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DUNS Number: 009214214 EIN: 941156365
Report Date: 30-Nov-2017 Date Received: 30-Apr-2018
Final Report for Period Beginning 01-Sep-2014 and Ending 31-Aug-2017
Title: Defect Engineering of Spin Polarized Transparent Conductors through Complex Oxide Epitaxy
Begin Performance Period: 01-Sep-2014 **End Performance Period:** 31-Aug-2017
Report Term: 0-Other
Submitted By: Yuri Suzuki Email: ysuzuki1@stanford.edu
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STEM Degrees: 1 **STEM Participants:** 1

Major Goals: A FINAL REPORT REQUEST FOR THE ARO INTRANET DATABASE WAS NEVER RECEIVED. A PROJECT SUMMARY WAS SUBMITTED TO THE PROGRAM OFFICER ON 12/7/17. THIS REPORT IS NOW BEING FILED TO ENSURE THAT ALL REPORT REQUIREMENTS ARE FULFILLED.

The main research objective of the proposed program is to develop a new class of spin polarized transparent conductors through cation defect ordering in epitaxial stannate oxide thin films. At a fundamental level, these efforts will enable us (i) to develop an understanding of charge transport in these transparent conductors, (ii) to address some long standing controversial claims as to the origin of ferromagnetism in transparent oxides as well as (iii) to explore the feasibility of materials design through cation defect ordering.

In order to develop a new class of transparent spin polarized conductors in stannate-based perovskite thin films, we will combine our expertise in atomic scale thin film synthesis and in the fabrication and characterization of junction devices to design and synthesize doped stannate thin film materials with optical transparency, metallic conductivity and magnetism. Our technical approach includes: the design and synthesis of stannate based spin polarized transparent conductors; the local structural, electronic and magnetic characterization via x-ray absorption spectroscopy, x-ray magnetic circular dichroism, photoemission electron microscopy, x-ray resonant magnetic scattering, magnetic force microscopy, transmission electron microscopy and electron energy loss spectroscopy; magnetic characterization of epitaxial doped stannate thin films; electronic characterization of epitaxial doped stannate thin films.

Accomplishments: In this three-year program, we have developed a new family of magnetically doped barium stannate epitaxial thin films that exhibit a combination of metallic conductivity, optical transparency and magnetism. In contrast to bulk samples which are grown under equilibrium conditions, epitaxial thin films grown via non-equilibrium processes should enable the incorporation of more magnetic dopants than otherwise possible with equilibrium processes. We have demonstrated the incorporation of up to 4% rare earth and transition metal dopants in epitaxial $BaSnO_3$ thin films with combined optical, electronic and magnetic functionality.

1. Transition metal doping of $BaSnO_3$. In order to induce magnetic functionality in $BaSnO_3$, the transition metal cation of Fe was doped into stannate films. From ionic radii considerations, Fe would prefer substitution on the B sites of the ABO_3 perovskite structure. Since the perovskite structure is composed of cornered shared BO_6 octahedra where magnetic functionality is generated via B-O-B exchange interactions, transition metal substitution of the Sn site is a promising route to generate magnetic functionality. We have successfully showed that up to 5% Fe doped $BaSn_{1-x}Fe_xO_3$ films does in fact exhibit ferromagnetism. Although Fe^{3+} valence has the most stable

half-filled electron configuration of 3d5, x-ray absorption spectroscopy suggests that the Fe valence is a combination of Fe^{2+} and Fe^{3+}. Due to the lower valence compared to Sn^{4+}, the Fe ions serve to trap carriers and suppress conductivity. Therefore Fe doped $BaSnO_3$ films exhibit long-range magnetic order and optical transparency but insulating behavior.

Moreover more detailed studies reveal that the magnetic functionality can be modulated with ambient oxygen growth pressure. More specifically growth in vacuum promotes the stabilization of weak ferromagnetism as evident in a nonzero x-ray magnetic circular dichroism signal at the Fe L3 edge (Figure 1 see pdf). Finger printing of the x-ray magnetic circular dichroism (XMCD) spectra indicates that the Fe ions are a combination of Fe^{2+} and Fe^{3+}. The ferromagnetism is also evident in bulk magnetometry measurements in low oxygen pressure whereas only paramagnetism is seen in higher oxygen pressures (Figure 2 see pdf). Ferromagnetism in vacuum-grown $BaSnO_3$ films may be attributed to the F-center exchange mechanism, which relies on the presence of oxygen vacancies to facilitate the ferromagnetism. However, other possible extrinsic contributions to the magnetic ordering, such as clusters of Fe_3O_4 and FeO or contamination should also be considered. While the weak ferromagnetism is promising, the charge doping as a result of Fe^{2+}/Fe^{3+} substitution for Sn^{4+} suppresses conductivity and results in insulating transport behavior.

2. Rare-earth doping of $BaSnO_3$. Another approach to magnetic doping of $BaSnO_3$ films has been to doped the A site with a magnetic cation akin to La doped $BaSnO_3$ films that have given rise to high mobility values. We have stabilized transparent, conducting, paramagnetic stannate thin films via rare-earth doping of $BaSnO_3$. Gd^{3+} (4f7) substitution on the Ba^{2+} site results in optical transparency in the visible regime, low resistivity and high electron mobility values, along with a significant magnetic moment. Although long range ferromagnetic order is not stabilized, all of the Gd moment is taken into account in the giant paramagnetic signal that can be described by a Brillouin function (Figure 3 see pdf).

Pulsed laser deposition was used to stabilize epitaxial $Ba_{0.96}Gd_{0.04}SnO_3$ thin films on (001) $SrTiO_3$ substrates, and compared with $Ba_{0.96}La_{0.04}SnO_3$ and undoped $BaSnO_3$ thin films. Gd as well as La doping schemes result in electron mobilities at room temperature that exceed those of conventional complex oxides, with values as high as 60 cm2/Vs (n~ 2.5x1020 cm3) and 30 cm2/Vs (n~1x1020 cm3) for La and Gd doping, respectively (Figure 4). The resistivity shows little temperature dependence across a broad temperature range, indicating that in both types of films the transport is not dominated by phonon scattering. Gd-doped $BaSnO_3$ films have a strong magnetic moment of 7 μB /Gd ion that is definitively associated with the Gd ions as determined by XMCD at the M4,5 edge of Gd (Figure 4 see pdf).

Detailed transmission electron microscopy studies of these films indicate that we have homogeneous distribution of the rare earth dopant in our samples (Figure 5). Combined with our x-ray diffraction results, we find that point defects more than grain boundaries are key ingredients in tuning the conduction $BaSnO_3$ films grown by pulsed laser deposition (Figure 5 see pdf).

More recently, we have explored additional rare earth dopants of Pr and Nd substituted in the Ba site of up to 8%. Pr and Nd doped samples exhibit similar transport and optical behavior to that of Gd doped samples but with lower magnetization as expected.

1. Urusa S. Alaan, Alpha T. N'Diaye, Padraic Shafer, Elke Arenholz, Yuri Suzuki, "Structure and Magnetism of Fe doped BaSnO3 Thin Films," AIP Advances 7 055716 (2017).
2. Urusa S. Alaan, Padraic Shafer, Alpha T. N'Diaye, Elke Arenholz, and Y. Suzuki, "Gd Doped BaSnO3: A Transparent Conducting Oxide with Local Magnetic Moments," Applied Physics Letters 108 042106 (2016).

Training Opportunities: Over the course of the program, one graduate student was fully funded. The graduate student explored and developed new doping schemes for the $BaSnO_3$ parent compound. Although the main focus of the project has been materials development, due to the transparent conducting nature of the compound, the student has acquired additional experimental skills associated with optical characterization, including ellipsometry and IR/VIS/UV optical spectrometry available at the Stanford Nano Shared Facilities. Professionally the student has been active in founding and organizing the Stanford Science Communication workshop, designing an introduction to materials science course for high school students as well as a nano-characterization methods crouse for middle and high school students and served as the president of the Stanford Materials Research Society student chapter. The student also presented her work at international conferences and wrote up her results in manuscripts.

Results Dissemination: We have (i) published papers in peer reviewed publications, (ii) presented the results at national conferences and seminars, (iii) collaborated with scientists at government laboratories.

We have disseminated our results to the scientific community via presentations in seminars and conferences (Joint Intermag and Conference on Magnetism and Magnetic Materials in San Diego, CA, the March Meeting of the American Physical Society and the Conference on Magnetism and Magnetic Materials) as well as publications. I have also developed an intersession class for a local high school in San Mateo, CA.

Papers:
Urusa S. Alaan, Padraic Shafer, Alpha T. N'Diaye, Elke Arenholz, and Y. Suzuki, "Gd Doped $BaSnO_3$: A Transparent Conducting Oxide with Local Magnetic Moments," Applied Physics Letters 108 042106 (2016).

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Honors and Awards: Yuri Suzuki, Department of Defense Vannevar Bush Faculty Fellowship (2014-2019)

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Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI
Participant: Yuri Suzuki
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Urusa Shahriar Alaan
Person Months Worked: 5.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Staff Scientist (doctoral level)
Participant: Carolina Adamo
Person Months Worked: 1.00 **Funding Support:**
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National Academy Member: N
Other Collaborators:

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RPPR Final Report
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Date Submitted: 4/28/18 12:00AM Date Published: 2/28/17 11:41PM
Publication Location:
Article Title: Structure and magnetism of Fe-doped BaSnO3 thin films
Authors: Urusa S. Alaan, Alpha T. N'Diaye, Padraic Shafer, Elke Arenholz, Yuri Suzuki
Keywords: BaSnO3, thin films
Abstract: BaSnO3 is an excellent candidate system for developing a new class of perovskitebased dilute magnetic semiconductors. In this study, we show that BaSn0.95Fe0.05O3 can be grown from a background pressure of ~2x10-3 mTorr to oxygen pressures of 300 mTorr with high crystallinity and excellent structural quality. When grown in vacuum, the films may be weakly ferromagnetic with a nonzero x-ray magnetic circular dichroism signal on the Fe L3 edge. Growth with oxygen flow appears to suppress magnetic ordering. Even for very thick films grown in 100 mTorr O2, the films are paramagnetic. The existence of ferromagnetism in vacuum-grown BaSnO3 may be attributed to the F-center exchange mechanism, which relies on the presence of oxygen vacancies to facilitate the ferromagnetism. However, other possible extrinsic contributions to the magnetic ordering, such as clusters of Fe3O4 and FeO or contamination can also explain the observed behavior.
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Acknowledged Federal Support: **Y**

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Paper Title: A new magnetically doped transparent conducting Oxide: Gd-Doped BaSnO3
Authors: Urusa S. Alaan, Franklin J. Wong, Alpha N'Diaye, Padraic Shafer, Elke Arenholz, Yuri Suzuki
Acknowledged Federal Support: **Y**

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Date Received: 30-Aug-2016 Conference Date: 15-Mar-2016 Date Published: 31-Aug-2016
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Paper Title: Gd-Doped BaSnO 3 Thin Films: High Mobility in a Magnetically- Doped Transparent Conducting Oxide
Authors: Urusa S. Alaan, Padraic Shafer, Alpha T. N'Diaye, Elke Arenholz, Yuri Suzuki
Acknowledged Federal Support: **Y**

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Conference Location: New Orleans, LA
Paper Title: The Effect of Paramagnetic Impurities in Transparent Conducting BaSnO3 Thin Films
Authors: U.S. Alaan, A.T. N'Diaye, P. Shafer, E. Arenholz, Y. Suzuki
Acknowledged Federal Support: **Y**

DISSERTATIONS:

RPPR Final Report
as of 24-Jul-2018

Publication Type: Thesis or Dissertation
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Title: Defect Control of Magnetism in Complex Oxides
Authors: Urusa Shahriar
Acknowledged Federal Support: **N**

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Major Goals

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Accomplished under Goals

In this three-year program, we have developed a new family of magnetically doped barium stannate epitaxial thin films that exhibit a combination of metallic conductivity, optical transparency and magnetism. In contrast to bulk samples which are grown under equilibrium conditions, epitaxial thin films grown via non-equilibrium processes should enable the incorporation of more magnetic dopants than otherwise possible with equilibrium processes. We have demonstrated the incorporation of up to 4% rare earth and transition metal dopants in epitaxial $BaSnO_3$ thin films with combined optical, electronic and magnetic functionality.

Transition metal doping of $BaSnO_3$.[1] In order to induce magnetic functionality in $BaSnO_3$, the transition metal cation of Fe was doped into stannate films. From ionic radii considerations, Fe would prefer substitution on the B sites of the ABO_3 perovskite structure. Since the perovskite structure is composed of cornered shared BO_6 octahedra where magnetic functionality is generated via B-O-B exchange interactions, transition metal substitution of the Sn site is a promising route to generate magnetic functionality. We have successfully showed that up to 5% Fe doped $BaSn_{1-x}Fe_xO_3$ films does in fact exhibit

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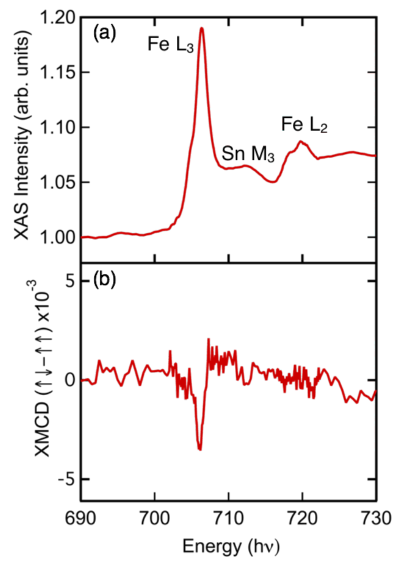

Figure 1. (a) X-ray absorption and (b) x-ray magnetic circular dichroism spectra at the Fe $L_{3,2}$ edges for a ferromagnetic $BaSn_{0.95}Fe_{0.05}O_3$ sample grown in vacuum.

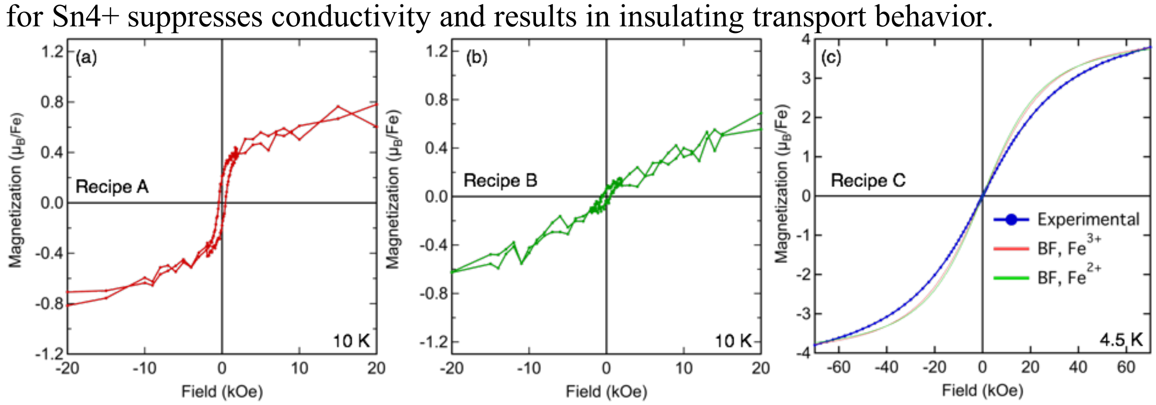

FIG. 2. Magnetization versus magnetic field loops as measured by SQUID magnetometry for samples grown using (a) Recipe A (no oxygen flow, 2×10^{-3} mTorr background pressure), (b) Recipe B (0.0425 mTorr O_2), and (c) Recipe C (100 mTorr O_2, thick film). In each case, the diamagnetic background from the substrate has been subtracted. All measurements were conducted after field-cooling in 70 kOe with the magnetic field oriented in the sample in-plane direction. For (a) and (b) the measurement was conducted at 10 K. In (c), the magnetization was measured are 4.5 K and the calculated Brillouin functions (BF) for high-spin Fe^{2+} and Fe^{3+} are also plotted.

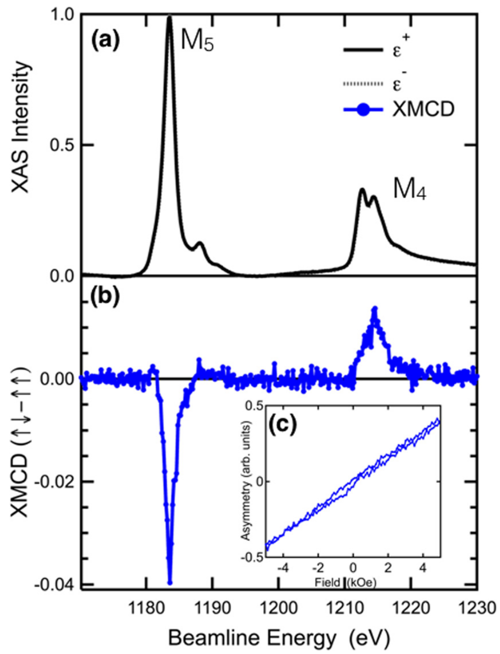

Figure 4. (a) X-ray absorption (XAS) spectra (with opposite circular polarizations ε^+ and ε^-) of the Gd M5 and M4 edges at 15K confirm Gd incorporation into the BaSnO3 films, and the (b) difference between these XASmeasurements with e. and e_ gives a clear XMCD signal. (c) Magnetic asymmetry versus field measurements in the range H.60.5 T are linear and non-hysteretic, consistent with a paramagnetic response.

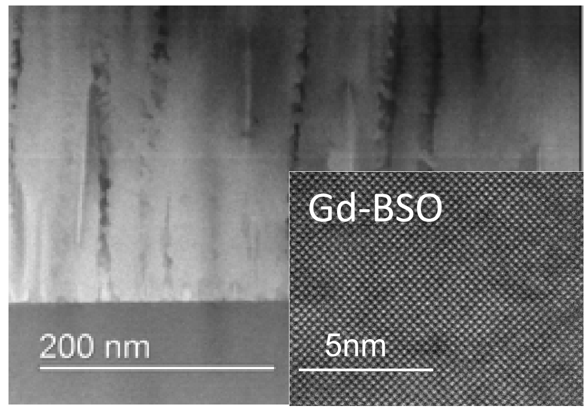

Figure 5. TEM shows columnar grains and large voids between the grains where there is Ba deficiency according to corresponding EELS data. Inset shows a high-resolution image of a crystalline region.

Rare-earth doping of $BaSnO_3$.[2] Another approach to magnetic doping of $BaSnO_3$ films has been to doped the A site with a magnetic cation akin to La doped $BaSnO_3$ films that have given rise to high mobility values. We have stabilized transparent, conducting, paramagnetic stannate thin films via rare-earth doping of $BaSnO_3$. Gd^{3+} ($4f^7$) substitution on the Ba^{2+} site results in optical transparency in the visible regime, low resistivity and high electron mobility values, along with a significant magnetic moment. Although long range ferromagnetic order is not stabilized, all of the Gd moment is taken into account in the giant paramagnetic signal that can be described by a Brillouin function (Figure 3).

Pulsed laser deposition was used to stabilize epitaxial $Ba_{0.96}Gd_{0.04}SnO_3$ thin films on (001) $SrTiO_3$ substrates, and compared with $Ba_{0.96}La_{0.04}SnO_3$ and undoped $BaSnO_3$ thin films. Gd as well as La doping schemes result in electron mobilities at room temperature that exceed those of conventional complex oxides, with values as high as 60 cm^2/Vs ($n\sim 2.5x10^{20}$ cm^3) and 30 cm^2/Vs ($n\sim 1x10^{20}$ cm^3) for La and Gd doping, respectively (Figure 4). The resistivity shows little temperature dependence across a broad temperature range, indicating that in both types of films the transport is not dominated by phonon scattering.

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Gd-doped $BaSnO_3$ films have a strong magnetic moment of 7 μ_B /Gd ion that is definitively associated with the Gd ions as determined by XMCD at the $M_{4,5}$ edge of Gd (Figure 4).

Detailed transmission electron microscopy studies of these films indicate that we have homogeneous distribution of the rare earth dopant in our samples (Figure 5). Combined with our x-ray diffraction results, we find that point defects more than grain boundaries are key ingredients in tuning the conduction $BaSnO_3$ films grown by pulsed laser deposition (Figure 5).

More recently, we have explored additional rare earth dopants of Pr and Nd substituted in the Ba site of up to 8%. Pr and Nd doped samples exhibit similar transport and optical behavior to that of Gd doped samples but with lower magnetization as expected.