by juxtaposing incompatible ground states. One might assume that atomically precise interfaces result from stoichiometric growth. Here we show that the most precise control is, however, obtained by using deliberate and specific non-stoichiometric growth conditions. For the precise growth of Srn+1TinO3n+1 Ruddlesden–Popper (RP) phases, stoichiometric deposition leads to the loss of the first RP rock-salt double layer, but growing with a strontium-rich surface layer restores the bulk stoichiometry and ordering of the subsurface RP structure. Our results dramatically expand the materials that can be prepared in epitaxial heterostructures with precise interface control—from just the n=? end members (perovskites) to the entire RP homologous series—enabling the exploration of novel quantum phenomena at a richer variety of oxide interfaces.

We recently used ~ 1% tensile strain to induce a ferroelectric instability in thin films of Srn+1TinO3n+1 (n=1-6) phases. We showed that the Curie temperature TC gradually increased with n, reaching 180 K for Sr7Ti6O19 (n = 6). The permittivity of this n=6 sample could also be tuned significantly by the application of an electric field with exceptionally low dielectric loss at 300 K, rivaling all known tunable microwave dielectrics. We have studied the microwave (MW), THz and infrared spectra of strained Srn+1TinO3n+1 thin films deposited on (110) DyScO3. Near the ferroelectric phase transitions we observe the splitting and shifting of phonon and central mode frequencies, demonstrating the change of crystal symmetry below TC. Moreover, our spectra reveal that the central mode contribution dominates MW loss. In the Sr7Ti6O19 thin film the central mode vanishes at 300 K, explaining its low MW loss. Finally we discuss the origin and general conditions for the appearance of central modes near ferroelectric phase transitions.

Technology Transfer

Statement of the Problem Studied

The purpose of our study was to improve the performance of tunable microwave dielectrics by better understanding Ruddlesden-Popper phases as tunable dielectrics. Specifically, we worked to understand why these materials, which we created and engineered with atomic-layer control, could have a higher figure of merit than all other known tunable dielectrics. Seeing that the layered structures we grew had a different stacking order at the atomic scale than the order in which we were supplying the constituent monolayers during growth, we also studied how they grow. The resulting phases are new and metastable, and our measurements show them to have unparalleled properties. Our results are consistent with the hypothesis that it is point defects that have been limiting the properties of tunable dielectrics in thin film form.

Summary of the Most Important Results

We have discovered a new family of tunable microwave dielectric with a figure of merit at room temperature that rivals all known tunable microwave dielectrics. This was achieved in a biaxially strained $Sr_{n+1}Ti_nO_{3n+1}$ film with n=6 at frequencies up to 125 GHz. We have also understood the growth mechanism of these new materials. The key achievements are described in attached figures.

Bibiography

C.H. Lee, N.D. Orloff, T. Birol, Y. Zhu, V. Goian, E. Rocas, R. Haislmaier, E. Vlahos, J.A. Mundy, L.F. Kourkoutis, Y. Nie, M.D. Biegalski, J. Zhang, M. Bernhagen, N.A. Benedek, Y. Kim, J.D. Brock, R. Uecker, X.X. Xi, V. Gopalan, D. Nuzhnyy, S. Kamba, D.A. Muller, I. Takeuchi, J.C. Booth, C.J. Fennie, and D.G. Schlom, "Exploiting Dimensionality and Defect Mitigation to Create Tunable Microwave Dielectrics," *Nature* **502** (2013) 532-536.
http://dx.doi.org/doi: 10.1038/nature12582

Press Release: http://www.news.cornell.edu/stories/2013/10/tunable-antenna-could-end-dropped-cell-phone-calls

Y.F. Nie, Y. Zhu, C.-H. Lee, L.F. Kourkoutis, J.A. Mundy, J. Junquera, P. Ghosez, D.J. Baek, S. Sung, X.X. Xi, K.M. Shen, D.A. Muller, and D.G. Schlom, "Atomically Precise Interfaces from Non-Stoichiometric Deposition," *Nature Communications* **5** (2014) 4530-1 – 4530-8.
http://dx.doi.org/doi: 10.1038/ncomms5530

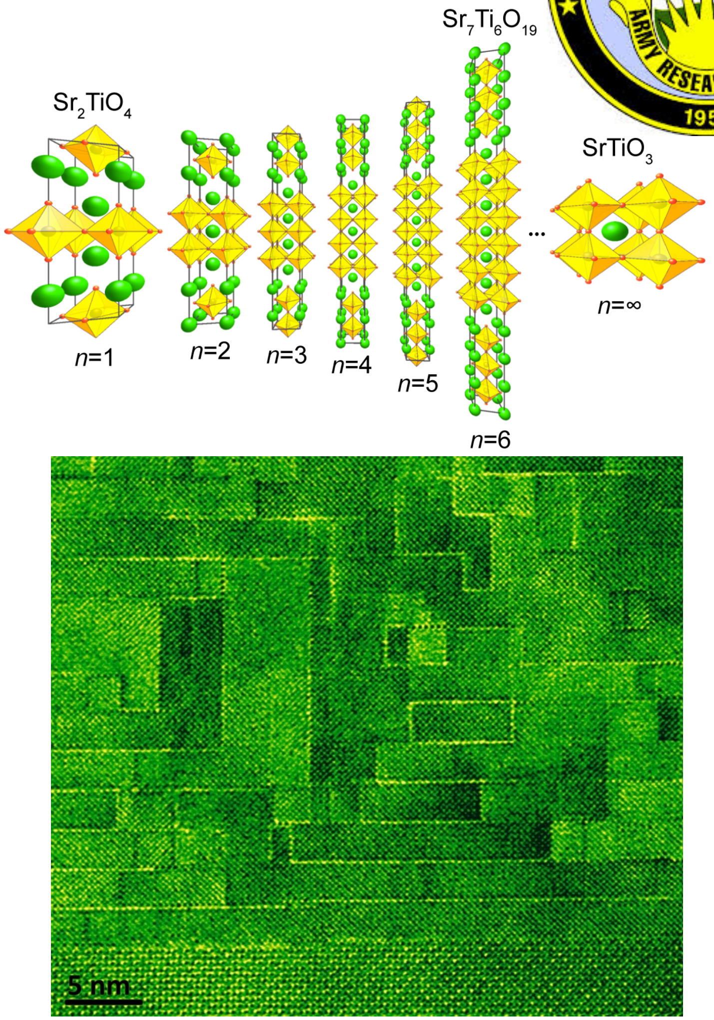
Press Release: http://www.news.cornell.edu/stories/2014/08/perfect-atom-sandwich-requires-extra-layer

V. Goian, S. Kamba, N. Orloff, T. Birol, C.H. Lee, D. Nuzhnyy, J.C. Booth, M. Bernhagen, R. Uecker, and D.G. Schlom, "Influence of the Central Mode and Soft Phonon on the Microwave Dielectric Loss near the Strain-Induced Ferroelectric Phase Transitions in $Sr_{n+1}Ti_nO_{3n+1}$," *Physical Review B* **90** (2014) 174105-1 – 174105-10.
http://dx.doi.org/doi: 10.1103/PhysRevB.90.174105

World's Highest Performance Microwave Dielectric

Strain and defect engineering used to create record-breaking material

We have designed and demonstrated the world's best tunable microwave dielectric to date operating with the highest reported Figure of Merit up to 125 GHz. This could result in a new generation of superior electronically tunable microwave filters, antennas, and phase shifters for improved wireless communications. Our research team predicted an unusual polar state in $Sr_{n+1}Ti_nO_{3n+1}$ Ruddlesden-Popper (RP) phases (inset) under tensile biaxial strain, where beyond a critical layer thickness $n>n_c$, an in-plane polarization sets in within the perovskite layers. This indicates the importance of the dimensionality "*n*" in turning on and off the ferroelectric properties. Moreover, these layered structures are believed to accommodate nonstoichiometry through the formation of additional rock-salt layers (SrO), thus significantly decreasing dielectric losses.



Schematic and cross-sectional transmission electron micrograph of $Sr_{n+1}Ti_nO_{3n+1}$ thin films grown by molecular beam epitaxy. The "bricks" are RP phases and the "mortar" are additional SrO layers that are believed to accommodate non-stoichiometry and lead to lower dielectric losses.

C.H. Lee *et al*. ***Nature*** **502**, 532-536 (2013)

Cornell University

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Assembling a Double Big Mac® at the Atomic Scale

Making the perfect atom sandwich is not as straightforward as it looks

Like the perfect sandwich, a perfect thin film for electronics requires not only the right ingredients, but also the right thickness of each ingredient in the desired order, down to individual layers of atoms. An important class of layered oxides for tunable microwave electronics resemble a double Big Mac® with alternating double and single layers of "meat patties" (strontium oxide) and "bread" (titanium oxide). Cornell scientists discovered that layer-by-layer atomic assembly—a powerful technology capable of making new materials for electronics—requires some unconventional "sandwich making" tricks to make this class of materials. To their surprise electron microscopy showed that sample after sample of their oxide sandwiches did not turn out as planned. In essence they laid down two meat patties on a bun, followed by a layer of bread, and another two meat patties, only to find that their sandwich had just one meat patty below the bread and three above it! Based on what they saw, they modified their growth procedure to make the targeted layered oxides by laying down an extra layer of meat (strontium oxide) at the start. It worked!

Understanding growth at the atomic scale enabled them to make atomically precise and sharp interfaces between layered oxides, which paves the way for creating improved materials for tunable microwave devices.

When Cornell scientists attempted to apply the same atomic layering technique they have been successfully using for years to make alternating single atomic layers, like occur in a hamburger, to make more sophisticated atomically layered structures such as the equivalent of a Double Big Mac® (upper image), what formed was the layering order shown in the lower image.

Cornell University

ARO Grant W911NF-12-1-0437

Y.F. Nie *et al*. ***Nature Communications*** **5**, 4530 (2014)