Abstract Book

XV International Workshop on Oxide Electronics

September 14-17, 2008
Stanley Hotel
Estes Park, Colorado
### Sunday, September 14

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
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<tbody>
<tr>
<td>4:00-6:00</td>
<td>Registration</td>
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<tr>
<td>6:00-8:00</td>
<td>Welcome reception</td>
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### Monday Morning

**C. B. Eom, University of Wisconsin-Madison**

**Opening remarks**

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**Session 1**

**Correlated Electron Systems**

Chair: M.S. Rzchowski, University of Wisconsin-Madison

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Institution</th>
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<tbody>
<tr>
<td>8:45-9:15</td>
<td><strong>E. Dagotto</strong> (Invited), U. Tennessee and Oak Ridge National Laboratory</td>
<td>Recent Results in the Computational Study of Models for Correlated Electrons</td>
<td></td>
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<tr>
<td>9:15-9:30</td>
<td><strong>H. Kumigashira</strong>, The University of Tokyo</td>
<td>Band Diagrams of Perovskite Oxide Heterojunctions</td>
<td></td>
</tr>
<tr>
<td>9:30-9:45</td>
<td><strong>G. Koster</strong>, University of Twente</td>
<td>A study of the relation of magnetism and the metal-insulator transition in SrRuO₃ as a function of thickness</td>
<td></td>
</tr>
<tr>
<td>9:45-10:00</td>
<td><strong>C. Beekman</strong>, Leiden University</td>
<td>Indications for Coulomb-gap formation in the MI transition of La₀.₇Sr₀.₃Mn₀₃</td>
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**10:00-10:30 Refreshment Break**

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**Session 2**

**Correlated Electron Systems II**

Chair: D.P. Norton, University of Florida

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<th>Time</th>
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<tr>
<td>10:30-11:00</td>
<td><strong>M. Salluzzo</strong> (Invited), INFM and Universite Federico II di Napoli</td>
<td>Indirect electric field doping of the CuO₂ planes in “123” cuprates</td>
<td></td>
</tr>
<tr>
<td>11:00-11:15</td>
<td><strong>T. Kawai</strong>, Osaka University</td>
<td>Heterostructured Nano-Oxides and Their Functionalities</td>
<td></td>
</tr>
<tr>
<td>11:15-11:30</td>
<td><strong>L. F. Kourkoutis</strong>, Cornell University</td>
<td>Stabilizing metallic ferromagnetism in (La₀.₇Sr₀.₃MnO₂)₅/(SrTiO₃)₅ multilayers</td>
<td></td>
</tr>
<tr>
<td>11:30-11:45</td>
<td><strong>Y. Shimakawa</strong>, Kyoto University</td>
<td>Single-crystal thin films of SrFeO₂ with FeO₂ infinite layers</td>
<td></td>
</tr>
<tr>
<td>11:45-12:00</td>
<td><strong>M. Kawasaki</strong>, Tohoku University</td>
<td>2D electron gas at (MgZn)O/ZnO interface grown by molecular beam epitaxy</td>
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**12:00-13:30 Lunch**
### Monday Afternoon

**1:30-3:30  Poster Session I**

### Session 3  
**Multiferroics I**

Chair: R. Ramesh, University of California-Berkeley

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<th>Time</th>
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<tr>
<td>3:30-4:00</td>
<td><strong>C. J. Fennie</strong> (Invited), Cornell University</td>
<td></td>
<td>Design of multifunctional oxides from first principles</td>
</tr>
<tr>
<td>4:00-4:15</td>
<td><strong>D. Kan</strong>, University of Maryland</td>
<td></td>
<td>Systematic investigation of morphotropic phase boundaries in rare-earth doped BiFeO$_3$</td>
</tr>
<tr>
<td>4:15-4:30</td>
<td><strong>H. W. Jang</strong>, University of Wisconsin-Madison</td>
<td></td>
<td>Strain-induced Polarization Rotation in Epitaxial (001) BiFeO$_3$ Thin Films</td>
</tr>
<tr>
<td>4:30-4:45</td>
<td><strong>J. F. Ihlefeld</strong>, Cornell University</td>
<td></td>
<td>Adsorption-controlled growth of BiFeO$_3$ by MBE and integration with wide band-gap semiconductors</td>
</tr>
</tbody>
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**4:45-5:15 Refreshment Break**

### Session 4  
**Multiferroics II**

Chair: C.B. Eom, University of Wisconsin-Madison

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<th>Time</th>
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<th>Topic</th>
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<tbody>
<tr>
<td>5:15-5:45</td>
<td><strong>E. Tsymbal</strong> (Invited), University of Nebraska</td>
<td></td>
<td>Ferroelectric and Multiferroic Tunnel Junctions</td>
</tr>
<tr>
<td>5:45-6:00</td>
<td><strong>M. Huijben</strong>, University of Twente</td>
<td></td>
<td>Magnetoelectric coupling through exchange bias at La$<em>{0.7}$Sr$</em>{0.3}$MnO$_3$/BiFeO$_3$ interfaces</td>
</tr>
<tr>
<td>6:00-6:15</td>
<td><strong>J. Hoffman</strong>, Yale University</td>
<td></td>
<td>Magnetoelectric coupling in complex oxides with competing ground states</td>
</tr>
<tr>
<td>6:15-6:30</td>
<td><strong>H. Béa</strong>, University of Geneva</td>
<td></td>
<td>Nanoscale study of coupled ferroelectric / antiferromagnetic domain walls in BiFeO$_3$ multiferroic thin films</td>
</tr>
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**7:00 Buffet Dinner**
### Tuesday Morning

#### Session 5
**Ferroelectrics I**

Chair: D.G. Schlom, *Cornell University*

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<tr>
<th>Time</th>
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<tbody>
<tr>
<td>8:30-9:00</td>
<td>L. Q. Chen (Invited)</td>
<td><em>Pennsylvania State University</em></td>
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<tr>
<td>9:00-9:30</td>
<td>A. M. Rappe (Invited)</td>
<td><em>University of Pennsylvania</em></td>
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<tr>
<td>9:30-9:45</td>
<td>P. Paruch</td>
<td><em>University of Geneva</em></td>
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<tr>
<td>9:45-10:00</td>
<td>D. A. Tenne</td>
<td><em>Boise State University</em></td>
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10:00-10:30 **Refreshment Break**

#### Session 6
**Ferroelectrics II**

Chair: D.H.A. Blank, *Universite Twente*

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
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<tbody>
<tr>
<td>10:30-11:00</td>
<td>T. W. Noh (Invited)</td>
<td><em>Seoul National University</em></td>
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<tr>
<td>11:00-11:15</td>
<td>M. Dawber</td>
<td><em>Stony Brook University</em></td>
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<tr>
<td>11:15-11:30</td>
<td>E. Bousquet</td>
<td><em>Liege University</em></td>
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<tr>
<td>11:30-11:45</td>
<td>R. Takahashi</td>
<td><em>Norwegian University of Science and Technology</em></td>
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<tr>
<td>11:45-12:00</td>
<td>M. J. Highland</td>
<td><em>Argonne National Laboratory</em></td>
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12:00-1:30 **Lunch**
## Tuesday Afternoon

### Session 7
**Oxide Heterostructures and Interfaces I**

Chair: J. Mannhart, *University of Augsburg*

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<thead>
<tr>
<th>Time</th>
<th>Speaker(s)</th>
<th>Title</th>
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<tbody>
<tr>
<td>1:30-2:00</td>
<td>G. Rijnders (Invited), University of Twente</td>
<td>Monitoring oxide thin film growth with in-situ scanning force microscopy</td>
</tr>
<tr>
<td>2:00-2:30</td>
<td>H. Y. Hwang (Invited), University of Tokyo</td>
<td>Modulation doping of electrons and holes at vanadate interfaces</td>
</tr>
<tr>
<td>2:30-2:45</td>
<td>A. Kalabukhov, Chalmers University of Technology</td>
<td>Depth profiling of lanthanum defects in the LaAlO$_3$/SrTiO$_3$ hetero-interfaces using middle energy ion spectroscopy</td>
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<th>Time</th>
<th>Session II (refreshments)</th>
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### Session 8
**Oxide Heterostructures and Interfaces II**

Chair: C. Ahn, *Yale University*

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker(s)</th>
<th>Title</th>
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<tbody>
<tr>
<td>5:00-5:15</td>
<td>S. Ismail-Beigi, Yale University</td>
<td>A First Principle Study of LaAlO$_3$/SrTiO$_3$ Heterointerface</td>
</tr>
<tr>
<td>5:15-5:45</td>
<td>J. M. Triscone (Invited), University of Geneva</td>
<td>Electrostatic tuning of the SrTiO$_3$/LaAlO$_3$ interface ground state</td>
</tr>
<tr>
<td>5:45-6:00</td>
<td>J. Mannhart, University of Augsburg</td>
<td>Impact of the microstructure on the transport properties of the electron gas at LaAlO$_3$-SrTiO$_3$ interfaces</td>
</tr>
<tr>
<td>6:00-6:15</td>
<td>J. Huijben, University of Twente</td>
<td>Magnetoresistance oscillations and relaxation effects at the SrTiO$_3$ – LaAlO$_3$ interface</td>
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<thead>
<tr>
<th>Time</th>
<th>Rump session on 2D Electron Gas Systems</th>
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<th>Time</th>
<th>Buffet Dinner</th>
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6:00-6:15 Rump session on 2D Electron Gas Systems

Moderator: M. Kawasaki, *Tohuku University*
### Session 9
**Device Applications I**
Chair: H. Koinuma, University of Tokyo

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<tr>
<th>Time</th>
<th>Speaker</th>
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<tbody>
<tr>
<td>8:30-9:00</td>
<td><strong>Y. Iwasa</strong> (Invited), Tohuka University</td>
<td><strong>Electric Double Layer Transistor</strong></td>
</tr>
<tr>
<td>9:00-9:15</td>
<td><strong>J. Levy</strong>, University of Pittsburgh</td>
<td><strong>Fabrication of Erasable Field-Effect Nanodevices at the LaAlO$_3$/SrTiO$_3$ Interface</strong></td>
</tr>
<tr>
<td>9:15-9:30</td>
<td><strong>X. Hong</strong>, Pennsylvania State University</td>
<td><strong>High mobility multi-layer graphene field effect transistors fabricated on epitaxial ferroelectric gate oxides</strong></td>
</tr>
<tr>
<td>9:30-9:45</td>
<td><strong>S. Guha</strong>, IBM Research</td>
<td><strong>Photocatalytic properties of ultrathin TiO$_2$ layers on Si substrates</strong></td>
</tr>
<tr>
<td>9:45-10:00</td>
<td><strong>L. Pellegrino</strong>, CNR-INMN-LAMIA</td>
<td><strong>All-Oxide Microelectromechanical Systems for Strain Manipulation of Epitaxial Oxide Thin Films</strong></td>
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10:00-10:30 Refreshment Break

### Session 10
**Device Applications II**
Chair: T. Kawai, Osaka University

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<tr>
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<th>Speaker</th>
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<tbody>
<tr>
<td>10:30-11:00</td>
<td><strong>R. Waser</strong> (Invited), Forschungszentrum Jülich</td>
<td><strong>Resistive switching in oxides - known facts, disregarded issues, and open questions</strong></td>
</tr>
<tr>
<td>11:00-11:15</td>
<td><strong>D. P. Norton</strong>, University of Florida</td>
<td><strong>Acceptor formation and light-emitting diode fabrication using phosphorus-doped ZnO</strong></td>
</tr>
<tr>
<td>11:15-11:30</td>
<td><strong>L. J. Brillson</strong>, The Ohio State University</td>
<td><strong>The role of morphology, polarity, and defects on ZnO near-surface optical emission</strong></td>
</tr>
<tr>
<td>11:30-11:45</td>
<td><strong>M. D. Biegalski</strong>, Oak Ridge National Laboratory</td>
<td><strong>Employing Uniform Reversible Film Strain from a Piezoelectric Substrate to Examine Effects of Strain in Epitaxial Oxide Thin Films</strong></td>
</tr>
<tr>
<td>11:45-12:00</td>
<td><strong>J. Schubert</strong>, Forschungszentrum Jülich</td>
<td><strong>Rare-earth based alternative gate-dielectrics for future integration in MOSFETs</strong></td>
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12:00 Box Lunch
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<thead>
<tr>
<th>Poster</th>
<th>Title</th>
<th>Authors</th>
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<tbody>
<tr>
<td>P1.1</td>
<td>Electronic structure of termination-controlled SrTiO$<em>3$/La$</em>{0.6}$Sr$_{0.4}$MnO$_3$ interface studied by hard X-ray photoemission spectroscopy</td>
<td>K. Yoshimatsu*, K. Horiba, H. Kumigashira, E. Ikenaga, M. Oshima</td>
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<td></td>
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<td>*Department of Applied Chemistry, The Univ. of Tokyo, Tokyo 113-8656, Japan</td>
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<tr>
<td>P1.2</td>
<td>Anomalous Hall effect in Eu$_{1-x}$La$_x$TiO$_3$ films</td>
<td>K. Takahashi*, M. Kawasaki, Y. Tokura</td>
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<td>*CMRG RIKEN</td>
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<tr>
<td>P1.3</td>
<td>Indications for Coulomb-gap formation in the metal-insulator transition of La$<em>{0.67}$Ca$</em>{0.33}$MnO$_3$</td>
<td>C. Beekman*, I. Komissarov, S. Kelly, F. Galli, J. Aarts</td>
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<td>*Kamerlingh Onnes Laboratory, Leiden University, P.O. box 9504, 2300RA Leiden, The Netherlands</td>
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<td>*Argonne National Laboratory</td>
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<tr>
<td>P1.5</td>
<td>ZrO$_2$-In$_2$O$_3$ Heterointerface Structure and Properties: Density Functional Theory Study</td>
<td>H. Iddir*, P. Zapol, D. Fong, P. Fuoss, J. Eastman</td>
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<td>*Argonne National Laboratory</td>
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<tr>
<td>P1.6</td>
<td>Spin-polarized current effects in disordered half-metal La$<em>{0.7}$Ba$</em>{0.3}$MnO$_3$ thin films</td>
<td>P. Orgiani*, C. Adamo, C. Aruta, C. Barone, A. Galdi, O. Quaranta, S. Pagano, L. Maritato</td>
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<td>*CNR-INFAM Coherentia and University of Salerno</td>
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<tr>
<td>P1.7</td>
<td>Gallium Implantation in LCMO and PCMO thin films</td>
<td>M. Porcu*, J. Aarts, C. Beekman, H. Zandbergen</td>
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<td>*Delft Technical University</td>
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<tr>
<td>P1.8</td>
<td>Scanning Tunneling Microscopy and Spectroscopy on La$<em>{0.7}$Sr$</em>{0.3}$MnO$_3$: Evidence for a pseudogap</td>
<td>U. Singh*, A. Gupta, G. Sheet, V. Chandrasekhar, H. Jang, C. Eom</td>
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<td>*Department of Physics, Indian Institute of Technology Kanpur, Kanpur 208016, India</td>
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<tr>
<td>P1.9</td>
<td>Epitaxial growth of atomically-flat LiCoO$_2$</td>
<td>T. Hitosugi*, T. Tsuruhama, Y. Hirose, T. Shimada, T. Hasegawa</td>
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<td>*WPI Advanced Institute for Materials Research (WPI-AIMR), Tohoku Univ., Japan</td>
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<tr>
<td>P1.10</td>
<td>Schottky Barrier Height Control by Interface Modulation in La$<em>{0.7}$Sr$</em>{0.3}$MnO$_3$/Nb:SrTiO$_3$ Junctions</td>
<td>Y. Hikita*, M. Nishikawa, T. Yajima, H. Hwang</td>
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<td>*Department of Advanced Materials Science, University of Tokyo, Kashiwa, Chiba Japan</td>
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<td>*Argonne National Laboratory</td>
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<td>*The University of Tokyo</td>
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<tr>
<td>P1.13</td>
<td>Spin transfer torque effects in La$<em>{0.8}$Sr$</em>{0.2}$MnO$_3$ single crystal</td>
<td>A. Ruyter*, J. Wolfman, A. Wahl, C. Simon, F. Giovannelli, I. Monot-Laffez, M. Rossel, G. Van Tendeloo, M. Dominikzak</td>
</tr>
<tr>
<td>P1.15</td>
<td>Electronic structural properties of SrRuO$_3$ ultrathin films on SrTiO$_3$ substrates</td>
<td>Y. Chang*, S. Phark, C. Kim, Y. Kim, J. Yu, T. Noh</td>
</tr>
<tr>
<td>P1.16</td>
<td>Asymmetry and rotation of the in-plane magnetic easy axis in La$<em>{0.67}$Sr$</em>{0.33}$MnO$_3$ thin film grown on NdGaO$_3$(112)</td>
<td>H. Nishikawa*, E. Houwman, H. Boschker, M. Mathews, G. Rijnders, D. Blank</td>
</tr>
<tr>
<td>P1.17</td>
<td>Magnetization induced resistance switching effects in YBa$_2$Cu$_3$O$<em>7$ - La$</em>{1-x}$Sr$_x$MnO$_3$ heterostructures</td>
<td>M. van Zalk*, M. Veldhorst, A. Brinkman, J. Aarts, H. Hilgenkamp</td>
</tr>
<tr>
<td>P1.18</td>
<td>Independent behavior of the antiferromagnetic and ferromagnetic properties in perovskite oxide superlattices</td>
<td>Y. Takamura*, F. Yang, N. Kemik, M. Biegalski, H. Christen, E. Arenholz</td>
</tr>
<tr>
<td>P1.19</td>
<td>Growth of (ultra) thin La$<em>{1.2}$Sr$</em>{1.8}$Mn$_{1.7}$Ru$_0.3$O$_7$ Ruddlesden-Popper films on SrTiO$_3$ substrate</td>
<td>M. Matvejeff*, T. Chikyow, M. Lippmaa</td>
</tr>
<tr>
<td>P1.20</td>
<td>Properties of epitaxial ferrimagnetic garnet thin films</td>
<td>Y. Krockenberger*, K. Yun, T. Hatano, M. Kawasaki, Y. Tokura</td>
</tr>
<tr>
<td>P1.21</td>
<td>Probing the nature of ferroelectric polarization dynamics in multiferroic BiFeO$_3$ by terahertz emission spectroscopy</td>
<td>D. Rana*, I. Kawayama, K. Takahashi, H. Murakami, M. Tonouchi</td>
</tr>
<tr>
<td>P1.22</td>
<td>Magnetoelastic effect at the Fe$_3$O$_4$/BaTiO$_3$ (001) interface: A first-principles study</td>
<td>M. Niranjan*, J. Velev, C. Duan, S. Jaswal, E. Tsymbal</td>
</tr>
<tr>
<td>P1.23</td>
<td>Charge driven magnetoelastic coupling in a ferromagnetic / ferroelectric bilayer</td>
<td>H. Molegraaf*, J. Hoffman, C. Vaz, S. Gariglio, D. van der Marel, C. Ahn, J. Triscone</td>
</tr>
<tr>
<td>P1.24</td>
<td>Magnetic anisotropy modulation of magnetite in Fe$_3$O$_4$/BaTiO$_3$(100) epitaxial structures</td>
<td>C. Vaz*, J. Hoffman, A. Posadas, C. Ahn</td>
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<tr>
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<td>Authors</td>
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<tr>
<td>P1.26</td>
<td>Structural distortion and magnetic properties in Bi&lt;sub&gt;2&lt;/sub&gt;FeCrO&lt;sub&gt;6&lt;/sub&gt; double perovskite films</td>
<td>R. Nechache*, C. Harnagea, L. Gunawan, M. Singh, P. Fournier, G. Botton, A. Pignolet</td>
</tr>
<tr>
<td>P1.27</td>
<td>Thin films of orthorhombic TbMnO&lt;sub&gt;3&lt;/sub&gt; under epitaxial strain</td>
<td>C. Daumont*, D. Rubi, D. Mannix, G. Catalan, B. Noheda</td>
</tr>
<tr>
<td>P1.29</td>
<td>Structural state of epitaxial (001) BiFeO&lt;sub&gt;3&lt;/sub&gt; films on cubic and orthorhombic substrates</td>
<td>C. Folkman*, H. Jang, D. Ortiz, S. Baek, C. Eom</td>
</tr>
<tr>
<td>P1.30</td>
<td>Nanoscale piezoresponse studies of ferroelectric domains in epitaxial BiFeO&lt;sub&gt;3&lt;/sub&gt; nanostructures defined by FIB lithography</td>
<td>S. Hong*, J. Klug, M. Park, A. Imre, M. Bedzyk, K. No, O. Auciello</td>
</tr>
<tr>
<td>P1.31</td>
<td>Magnetic Field Control of Dielectric Properties in Strained Garnet Ferrite Thin Films</td>
<td>M. Seki*, M. Mikami, Y. Ono, H. Tabata</td>
</tr>
<tr>
<td>P1.32</td>
<td>Magnetic and dielectric properties of strained Sm&lt;sub&gt;3&lt;/sub&gt;Fe&lt;sub&gt;5&lt;/sub&gt;O&lt;sub&gt;12&lt;/sub&gt; garnet ferrite</td>
<td>M. Mikami*, Y. Ono, M. Seki, H. Tabata</td>
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*ReCOE & FPRD, Department of Physics and Astronomy, Seoul National University, Seoul Korea |
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*CNR-INFN-LAMIA & Dipartimento di Fisica, Universit‡ di Genova |
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Opening remarks for the 15th International Workshop on Oxide Electronics

Chang-Beom Eom
*Department of Materials Science and Engineering, University of Wisconsin-Madison*
Recent results in the computational study of models for correlated electrons

Elbio Dagotto

Department of Physics, University of Tennessee, and Materials Science and Technology Division, Oak Ridge National Laboratory

In this presentation, some recent computational results for models of correlated electrons will be discussed. First, the presence of large magneto-resistance effects in double-exchange models for manganites will be addressed [1]. Phase competition appears to be the cause of the CMR effect in these materials. Second, recent results for oxide interfaces will be presented, using model Hamiltonians. The materials studied include manganites LMO-SMO, superconductors, and other compounds [2]. Orbital order at the interface will be analyzed, together with charge transfer effects. Time allowing, the presentation will also include results explaining the Fermi arcs of underdoped cuprates [3], and new results for two-orbital models for undoped and lightly doped LaOFeAs [4].


Research supported by NSF and DOE.
Band Diagrams of Perovskite Oxide Heterojunctions

H. Kumigashira\textsuperscript{1,3*}, M. Minohara\textsuperscript{4}, K. Yoshimatsu\textsuperscript{1}, and M. Oshima\textsuperscript{1-4}

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Heterojunctions based on perovskite oxides have heralded the possibility of creating new multifunctional properties in ways that would not have been possible by using single-phase bulk materials. For designing the functionalities of the heterojunctions, the precise determination of their band diagram is indispensable, together with the exact understanding of their interfacial electronic structures. In this study, we have performed \textit{in situ} photoemission spectroscopy (PES) to determine the band diagram of promising oxide heterojunctions between (a) a half-metallic ferromagnet La\textsubscript{0.6}Sr\textsubscript{0.4}MnO\textsubscript{3} (LSMO) and a semiconductor Nb-doped SrTiO\textsubscript{3} (Nb:STO), (b) itinerant ferromagnet SrRuO\textsubscript{3} (SRO) and Nb:STO, and (c) band insulators LaAlO\textsubscript{3} (LAO) and STO. We have found that the ideal Schottky barrier is formed in SRO/Nb:STO junctions with Schottky barrier height (SBH) of 1.2±0.1 eV, while the measured SBH of LSMO/Nb:STO (1.2±0.1 eV) is much larger than the prediction from the Schottky-Mott rule (0.7±0.1 eV), indicating that a certain interface dipole is formed at the LSMO/Nb:STO interface \cite{1}. On the other hand, we have observed that the band discontinuity at polar/nonpolar interfaces, namely LSMO/STO and LAO/STO, varies depending on the terminating layer at the interface \cite{2}. The result suggests that the terminating layer and resultant polar direction play an important role in the band discontinuity at the polar/nonpolar interface.

\cite{1} M. Minohara \textit{et al.}, Appl. Phys. Lett. 90, 132123 (2007).
A study of the relation of magnetism and the metal-insulator transition in SrRuO3 as a function of thickness

Wolter Siemons, Jing Xia, Gertjan Koster, Dave H.A. Blank, M.R. Beasley, A. Kapiltunik

Thin films of the perovskite SrRuO3 have attracted considerable interest due to their low room temperature resistivity and small lattice mismatch with a range of functional oxide materials. In addition they exhibit “bad metal” behavior, which is one of the unsolved problems of contemporary condensed matter physics, show signs of electron correlation in the material, and are ferromagnetic below a temperature of 160 K. For these reasons thin films of SrRuO3 are of great current interest, both from the materials science and the physics point of view.

Indeed, recent studies from several groups emphasized the interplay between itineracy and ferromagnetism in thin films of SrRuO3. In particular, Toyota et al.\cite{1} presented results on the thickness dependence of metallicity and ferromagnetism in SrRuO3 films concluding that a metal-insulator transition (MIT) accompanied by the disappearance of ferromagnetism occurs in these films at a critical film thickness of 4 to 5 monolayers (ML).

In this presentation we present new results on the MIT in ultrathin SrRuO3 films and the magnetic properties of such films. We show that in homogeneous films of SrRuO3 a MIT occurs at a critical thickness below 4 monolayers (ML), below which ferromagnetism is undetectable using an ultra-sensitive Sagnac magneto-optic interferometer \cite{2}. While T_C drops rapidly below ~10 ML, the size of the moment remains unchanged from its 1.6 \mu_B in thick films. Examination of the transport properties of the measured films shows an increase in the sheet resistance with decreasing thickness. At 4 ML the extrapolated low-temperature sheet resistance is ~7 k\Omega (about a quarter of the two-dimensional quantum of resistance), jumping to several megaohm just below the transition.

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Indications for Coulomb-gap formation in the metal-insulator transition of La_{0.67}Ca_{0.33}MnO_3

C. Beekman*, I. Komissarov, S. Kelly, F. Galli, J. Aarts
*Kamerlingh Onnes Laboratory, Leiden University, P.O. box 9504, 2300RA Leiden, The Netherlands

Although much by now is known about the physics of doped manganese oxides such as La_{1-x}Ca_xMnO_3, a question of both practical and fundamental interest still is at what length scales the (connected) phenomena of the Metal-Insulator transition (at a temperature T_{MI}) and phase separation influence the physical properties of the system, and what role is played by the disorder. We have studied 10 nm thick La_{0.67}Ca_{0.33}MnO_3 (LCMO) thin films structured into microbridges by e-beam lithography and Ar-etching. They were grown on 1°-miscut SrTiO_3 (STO) substrates, which puts the film under a small tensile strain. Special care has to be taken in structuring the microbridges since the Ar-etching can damage the STO, creating a conducting surface layer, but a brief oxygen plasma etch recovers the insulating state of the STO surface[1]. Upon cooling, such bridges show linear current (I)-voltage (V) characteristics both above and below T_{MI}. However, around T_{MI} we always find a (small) regime of non-linear behavior, described by a differential resistance peak at zero bias which disappears under influence of a magnetic field. We suggest that this effect is due to the combination of disorder and a low carrier concentration in the transition, which are known ingredients for the formation of a Coulomb gap. Given variations in disorder and percolation behavior it can be expected that structured samples are quite sensitive to such a gap. The interpretation is further supported by Scanning Tunneling Microscopy measurements on similar samples grown on NdGaO_3, as well as by electric field effect measurements with STO as the gate electrode. The gap formation appears to be a generic feature of the phase transition, and can explain the observation of various anomalies reported in the literature.

Indirect electric field doping of the CuO$_2$ planes in “123” cuprates

M. Salluzzo
INFM and Universite Federico II di Napoli

The electric field-effect is a method to change the electrical properties of a thin film using an external gate voltage. In superconductors, including the copper based high critical temperature superconductors (HTS), it has been used to shift the critical temperature and even to induce phase transitions. Field effect experiments in ultra-thin HTS are usually interpreted by supposing that the induced charges develop into carriers in the CuO$_2$ conducting planes, thus changing the filling of the Zhang-Rice (ZR) band without changing disorder or the structure. By using x-ray absorption spectroscopy in the presence of an electric field, here we show that in hole doped Nd$_{1+x}$Ba$_{2-x}$Cu$_3$O$_7$ films the polarization charges are mainly confined at the CuO chains of the charge reservoir layer. Doping of the CuO$_2$ planes is rather indirect and it occurs via the transfer from the charge reservoir of a fraction of the total injected charges. It turns out that the actual carrier density is substantially lower than expected from a direct injection of holes into the superconducting layer. The results also show that electric field effect mechanism have strong similarities with the chemical doping effect, i.e. carriers are introduced as a consequence of a charge redistribution between charge reservoir and CuO$_2$ planes that minimize the accumulated electrostatic energy in the system. Consequently, the electronic properties of the charge reservoir and of the dielectric/HTS interface determine to what extent the electric field effect can modify the conduction properties of high critical temperature superconductors.
Heterostructured Nano-Oxides and Their Functionalities


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* Corresponding Author: e-mail: kawai@sanken.osaka-u.ac.jp

A heterostructure in transition metal oxides (TMOs) has attracted considerable attentions due to the fascinating physical properties. Although the major concerns of TMOs heterostructures have been directed at the 2D thin films via utilizing advanced laser MBE techniques, exploring the TMOs heterostructures of lower dimensional systems (1D or 0D) would be invaluable and indispensable to realize and discover novel properties and functionalities of nano-TMOs, and the device applications. However compared with the well-established 2D thin film heterostructures, the knowledge as to methodologies for creating and evaluating “TMOs Nano-Heterostructures” is still much scarce. Here we report on our recent developments as to “TMOs Nano-Heterostructures” utilizing several methodologies combined with laser MBE technique, including AFML (Atomic Force Microscopy Lithography) 1-4), NIL (Nano-Imprint Lithography) with selective nano-area deposition 5), and VLS (Vapor-Liquid-Solid) nanowire growth techniques 6-9). TMOs heterostructures of highly spin-polarized spinel ferrites, including (Fe,Mn)$_3$O$_4$ and (Fe,Zn)$_3$O$_4$, were constructed via AFML and NIL techniques 1-5). The well-defined structures were confirmed in terms of the spectroscopy measurements. The characteristic magneto-transport properties of these spinel hetero-nanostructures are presented. Heterostructured nanowires using binary oxides, including rock-salt-NiO and MgO, rutile-TiO$_2$ and SnO$_2$, and spinel-Fe$_3$O$_4$, have been fabricated by in-situ laser MBE technique with VLS growths 8-9). The transport properties, evaluated by the microwave conductivity and the direct single-nanowire measurements, are presented. We will discuss the underlying mechanisms within these dimensionally confined oxide heterostructures and perspective of “Heterostructured Nano-Oxides”.


(a) (Fe,Mn)$_3$O$_4$ nano-channel via AFML, (b) (Fe,Mn)$_3$O$_4$/NiO heterostructured nano-dot array via NIL, (c) TiO$_2$/SnO$_2$ heterostructured nanowire via VLS.

Figures
Stabilizing metallic ferromagnetism in (La$_{0.7}$Sr$_{0.3}$MnO$_3$)$_5$(SrTiO$_3$)$_5$ multilayers

L. Fitting Kourkoutis, J. H. Song, H. Y. Hwang, and D. A. Muller

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Abstract:

Colossal magnetoresistance, metal-insulator transition and half-metal ferromagnetism are only some of the intriguing phenomena that occur in manganites and have driven the interest in the family of perovskite manganese oxides. With a Curie temperature, $T_c$, of ~370K, the half-metal La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) has been considered a promising candidate for spintronics applications. However, while complete spin polarizations in LSMO was inferred from photoemission measurement [1] and a record tunneling magnetoresistance (TMR) ratio of 1800% was obtained in tunnel junctions with half-metallic manganite electrodes separated by a thin insulating layer of SrTiO$_3$ (STO) [2], the TMR decreases rapidly with temperature and diminishes far below $T_c$. It has been suggested that the ferromagnetic ordering at the LSMO/STO interface degrades, causing the magnetization and $T_c$ to degrade and the resistivity to increase; ultimately resulting in films that are insulating at all temperatures as the layer thickness decreases below a critical value of 3-5 nm. This critical thickness for sustaining conductivity below $T_c$ is attributed to an inherent “dead layer” at the interface between LSMO and STO.

Here, we show that LSMO/STO multilayers with layer thicknesses of ~2nm can exhibit ferromagnetism with $T_c$ above room temperature and remain metallic below $T_c$, if the structure is optimized by tuning not only the oxygen partial pressure and growth temperature but also the laser fluence. For larger fluences the LSMO A-site/B-site cation ratio exceeds one which is accommodated by the introduction of extended defects and leads to a reduction of the magnetization and an increase of the resistivity such that the multilayers remain insulating at all temperatures.

Single-crystal thin films of SrFeO$_2$ with FeO$_2$ infinite layers

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Square-planar oxygen coordination of Fe$^{2+}$ is extremely rare because iron ions are favorably coordinated by oxygen ions tetrahedrally or octahedrally. Recently SrFeO$_2$ with “infinite layers” of Fe$^{2+}$O$_2$ was reported to be synthesized by a low temperature treatment of SrFeO$_{2.875}$ (Sr$_8$Fe$_8$O$_{23}$) with CaH$_2$ [Y. Tsujimoto, et al., Nature 450, 1062 (2007)]. We have succeeded in preparing single-crystal thin films of SrFeO$_2$ by using CaH$_2$ for low-temperature reduction of epitaxial SrFeO$_{2.5}$ single-crystal films deposited on KTaO$_3$ and SrTiO$_3$ substrates by a pulsed laser deposition method [S. Inoue, et al., Appl. Phys. Lett. 92, 161911 (2008)]. This reduction process, removing oxygen ions from the perovskite structure framework and causing rearrangements of oxygen ions, topotactically transforms the brownmillerite SrFeO$_{2.5}$ to $c$-axis oriented SrFeO$_2$. Attempts for preparing other single-crystal thin films of infinite layer oxides, CaFeO$_2$, BaFeO$_2$, SrCoO$_2$ and LaNiO$_2$, are also reported.
Two dimensional electron gas at (MgZn)O/ZnO interface grown by molecular beam epitaxy

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Nominally undoped Mg0.05Zn0.95O/ZnO (x = 0.05 and 0.08) single heterostructures were prepared on Zn-polar ZnO substrates by using plasma assisted molecular beam epitaxy (MBE). The samples showed a metallic conductivity below 50K and a mobility exceeding 10^4 cm^2/Vs at 0.5 K. We observed quantum Hall effect accompanying Shubnikov–de Haas oscillations, in which zero-resistance states were clearly seen above 5 T. Rotation experiments in magnetic field suggest strong two-dimensional carrier confinement at low temperatures. The results indicate that the MBE grown films [1] have much higher quality than the previously reported samples grown by pulsed laser deposition [2].

Design of multifunctional oxides from first principles

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Multifunctional materials have the ability to respond in a useful way to several external stimuli and as such have tremendous potential for meeting the demands of emerging technological applications. Multiferroic oxides, which combine more than one “ferro” property, such as ferroelectricity, ferroelasticity, and ferromagnetism, are promising materials to achieve such responses. The key challenge in multiferroics is to produce a strong coupling among the physically distinct order parameters and thus increase functionality via cross-coupling responses. First-principles density-functional methods recently have proved a powerful tool for studying the properties of complex materials at the level of atoms and electrons, without the need for empirical input. In this Talk, I will discuss our recent work on the design of multifunctional oxides from first principles.
Systematic investigation of morphotropic phase boundaries in rare-earth doped BiFeO₃

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We have recently discovered a morphotropic phase boundary (MPB) in Sm doped BiFeO₃ (BFO).[1] The boundary is a rhombohedral to pseudo-orthorhombic cell-doubling structural transition which occurs at approximately the same composition in the measured temperature range (room temperature up to 400 °C). Substantial enhancement in dielectric/ferroelectric/piezoelectric properties are observed at the boundary. In this study, we have investigated structural and ferroelectric properties of various other rare-earth (RE) doped BFO. In particular, La, Sm, Gd, Dy, Lu were used as dopants. A series of doped BFO with continuously changing dopant concentration were fabricated by combinatorial pulsed laser deposition on SrTiO₃ (100) substrates with a SrRuO₃ buffer layer. Thin film composition spreads were used to map systematic changes in the structure and ferroelectric properties as a function of dopant concentration. For RE dopants with different ionic radii, the structural transition occurs at concentrations roughly consistent with their radii: the smaller the ion, the smaller the concentration at which the transition takes place. This confirms that the primary cause of the transition is the chemical pressure effect. The details of this trend will be reported. Lowering of the coercive field as well as the ferroelectric-antiferroelectric transition previously seen in Sm-BFO are also observed for different RE dopants. The correlation between the structural properties and ferroelectric properties will be discussed. This work is supported by DMR 0520471, NSF DMR 0603644, ARO W911NF-07-1-0410 and the W. M. Keck Foundation.

**Strain-induced Polarization Rotation in Epitaxial (001) BiFeO$_3$ Thin Films**


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The strong coupling between polarization and strain in ferroelectrics allows the control of properties by strain, namely, strain engineering. Indeed, drastic strain-induced enhancements in ferroelectric Curie temperatures and polarization have been observed in a number of epitaxial complex oxide thin films. However, a recent study on BiFeO$_3$ shows a dramatic different behavior; the polarization of a (111)-oriented BiFeO$_3$ film is almost independent of strain.

Epitaxial (001) BiFeO$_3$ films grown on (001) SrTiO$_3$ substrates are subjected to a compressive strain due to the lattice mismatch of $-1.4\%$. In contrast, epitaxial (001)$_p$ BiFeO$_3$ films grown on (001) Si substrates are under biaxial tensile strain due to the difference in thermal expansion between the film and the substrate. Since the amount of strain due to lattice mismatch decreases with the thickness of the BiFeO$_3$ films due to strain relaxation, different states of compressive and tensile strains can be obtained by changing the thickness of the BiFeO$_3$ films. Domain engineered high-quality (001) BiFeO$_3$ films have been achieved using substrate miscut [1]. Decent procedure was used to lift off the BiFeO$_3$ films from the Si substrate [2]. Thus we could examined the strain dependence of the ferroelectric properties of BiFeO$_3$ using compressively strained films on (001) SrTiO$_3$ substrates, tensilely strained films on (001) Si substrates, and strain-free membranes after lift-off [3].

Our measurements show that the remanent polarization of (001)-oriented BiFeO$_3$ thin films has a strong strain dependence, even stronger than (001)-oriented PbTiO$_3$ films. This is in direct contrast to (111)-oriented BiFeO$_3$ which, according to first-principles calculations, shows a very little strain dependence of...
spontaneous polarization. Thermodynamic analysis reveals that a strain-induced polarization rotation mechanism is responsible for the large change in the out-of-plane polarization of (001) BiFeO$_3$ with biaxial strain while the spontaneous polarization along the [111] direction itself remains almost constant.

Adsorption-controlled growth of BiFeO$_3$ by MBE and integration with wide band-gap semiconductors

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Epitaxial (111)$_p$ BiFeO$_3$ thin films have been deposited on (0001)-oriented GaN and AlGaN/GaN high electron mobility transistor (HEMT) structures by reactive molecular-beam epitaxy in an adsorption-controlled growth regime. Integration with GaN was realized by using intervening epitaxial (111) SrTiO$_3$ / (100) TiO$_2$ buffer layers and (111)$_p$ GdScO$_3$ and (111)$_p$ LaAlO$_3$ wide bandgap insulation layers. BiFeO$_3$ growth is achieved by supplying a bismuth over-pressure and utilizing the differential vapor pressures between bismuth oxides and BiFeO$_3$ to control stoichiometry. Four-circle x-ray diffraction and transmission electron microscopy reveal phase-pure epitaxial films. The epitaxial BiFeO$_3$ thin films have two in-plane orientations: [1$\bar{1}$20] BiFeO$_3$ $\parallel$ [1$\bar{1}$20] GaN plus a twin variant related by a 180° in-plane rotation. X-ray spectroscopic measurements of the band offsets of GdScO$_3$/SrTiO$_3$ and LaAlO$_3$/SrTiO$_3$ and GaN reveal large (∼2 eV) oxide/nitride conduction band offsets. Device simulations indicate that these layers are promising for $n$-channel GaN-based devices.
So far almost all the existing tunnel junctions were based on non-polar dielectrics. An interesting possibility to extend the functionality of tunnel junctions is to use a ferroelectric insulator as a barrier to make a ferroelectric tunnel junction (FTJ). Recent experimental and theoretical findings demonstrate that ferroelectricity persists down to vanishingly small sizes which make FTJs feasible. FTJs offer exciting prospects for device applications. In particular, the electric-field-induced polarization reversal in a ferroelectric barrier may have a profound effect on the conductance of a FTJ. One of the mechanisms is the incomplete screening of polarization charges which makes the depolarization field and hence the potential profile seen by transport electrons different for the opposite polarization orientations. In addition, the polarization switching changes positions of ions near the interfaces which affect the atomic orbital hybridizations at the interface and electronic properties of the barrier and hence alter the transmission probability. Functional properties of a FTJ can be extended by replacing normal metal electrodes by ferromagnets which makes the junction multiferroic. In such a multiferroic tunnel junction (MFTJ), where a thin ferroelectric film is used as a barrier, spin-dependent tunneling may be controlled by reversing the electric polarization of the ferroelectric. In other words, by changing the electric polarization of the barrier one can influence the spin polarization of the tunneling current and the tunneling magnetoresistance. This talk will address the physics of FTJs and MFTJs based on our recent model and first-principles calculations. We will also discuss possible implications following from the interplay between ferroelectric and ferromagnetic properties of the two ferroic constituents in these junctions resulting in the interface magnetoelectric effects.

Magnetoelectric coupling through exchange bias at La$_{0.7}$Sr$_{0.3}$MnO$_3$/BiFeO$_3$ interfaces

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Multiferroics exhibiting simultaneously multiple order parameters, such as magnetism and ferroelectricity, offer an exciting way to explore coupled phenomena in solids. These investigations are driven by the prospect of magnetoelectric coupling in which charges are controlled by applied magnetic fields and spins by applied voltages. The recent availability of high-quality thin-film samples of hexagonal manganites and Bi-based perovskites, has improved the ability to accurately characterize multiferroic behavior, and has opened the door to the fabrication of practical devices based on magnetoelectric coupling. Currently, bismuth ferrite BiFeO$_3$ (BFO) is being intensely explored since both ferroelectric (~820 °C) and antiferromagnetic (~370 °C) ordering temperatures are much higher than room temperature, which make it appealing for ambient applications. Recent studies have demonstrated the existence of strong coupling between ferroelectricity and antiferromagnetism. Since the intrinsic canted ferromagnetism in BFO is too small in magnitude to be useful, current approaches have focused on heterostructures consisting of a ferromagnet in intimate contact with the multiferroic. These studies have used a conventional metallic ferromagnet such as Co$_{0.9}$Fe$_{0.1}$ to couple to the BFO through exchange coupling at the interface. The existence of double exchange coupled
ferromagnets such as La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) provides us with an alternative approach to probe magnetic coupling at epitaxial oxide interfaces. Within this framework, we report the first observation of exchange bias coupling between the ferroelectric/antiferromagnet (multiferroic) BFO and the ferromagnet (LSMO) in high quality heterostructures. We will provide a suggestion for the cause of this interesting interface effect based on results from an extensive amount of magnetic measurements, structural analysis measurements (such as STEM-EELS) and first principles calculations. Finally, we will show the first indications of magnetoelectric coupling at these interfaces by magneto-optical Kerr effect measurements, while switching the polarization direction.
Magnetoelectric coupling in complex oxides with competing ground states

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Recent efforts to exploit materials with multifunctional capabilities have rekindled interest in multiferroic materials, which are characterized by a coupling between ferroic order parameters. Recently, artificially formed structures that combine separate magnetic and ferroelectric materials epitaxially have been recognized as materials that exhibit enhanced magnetoelectric coupling. While composite multiferroics relying on piezo- or magnetoelastic coupling to modulate magnetic anisotropies have been proposed, here, we demonstrate a carrier-based coupling between magnetic and electric order parameters in ferroelectric / Sr-doped lanthanum manganite heterostructures.

Off-axis RF magnetron sputtering was used to deposit epitaxial ferroelectric Pb(Zr,Ti)O\textsubscript{3} (PZT) / La\textsubscript{0.8}Sr\textsubscript{0.2}MnO\textsubscript{3} (LSMO) heterostructures with low leakage current density, high crystalline quality, and atomically smooth surfaces. X-ray diffraction shows c-axis oriented growth of PZT, with a typical root-mean-square (RMS) surface roughness of \( \sim 5\text{Å} \). We use magneto-optic Kerr effect (MOKE) magnetometry to directly probe the local magnetic state of the LSMO as a function of the PZT polarization states. We demonstrate direct control of magnetism via applied electric fields, including on/off switching of magnetism. The coupling between magnetic and electric order parameters in ferroelectric / Sr-doped lanthanum manganite heterostructures is illustrated by hysteretic M-E (magnetization vs. electric field) loops, with a measured magnetoelectric susceptibility of \( \alpha^3_{33} = 1.6 \text{ Oe cm / kV}^{-1} \).
Nanoscale study of coupled ferroelectric / antiferromagnetic domain walls in BiFeO$_3$ multiferroic thin films

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Multiferroics, displaying several ferroic orders among ferroelectricity, ferro (or antiferro-)magnetism and ferroelasticity are of significant interest for applications due to the possibility of a magnetoelectric effect allowing a change of the magnetic order by an electric field or of the electric polarization by a magnetic field. A promising candidate for room temperature devices is BiFeO$_3$ (BFO) which is antiferromagnetic (AFM) and ferroelectric up to high temperatures. Due to its AFM ordering, this material can be exchange coupled with a ferromagnetic electrode [1] allowing the magnetic state of the device to be tuned by an electric field via the magnetoelectric effect [2].

Comparing the exchange field in such devices with nanoscale measurements of the intrinsic (as-grown) ferroelectric domain configuration [1], we showed that antiferromagnetic and ferroelectric domains are coupled. Moreover, the exchange field varies inversely with the size of the multiferroic domains [1]. Multiferroic domains and domain walls are thus of crucial interest for the electrical control of magnetization through magnetoelectric coupling.

To better understand the magnetoelectric coupling mechanisms at the nanoscale, we studied the ferroelectric domain switching and growth under an applied electric field, as well as the static equilibrium configuration of the domain walls in BiFeO$_3$ thin films using Piezoresponse Force Microscopy. We observed a behavior different from that of pure ferroelectric or ferromagnetic 180° domain walls [4]. The possible influence of the magnetic contribution on the ferroelectric domain wall behavior will be discussed.

Predicting domain structures and properties of ferroelectric thin films using the mesoscale phase-field approach

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This presentation will discuss the applications of the phase-field approach to predicting phase transitions, domain structures, and properties of ferroelectric thin films. In this approach, a nanoscale domain structure is described using a set of spatially inhomogeneous distributions of order parameters such as polarization and strains. Their temporal evolution toward equilibrium is obtained by solving the coupled time-dependent Ginzburg-Landau equations as well as the electrostatic and mechanical equilibrium equations. In particular, it will be shown that one can use it to not only help interpreting experimental observations but also provide guidance to achieve desirable transition temperatures, specific domain states, domain wall orientations, and domain wall mobility. It will also be shown that mechanical boundary conditions and stress distributions may be manipulated to tune the coercive field and dramatically enhance piezoelectric responses of ferroelectric thin films as well as the mangetoelectric responses of multiferroic nanocomposites. Examples to be discussed are drawn from recent collaborations between the author’s group in continuum and mesoscale modeling and a number of experimental groups on oxide film growth and characterizations.
Nucleation and growth mechanism of ferroelectric domain-wall motion
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University of Pennsylvania

The motion of domain walls is critical to many applications involving ferroelectric materials, such as fast high-density non-volatile random access memory. [1] In memories of this sort, storing a data bit means increasing the size of one polar region at the expense of another, and hence the movement of a domain wall separating these regions. Experimental measurements of domain growth rates in the well-established ferroelectrics PbTiO$_3$ and BaTiO$_3$ have been performed, but the development of new materials has been hampered by a lack of microscopic understanding of how domain walls move. [2–11] Despite some success in interpreting domain-wall motion in terms of classical nucleation and growth models [12–16], these models were formulated without insight from first-principles-based calculations, and they portray a picture of a large, triangular nucleus that leads to unrealistically large depolarization and nucleation energies. [5] Here we use atomistic molecular dynamics and coarse-grained Monte Carlo simulations to analyse these processes, and demonstrate that the prevailing models are incorrect. Our multi-scale simulations [17] reproduce experimental domain growth rates in PbTiO$_3$ and reveal small, square critical nuclei with a diffuse interface. A simple analytic model is also proposed, relating bulk polarization and gradient energies to wall nucleation and growth, and thus rationalizing all experimental rate measurements in PbTiO$_3$ and BaTiO$_3$. 

![Diagram](image-url)
References


Polarization switching using single-walled carbon nanotubes grown on epitaxial ferroelectric BaTiO$_3$ thin films

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The unique electronic properties of carbon nanotubes (CNTs) have been extensively investigated using field effect in devices where Si and SiO$_2$ function as the gate electrode and gate dielectric, respectively. An interesting alternative is to use the ferroelectric field effect, replacing the Si-based system by a thin ferroelectric (FE) film, whose remanent, locally reversible polarization can be used to control the charge-carrier density in the overlying CNT. In such devices, the CNT could also be used as a local field source for polarization switching.

We have directly grown single-walled carbon nanotubes on epitaxial BaTiO$_3$ thin films, fabricating a prototype carbon nanotube-ferroelectric device. In such devices, we demonstrated polarization switching using the carbon nanotube as a local field source, and compared this to switching mediated by an atomic force microscopy tip. The observed variation of domain growth rates in the two cases agrees with the changes in electric field intensity at the ferroelectric surface. We also observe a “memory effect” during electric transport measurements, although this appears to be due to interaction with neighboring surface states rather than to the ferroelectric polarization.


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Ultraviolet (UV) Raman scattering studies of the effects of strain and film thickness on phase transitions in nanoscale BaTiO$_3$/SrTiO$_3$ ferroelectric heterostructures, grown by molecular beam epitaxy. A series of high quality coherently strained (BaTiO$_3$)$_8$/(SrTiO$_3$)$_4$ SLs having the same thicknesses of BaTiO$_3$ and SrTiO$_3$ layers have been grown on rare earth scandate (GdScO$_3$, DyScO$_3$, SmScO$_3$) as well as SrTiO$_3$ substrates. Utilizing these substrates allowed a systematic variation of strain state in superlattices by varying the in-plane lattice constant from 3.905 Å (BaTiO$_3$ under 2.2% compressive biaxial strain, SrTiO$_3$ unstrained) to 3.99 Å (BaTiO$_3$ nearly unstrained, SrTiO$_3$ under 2.2% tensile strain). UV Raman studies provided information on the temperature-strain phase diagram of the superlattices. Raman data allowed the determination of the ferroelectric phase transition temperature ($T_c$) and indicated the presence of different ferroelectric phases with out-of-plane and in-plane components of polarization in superlattices, depending on strain and temperature. We have also applied UV Raman spectroscopy for studies of phase transitions in a series of strained single-layer ultrathin BaTiO$_3$ films with layer thicknesses varied from 4 to 25 unit cells, commensurately grown on SrTiO$_3$ substrates. Using UV excitation allowed observing the Raman peaks in single-layer BaTiO$_3$ films as thin as 4 unit cells (1.6 nm). Raman data indicate that even that thin films become ferroelectric at low temperatures (~75K). According to the UV Raman data, the $T_c$ varies in a very broad range as a function of BaTiO$_3$ layer thickness, being as high as about 920 K for the 10-nm-thick BaTiO$_3$ film, which is more than 500 K above the bulk BaTiO$_3$ value. Experimental Raman results will be compared with the thermodynamic phase-field model calculations of strain-temperature phase diagrams and ferroelectric polarization as a function of temperature and strain.

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Domain nucleation and wall dynamics in epitaxial Pb(Zr,Ti)O$_3$ films

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There have been extensive studies on ferroelectric (FE) domain dynamics due to their scientific and technological importance.[1,2] However, most techniques have serious limitations in providing the information required to understand time-dependent domain wall motion during the FE polarization switching process. The FE domain wall width is typically 1 nm or less, and the domain size typically varies from a few nm to above 1 $\mu$m. In addition, polarization switching is known to occur on a timescale between nanoseconds and seconds. Therefore, the study on domain wall dynamics in FE thin films poses a challenge due to the lengths and timescales involved.

Recently, we developed a new piezoresponse force microscopy (PFM), which can trace microscopic images of domain wall in the above-mentioned time scale. Using this technique, we systematically investigated domain dynamics in epitaxial Pb(Zr,Ti)O$_3$ thin films of 100 nm thickness.[3,4] First, we obtained experimental evidences of inhomogeneous nucleation process.[3] We found that the nucleation should play an important role in an early stage of switching and under a high electric field. Second, we measured domain wall speed $<v>$ directly from successive PFM images.[4] We observed dependence of $<v>$ on domain size and electric field. Third, we found that $<v>$ can be also obtained from switching current measurements. By combining with PFM results, we could determine $<v>$ at the creep, depinning, and flow regimes. The obtained values of the velocity and dynamical exponents indicate that the FE domain walls are fractal and pinned by disorder-induced local field.

Improper ferroelectricity in perovskite oxide artificial superlattices

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A large body of work has shown that in paraelectric/ferroelectric heterostructures with thick constituent layers electrostatics is the dominant interaction between layers. From a practical sense this provides a useful route for the tailoring of materials to particular applications [1], however, the real excitement concerning artificially layered fine period multilayers lies in the potential for phenomena that are driven by the interfaces and present markedly different behaviors from the parent compounds. Here we discuss an example of this kind of behavior; interfacially driven improper ferroelectricity in lead titanate/strontium titanate superlattices [2]. A combination of experimental measurements and first principles calculations are used to reveal the manner in which oxygen rotations at the interfaces in the structure couple in such a way as to drive a macroscopic polarization that, apart from being larger [3], also has properties that differ substantially from those associated with conventional ferroelectricity. These observations suggest an approach, based on interface engineering, to produce artificial materials with unique properties. We discuss some perspectives on how best to utilize these kinds of interactions for the design of new materials, and present a brief progress report on the new ferroelectrics lab at Stony Brook University.

References:
Combining ferroelectric and antiferrodistortive structural instabilities in perovskite oxide artificial superlattices

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Recently, we have shown that PbTiO$_3$/SrTiO$_3$ superlattices exhibit in the limit of ultra-short periods an unexpected behaviour, distinct from that of the parent compounds. This was explained from a specific coupling between ferroelectric (FE) and antiferrodistortive (AFD) structural instabilities at the layer interfaces, yielding improper ferroelectric behaviour [1]. Here, we investigate to which extent a similar type of FE/AFD coupling can be induced in other artificially layered systems. We consider different bicolor superlattices obtained from the combination of PbTiO$_3$, SrTiO$_3$, CaTiO$_3$ or BaTiO$_3$ and discuss how the intrinsic tendency of these compounds to favor either the ferroelectric or the antiferrodistortive instabilities shifts or even supresses the FE/AFD coupling. Work supported by FAME-EMMI and MaCoMuFi.

Transition between domain states in ferroelectric PbTiO$_3$ thin films driven by photochemical reaction

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The recently reported stripe-domain ground state in ferroelectric thin films [1] serve to minimize the free energy, including contributions from domain walls and depolarization effects. Here, we present evidence for a transition from this stripe-domain ground state to a monodomain state in ferroelectric films of PbTiO$_3$ driven by a photochemical reaction. The data was obtained by X-ray diffraction (XRD) and pyroelectric measurements [2].

Epitaxial thin films of PbTiO$_3$ were grown on Nb: SrTiO$_3$ (001) substrates by off-axis rf magnetron sputtering. High-resolution XRD profiles recorded along the Q$_x$ direction in reciprocal space showed distinct satellite peaks on either side of the Bragg peak, characteristic of the stripe-domain ground state. In order to control the stripe-domains over a large surface area, a photochemical technique was adopted. The stripe-domain films were dipped in a AgNO$_3$ solution under UV illumination from a high pressure mercury lamp. Upon immersion in this AgNO$_3$ electrolyte, a negative galvanic potential is established at the PbTiO$_3$ surface, and photo-assisted deposition of a surface reaction layer of Ag-rich oxide particles, which serve to screen the depolarization field, was observed.

From XRD analysis, we found that films thinner than 50 unit cells with a stripe-domain ground state switched to a monodomain state after the photochemical reaction. This transition was found to coincide with a change in crystal symmetry. Pyroelectric measurements corroborate the XRD results, showing that the monodomain state corresponds to a negatively polarized thin film, in keeping with the polarity of the estimated galvanic potential.


Reaching the Intrinsic Coercive Field of PbTiO$_3$ during Polarization Switching Induced by Changing Oxygen Partial Pressure


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In this talk we describe measurements showing that polarization switching in a ferroelectric film resulting from an applied chemical gradient can occur by a non-nucleated (continuous) process, consistent with reaching the intrinsic value of the coercive field. Earlier work has shown that the polarization state of an ultrathin ferroelectric oxide can be altered by changing the chemistry of its environment. Our experiments have found that changing the partial pressure of oxygen (pO$_2$) in the gas above an epitaxial PbTiO$_3$ film can induce inversion in the sign of the polarization. Here we have investigated the unexpectedly large changes in polarization that can be achieved before switching occurs. We present in-situ x-ray scattering measurements during chemical switching of 5-nm-thick PbTiO$_3$ on SrRuO$_3$, lattice matched to SrTiO$_3$ (001). These x-ray measurements allow us to determine the polarization magnitude and domain distribution as a function of pO$_2$ during switching. At temperatures below 500°C, switching occurs by the usual mechanism of nucleation and growth of 180° domains having the same polarization magnitude but opposite signs. At 550°C, switching of the polarization occurs without nucleation: the polarization magnitude decreases to zero and changes sign uniformly without domain formation. This behavior is in quantitative agreement with the predictions of Landau theory for the case in which nucleation is suppressed and switching occurs at the intrinsic coercive field. Since the measured coercive field for oxide ferroelectrics never reaches the intrinsic value in experiments using applied electric field, our results indicate that the barrier to nucleation of inverted domains is unexpectedly large during chemical switching. Work supported by the U. S. Department of Energy under Contract No. DE-AC02-06CH11357.

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Monitoring oxide thin film growth with in-situ scanning force microscopy

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Scanning Force Microscopy (SFM) is one of the most important tools in nanotechnology and surface science. Because of recent developments, it is nowadays also used to study dynamic processes, such as thin film growth and surface reaction mechanisms.

We have realized a system, in which SFM can be performed during Pulsed Laser Deposition (PLD). Deposition and force microscopy are performed in one vacuum chamber and via a fast transfer (in the order of seconds) the surface of a sample can be scanned. In our system we take advantage of the pulsed deposition process, because microscopy measurements can be carried out between the pulses. This provides real-time morphology information on the microscopic scale during growth. The transfer mechanism allows switching between microscopy and deposition with a re-position accuracy of ±500 nm which gives new opportunities to study growth processes. Furthermore, it can provide information if RHEED is not possible, for example during amorphous and polycrystalline growth.

In our experiments, we used an inverted fiber SFM, based on a commercially available SFM (Ultraobjective from SIS GmbH, Germany). The piezo-scanner is thermally isolated from the heat source by placing a 20mm long macor-tube on top of the scanner. The geometry of the electrodes of the piezo scanner is such that, at the maximum applied voltage, no voltage breakdown is expected in the pressure range of interest.

Using the modified SFM, measurements at elevated temperature are possible in which the maximum operating temperature merely depends on the thermal load. To minimize this load, we developed a low power heating stage. Small thermal mass heaters are designed to obtain stable monitoring at temperatures >700ºC in a high-pressure environment.

In this contribution, the in-situ SFM will be presented as well as the latest equipment developments. With high-temperature microscopy, growth characterization at typical deposition conditions of complex oxides becomes feasible.
Modulation doping of electrons and holes at vanadate interfaces

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Recently, there has been significant interest to explore and utilize electronic reconstructions at transition metal oxide interfaces. Here we survey our current understanding of the valence changes that can be induced at interfaces with vanadium oxides. These materials are fertile ground for such studies, since they can be formed with a wide range of valences from $V^{2+}$ to $V^{5+}$, spanning Mott insulators, band insulators, and correlated metals.

The growth phase diagram of thin film LaVO$_x$ varies from perovskite LaV$^{3+}$O$_3$ to monazite LaV$^{5+}$O$_4$ with increasing oxygen partial pressure, with an extended region of mixed phase growth [1]. At an abrupt interface between LaVO$_3$ and LaVO$_4$, although no bulk structure of LaV$^{4+}$O$_x$ exists (i.e., pyrochlore La$_2$V$_2$O$_7$ cannot form in bulk), the valence smoothly varies from $V^{3+}$ to $V^{5+}$, inducing a nanometer-wide region of V$^{4+}$ at the interface[2].

LaVO$_3$/SrTiO$_3$ heterointerfaces exhibit a strong interface dependence on their electronic properties [3]. The (001)-oriented $n$-type VO$_2$/LaO/TiO$_2$ polar discontinuity is conducting, while the (001) $p$-type VO$_2$/SrO/TiO$_2$ interface, formed by inserting a single layer of bulk metallic SrVO$_3$ or SrO, drives the interface insulating. The (110) heterointerface is also insulating, indicating interface conduction arising from electronic reconstructions.

Conductivity at the $n$-type LaVO$_3$/SrTiO$_3$ interface requires a minimum critical thickness of 5 unit cells of LaVO$_3$, similar to that found for LaAlO$_3$/SrTiO$_3$ structures [4], which can be understood by considering the electrostatic coupling between the polar surface and the interface at short length-scales. This coupling can be used to induce hole-doping in LaAlO$_3$/LaVO$_3$/LaAlO$_3$ quantum wells by providing an alternative electronic reconstruction to the usual polar surface reconstruction of LaAlO$_3$ [5, 6].

Depth profiling of lanthanum defects in the LaAlO$_3$/SrTiO$_3$ hetero-interfaces using middle energy ion spectroscopy

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Since the discovery of the conducting LaAlO$_3$/SrTiO$_3$ (LAO/STO) interface [1], doping mechanism of these separately insulating perovskite oxide materials have been widely discussed. Mainly two possible mechanisms have been considered: a polar catastrophe model and oxygen vacancies. Recently, cationic mixing at the interfaces has been reported by Willmott et. al., and may result in the formation of metalic La$_{1-x}$Sr$_x$TiO$_3$ layer [2]. In order to better understand the microscopic origin of conducting interfaces, we have used middle-energy ion scattering spectroscopy (MEIS). The MEIS technique is based on the analysis of the energy spectra and angular dependencies of ions backscattered from the film with incoming ion energies of 100 keV. It allows a careful, non-destructive determination of the composition and depth profiling in very thin films [3]. We have studied the heterostructures of LAO/(100) STO grown at different oxygen pressures (10$^{-2}$ mbar, non-conducting, and 10$^{-4}$ mbar, conducting). The thickness of the LAO films was varied from 1 to 15 unit-cells. A pronounced distortion of the La sub-lattice was detected for the 1-3 unit cell thick LAO films. The distortion is decreasing with in creasing of film thickness, becoming non-detectable in 8 unit cell thick film. The best fit of an experimental MEIS spectra and results of computer simulations was achieved if about 10% of the La ions from LAO layer are concentrated near the interface. Our observations support the possibility of doping due to cationic mixing at the interface. On the other hand, cationic defects may also stabilize oxygen vacancies in the STO substrate.

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A First Principle Study of LaAlO$_3$/SrTiO$_3$ Heterointerfaces

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In order to understand the origin of the intriguing high-mobility quasi two dimensional electron gas formed at LaAlO$_3$/SrTiO$_3$(001) heterointerfaces, we carry out first principle calculations on the electronic structure and properties of these oxide interfaces. The intrinsic polar properties are investigated and the average electronic potential increase by each LaAlO$_3$ layer is calculated, explaining the recent observations of an insulating-to-metallic transition above a critical LaAlO$_3$ thickness. When the interface becomes metallic, we find that the spatial distributions of mobile electrons and holes reveal a fundamental asymmetry between the n-type and p-type interfaces. This may provide an explanation for the observed drastic difference in conductivities of these two types of interface. A large cation-cation hopping matrix element across the interface which only exists at the n-type interface turns out to be the key reason for this asymmetry. This novel mechanism may provide a robust means of tuning interfacial conductivities and open a new pathway to nanoengineering oxide interfaces.
Electrostatic tuning of the SrTiO$_3$/LaAlO$_3$ interface ground state


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At interfaces between complex oxides, electronic systems with unusual properties can be generated. As reported first by Ohtomo and Hwang [1], a highly mobile electron gas is formed at the interface between LaAlO$_3$ and SrTiO$_3$, two insulating dielectric perovskite oxides. Recently, two possible ground states have been experimentally identified: a magnetic state [2] and a two dimensional superconducting condensate [3]. We have used the electric field effect to explore the phase diagram of the system. The electrostatic tuning of the carrier density allows an on/off switching of superconductivity and drives a quantum phase transition between a 2D superconducting state and an insulating state. Analyses of the magnetotransport properties in the insulating state are consistent with weak localization and do not provide evidence for magnetism.

References

Impact of the microstructure on the transport properties of the electron gas at LaAlO₃-SrTiO₃ interfaces

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We report on first experiments in which well defined defects have been incorporated into the electron gas generated by LaAlO₃-SrTiO₃ interfaces. These experiments reveal that besides the LaAlO₃ layer thickness, possible oxygen vacancies, and substrate termination, dislocation scattering is a key parameter in controlling the properties of the interface electron gas. The data suggest that a reduction of the dislocation density will enhance the mobility of the electron gas, which is a function of the microstructural quality of the SrTiO₃ substrates and the LaAlO₃ films.
Magnetoresistance oscillations and relaxation effects at the SrTiO$_3$–LaAlO$_3$ interface

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The discovery of conducting interfaces between the insulating perovskites SrTiO$_3$ and LaAlO$_3$ [1] has generated intensive research in recent years. The conduction arises from a charge redistribution that occurs at the interface in order to counteract an otherwise diverging electric potential in a polar material. So far, oxide interface samples exhibited metallicity, superconductivity below 200 mK and magnetic hysteresis below 300 mK [2]. Here we present transport measurements on SrTiO$_3$ — LaAlO$_3$ interfaces at 50 mK in magnetic fields up to 30 T [3]. The data provide insight in the nature of the magnetic phenomena and dimensionality of the transport. The hysteresis relaxes logarithmically as a function of time, suggestive of the presence of magnetic frustration. We observe magnetoresistance oscillations, which are periodic in $\sqrt{B}$, and not periodic in $1/B$, as is the case for the well-known Shubnikov-de Haas oscillations. A possible relation with the formation of edge states on substrate terrace edges is discussed. The presence of such states would imply the existence of a highly mobile 2D electron gas at the interface.


FIG. 1. Magnetoresistance as a function of applied magnetic field at 50 mK, showing both hysteresis and oscillations.
Electric Double Layer Transistor

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Electrostatic carrier doping in MIS-FET structures has been expected as a potentially powerful tool for controlling electronic states of matter for many years, because it is basically free from disorder effects. However, the phase control by electric field has been seriously limited so far, because the maximum voltage available in the conventional MIS-FETs is not sufficient for inducing electronic phase changes. Here we propose a novel approach for this purpose by employing an electrochemical device concept.

When voltage is applied between two electrodes in an electrochemical cell, ions in electrolyte move toward both electrodes driven by the electric field. Finally, ions are stabilized right above the electrode surface to form an electric double layer (EDL), a kind of capacitor, which has an ability of high density charge accumulation. This capacitor device, called electric double layer capacitor (EDLC) is already on market as a high density and high speed capacitor. If one of the electrodes is replaced by a semiconductor with a source and drain electrodes, this device works as a field effect transistor, which can be called an electric double layer transistor (EDLT). EDLT can be also formed using another type of ionic conductors, which is ionic liquid.

We have tested this type device on a number of semiconductor materials, including oxide semiconductors, using electrolytes and ionic liquids, and found that the high density charge accumulation up to $6 \times 10^{14} \text{ cm}^2$ is indeed achieved in the EDLTs. We talk about charge accumulation behavior in EDLTs with particular emphasis on oxide semiconductors, and associated electronic behaviors, such as gate-induced insulator-metal transition in ZnO and superconductivity in SrTiO$_3$.

This work has been carried out in collaboration with H. Shimotani, H. T. Yuan, J. T. Ye, A. Tsukazaki, A. Ohtomo, K. Ueno, and M. Kawasaki.
Fabrication of Erasable Field-Effect Nanodevices at the LaAlO$_3$/SrTiO$_3$ Interface

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Future contributions of oxide electronics to information technology will depend on their ability to scale properties of interest to nanometer dimensions. Previously, we reported$^1$ that the metal-insulator transition at the interface between LaAlO$_3$ and SrTiO$_3$ can be controlled locally and reversibly at room temperature. Using a biased conducting atomic force microscope (AFM) probe, it is possible to create conducting lines with widths < 4 nm and dots with diameters < 2 nm. Here we describe the creation and erasure of sub-10-nm tunnel junctions and field-effect transistors in this system, using voltages applied in a similar manner. These two and three-terminal devices are constructed using a combination of writing and erasing steps. This demonstrated ability to place and route nanoscale active devices may provide a new method for reconfigurable electronics.


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High mobility multi-layer graphene field effect transistors fabricated on epitaxial ferroelectric gate oxides

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We report the first successful implementation of an epitaxial ferroelectric thin film as the substrate gate oxide to fabricate multi-layer graphene (MLG) field effect transistors (FETs). Recent studies show that the intrinsic mobility $\mu$ of graphene, set by longitudinal acoustic (LA) phonon scattering, can reach $\sim 10^5$ cm$^2$/Vs at room temperature. However, extrinsic scattering sources, many of which arise from the surface morphology, chemistry, structural and electronic properties of the widely used SiO$_2$ substrate limit the mobility to the current range of $2 \times 10^3$ – $2 \times 10^4$ cm$^2$/Vs. Increasing the mobility beyond these extrinsic limits is one of the central challenges of the graphene community. Very recently, two groups have reported a significant improvement in $\mu$ on suspended graphene after current-heating annealing. A more device-friendly solution involves replacing SiO$_2$ with a substrate oxide with higher dielectric constant or lower impurity density.

Here we have demonstrated a significant performance improvement in multi-layer graphene FETs by using the crystalline ferroelectric gate oxide Pb(Zr$_{0.2}$Ti$_{0.8}$)O$_3$ (PZT). The PZT gate shows high charge injection efficiency, corresponding to a dielectric constant ($k$) of $\sim 100$. The carrier mobility $\mu$ of the device shows a ten-fold increase compared with that of SiO$_2$-gated devices. At a technologically relevant density of $n = 2.4 \times 10^{12}$/cm$^2$, $\mu$ is $7 \times 10^4$ cm$^2$/Vs at 300 K, 70% of the intrinsic limit set by LA phonons; it reaches $1.4 \times 10^5$ cm$^2$/Vs at low temperature. The temperature-dependent resistivity $\rho (T)$ reveals a clear signature of LA phonon scattering. We attribute this remarkable improvement to the strong screening capacity of PZT due to its high $k$ nature and possibly a high degree of ordering in the interfacial adsorbate layer, which forms in registry to the lattice sites of the crystalline PZT substrate. Our results open up a promising route into realizing graphene’s full scientific and technological potential.
Photocatalytic properties of ultrathin TiO$_2$ layers on Si substrates

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Ionic oxides such as TiO$_2$ have been promising as surfaces for photocatalytic cleavage of water or oxidation of toxic molecules for pollutant remediation. Using an in-situ mass spectrometry based technique, we have studied the photocatalytic properties of ultra-thin nm scale films of TiO$_2$ on silicon substrates, using the isopropyl alcohol (IPA) to acetone conversion reaction under UV irradiation as a model reaction. We show that TiO$_2$ films as thin as 2nm exhibit photocatalytic behavior, and that by controlling the Fermi level in the non photoactive semiconductor (i.e. Si substrate), we can control the photocatalytic activity in the photoactive layer (i.e. TiO$_2$). Based upon the results we present a model for the photocatalysis that points to the role of oxygen vacancies in the metal oxide, and that the reaction rate is limited by the annihilation of these vacancies by ambient oxygen.
All-Oxide Microelectromechanical Systems for Strain Manipulation of Epitaxial Oxide Thin Films

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Microelectromechanical Systems (MEMS) are widely employed in different technological fields as sensors and actuators. MEMS technology is mainly based on silicon manufacturing processes and thus on silicon-compatible materials which often are not crystalline.

The functionalities of MEMS can be greatly enriched with the use of crystalline oxide thin films and heterostructures. Transition metal oxides (TMO), especially perovskite-type compounds, have a broad range of physical properties and can be grown epitaxially in thin films and multilayers. Many of these materials show transport, magnetic and optical properties which can be tuned by chemical doping or, in a reversible way, by electric charge induction or mechanical stress. So far, few works on functional oxide MEMS have been reported, mainly with ferro-piezoelectric materials grown on structures made of silicon.

In this work, we report the fabrication and the characterization of MEMS entirely based on crystalline transition metal oxide thin films. A suspended element made of SrTiO₃ (STO) is mechanically bent by external pressure through an AFM tip or by an external electric field. Strain due to bending of the STO cantilever is mechanically transferred to epitaxial films deposited over the STO element by Pulsed Laser Deposition. Strain manipulation of epitaxial oxide thin films can be thus realized with these devices. Electrical characterization of all-oxide MEMS will be presented with first applications to strain modulation of the electrical state of manganite thin films.
Resistive switching in oxides - known facts, disregarded issues, and open questions

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A classification of oxide-based resistive switching phenomena for potential non-volatile memory devices, will be proposed and the conceivable microscopic mechanisms will be discussed. A critical review of the literature will show that wishful thinking and speculations sometimes dominate over scientific proof. The paper will try to collect the hard facts, separate them from speculations, and discuss some frequently disregarded issues. In addition, the major open questions in conjunction with resistive switching in oxides will be worked out.
Acceptor formation and light-emitting diode fabrication using phosphorus-doped ZnO


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The formation of p-type ZnO films and subsequent synthesis of light emitting junctions (LED) will be reported. A significant challenge for ZnO LEDs is the formation of p-type material. In recent studies, we have reported the growth of p-type ZnO in P-doped ZnO grown by pulsed laser deposition (PLD). As-grown ZnO:P samples show n-type characteristics, presumably due to the formation of anti-site P$_{Zn}$ defects. Rapid thermal annealing yields a carrier type conversion from n- to p-type for the ZnO:P films grown at ~ 700ºC; samples grown at substantially lower or higher temperatures tended to remain n-type even after thermal annealing process. The properties and behavior of the n-to-p conversion is consistent with the formation of P$_{Zn}$-2V$_{Zn}$ as the active acceptor state. The synthesis and properties of ZnO LED heterojunctions employing these P-doped ZnO materials will also be discussed. ZnO-based light emitting diodes were fabricated on c-plane sapphire using ZnO:P/ Zn$_{0.9}$Mg$_{0.1}$O/ZnO/ Zn$_{0.9}$Mg$_{0.1}$O/ZnO:Ga p-i-n heterostructures. Annealed p-i-n heterojunction diodes diodes show band-edge electroluminescence and a broad defect band with a peak at 930nm at room temperature. Properties of the materials and devices, along with prospects for significant improvement in LED performance will be discussed.

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The role of morphology, polarity, and defects on ZnO near-surface optical emission

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Advances in ZnO growth and processing are enabling optoelectronic applications, yet ZnO’s optical emission properties at the nanoscale are relatively unexplored. We used nanoscale depth-resolved cathodoluminescence spectroscopy (DRCLS), atomic force microscopy (AFM), and Kelvin probe force microscopy (KPFM) to measure the spatial distribution of native point defects within the outer few hundred nanometers of the surface for leading ZnO growth and processing techniques and identified how surface morphology and polarity impact sub-gap recombination and the efficiency of near band edge (NBE) optical emission. ZnO crystals grown by melt, hydrothermal, and vapor-phase transport methods display independent, orders-of-magnitude variation in 2.1, 2.5, and 3.0 eV native point defect optical transitions at their free surface and as a function of nanometer depth from <5 to ~1000 nm below the surface. AFM reveals large variations in surface roughness, asperities, and extended features related to the growth method, subsequent polishing and etching. UHV-clean Zn-polar surfaces exhibit significantly higher NBE emission, lower (0.2 vs. 0.4 nm) rms roughness, lower point defects, and lower near-surface donor segregation than O-polar surfaces of the same crystals. KPFM maps of surface and subsurface electric potential acquired simultaneously exhibit systematic correlations with DRCLS-measured native point defect distributions. When DRCLS emissions vary with depth, potential maps can vary by hundreds of meV over smooth morphologies, emphasizing the impact of sub-surface defects on surface electronic properties. Detailed depth correlations show that chemomechanical polishing can reduce outer layer roughness and native defects while sub-surface defect and potential features remain. The relative strength of near band edge to deep level defect emissions exhibits a dramatic threshold dependence on surface roughness: surface optical emission efficiency increases over ten-fold as roughness decreases to unit cell dimensions, highlighting the coupled role of surface morphology, polarity, and depth-dependent defects for high efficiency ZnO emitters.
Employing Uniform Reversible Film Strain from a Piezoelectric Substrate to Examine Effects of Strain in Epitaxial Oxide Thin Films.

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Epitaxial oxide thin films frequently exhibit different properties than their bulk counterparts. Epitaxial strain can play a key role in these changes and can be induced in a thin film by using piezoelectric substrates. This reversible approach differs significantly from that in which similar films are grown on different substrates with varying lattice mismatch and thickness. In the latter method, the intrinsic effect of strain may be obscured by variations in defect structure and composition between different films. Therefore, in this work piezoelectric 0.70Pb(Mg₀.₅,Nb₀.₅)O₃-0.30PbTiO₃ (PMN-PT) was utilized as a substrate, allowing us to vary the epitaxial strain in a single film by up to 1%, with the elastic response of the film being monitored by in and out-of-plane x-ray diffraction, yielding a reliable and direct method to determine the Poisson ratio of several oxide films. SrTiO₃, BiFeO₃, MgO, and LaScO₃ thin films were grown epitaxially on polished PMN-PT substrates by pulsed-laser deposition. Thin bottom electrodes of La₁₋ₓSrₓMnO₃ were used to apply the electric field across the substrate. The Poisson’s ratio for the monoclinic phase of BiFeO₃, which had not previously been determined, was found to agree with theoretical predictions, and the values for MgO and SrTiO₃ were found to agree with bulk values. The structural changes in the BiFeO₃ and SrTiO₃ thin films were mapped as a function of strain to characterize how the structure of the thin films change as a function of strain. The details of these results and the ability of this technique to change the strain of an epitaxial thin film will be discussed.

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Rare-earth based alternative gate-dielectrics for future integration in MOSFETs

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The dielectric SiO$_2$ has been the key to the tremendous improvements in Si-based metal-oxide-semiconductor (MOS) device performance over the past four decades. It has, however, reached its limit in terms of scaling since it exhibits a leakage current density higher than 1 A/cm$^2$ and does not retain its intrinsic physical properties at thicknesses below 1.5 nm. In order to overcome these problems and keep Moore’s law ongoing, the use of higher dielectric constant ($\kappa$) gate oxides has been suggested. These high-$\kappa$ materials must satisfy numerous requirements such as the high $\kappa$, low leakage currents, suitable band gap and offsets to silicon. Rare-earth based dielectrics are promising materials which fulfill these needs. We will review the properties of $RES\text{ScO}_3$ ($RE =$ La, Dy, Gd, Sm, Tb) and LaLuO$_3$ thin films, grown with pulsed laser deposition, e-gun evaporation or molecular beam deposition, integrated in capacitors and transistors. A $\kappa > 20$ for the $RES\text{ScO}_3$ ($RE =$ Dy, Gd) and around 30 for ($RE =$ La, Sm, Tb) and LaLuO$_3$ are obtained. Transistors prepared on SOI and sSOI show mobility values up to 380 cm$^2$/Vs on sSOI, which are comparable to such prepared with HfO$_2$.

References

Electronic structure of termination-controlled SrTiO$_3$/La$_{0.6}$Sr$_{0.4}$MnO$_3$ interface studied by hard X-ray photoemission spectroscopy

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Spin tunneling junction based on the half-metallic materials like La$_{0.6}$Sr$_{0.4}$MnO$_3$ (LSMO) has a great potential to apply tunneling magnetoresistance (TMR) devices. However, the performance of the TMR devices composed of LSMO and SrTiO$_3$ (STO) is far worse than what is expected from the half metallic nature, suggesting the formation of dead layers at the interface [1]. One of the possible origins of the dead layer formation is over hole doping in Mn ions from the SrO layers of STO across the interface [1]. Since STO/LSMO junctions along c-axis have two types of terminating interfaces, TiO$_2$-La$_{0.6}$Sr$_{0.4}$O-MnO$_2$ or TiO$_2$-SrO-MnO$_2$, the charge redistribution by the different terminating layers will play a key role in the interfacial electronic structures of LSMO. In order to investigate the termination dependence of interfacial electronic structures, we have carried out hard X-ray photoemission spectroscopy. We have found that Mn 2p core level spectra show the clear difference between the two interfaces. The detailed analysis revealed that the Mn ions at the TiO$_2$-La$_{0.6}$Sr$_{0.4}$O-MnO$_2$ terminated interface were much reduced in comparison with the TiO$_2$-La$_{0.6}$Sr$_{0.4}$O-MnO$_2$ terminated interfaces. The difference may originate from the over hole doping in Mn ions from the SrO atomic layer at the interface. These results suggest that the precise control of chemical composition in terminating layers is necessary to realize high performance TMR devices.

Anomalous Hall effect in Eu$_{1-x}$La$_x$TiO$_3$ films

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We have fabricated epitaxial films of Eu$_{1-x}$La$_x$TiO$_3$ (x=0-0.1) on (001) LSA T substrates by a pulsed-laser deposition method. High temperature growth in reductive atmosphere enabled a step flow growth mode, resulting in atomically flat and high crystallinity films. Eu$_{1-x}$La$_x$TiO$_3$ films show antiferromagnetic transitions below 9 K and external magnetic field induces ferromagnetic transition as previously reported in single crystal samples [1]. The La doping induces an insulator to metal transition, where the carrier density could be controlled from $1 \times 10^{18}$ to $1.5 \times 10^{21}$ cm$^{-3}$ as determined by the normal contribution (negative sign) of Hall effect. Below the antiferromagnetic transition temperature, an anomalous Hall effect was clearly observed in all the conductive films. This is the first observation of the anomalous Hall effect in electron doped EuTiO$_3$ system. Interestingly, the sign of the anomalous Hall effect changes from negative to positive as the carrier density increases. Such unusual behavior of anomalous Hall effect might be related to the mechanism of anomalous Hall effect in SrRuO$_3$ that is explained by the Berry phase at the singularity point in band structure [2].

Indications for Coulomb-gap formation in the metal-insulator transition of La\textsubscript{0.67}Ca\textsubscript{0.33}MnO\textsubscript{3}

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Although much by now is known about the physics of doped manganese oxides such as La\textsubscript{1-x}Ca\textsubscript{x}MnO\textsubscript{3}, a question of both practical and fundamental interest still is at what length scales the (connected) phenomena of the Metal-Insulator transition (at a temperature T\textsubscript{MI}) and phase separation influence the physical properties of the system, and what role is played by the disorder. We have studied 10 nm thick La\textsubscript{0.67}Ca\textsubscript{0.33}MnO\textsubscript{3} (LCMO) thin films structured into microbridges by e-beam lithography and Ar-etching. They were grown on 1°-miscut SrTiO\textsubscript{3} (STO) substrates, which puts the film under a small tensile strain. Special care has to be taken in structuring the microbridges since the Ar-etching can damage the STO, creating a conducting surface layer, but a brief oxygen plasma etch recovers the insulating state of the STO surface[1]. Upon cooling, such bridges show linear current (I)-voltage (V) characteristics both above and below T\textsubscript{MI}. However, around T\textsubscript{MI} we always find a (small) regime of non-linear behavior, described by a differential resistance peak at zero bias which disappears under influence of a magnetic field. We suggest that this effect is due to the combination of disorder and a low carrier concentration in the transition, which are known ingredients for the formation of a Coulomb gap. Given variations in disorder and percolation behavior it can be expected that structured samples are quite sensitive to such a gap. The interpretation is further supported by Scanning Tunneling Microscopy measurements on similar samples grown on NdGaO\textsubscript{3}, as well as by electric field effect measurements with STO as the gate electrode. The gap formation appears to be a generic feature of the phase transition, and can explain the observation of various anomalies reported in the literature.

Growth on polar interfaces: enhanced segregation in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$

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The rich electronic and magnetic properties of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO) have given rise to a wide range of research on topics including colossal magnetoresistance, giant electroresistance, spin injection applications, and strain-induced orbital ordering. LSMO is also a widely used cathode material in solid oxide fuel cells (SOFCs) because of its excellent catalytic properties, good electronic conductivity, and chemical stability at high temperatures. In each case, the relevant properties depend on the interplay between the strontium concentration, the manganese charge state, and oxygen nonstoichiometry. Surface composition can be strongly influenced both by thermally driven rearrangements during high temperature operation and by intrinsic driving forces (e.g. interface polarity) during crystal growth where atoms respond with relatively high mobility. We have measured both equilibrium and growth induced strontium surface segregation using in situ synchrotron measurements of total reflection x-ray fluorescence. We observe strontium surface segregation in (001)-oriented $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films over a wide range of temperatures (25-900°C) and oxygen partial pressures ($p_{O_2} = 0.15$-150 Torr). The strontium surface concentration is observed to increase with decreasing $p_{O_2}$, suggesting that the surface oxygen vacancy concentration plays a significant role in controlling the degree of segregation. In contrast, the $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ film thickness and epitaxial strain state has little impact on segregation behavior. The surface strontium enrichment persists in $\text{LaMnO}_3$-capped LSMO thin films, suggesting that segregation occurs during the pulsed laser deposition growth in response to the polar $\text{LaMnO}_3$ surface. Using these results, we discuss the impact of surface polarity and point defect chemistry on the surface composition and growth of LSMO thin films.
ZrO$_2$ – In$_2$O$_3$ Heterointerface Structure and Properties: a Density Functional Theory Study

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The combination of an ionic oxide conductor with an electronic oxide conductor in a heterostructure configuration has great potential to generate new and interesting properties through proximity effects at interfaces. These effects may be especially prominent in nanoscale superlattices, where the high density of such interfaces can lead to novel transport properties distinct from those in their bulk counterparts. A first-principles study based on density functional theory calculations of epitaxially matched ZrO$_2$ – In$_2$O$_3$ (001) heterostructures is performed to identify stable interface configurations as a function of oxygen and electron chemical potentials. Two different interfaces, each sharing a common oxygen plane, are considered for the (001) orientation: (1) a flat interface with two types of In atoms (8b and 24d) present at the interface, and (2) a buckled interface with one type of In atom (24d). We present results on the atomic and electronic structure of these interfaces as a function of oxygen partial pressure. Calculations of oxygen vacancy diffusion at the interface have also been carried out, providing insight into the effects of interfacial proximity on optical and conduction properties. The results are compared with those from synchrotron x-ray scattering and transport measurements on sputter-deposited ZrO$_2$ – In$_2$O$_3$ heterostructures. The impact of Y and Sn dopants in ZrO$_2$ and In$_2$O$_3$, respectively, on interfacial segregation behavior and electrical transport will also be discussed. This work is supported by the U.S. Department of Energy under Contract No. DE-AC02-06CH11357.
Spin-polarized current effects in disordered half-metal

La$_{0.7}$Ba$_{0.3}$MnO$_3$ thin films

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We investigate the transport properties of half-metal La$_{0.7}$Ba$_{0.3}$MnO$_3$ (LBMO) thin films deposited on SrTiO$_3$ (STO) and MgO substrates. Despite the quite similar structural features if compared to crystalline manganite films, the dc transport measurements show different metal-insulator transition temperatures for the two analyzed systems (345K and 200K for LBMO films grown on STO and MgO substrates, respectively). An unusual noise behavior is observed in the more disordered films grown on MgO substrates when compared with that of STO substrates. In particular, a large increase of noise is observed below the metal-insulator transition temperature on samples deposited on MgO, associated to a current induced reduction of the noise level. This peculiar finding is explained by the presence of noise active grain boundaries between small regions with depressed Curie temperatures among the ferromagnetic metallic domains. All these findings are analysed in terms of possible physical mechanisms related to the growth in the presence of large mismatch between film and substrate lattice parameters. By the use of noise spectroscopy, a quantitative model taking into account the half-metal character of manganites describes excellently the experimental data.
Gallium Implantation in LCMO and PCMO thin films

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Pr0.5Ca0.5MnO3 (PCMO, thickness 120 nm) and La0.7Ca0.3MnO3 (LCMO, thickness 10 nm) are grown on SrTiO3 (STO) [100] oriented. The samples were patterned by means of a Focused Ion Beam (Ga⁺). In the case of PCMO film a volume of 3 mm X 1 mm X 40 nm was removed from the film with a 1000 pA ion-current and a suitable cross section specimen was prepared to perform TEM analyses. The high resolution images show the common Pnma structure, apart from a region close to the surface of the patterned region, due to the gallium implantation which is likely to have caused structural changes. The spectroscopic data confirm this finding: indeed EDX data point towards a high gallium concentration within a region that extends by 25 nm underneath the film surface. Moreover, electron energy loss (EEL) spectra reveal a change in the Oxygen absorption edge, due to a different oxygen coordination. In the case of LCMO film, microbridges were created and then patterned to reduce the width from 10 µm to 200 nm. The film did not show any IM transition at 0 T; only by applying a 5 T field it was possible to recover the IM transition. TEM data from the nanobridges will be presented.
Scanning Tunneling Microscopy and Spectroscopy on La$_{0.7}$Sr$_{0.3}$MnO$_3$: Evidence for a pseudogap

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Physical properties of the manganites have been investigated for nearly five decades. Still the nature of metal-insulator (MI) transition observed in heavily doped manganites is an outstanding issue. The most widely accepted explanation says that intrinsic inhomogeneities in such systems lead to phase separations into conducting and insulating domains in the sample. The system is at its metallic (ferromagnetic) ground state at very low temperature and at higher temperatures the insulating (non-magnetic) regions are expected to emerge slowly. With such inhomogeneities, the interesting nature of the metal-insulator transition can be explained within a percolation transition model. Scanning tunneling microscopy (STM) and spectroscopy (STS) can be powerful tools in probing the mentioned electronic inhomogeneities. In the past some groups reported observation of electronic inhomogeneities in the conductance map of the surface of manganites by STM while some other groups reported that such inhomogeneities are not probed by STM. We have performed STM and STS on an epitaxial thin film of La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) grown by pulsed laser deposition (PLD). The as-grown sample showed a granular surface. However, the annealed LSMO film showed nice atomic terraces of 0.4 nm height. We did not find direct signatures of electronic inhomogeneities in the conductance map. Interestingly, we have observed a pseudogap forming at low temperature i.e. in the metallic state of the film. We will discuss these results in the light of the existing theoretical models.
Epitaxial growth of atomically-flat LiCoO$_2$

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LiCoO$_2$, in bulk powder form, is, at present, the most commonly used cathode material for commercial Li-ion rechargeable batteries. It is very difficult to fabricate large single crystals, and therefore, detailed transport and magnetic properties are still not well understood. Furthermore, epitaxial growth of atomically flat thin films with “step and terrace” surfaces has not been reported so far.

Here, we report on pulsed laser deposition (PLD) of LiCoO$_2$ epitaxial thin films grown on Al$_2$O$_3$(0001). Films were grown at substrate temperatures ranging from room temperature to 650°C under oxygen partial pressure of 1x10$^{-3}$ Torr.

When the substrate temperature was 250-300 °C, LiCoO$_2$ epitaxial thin films with the rhombohedral layered structure were grown. We also obtained epitaxial films by annealing the films deposited at room temperature. The latter films exhibited step and terrace surface structures, as observed from atomic force microscopy, with surface roughness ($R_a$) of ~ 0.2 nm. Detailed study of transport and magnetic properties are under way, and this study may pave the way for constructing oxide superlattices, which would be expected to demonstrate new interface properties involving both electrons and Li atoms.
Schottky Barrier Height Control by Interface Modulation in \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{Nb:SrTiO}_3 \) Junctions

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The recent discoveries of novel ground states at perovskite interfaces have triggered a number of studies on interfaces in this materials system. One of the central issues governing the fundamental properties of interfaces is the formation of band alignments, which is crucial in designing electronic and optical devices based on these functional oxides. Recent development in the technique to fabricate heterointerfaces with atomic scale precision has made microscopically tuned heterostructures more accessible for exploring the basic mechanism for interface band alignments.

We present results on the characterization of the Schottky barrier height at epitaxial \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{Nb:SrTiO}_3 \) (100) Schottky interfaces, in which the chemical composition of the first interface layer was modified systematically. The interface composition was varied from a \( \text{TiO}_2 \)-terminated interface (\( \text{La}_{0.7}\text{Sr}_{0.3}\text{O}/\text{TiO}_2 \)) to a \( \text{SrO} \)-terminated interface (\( \text{MnO}_2/\text{SrO} \)) by varying the Sr concentration at the first atomic layer of the thin film. Evaluation of the barrier heights was carried out using internal photoemission\(^1\), a technique known to be insensitive to effects from biasing, as well as conventional electrical measurements. We have found a systematic increase in the barrier height with the increase in the Sr content at the interface, which can be explained by considering the screening of the polarity mismatch of the interface by \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 \).

Interfacial Proximity Effects on the Structure and Conduction Behavior of ZrO$_2$ – In$_2$O$_3$ Heterostructures

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Nanocomposite oxides comprised of electronic and ionic conducting phases have the potential to produce materials with novel properties. Not only is mixed conductivity expected, but the high density of oxide heterointerfaces may also lead to pronounced deviations from bulk electronic, ionic, and thermal transport behavior. The resulting properties may be of interest for a wide variety of applications including thermoelectric devices, transparent conductors, and solid oxide fuel cells. Here we describe the synthesis, structural characterization, and electrical properties of epitaxial In$_2$O$_3$/ZrO$_2$ (or Y$_2$O$_3$-stabilized ZrO$_2$ (YSZ)) heterostructures grown on YSZ (001) substrates. Using synchrotron x-ray scattering and high-resolution transmission electron microscopy, we find that co-deposition of YSZ and In$_2$O$_3$ results in the formation of a single-crystal nanocomposite with epitaxial In$_2$O$_3$ nanopillars/nanolamellae dispersed in a YSZ matrix. The embedded In$_2$O$_3$ phase is coherently strained with the matrix in all three-dimensions. We compare the oxygen partial pressure- and temperature-dependent in-plane and out-of-plane electrical properties of these nanocomposites with those of epitaxial In$_2$O$_3$/ZrO$_2$(YSZ) superlattices using an environmental four-point probe station. This allows investigations into the effects of oxide interfaces, nanostructure morphology, and different phase mixtures on electrical transport. First-principles calculations are also carried out on superlattice heterostructures to provide insight into the effects of interfacial proximity on electronic structure. The role of surface/interface polarity on interfacial structure, segregation behavior, and transport will be discussed.

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HAADF-STEM study of FeTiO$_3$-Fe$_2$O$_3$ solid solution thin films

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Magnetic semiconductors have arrested considerable attention in recent years to develop the next generation of spin electronics applications. One approach toward the development of magnetic oxide semiconductors is to explore materials that are intrinsically ferromagnetic and semiconducting. As an example of such materials, we have studied a series of solid solutions between ilmenite (FeTiO$_3$) and hematite (Fe$_2$O$_3$).

Although both FeTiO$_3$ and Fe$_2$O$_3$ are antiferromagnetic insulators, their solid solutions exhibit both semiconducting and ferrimagnetic properties. It is generally known that cation ordering has a crucial role in determining the magnetic properties of the solid solutions. The magnetic properties are also greatly affected by nanostructures associated with FeTiO$_3$ and Fe$_2$O$_3$ exsolution lamellae. Therefore, determination of nanostructures including cation ordering has been an important issue to understand comprehensively the magnetic properties of this system.

We have recently reported the preparation of $x$FeTiO$_3$-(1-$x$)Fe$_2$O$_3$ ($x$=0.6, 0.7, and 0.8) solid solution thin films on $\alpha$-Al$_2$O$_3$ (0001) substrates using a pulsed laser deposition (PLD) technique [1,2].

In this study, we report the nanostructural analysis of FeTiO$_3$-Fe$_2$O$_3$ solid solution thin films using aberration-corrected scanning transmission electron microscopy (STEM) with a high angle annular dark field (HAADF) detector. FeTiO$_3$-Fe$_2$O$_3$ solid solutions crystallize in corundum-based structures and are generally known to consist of the alternate stacking of Fe and Fe$^+$Ti layers along c axis in the ordered phase. Despite the rather small difference in the average atomic number between the Fe and Fe$^+$Ti columns, each of the layers in the ordered structure is distinguishable in the HAADF images. The effect of the nanostructures on the magnetic properties of the films composed of disordered as well as ordered phases is discussed in detail.

Spin transfer torque effects in La$_{0.8}$Sr$_{0.2}$MnO$_3$ single crystal

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The electrical and magnetic response to a bias current has been investigated in a La$_{0.8}$Sr$_{0.2}$MnO$_3$ single crystal. In the vicinity of the ferromagnetic-paramagnetic transition temperature, a significant increase of the magnetization with the current is observed when V-I characteristics exhibit a linear behaviour [1]. These results are explained taking into account the crystal nanostructure, local distribution of the Curie temperature, and the s-d exchange coupling between conduction electrons spins and localized spins. For high enough current, the ohmic regim holds no more, and local heating results in magnetization decrease [2].

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Anisotropic electron transport in twin-free epitaxial SrRuO$_3$ thin films

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We have studied the electron transport properties along the perpendicular in-plane [001] and [110] directions in SrRuO$_3$ thin films. In particular we have measured the magneto-transport as function of the direction of the applied magnetic field.

Epitaxial thin films of SrRuO$_3$ were grown on closely lattice matched SrTiO$_3$ substrates by pulsed laser deposition using different growth conditions. The film quality was examined by transmission electron microscopy and the number of defects could be related to the substrate temperature during growth. The resistance of the samples, measured in a van der Pauw configuration, was found to be different in the two in-plane directions, [001] and [110]. The sample with the strongest anisotropy was also the most defect-free, as revealed by TEM. This sample was therefore selected for this particular study where we control the current paths and can most likely exclude the possibility of an anisotropic density of defects. The 50 nm thick twin-free sample was patterned into Hall-bars in different directions, in particular along [110] and [001]. The residual resistance ratio (RRR) of the sample was about 6. The overall behavior of the resistance is the same for the two perpendicular directions. However, pronounced differences were revealed in the longitudinal magneto-resistance well into the ferromagnetic state. The magneto-resistance is found to be a function of the direction of the external magnetic field. The shapes of the magneto-conductance curves reveal a single minimum for $H \parallel [110]$ and two minima for $H \parallel [001]$. 


Electronic structural properties of SrRuO\textsubscript{3} ultrathin films on SrTiO\textsubscript{3} substrates

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Heterostructures between different oxide perovskite compounds attracts lots of attention due to its potential application in oxide electronics. One fundamental question that we have to face in utilizing the heterostructures is just how thin film can maintain their own physical properties. Among various functionalities of oxides, ferromagnetic metallic characters are essential elements due to various applications, such as spin-polarized ferromagnetic tunnel junction\cite{1}, multiferroic composite device\cite{2} as well as ferroelectric capacitors\cite{3}. The 4\textit{d} ferromagnetic metal SrRuO\textsubscript{3} films on the band insulator SrTiO\textsubscript{3} provide a good model system to test the thickness limit of ferromagnetic metallic properties in the complex materials.

We fabricated ultrathin films of SrRuO\textsubscript{3} on TiO\textsubscript{2} terminated SrTiO\textsubscript{3} by pulsed laser deposition. We carefully controlled thicknesses of the SrRuO\textsubscript{3} films from one to 50 unit cell by monitoring the growth mode with high-pressure reflection high energy electron diffraction and checked the thicknesses with X-ray reflectivity measurements. Atomic force microscopy studies show clear step-terrace structures of the films, which reflects 2-dimensional growth mode.

Temperature-dependent resistivity measurements revealed that the atomically flat films are metallic down to the 2 unit cell in thickness. As the film thickness decreased, the resistivity increased and the ferromagnetic transition temperature decreased. However, the ferromagnetic transition signature in the resistivity curve could not be observed for the 2 unit cell SrRuO\textsubscript{3} films. We investigated thickness-dependent electronic structural changes of ultrathin SrRuO\textsubscript{3} layer by \textit{in-situ} scanning tunneling spectroscopy. The electronic structural evolution will be discussed with the predictions of the first principles calculations.

Asymmetry and rotation of the in-plane magnetic easy axis in La$_{0.67}$Sr$_{0.33}$MnO$_3$ thin film grown on NdGaO$_3$(112)

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The manganite La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO), is of great interest because of its colossal magnetoresistance and the predicted full spin polarization. These properties make it an interesting material for a number of spintronic device applications, especially tunneling magnetoresistance (TMR) junctions. For achieving very high TMR ratios, some of the issues to be resolved are the magnetization properties and magnetic domain structure of the LSMO electrodes. To this end we are investigating the relationships between the strain state, the structure change and the magnetic anisotropy of the LSMO grown on various substrates. In this study, we have investigated the thickness dependence of the in-plane magnetic anisotropy of LSMO thin films grown on NdGaO$_3$ (NGO), with a (112)$_o$ surface (we will use subindex “$o$” for the NGO orthorhombic and “pc” for the LSMO pseudo-cubic crystal structure). The NGO(112)$_o$ plane has a similar structure as the perovskite pseudo-cubic (011)$_pc$ plane. Therefore the orientation of LSMO grown on NGO(112)$_o$ is {011}$_pc$.

LSMO thin films were grown on atomically smooth NGO(112)$_o$ by the pulsed laser deposition technique. In-plane magnetization loops were measured as a function of the angle of the in-plane field by a vibrating sample magnetometer. It is shown that with increasing film thickness the in-plane magnetic anisotropy changes from uniaxial to biaxial. The surface unit of the NGO(112)$_o$ is not a rectangle but a parallelogram with 89.5 ° and 90.5 ° angles. Due to this asymmetry the easy axes of the LSMO thin films are not along any low index (in-plane) crystal vectors of NGO or LSMO. Moreover, the total value and the rotation angle of the in-plane remanence as function of the field angle with increasing film thickness is measured directly for the first time on LSMO thin films.
Magnetization induced resistance switching effects in YBa$_2$Cu$_3$O$_7$ - La$_{1-x}$Sr$_x$MnO$_3$ heterostructures

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We have fabricated bi- and trilayers composed of the high-temperature superconductor YBa$_2$Cu$_3$O$_7$ (YBCO) and the half-metallic ferromagnet La$_{1-x}$Sr$_x$MnO$_3$ (LSMO). Heterostructures are pulsed laser deposited on SrTiO$_3$ (001) as well as on SrTiO$_3$ (305). On the latter, tilted epitaxial growth partly yields ab-plane contact between YBCO and LSMO. As a result of the uniaxial magnetic anisotropy in the (305)-oriented structures, we observe sharp magnetization switching behavior. At temperatures close to the superconducting transition temperature ($T_c$), we find resistance jumps induced by magnetization switching, resulting in a magnetization dependence of $T_c$. The results are similar to what is commonly being interpreted as the (inverse) spin switch effect. For the bilayers, we find that the switching effect can also be observed, provided that the ferromagnetic layer is grown with considerable roughness. Our results indicate that the switching behavior arises from magnetic stray fields from the ferromagnetic layers that penetrate into the superconductor.

**Figure 1** (a) Trilayer structure grown on SrTiO$_3$ (305). Indicated are the YBCO crystal directions. (b) Magnetization loop of the trilayer. The dashed lines denote the coercive fields of the top and bottom layer. (c) Resistance of the middle YBCO layer in the superconducting transition as a function of magnetic field.
Independent behavior of the antiferromagnetic and ferromagnetic properties in perovskite oxide superlattices

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Recent studies of perovskite oxide superlattices have demonstrated enhanced or completely unexpected properties when compared to the individual constituent materials. These effects are attributed to structural distortions as well as band or charge discontinuities at these interfaces. We have examined superlattices of two perovskite oxide layers, the antiferromagnetic insulator La$_{0.7}$Sr$_{0.3}$FeO$_3$ (LSFO) and the ferromagnetic metal La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO). We used a combination of structural, magnetic, and electrical characterization techniques to probe both the global and interfacial properties of the superlattices. In particular, x-ray magnetic dichroism provided chemically selective information on the electronic structure and the magnetic (ferromagnetic and antiferromagnetic) characteristics of each layer. As single layer thin films, the easy magnetization direction of LSMO and the direction of the antiferromagnetic axis, A, of LSFO both lie in the plane of the film. However, when incorporated in superlattice structures, the ferromagnetic and antiferromagnetic orders act independently with decreasing superlattice period. In the case of the ferromagnetic LSMO layers within the superlattices, the magnetic and electrical properties behave as expected, gradually approaching the case of the solid solution with decreasing superlattice period, namely decreasing saturation magnetization and Curie temperature, and increasing resistivity. In contrast, the Néel temperature of the LSFO layers is almost independent of the superlattice period and the orientation of the A axis differs from the solid solution film irrespective of superlattice period, by canting out of the plane of the film. This diverging behavior illustrates how the neighboring LSFO and LSMO layers respond differently to a charge transfer between the Mn and Fe ions across the interfaces and provides an interesting new means to control of the global magnetic properties of the superlattices.

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Growth of (ultra) thin La$_{1.2}$Sr$_{1.8}$Mn$_{1.7}$Ru$_{0.3}$O$_7$ Ruddlesden-Popper films on SrTiO$_3$ substrate

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Ruddlesden-Popper (RP) oxides, with the general formula of $A_{n+1}B_nO_{3n+1}$, are derived from the respective perovskite oxides with the addition of one AO layer per formula unit, leading to the introduction of the rock-salt structured (AO)$_2$ block between the two consecutive formula units. It is expected that, due to the presence of insulating (AO)$_2$ double layer, the incorporation of RP oxides into existing (perovskite) oxide devices would help to avert the common problems encountered at the perovskite heterointerfaces, such as the modulation of the carrier concentration resulting from charge transfer over the interface. However, the nucleation and initial growth mode of the RP oxides at the perovskite interface, essential for obtaining a clean and well defined interface, often remain poorly understood yet, especially for the films grown from a single RP target by laser ablation. In the current contribution we have therefore studied the growth of (ultra) thin La$_{1.2}$Sr$_{1.8}$Mn$_{1.7}$Ru$_{0.3}$O$_7$ films on SrTiO$_3$ substrate. Deviations from the relatively narrow growth window were observed to result in the random nucleation of (AO)$_2$ double layers along all crystal directions. For films where $n = 2$ RP type growth was dominant, the observed magnetic and transport properties corresponded well with the behavior observed for the bulk samples, although with the increasing film thickness the nucleation of both the perovskite and the $n = 1$ RP defects were confirmed. Near the interface region, a coherent $n = 2$ RP-type growth was observed, although the growth commenced with the nucleation of two perovskite sub-units at before the formation of first (AO)$_2$ block as seen in the Fig. 1. However, the nucleation of the (AO)$_2$ block directly at the interface can be facilitated by buffering the SrTiO$_3$ substrate with SrO before the deposition of the RP phase.

Fig. 1 The growth of La$_{1.2}$Sr$_{1.8}$Mn$_{1.7}$Ru$_{0.3}$O$_7$ on SrTiO$_3$ as monitored with RHEED.
Layer-by-layer growth of $Y_3Fe_5O_{12}$ thin films on $Gd_3Ga_5O_{12}$

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Heterostructures and superlattices of magnetic oxides attract considerable interest both from application and basic physics viewpoints. Most of them have been constructed with perovskite oxides and few reports have been presented for other magnetic oxides such as garnet. Ferrimagnetic garnets have been extensively studied and practically used in magneto-optical devices. However, most of the studies were carried out with rather thick films made by liquid phase epitaxy. In order to construct atomically defined interfaces, we optimized the growth conditions of very thin and flat films. Thin films of $Y_3Fe_5O_{12}$ have been grown by pulsed laser deposition on $Gd_3Ga_5O_{12}$ substrates with different orientations. We varied oxygen pressure, temperature and laser repetition frequency. Under the optimum conditions, we could observe clear RHEED oscillation with a period corresponding to the charge neutral unit. The films had quite smooth surface (roughness $\leq$ 1 unit cell) and the magnetic properties were comparable to those of bulk ($T_C = 560$ K, $M_s(300K)=3\mu_B$/f.u.). For the films grown on (110)GGG, the magnetic easy axis lies in-plane.

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Probing the nature of ferroelectric polarization dynamics in multiferroic BiFeO$_3$ by terahertz emission spectroscopy

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Since ever mounting quest for superior operating speed of data storage devices, the speed at which the memory parameter is consecutively accessible for read/write operation has become indispensible subject of research. The dynamic response of the memory parameter to the ultrafast electric, magnetic or optical stimuli is vital to determine the speed. Though the ultrafast dynamics of spin (magnetic) memory in about a pico-second upon femto-second excitation are well-established, the analogous ultrafast functionality of spontaneous polarization ($P_s$) in ferroelectric memory is not known. In this work, we have investigated the ultrafast polarization dynamics of the room temperature ferroelectric-antiferromagnet BiFeO$_3$ by employing the terahertz (THz) emission spectroscopy. The ferroelectric polarization of BiFeO$_3$ is oriented in (111) crystallographic plane, which implies that THz emission along all the three (100), (110) and (111) orientations should have distinct features evolving from crystallographic preference of $P_s$. This was realized experimentally as the electric-field dependent THz-emission exhibits the ferroelectric like hysteretic behavior in (100) and (100) films vis-à-vis linear behavior in (111) BiFeO$_3$ films. Extracting the ultrafast dynamics of $P_s$ from these data, we demonstrate the ultrafast depolarization of ferroelectric order in about a pico-second, followed by its non-destructive retrieval. The non-thermal mechanism of depolarization and the photo-induced suppression of coercivity signifying, respectively, ultrafast non-destructive data read-out and laser-assisted electrical data recording can potentially inspire fabrication of ultrafast opto-electric hybrid data storage devices based on ferroelectric/multiferroic materials.
Magnetoelectric effect at the Fe$_3$O$_4$/BaTiO$_3$ (001) interface: A first-principles study

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Multiferroic materials have recently attracted much scientific interest due to unconventional magnetoelectric (ME) coupling between ferroelectricity and ferromagnetism. There are two major sources of ME coupling: (1) an intrinsic ME coupling that occurs in compounds with no time-reversal and space-inversion symmetries; and (2) the coupling mediated by strain across interfaces that occurs in composites of piezoelectric (ferroelectric) and magnetostrictive (ferro- or ferrimagnetic) materials. Recently, a different mechanism of the ME coupling has been proposed.$^1$ It was predicted that the chemical bonding at the ferromagnet/ferroelectric interface may lead to a sizable change in the surface magnetization with reversal of the ferroelectric polarization. Here we present a density functional study of this ME effect at the ferrimagnetic/ferroelectric Fe$_3$O$_4$/BaTiO$_3$(001) interfaces. We find that there are induced magnetic moments on interface Ti and O atoms which are sensitive to ferroelectric displacements in the ferroelectric BaTiO$_3$. The reversal of the ferroelectric polarization in BaTiO$_3$ leads to notable changes of the interface magnetic moments indicating a ME coupling. The magnitude of the ME effect depends on the interface termination. Two different interfaces have been studied: oxygen rich TiO$_2$-FeO$_2$(B) and oxygen deficient TiO$_2$-Fe(A). We find that the effect is much stronger for the oxygen-deficient BaTiO$_3$/Fe$_3$O$_4$ interface. This is due to the bonding between Fe and Ti atoms which induces magnetic moments on the interface Ti atoms sensitive to the Fe-Ti bond length. The magnitude of the magnetic moment change per surface unit cell is predicted as large as 0.6$\mu_B$ for the oxygen deficient TiO$_2$-Fe(A) and 0.2$\mu_B$ for the oxygen rich TiO$_2$-FeO$_2$(B) interface. The sensitivity to the oxygen content suggests that oxidation or oxygen vacancies at the interface may play an important role in determining the strength of the coupling. BaTiO$_3$/Fe$_3$O$_4$(001) heterostructures can be grown epitaxially which opens the possibility to verify our predictions experimentally.

Charge driven magnetoelectric coupling
in a ferromagnetic / ferroelectric bilayer

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The present drive towards materials functionalization has rekindled interest in the
so-called multiferroic materials, which are characterised by a coupling between mag-
netic and electric properties. While the magnetoelectric coupling exhibited by the
classical ferroic compounds is very weak, and improvements in the material prop-
erties of these materials has remained elusive, a new class of composite materials,
combining dissimilar magnetic and electric materials, are expected to deliver the re-
quired functionality through artificially enhanced magnetoelectric couplings. Here,
we present direct, charge-mediated magnetoelectric coupling in a bilayer of ferro-
magnetic La0.8Sr0.2MnO3 and ferroelectric Pb(Zr,Ti)O3. Using magneto-optic Kerr
effect magnetometry, we demonstrate the control of magnetic order through the fer-
roelectric field effect, by direct measurement of the magnetic order parameter. Key
results include a direct measurement of the magnetoelectric coupling parameter by
measuring the magnetic response of the PZT/LSMO system as a function of applied
electric field, a 20K shift of the magnetic Curie temperature of the LSMO layer upon
switching the electric polarization of the PZT layer and an electric field-controlled
on/off switching of magnetism in the LSMO layer. These experiments show that
artificial multiferroics made of multilayers of ferromagnetic and ferroelectric materi-
als open new possibilities for the development of magnetoelectric devices with large
coupling between electric and magnetic degrees of freedom.
Magnetic anisotropy modulation of magnetite in Fe₃O₄/BaTiO₃(100) epitaxial structures


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Abstract

A defining characteristic of complex oxides is the display of a wide variety of magnetic and dielectric properties. Such multifunctional behavior has motivated much effort aimed at controlling the materials properties by means of external applied fields, which is key for device applications. In addition, recent advances in the growth of epitaxial oxide multilayers have enabled the fabrication and study of composite material heterostructures, where the properties of the individual components are engineered to yield an effective coupling between different order parameters, for example magnetic and ferroelectric ordering for multiferroic behavior. In this context, we have investigated the strain-induced magnetic anisotropy modulation of 10 nm epitaxial magnetite (Fe₃O₄) films grown on BaTiO₃(001) single crystals by off-axis magnetron sputtering and oxygen-assisted molecular beam epitaxy (MBE). SQUID and magnetoresistance measurements as a function of temperature show a series of discontinuities that are attributed to changes in the strain of the magnetite film via elastic coupling to the ferroelectric substrate as the latter undergoes a series of structural phase transitions. The trends in the magnetic anisotropy variation along the ⟨110⟩ and ⟨100⟩ directions are gauged from the variation of the magnetic moment with temperature under an applied field and are related to the variation in anisotropy derived from the bulk magnetoelastic coefficients of magnetite. The possibility of using the piezoelectric response of BaTiO₃ to modulate the magnetic anisotropy of magnetite films is discussed.
Domain engineering for enhanced ferroelectric properties of epitaxial (001) BiFeO₃ thin films

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We have demonstrated the selection of domain structure variants in epitaxial BiFeO₃ films and consequently significant improvement in ferroelectric switching behavior and leakage current by employing miscut in cubic (001) SrTiO₃ substrates. BiFeO₃ films on miscut SrTiO₃ have a step-flow growth and the preferential rhombohedral distortion toward the miscut direction. This result indicates that both the substrate anisotropy and the step-flow growth of BiFeO₃ are the origins of the two-variant stripe domains in BiFeO₃ films. Square-like P-E loops and very low leakage current density are obtained from the BiFeO₃ films with two-variant stripe domains. In contrast, BiFeO₃ films on exact (001) SrTiO₃ exhibit low Pₑ values and high leakage current. From this results, we suggest that 109° domain walls prevent the complete ferroelectric switching of (001) BiFeO₃ domains and act as dominant leakage paths in the four-variant BiFeO₃ films, whereas the intrinsic ferroelectric properties of BiFeO₃ can be observed from two-variant BiFeO₃ films with 71° domain walls. The dependence of ferroelectric properties on domain wall configuration opens the exciting opportunity to investigate the correlation between domain walls and the antiferromagnetic order in BiFeO₃. We believe that such a domain engineering can be very useful for growing high-quality BiFeO₃ films on cubic (001) Si substrate for device applications, and generalized for heterostructures with rhombohedral thin films such as Pb(ZrₓTi₁₋ₓ)O₃, Pb(Mg₁/₃Nb₂/₃)O₃-PbTiO₃, La₁₋ₓSrₓMnO₃, and LaAlO₃.
Structural Distortion and Magnetic Properties in Bi$_2$FeCrO$_6$ Double Perovskite Films

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Beside their potential applications, the fundamental physics of multiferroic materials is rich and fascinating. Good magnetic and ferroelectric properties have recently been observed at room temperature in pulsed laser deposition (PLD) grown epitaxial single phase Bi$_2$FeCrO$_6$ (BFCO) thin film.

We report here the effect of structural distortion on the magnetic properties of BFCO thin films. Detailed studies have shown that BFCO exhibits a double perovskite structure with a cationic ordering on the B-site, where the Fe$^{3+}$ and Cr$^{3+}$ ions make up a rock-salt type magnetic cation lattice. BFCO magnetic insulating properties are basically governed by the Goodenough-Kanamori rules, with their ferro-ferrimagnetic coupling arising from a 180° superexchange interaction between Fe$^{3+}$ and Cr$^{3+}$ transition metal ions via the oxygen ion of the Fe-O-Cr bond. The crystal structure and the magnetic properties of BFCO thin films under different compressive strains vary and we found that the strength of the superexchange interaction correlates well with the octahedral tilting and the resulting Fe-O-Cr bond angles. The dominant distortion mechanism present under compression causes not only octahedral tilting, but also a bond distance variation. In turn, the superexchange Fe$^{3+}$-O$^{2-}$-Cr$^{3+}$ magnetic interaction also depends on the bond angles.

We also report here the growth of epitaxial BFCO thin films on different single crystalline substrates in order to vary the epitaxial strain imposed on the films. Experimental results about the influence of the epitaxial strain on the films properties will be presented, and a particular attention will be paid on the evolution of the magnetic properties of BFCO thin films with the variation of the film compressive strain. In particular, detailed results for high-quality BFCO thin films of different thicknesses onto 100-oriented SrTiO$_3$ (STO) substrates will be presented.
Thin films of orthorhombic TbMnO$_3$ under epitaxial strain

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Among the rare earth manganites, orthorhombic TbMnO$_3$ has attracted much attention due to its multiferroic character and giant magnetoelectric coupling[1]. Despite the large interest of multiferroics for applications, only a few reports in the literature deal with this material in thin film form [1]. In this work we have grown for the first time thin films of TbMnO$_3$ under epitaxial strain. Films with thickness ranging between 8nm and 125nm were successfully grown on SrTiO$_3$(100) substrates using RHEED-assisted pulsed laser deposition, and have been characterized using x-ray diffraction, atomic force microscopy, x-ray photoelectron spectroscopy and magnetometry. Grazing incidence x-ray diffraction has also been performed using synchrotron radiation. The films are orthorhombic for all thicknesses under investigation, with the orthorhombic c-axis out of plane. The orthorhombic unit cell evolves as a function of thickness only in the in-plane directions, revealing an unusual strain relaxation mechanism. For the thinnest films the in-plane orthorhombic distortion is largely decreased with respect to that in the bulk and the in-plane structure relaxes as function of thickness towards the bulk value. The $a_0$ and $b_0$ lattice parameters reach their minimum and maximum values, respectively, for thickness of ~80nm and above this thickness, two lattices, corresponding the partially strained and the bulk-like structure, are observed. The magnetic properties of the films differ considerably from those of the bulk material and are found to be unchanged with increasing thickness, growth oxygen pressure (pressures up to 0.9 mbar have been used) or annealing conditions. Only one magnetic transition and no signs of the lock-in transition at 23K have been found. The magnetization and susceptibility measurements show dominant AFM interaction along with the presence of weak FM interactions below $T=30$-40K. This works highlights need of a more subtle control of the epitaxial strain to tune the magnetic properties in TbMnO$_3$.

Adsorption-controlled growth of BiMnO$_3$ by reactive molecular-beam epitaxy


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Adsorption-controlled conditions for the epitaxial growth of multiferroic BiMnO$_3$ thin films have been established using reactive molecular-beam epitaxy (MBE). The combination of substrate temperature and bismuth overpressure under ozone atmosphere enables the growth of stoichiometric BiMnO$_3$ thin films without either bismuth or manganese oxide second phases. The adsorption-controlled growth was monitored by in situ reflection high-energy electron diffraction and band-edge thermometry during the deposition. The bismuth flux was maintained about three times higher than the manganese flux to compensate for the bismuth desorption and achieve stoichiometric BiMnO$_3$ within the error of Rutherford backscattering spectrometry. Epitaxial BiMnO$_3$ thin films have been deposited on (100) SrTiO$_3$, (110) DyScO$_3$, and (110) GdScO$_3$ at substrate temperatures between 600°C and 650°C. When the substrate temperature was below 600°C, excess bismuth adsorption occurred and bismuth oxide phases were formed. When it was above 650°C, manganese oxide phases were formed due to the excess desorption of bismuth on the substrate. X-ray diffraction rocking curves of films grown on (100) SrTiO$_3$, (110) DyScO$_3$, and (110) GdScO$_3$ show a full width at half maximum (FWHM) of 62, 8, and 11 arc sec, respectively in $\omega$, which are close to the rocking curve FWHM of the underlying substrates. These narrow rocking curves demonstrate more than an order of magnitude improvement in comparison with prior BiMnO$_3$ thin films grown by pulsed-laser deposition (PLD) or nebulized spray pyrolysis. The epitaxial relationship and twin variants of monoclinic BiMnO$_3$, and its effect on ferromagnetic properties will be discussed.
Structural state of epitaxial (001) BiFeO$_3$ films on cubic and orthorhombic substrates

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Bismuth ferrite is a promising ferroelectric and magnetoelectric material with a bulk rhombohedral structure. In thin film form, the structural properties of BiFeO$_3$ can be altered from substrate clamping, which in turn have large effects film properties. Hence, a large amount of research has been invested into uncovering the as-deposited structural state of BiFeO$_3$ thin films epitaxially deposited on single crystal substrates. Although many of these publications report interesting findings, there are some remaining discrepancies and none as we could find reported results in the context of the predicted rhombohedral overlayer domain patterns on (001) cubic surfaces.\(^1\)\(^2\) To demonstrate our findings in this context, we have analyzed the structure of epitaxial (001) BiFeO$_3$ films on various substrates with x-ray diffraction and reciprocal space mapping (RSM). BiFeO$_3$ films grown on exact (001) SrTiO$_3$ exhibited highly obscured reflections resulting from poor crystallinity. However, sharp reflections resulting from high crystallinity were observed when anisotropic substrates were introduced that included: miscut (001) SrTiO$_3$ and orthorhombic rare-earth scandate substrates. The structural state of these films was defined by the ferroelastic domain patterns and phase symmetries. Domain patterns were determined with RSM in conjunction with transmission electron microscopy and atomic force microscopy. The symmetry of BiFeO$_3$ on SrTiO$_3$ was triclinic, but BiFeO$_3$ on DyScO$_3$, TbScO$_3$ and NdScO$_3$ exhibited bulk rhombohedral symmetry. The rhombohedral phase accompanied vertical (010) domain boundaries where wedge disclinations are predicted for coherency at the film substrate interface.\(^2\)

Direct evidence for these defects was observed with RSM in localized tilting of domains and in diffuse scattering.


Nanoscale piezoresponse studies of ferroelectric domains in epitaxial BiFeO$_3$ nanostructures defined by FIB lithography

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We present a report on recent studies of local ferroelectric domain configuration and response of epitaxially grown BiFeO$_3$ (BFO) thin films structured into nanocapacitors defined by focused ion beam (FIB) lithography. The BFO films were grown by rf magnetron sputtering on epitaxial SrRuO$_3$ (SRO) layers grown on SrTiO$_3$ (STO) (001) oriented single crystal substrates. XRD revealed epitaxial growth of BFO on (001) SRO/(001) STO. X-ray measurements of the heterostructures were used to calculate the thickness of the BFO (120 nm) and SRO (125 nm) layers.

AFM topographical and piezo force microscopy (PFM) images were obtained using Pt/Ir coated silicon tips (Olympus) on square and round shaped nanostructures. The square shaped one shows only one polarization variant along [-11-1] direction whereas the round shaped one shows 5 variants of [-11-1], [111], [1-11] and [-111]. Shape dependence of domain configuration suggest that the geometry can influence the electrostatic and strain field distribution inside the nanostructure in a significant way, which impact the design of future energy harvesting or memory devices.

In addition to shape dependence, size and edge shape dependence of piezoelectric properties and domain behavior will be discussed, which will serve as a corner stone of future environment friendly high-density ferroelectric memory devices.

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Magnetic Field Control of Dielectric Properties in Strained Garnet Ferrite Thin Films

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Rare earth iron garnet (RIG) forms a prototypic class of ferrimagnetic oxides with applications in magneto-optical devices, waveguide optical isolators and magnetic memories. The study of ultrathin garnet ferrite thin films is an active field and many efforts being devoted to investigate the ferrimagnetic interaction among cations, magnetic anisotropy and magnetooptical properties of the films. On the other hand, there exist not so many reports on the dielectric properties of garnet ferrites. The coupling of electric polarization and spins in garnet ferrites will bring the novel type of multiferroic devices. However, the normal garnet ferrite exhibits no ferroelectric behaviors because of the cubic garnet structures with a central symmetry. In order to break the central symmetry and enhance the dielectric properties of the film, the epitaxial strain from a substrate is effective.

We focused on the (Y, Lu, Bi)₃Fe₅O₁₂ thin films formed on substituted-gadolinium gallium garnet (SGGG; (Gd₂.7Caₐ.₃)(Ga₄.₀Mg₀.₃₂Zr₀.₆₅Ca₀.₀₃)O₁₂) substrates using a pulsed laser deposition technique. The lattice parameter of SGGG is 0.93 ~1.78 % larger than that of the (Y, Lu, Bi)₃Fe₅O₁₂, which is considered to cause tensile strain in the film. The dependence of MCD and dielectric properties on the film thickness and composition implies that the enhancement of the magnetic and ferroelectric properties observed in these thin films is due to the strain originating from the lattice mismatch between the films and substrates. As shown in Fig.1, the modulation of the ferroelectric properties of the films by means of a magnetic field is achieved at room temperature. We believe that these results can be utilized in the development of novel multi-functional devices based on multiferroic materials.

Figure 1: D-E curves of Y₁.₂Bi₁.₈Fe₅O₁₂/Gd₃Ga₅O₁₂(100) with and without a magnetic field (1T).
Magnetic and dielectric properties of strained Sm$_3$Fe$_5$O$_{12}$ garnet ferrite

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Recently, multiferroic materials which simultaneously show ferroelectricity and ferromagnetism have attracted much attention from the viewpoint of not only new device such as memories but also new physical properties originating from the coupling of spin and electric dipole moment. However, multiferroic materials are very rare. In this work, we have focused on the strained garnet ferrite thin films. The lattice mismatch between substrate and thin film result in presenting a remanence charge property.

The Sm$_3$Fe$_5$O$_{12}$ (SmIG) thin films were deposited on the substrate of Gd$_3$Ga$_5$O$_{12}$ (GGG) using a pulsed laser deposition technique. The lattice mismatch between SmIG and GGG is 1.187%, which is expected to cause a compressive tensile along the c axis and induce the tetragonalinity of films. During film deposition the substrate temperature and ambient oxygen pressure were maintained at 700°C and 0.1 Pa respectively. Bottom ITO electrodes were deposited by RF magnetron sputtering on the GGG. Ag past or ITO was used for top electrodes. The films were post-annealed at 800°C for 6 hours to improve the crystallinity and enhance the dielectric property. Figure 1 shows the results of D-E measurement at 150 Hz. Non-linear D-E hysteresis loops were observed, however, the D value was not saturated at an electric field of 400 kV/cm and minor loops are observed. The dependence of annealing processes and preparation condition on the magnetic and dielectric properties of the films were investigated.

Fig.1 D-E hysteresis of SmIG film
Ferroelectric switching behavior of (001) mono-domain BiFeO$_3$ thin film

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BiFeO$_3$ has drawn a great deal of attention as a single phase multiferroic material for the magnetoelectric device and non-volatile memory application. BiFeO$_3$ has a rhombohedral symmetry with the [111] polar axis. Due to this rhombohedral geometry of unit cell, it can form multi-domains which have maximum four structural ferroelastic and eight ferroelectric variants, thus domain boundaries between each domain. This multi-domain system makes it complicated to understand fundamental properties of BiFeO$_3$ because the measured properties come from both intrinsic and extrinsic characteristics. Furthermore, this complex domain structure makes it difficult to control electric and magnetic properties in a simple way for device application. Therefore, it is desirable to fabricate mono-domain single crystal BiFeO$_3$ thin films as the simplest model system for both fundamental study and device applications. Structural domains can be controlled by structural anisotropy of the substrate while the resulting ferroelectric domains can be determined by the electrical boundary condition. We have successfully grown epitaxial mono-domain (001) BiFeO$_3$ thin film on (001) SrTiO$_3$ substrates with miscut toward [110] by off-axis sputtering. Mono-domain BiFeO$_3$ thin film shows higher remanent polarization and lower coercive field than multi-domain BiFeO$_3$ thin films. We will discuss the difference of ferroelectric switching behavior between local switching by AFM tip and uniform switching by large area top electrodes. These discussions will lead us to understand how to engineer the intrinsic and extrinsic characteristics to enhance the performances of the low symmetry material system.
Exchange Coupling Across the La$_{0.7}$Sr$_{0.3}$MnO$_3$ and BiFeO$_3$ Interface


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We are exploring the exchange coupling between epitaxial ferromagnetic La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) and multiferroic BiFeO$_3$ (BFO) heterostructures. Negative exchange bias with a “blocking” temperature ~100K has been observed. Thickness dependence studies reveal that the exchange bias field is inversely proportional to the thickness of LSMO layer, consistent with conventional exchange bias systems. By taking the advantage of the layer-by-layer control available in laser MBE, we are studying the influence of different types of interface terminations on the exchange bias. We find that the magnitude of the exchange bias is systematically dependent on the LSMO layer termination. Photoemission electron microscope (PEEM) studies give us complementary evidence for the strong coupling between the LSMO domain structures and antiferromagnetic BFO domain structures. The possibility of electric control of the magnetic domain is also studied by SMOKE measurement.

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Dynamics of optically controlled Josephson vortices and their application to an ultrafast optical switch

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Ultrafast optical devices are strongly desired to process large-capacity data-traffic on expanding information networks. Some attractive optical devices using semiconductors operative in terahertz region have been realized, however, the power consumption become quite large in a high frequency region. On the other hand, a superconductive electronic device with high Tc superconductor is an attractive candidate for an ultrafast signal processing with very low power consumption. We discovered that the local superconducting current could be modulated by the illumination of femtosecond laser pulses, as a result, magnetic fluxes were generated around the laser spot. Such phenomena are not only interesting for fundamental physics concerning an optical excitation of quantized states but also important from a viewpoint of application to ultrafast optical devices using magnetic fluxes.

Recently we have fabricated a novel superconducting photonic device based on a Josephson vortex flow transistor (JVFT) with a YBCO thin film, and investigated dynamics of optically controlled vortices and the optical properties of this type of device using an ultrafast optical measurement system with a femtosecond laser. In my presentation, I introduce our approaches to realize the ultrafast optical devices and show the recent results of optical signal processing with JVFTs.

This research was partially supported by a grant for Osaka University Global COE Program, “Center for Electronic Devices Innovation”, from the Ministry of Education, Culture, Sports, Science and Technology of Japan.
Impact of The Starting Powder Composition on GdSr$_2$RuCu$_2$O$_8$ Melt-Textured Samples

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The superposition of strongly anisotropic magnetic and superconducting properties, in Gd$_{12}$ (Gd$_{2}$Sr$_2$Ru$_2$O$_{8}$) makes relevant the fabrication of oriented samples of macroscopic size by Melt-Texturing techniques. Up to now, the results obtained are unsatisfactory due to the small size and the random distribution of the oriented domains.

In order to achieve MTG samples with higher oriented volume fractions, we prepared pellets adding either CuO or Gd$_{12}$ (Gd$_{2}$Sr$_2$O$_6$) to highly pure Gd$_{12}$ powders. XRD analysis shows that a certain degree of orientation is present only in Gd$_{12}$-Gd$_{12}$ samples. The analysis on the microstructures of the two samples carried out by Scanning Electron Microscopy with implemented Energy Dispersive Spectroscopy (EDS) revealed a substantial difference between the two systems: in the case of Gd$_{12}$-CuO samples micro-sized precipitates of Gd$_{12}$ are homogeneously distributed throughout a CuO matrix. However, in the Gd$_{12}$-Gd$_{12}$ samples oriented domains of Gd$_{12}$ are predominantly observed with amount of solid Gd$_2$CuO$_4$ and Gd$_{12}$. These features have a profound impact on the transport and magnetic properties of the two samples. We believe that the addition of Gd$_{12}$ in highly pure Gd$_{12}$ powders represent a favourable condition to obtain Gd$_{12}$ MTG samples.
Growth and dielectric properties of epitaxial MgO on SiC

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The integration of oxides with semiconductors by means of epitaxial growth is an active area of research due to desire for an increased understanding of the structure of dissimilar interfaces, as well as for the potential payoff in the development of new types of device applications. For the case of wide bandgap semiconductors such as SiC, current devices are limited by the breakdown of the dielectric before reaching the electric fields needed for optimum performance. One possible solution is to grow epitaxial high dielectric constant oxides that allow one to apply larger electric fields and increase the performance of transistors based on these materials. We report here on the growth and electrical characterization of epitaxial MgO (111) on 6H-SiC (0001) as an alternative gate dielectric. We find that epitaxial MgO can sustain large fields before breaking down and has a dielectric constant matched to the SiC, showing that the structure has potential for SiC field effect transistor applications.
Photo-induced effect in tin dioxide thin films

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Background Photo-induced change in physical properties of oxides has been attracting much interest recently in search of a novel material control in condensed matter as well as in terms of application. In response to this, a variety of changes in physical properties caused by photo irradiation have been reported. For example, photo-induced phase transition in manganite [1], and photo-carrier injection in cupric oxide superconductor were reported [2]. In this study, we focused on photo-induced effect at the surface of oxide in terms of physical properties control. Specifically, we are aiming at controlling the electrical conductivity of oxide thin film using light irradiation.

Method Tin dioxide we focused in this study is an n-type semiconductor and its conductivity drastically changes as a result of oxygen vacancies in the lattice and adsorption at the surface. SnO$_2$-$x$ thin films were fabricated on Al$_2$O$_3$ substrate by using a pulsed laser deposition. We measured resistance of the sample under photo irradiation.

Experimental results The resistance of SnO$_2$-$x$ thin film decreased by several orders of magnitude as a result of UV light irradiation at room temperature in vacuum and the low resistance state was retained after the irradiation.

Discussion Experimental results suggest that the resistance decrease is related to oxygen desorption from the surface of SnO$_2$-$x$ as a result of UV light irradiation.

References
On some Peculiarities of Electronic Surface Properties
of Niobium Anodic Oxide Films

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Previously \cite{1} it had been established by structural investigation that extraction of oxygen anions from surface layers of anodic oxide films Nb\textsubscript{2}O\textsubscript{5} is the typical special feature of ion-exchange processes occurring at the oxide/electrolyte interface during cathodic polarization of oxide in aqueous electrolytes (in this case, the extraction process is attended by proton injection into the oxide). This gives rise to appreciable changes in the bulk of the oxide because of a loss of order of the anionic sublattice of Nb\textsubscript{2}O\textsubscript{5}.

It will be logical to suggest that oxygen extraction also will be able to substantially influence the surface properties of oxide, hence in the present communication we analyze the capacitance-voltage characteristics of anodic niobium pentoxide in order to discuss the changes which occur in the surface properties of oxide as a result of oxygen anion extraction by cathodic polarization.

The donor concentration, N\textsubscript{D}, calculated from the experimental data with Mott-Schottky relation is 4,6 $10^{17}$ cm\textsuperscript{-3} for the original sample, while the flat-band potential $U_{FB} = -0.37$ V. Cathodic polarization of the oxide leads to an increase in N\textsubscript{D} to 2,9 $10^{20}$ cm\textsuperscript{-3}, which in turn is evidence for oxygen occurring as an ion-exchange process during cathodic polarization of niobium pentoxide. The increase in donor concentration is attended by a negative shift of $U_{FB}$ to $-0.57$ V.

Thus, the extraction of oxygen anions from oxide leads to a rise in Fermi level $E_{FS}$ at the surface, which in turn gives rise to higher adsorptive power of the oxide surface for donor species, which in our case are the $H^\text{+}$ ions. The higher adsorptive power of niobium pentoxide surface was shown in \cite{2} to facilitate proton conductivity into the bulk of oxide.

Polaron and phonon modes in tungsten oxide: oxygen vacancies and electrochromism

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Tungsten oxide is one of the most investigated inorganic electrochromic materials, however, up to now the coloration mechanism is not fully understood yet. We report on the dependence of the polaron and phonon mode properties in amorphous tungsten oxide thin films measured by spectroscopic ellipsometry in the infrared to ultraviolet spectral regions as a function of the intercalated charge density. A parametric physical model dielectric function is presented, which excellently describes the ellipsometry data over a large intercalated charge density range. Upon increased amounts of intercalated charge we observe a strong increase of the polaron absorption in the visible spectral range, a decrease of the infrared W-O bond polarity, and an increase of the W=O bond polarity. Our findings support the oxygen extraction model as the polaron formation mechanism in tungsten oxide in agreement with previous theoretical works based on first principles pseudopotential calculations [1]. We discuss polaron formation by oxygen vacancy generation as origin for the coloration mechanism in tungsten oxide. The research is funded by NSF in MRSEC QSPIN at the University of Nebraska-Lincoln.

Surface structures of doped SrTiO₃ (100) substrate

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SrTiO₃ single crystals are widely used as substrates for the epitaxial growth of perovskite oxide thin films. To obtain high quality films, it is necessary to control the surface structures of the substrates at an atomic scale. So far, many studies have been reported for the surface structures concerned with the surface termination layer, second phase precipitation and surface reconstruction. In those studies, it has been revealed that atomic structure on SrTiO₃ (100) surface significantly changes against annealing conditions such as temperature, time, and oxygen partial pressure. However, there are few reports about the dopant effects. In this study, we examined the dopant effects on the formation of surface structure in SrTiO₃ (100) surface by HRTEM (High Resolution Transmission Electron Microscopy) and HAADF-STEM (High Angle Annular Dark Field-Scanning Transmission Electron Microscopy).

Undoped, 0.1wt% Nb-doped and 0.1wt% Fe-doped SrTiO₃ single-crystals with (100) orientation commercially supplied by Furuuchi Co.,Ltd. were used in this study. Respective crystals were annealed at 1000°C for 20h in air. Analysis at an atomic scale was carried out in Plan-view and cross-sectional view directions by HRTEM (EM-002BF, TOPCON, 200kV) and HAADF-STEM (JEM-2100F, JEOL, 200kV, Cs-corrected). Cross-sectional thin foils were prepared by ordinary method including ion-milling technique.

Figure (a) shows HRTEM image of the 0.1wt% Nb-doped sample after annealing. Atomically flat surface was observed. Figure (b) and (c) were EDS spectrum taken from the surface and the bulk area respectively. The intensity ratio of Sr to Ti decreased at the surface. The behavior of compositional change was found to be dependent on a type of dopant. In addition, we analyzed atomic structures on (100) surface by HAADF-STEM. We will summarize the dopant effects for surface structures on SrTiO₃ (100) surface.
Atomic-scale investigation of chemically prepared rutile TiO\textsubscript{2}(110) step/terrace surface

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Control of the single crystal oxide surface at the atomic level may open an avenue for high quality thin films and interfaces. For example, it was demonstrated in a recent study that the sharp interface of LaAlO\textsubscript{3}/SrTiO\textsubscript{3} yields superior conductivity, magnetism and superconducting properties. In order to study these properties and extract new functionalities arising from interfaces, thorough understanding of the interface on an atomic scale is essential. However, atomic-scale topographic and electronic structures of step/terrace substrates prior to depositing thin films have not been clarified so far.

Here, we report on our study of the step/terrace structures on an atomic scale using the rutile-TiO\textsubscript{2}(110) substrate as an model system. Chemically prepared Nb-doped rutile-TiO\textsubscript{2}(110) single crystal with steps and terraces \textsuperscript{[1]} was annealed in the range of 300 to 950\textdegree C in UHV, and the structures of the quenched surface were investigated by using scanning tunneling microscopy (STM) at room temperature. It was found that the surface structure varies dramatically, depending on annealing temperature. Step and terrace structures were disordered (meandered) at 600-800\textdegree C and the flat atomic scale structure was recovered at 850-900\textdegree C. Step bunching and segregation of impurities were observed at 950\textdegree C. These results suggest that annealing to 900\textdegree C prior to the deposition results in the desired sharp interface between substrate and films.


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Synchrotron x-ray scattering determination of BaO / Silicon (001) interface structure

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The successful integration of functional crystalline oxides with covalent semiconductors requires atomic level control and understanding of the interface structure between the two sets of materials. While methods for atomic level control during deposition have been developed over the last decade, determination of the resulting interface structures has been incomplete, leaving questions about oxygen and silicon stoichiometry unresolved. To address these questions, we have developed a characterization approach with interface specificity based on a combination of synchrotron x-ray diffraction and first-principles density functional theory (DFT). We use this approach to study barium oxide on silicon grown by molecular beam epitaxy using a sub-monolayer strontium interfacial passivation layer. We observe x-ray diffraction from an interface phase that exhibits a 2×1 unit cell reconstruction. This scattering must be from the interfacial structure, since bulk silicon and BaO do not have this in-plane periodicity. We find that the diffraction is dominated by sub-Å rumpling of the BaO. By comparing this diffraction to that predicted for candidate DFT structures, we find that the 2×1 interfacial reconstruction is driven by the bonding configuration of the first monolayer of oxygen in the BaO. A monolayer of oxygen is bonded to the surface silicon atoms, increasing the conduction band offset by 0.7 eV, compared to the calculated band offset for a structure where the reconstruction is absent.
The role of strontium in oxide epitaxy on silicon (001)

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The ability to grow crystalline SrTiO$_3$ on the silicon (001) surface, developed in the last decade, enables the integration of crystalline oxides and semiconductors for both technological applications and fundamental scientific inquiries. This promise is related to the wide range of behavior exhibited by crystalline oxides, including magnetism, ferroelectricity, superconductivity, and colossal magnetoresistance. The most successful approach to realizing these epitaxial oxide-silicon (001) heterostructures requires manipulating substrate temperature and oxygen pressure on a layer by layer basis during the deposition of the metal-oxide layers. The transition layer between the semiconductor and crystalline oxide is an alkaline earth metal, most often strontium, that is deposited on the silicon surface at around 650°C. This strontium sub-monolayer forms ordered surface structures that have been extensively studied, both experimentally and theoretically. Despite this attention, inconsistencies remain between experimental results and theoretical predictions for this surface structure. Motivated by a desire to resolve these questions and develop a fundamental understanding of this important transition layer between silicon and oxide, we have studied the surface structures formed by strontium on miscut silicon wafers, which, unlike the regular silicon wafers, have a unique surface termination. These experiments avoid ambiguities in surface symmetry and reveal an unexpected reaction of strontium with the silicon surface. At high temperatures, this reaction rearranges the top layer of silicon to replace the original top layer with strontium. At low temperatures, this reaction is suppressed, leading to a different, but symmetry related, surface structure. Although all previous approaches to oxide epitaxy on silicon have required high temperature, we find that crystalline oxides can be grown on a clean silicon surface without the need to heat the wafer above 100°C.
Magnetic anisotropy and magnetoelectric coupling in hexagonal Ga-Fe oxides

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Multiferroism which signifies a coexistence of magnetism and ferroelectricity in a single phase has been an important research subject in functionally correlated oxides. Ga–Fe oxides (Ga<sub>2-x</sub>Fe<sub>x</sub>O<sub>3</sub>) are considered to be promising multiferroic materials because of their possible piezoelectric and magnetoelectric (ME) coupling effects near room temperature. The lattice symmetry of a GaFeO<sub>3</sub> (GFO) single-crystal is known to be orthorhombic with the space group P<sub>c2</sub>1<sub>n</sub>. Recent x-ray absorption spectroscopic study indicated that the GFO were characterized by orbital and bonding anisotropies with exotic off-centering local distortions in the a-b plane of D<sub>3d</sub> symmetry.

In this work, we will present our recent investigation on the structure and the ME coupling properties of the flux-grown single-crystal GFO. X-ray diffraction study and compositional analysis indicate that our flux-grown GFO is stoichiometric (i.e., Ga:Fe=1:1) but its crystal symmetry is hexagonal, which is in contrast to the well-known orthorhombic P<sub>c2</sub>1<sub>n</sub> crystals with their T<sub>N</sub> between 200 and 260 K. Interestingly, our hexagonal GFO exhibits a strong magnetic anisotropy at room temperature with its magnetic easy axis along the c-axis. A further study showed that the relative dielectric permittivity of the hexagonal GFO underwent some changes under the applied dc magnetic field (i.e., magnetocapacitance effects), suggesting that the hexagonal GFO is room-temperature multiferroic with a non-zero degree of the ME coupling.
Ferroelectric Size-effect on Switching and Imaging of Nanoscale BiFeO$_3$ Films in Ultra-High Vacuum

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One of the highly pursued topics in modern ferroelectricity is the ferroelectric size effect, which includes the scaling of the polar distortion in ferroelectric materials, the domain structure in nanoscale ferroelectrics and most importantly the limits of our ability to switch polarization by applying electric field which is closely related to polarization charge screening mechanisms in nanoscale materials. Probing ferroelectric switching in ultrathin oxides requires new techniques since standard capacitor measurements hindered by increased leakage and measurement time-constant and with a few exceptions can not be reliably scaled below ~20 nm. We have explored the limits of ferroelectric switching using a new Piezoresponse Force Microscope in Ultrahigh Vacuum (UHV-PFM) and a recently invented Band-Excitation Piezo Force Spectroscopy (BEPFS). This combination of the environment, instrumental platform, and measurement technique offers several crucial advantages that allows for quantitative and reproducible ferroelectric measurements in few unit-cell films. The key finding of our work is that epitaxial BiFeO$_3$ films grown by pulsed-laser deposition on La(Sr,Mn)O$_3$ electrode can be repeatedly and reproducibly switched down to a thickness of 5 unit cells (2.0 nm) in ultrahigh vacuum without electric breakdown or topographic damage. In addition the polarization domain structure in these films is found to be strongly correlated with topography, yielding significant enhancement of piezoresponse upon unit-cell increments in the film thickness.

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2D Superconductivity at the LaAlO$_3$SrTiO$_3$ interface


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The interface between two insulating oxides, LaAlO$_3$ and SrTiO$_3$ (both band insulators), is metallic with a high mobility. We have recently shown that the ground state of this system is a superconducting condensate [1]. The epitaxial LaAlO$_3$ films are grown by pulsed laser deposition on TiO$_2$-terminated (001) SrTiO$_3$ substrates and are annealed in situ in oxygen.

The superconducting properties of the LaAlO$_3$/SrTiO$_3$ heterostructures display signatures of 2D superconductivity. We will discuss critical field anisotropy measurements, which allow the thickness of the superconducting gas to be determined. The superconducting properties are consistent with the Beresinskii-Kosterlitz-Thouless (BKT) predictions. However, for low current densities, I-V curves show some deviation from the expected behaviour for a perfect infinite 2D system. These deviations are attributed to the finite lateral size of the samples. To check this interpretation, experiments to probe this size effect have been performed and will be presented.

Electronic structure of the SrTiO$_3$/LaAlO$_3$ interface revealed by resonant soft x-ray scattering

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The interfaces of hetero-junctions composed of transition-metal oxides have recently attracted great interest. Among them, the interface between two band insulators SrTiO$_3$ (STO) and LaAlO$_3$ (LAO) is especially interesting due to the metallic conductivity [1] and even superconductivity [2]. There has been intense debate on the origin of this metallicity, that is, whether it is due to oxygen vacancies (“extrinsic”) or due to the polar nature of the LAO structure (“electronic reconstruction”). In this study we investigated the electronic structure of the STO-LAO superlattice by resonant soft x-ray scattering, which has recently been used to study SrMnO$_3$-LaMnO$_3$ superlattices [3]. Our superlattice consisted of seven periods of 12 unit cells (uc) of STO and 6 uc of LAO grown on a STO (001) substrate. Figure 1 shows the photon-energy dependence of the (003) peak at the Ti 2p edge. The (003) peak is only allowed if the interface differs from a bulk termination. Both (002) and (003) peaks show resonant enhancement at the Ti 2p, O 1s, and La 3d absorption edges. From the peak position analyses taking into account the effects of refraction, we found disagreement between experiment and calculation based on a simple model consisting of just STO and LAO and obtained evidence for electronic reconstruction of Ti 3d and O 2p occurring at the interface without interdiffusion of La atoms. From reflectivity analyses, highly asymmetric properties of the STO/LAO superlattice were concluded, which means that the n-type interface (AlO$_2$/LaO/TiO$_2$/SrO) is different from the p-type (TiO$_2$/SrO/AlO$_2$/LaO).

Electric field driven superconductor to insulator quantum phase transition at the LaAlO$_3$/SrTiO$_3$ interface


Electronic states with unusual properties can be promoted at interfaces between complex oxides. A particularly fascinating system is the interface between band insulators LaAlO$_3$ and SrTiO$_3$, which displays conductivity with high mobility. Recently two possible ground states have been experimentally identified: a magnetic state (1) and a two dimensional (2D) superconducting condensate (2). In this contribution, field effect experiments performed on this system will be discussed. Using the electrostatic tuning of the carrier density, the phase diagram of the system has been explored, revealing a quantum phase transition (QPT) separating a 2D superconducting state from an insulating state. The critical exponents of the QPT are compatible with a 3D-XY model pointing at the key role of quantum phase fluctuations in this 2D low carrier density superconductor. The insulating phase displays signatures of weak localisation. Down to 30 mK no magnetism has been detected.

Switchable 2DEG at a ferroelectric KNbO$_3$/BaTiO$_3$(001) interface: A first-principles study

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In recent years, all-oxide heterostructures with atomically abrupt interfaces have attracted considerable interest. In particular, the demonstration of a quasi-two dimensional electron gas (2DEG) at the (LaO)$^+$/TiO$_2^0$ interface in LaAlO$_3$/KNbO$_3$ (001) heterostructures fuelled intense experimental and theoretical research activity. It was found that the 2DEG has a high carrier mobility and electron density that are interesting for applications in all-oxide electronic devices. For such applications it is desirable to have the ability to control the properties of the 2DEG by external stimulus, e.g., by an electric field. In this study we use density functional calculations to explore a ferroelectric KNbO$_3$/BaTiO$_3$ (001) heterostructure for this purpose. We find that electronic reconstruction at the polar (NbO$_2^+$)/(BaO)$^0$ interface and ferroelectricity of the constituents create a 2DEG, properties of which are determined by the orientation of the electric polarization. Along the [001] direction, KNbO$_3$ consists of alternating planes of (NbO$_2^+$) and (KO)$^-$ which are analogous to the polar planes in LaAlO$_3$. Likewise, BaTiO$_3$ consists alternating planes of (TiO$_2^0$) and (BaO)$^0$ and are analogous to the neutral planes in SrTiO$_3$. The polar discontinuity at the (NbO$_2^+$/BaO)$^0$ interface in KNbO$_3$/BaTiO$_3$ heterostructure is similar to that at the (LaO)$^+$/TiO$_2^+$ interface in LaAlO$_3$/SrTiO$_3$ heterostructure. This leads to the electronic reconstruction resulting in a 2DEG formed at this interface. Our calculations reveal that the (NbO$_2^+$)/(BaO)$^0$ interface in KNbO$_3$/BaTiO$_3$ (001) superlattice is conducting due to partially occupied Nb 4$d$-states confined at the interface. We predict that occupancy of the conducting states at the Fermi energy and hence conducting properties of the interface are strongly dependent of the orientation of electric polarization and consequently can be controlled by an applied electric field.
Electric-field-induced resistance switching of VO\textsubscript{2} thin films – mechanism, and application as an oscillator

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The electric-field-induced resistance switching (EIRS) of VO\textsubscript{2} is widely believed as an appearance of a thermally-induced low resistance state (T-LRS) through a Joule heating, although no direct evidence for this picture has been presented. In this report we discuss the mechanism of the EIRS of VO\textsubscript{2} on the basis of hydrostatic pressure experiments.\textsuperscript{[1]} Moreover, we demonstrate an application of a VO\textsubscript{2} EIRS device as a simple voltage-control oscillator which consists of only two circuit components.\textsuperscript{[2]}

VO\textsubscript{2} thin film planar-type junctions were fabricated on Al\textsubscript{2}O\textsubscript{3} (0001) substrates. EIRS characteristics of the junctions were investigated at hydrostatic pressures up to 2 GPa and room temperature. As the results, the resistance in the electric-field-induced low resistance state (E-LRS) was revealed to be insensitive to the hydrostatic pressure, in contrast to the apparent suppression of resistance in the T-LRS.\textsuperscript{[3]} The critical current to induce the E-LRS is increased as the pressure is increased, while the voltage at the transition is independent of the pressure. These EIRS behaviors under hydrostatic pressures suggest that neither the trigger nor the maintenance of the E-LRS is caused by thermal effect.

A voltage application to the pair of a VO\textsubscript{2} junction and a load resistor drives an oscillation of the junction voltage, when the combination of the source voltage and the load resistance satisfies certain conditions. The frequency can be tuned by the source voltage and the load resistance. The mechanism of the oscillation is considered to be the alternate occurrence of an EIRS in the VO\textsubscript{2} junction and a rapid dielectric relaxation in the load resistor.

Fabrication of nanostructured optical waveguides in (Pb,La)(Zr,Ti)O₃ epitaxial thin films

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High transparency at infrared frequencies and strong electro-optic effect make the ferroelectric perovskite (Pb,La)(Zr,Ti)O₃ (PLZT) a material of special interest to electro-optical devices. In this study, the structural, ferroelectric, and optical properties of PLZT thin films, sputter-deposited on MgO(100), are investigated with the objective of incorporating this material in future optical components. Fabrication of nanostructured waveguides in the PLZT epilayer and propagation of light through these structures will be discussed.

X-ray diffraction analysis shows epitaxial growth of single-crystalline PLZT thin films, with a (001) rocking curve half-width of ~0.3°. Atomic force microscopy measurements confirm that the PLZT films feature smooth surfaces, which meet the requirements for optical waveguide applications. Recorded P–E loops show a remanent polarization, \( P_r \approx 27 \ \mu\text{C/cm}^2 \) and a coercive field, \( E_c \approx 130 \ \text{kV/cm} \). Estimates of the thickness and refractive index for the PLZT epilayer were derived using rutile prism coupling, and this data corresponds well with data obtained from spectroscopic ellipsometry measurements.

Numerical simulations were carried out to help design optical waveguides and photonic band gap structures in the PLZT thin film epilayers. Single-mode ridge type optical waveguides were defined using standard photolithographic techniques and chemical wet etching, with the purpose of guiding light in and out of regions with photonic band gap structures defined by focused ion beam processing. A tapered fiber arrangement was used for butt-coupling of infrared light (\( \lambda_0 = 1550 \ \text{nm} \)) into those waveguiding structures.
A possible mechanism of resistive switching in perovskite oxide heterojunctions

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Recently, reversible resistive switching between two or multilevel resistance states has been found to take place by short voltage pulses at room temperature in capacitor-like devices composed of a wide variety of insulating transition metal oxides [1]. This resistive switching attracts considerable attention due to the potential for device application such as resistance random access memory (ReRAM). Although the resistive switching effect has been extensively studied both experimentally and theoretically, the definitive mechanism involved has not been attained, yet.

To elucidate the origin of resistive switching, we studied the effect of annealing in oxidative atmosphere on resistive switching behaviors of the devices composed of p-type and n-type semiconducting oxides such as Pr0.7Ca0.3MnO3 (PCMO) [2] and Nb-doped SrTiO3 (Nb:STO) [3], respectively. The as-prepared devices, (before annealing) showed hysteretic I-V characteristics. After acquiring the I-V curves, the PCMO and Nb:STO devices were annealed at 400 ºC in air or O2 atmosphere. The annealed PCMO and Nb:STO devices converted into a LRS and a HRS, respectively, and the hysteretic behavior (resistive switching) was suppressed by the annealing. These results indicate that the density of oxygen vacancies plays an important role in the bistability in the resistance. Based on the experimental results, we propose that electrochemical migration of oxygen vacancies in the vicinity of the interfaces is the origin of the resistive switching.

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Correlation between stacking defect and resistive switching in Sr₂TiO₄ thin films

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A great deal of effort on reversible resistive switching has been done in oxide materials. However, the precise mechanisms are still unclear. One of the reasons is due to relatively high defect density in oxides. Unfortunately it is not easy to exclude the influence of lattice defects, even in a high quality single crystal [1]. On the contrary, lattice defect has a potential to work as charge traps, conduction filaments, and/or easy diffusion ion paths. In the sense, it is useful for understanding the mechanism to investigate resistive switching properties under control of lattice defects in channel.

Sr₂TiO₄ films were epitaxially grown on SrTiO₃ (001) substrates by pulsed laser deposition. Laser energy density, substrate temperature, and oxygen pressure during deposition were carefully adjusted to obtain stoichiometric films. At a low growth temperature of 700 °C, random distribution of SrO double layers both laterally and vertically was observed in Fig. 1 (a). This resulted in the disappearance of some peaks in XRD because a new extinction rule was created by the random distribution. On the other hand, films grown at a higher temperature of 900 °C showed well-ordered structure in Fig. 1 (b) due to large thermal energy which compensates local nanometer-scale nonstoichiometry of deposited adatoms [2]. For electrical measurements, a gold layer and Nb-doped SrTiO₃ substrates were used as top and bottom electrodes, respectively. Films grown at the low temperature that include high-density defects showed clear switching properties with a high on/off resistance ratio after an electrical forming process as shown in Fig. 2 (a). In contrast, poor switching hysteresis was seen in well-ordered films as presented in Fig. 2 (b). This clearly demonstrated the correlation between stacking defect and resistive switching in Sr₂TiO₄ thin films.

Fig. 1: TEM images of Sr₂TiO₄ films grown at (a) 700 °C and (b) 900 °C.

Fig. 2: Switching curves of Sr₂TiO₄ films grown at (a) 700 °C and (b) 900 °C.

Observation of inhomogeneous chemical states associated with resistance changes of Pt/CuO/Pt structures by photoemission electron microscopy

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Resistance random access memory (ReRAM) with metal/insulating-oxide/metal structures has recently attracted much attention as a candidate for next generation non-volatile random access memories. Among them, the characteristics of ReRAM based on binary transition metal oxides is considered to be dominated by low resistance conductive paths that are formed by red-ox reactions [1]. It has been reported that planar-type Pt/CuO/Pt structures show a unipolar resistance-switching phenomenon, and the low resistance “bridge” structure formed in CuO channels between Pt electrodes play an important role in the resistance-switching behavior [2]. However, due to a lack of information on the spatial distribution of chemical states, the origin of resistance changes induced by bias application has not been elucidated. In this study, we report the direct observation of the chemical state distribution in the bridge structures using photoemission electron microscopy (PEEM) which enables us to detect x-ray absorption from micro regions with the spatial resolution of sub-microns. Consequently the lateral chemical state distribution can be displayed by mapping of chemical valences. We have found that lighting-shaped paths run across the CuO channels between Pt electrodes in the “reduction” mapping images. Combined with scanning electron microscopic images, reduced areas were obtained only in the bridge structures. Furthermore, the micro XAS spectra obtained from PEEM images indicate that CuO (Cu (II)) is reduced to Cu2O (Cu (I)) or Cu metal in the bridge structures. These results strongly suggest that the bridge structures are generated from the reduction reaction in the CuO channels, and the reduced conductive path is responsible for the resistance-switching phenomenon.

Predictable resistance switching of Pt/NiO/Pt based on Joule heating effects

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The semiconductor industry has long searched for a next-generation nonvolatile memory device, which can retain its data even when the power is interrupted. A new concept called resistance random access memory, in which its resistance can be repeatedly switched between a high and a low value by applying electric field, has recently attracted lots of scientific and technological interests. Especially for the unipolar resistance switching, which shows the low-/high-resistance switching along the single bias voltage, switching mechanism are largely classified into formation and rupture of conducting path based on a thermal effect or electronic charge injection effects [1]. All models, however, leave unanswered questions.

In this works, normalized third harmonic $B_{3f}$, which is thermal response to an external voltage, is measured for low resistance state of Pt/NiO/Pt thin films. $B_{3f}$ is theoretically based on Joule heating effects of local conducting path, and provides a direct measurement of the microscopic current distribution [2]. The scaling of $B_{3f}$ as a function of resistance suggests that nonlinear current-voltage curve is due to Joule heating effects. $B_{3f}$ versus maximum current at the moment of conducting path rupture has a scaling relation. Therefore, $B_{3f}$ can be a new nondestructive parameter to predict rupture of conducting path. All experimental results can be explained by computer simulation based on bond percolation model with Joule heating effects.

Our results support that the switching mechanism can be understood by formation and rupture of the conducting path, which can be governed by the percolation nature. Especially, rupture of conducting path is driven by Joule heating effects. Furthermore, these results suggest that broad switching voltage distribution can be reduced by nanoscale-confined conducting paths.

Fabrication and Characterization of All-Oxide Microelectromechanical Systems

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In this work, we report the fabrication processes and the mechanical characterization of Microelectromechanical systems (MEMS) entirely made with epitaxial oxide thin films deposited with Pulsed Laser Deposition with the aim of realizing all-oxide MEMS for stress manipulation of epitaxial transition metal oxide thin films. SrTiO₃(STO) based micrometric cantilevers are thus fabricated and mechanically deformed by external pressure or external electric fields. Mechanical characterization of STO MEMS is performed by Force-Distance curves through the tip of an Atomic Force Microscope. We discuss how the cantilever geometry and its dimensions affect both the mechanical parameters of the MEMS device (i.e. its elastic constant) and the maximum epitaxial strain that can be realized with these devices. The occurrence of mechanical hysteresis (i.e. pull-in and pull-off voltages) and strain distribution along the MEMS will be also quantified and modelled. The modelled quantities will be compared with the electrical measurements on MEMS structures showing electric-field-assisted strain modulation of epitaxial conducting oxide films.
Single Crystal SrTiO$_3$ (100) Field Effect Transistors with epitaxial DyScO$_3$ gate insulator

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A field-effect transistor (FET) is a useful tool for the study of electronic states at oxide heterointerfaces because a transistor it is possible to modulate the density of carriers in a thin, nm-order interface layer and probe the carrier density by simple transport measurements. Transistor switching performance is thus a good measure of the structural quality of the gate-channel heterostructure. In this work we use SrTiO$_3$ as a channel material because of the very low carrier density at which a metal-insulator transition occurs. The gate insulator is an epitaxial layer of DyScO$_3$, which is a wide-gap insulator that has only a 1% lattice mismatch with SrTiO$_3$ and can thus be grown epitaxially in atomically flat layers on a SrTiO$_3$ (001) surface up to a thickness of about 20 monolayers. The insulator growth was done by pulse laser deposition at a relatively low temperature and high oxygen pressure (700°C and 1 mTorr) in order to avoid cation segregation and oxygen loss at the SrTiO$_3$ substrate surface. Post annealing in oxygen was used to compensate for any residual oxygen loss at the channel interface. Device patterning was done by photolithography [1] with the channel length/width ranging from 100 $\mu$m/500 $\mu$m to 10 $\mu$m/50 $\mu$m. In this presentation we report the characteristics of the epitaxial DyScO$_3$/SrTiO$_3$ FETs at low temperature. Smaller devices gave better performance at room temperature but device scaling had less effect at low temperature. The field-effect mobility reached 300 cm$^2$/Vs at 30 K, which is close to the expected bulk value. We measured time-dependent channel current relaxation under high gate field conditions. The relaxation measurements appear to show that under MV/cm order fields there is relaxation both in the dielectric properties of the gate insulator and in the mobility of carriers in the SrTiO$_3$ channel.

Electrical control of rectification in Pt/TiO$_x$/Pt trilayer

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We report the reproducible rectification switching in the PtBE/TiO$_x$/PtTE trilayer synthesized by magnetron sputtering, where BE and TE are the bottom and top electrodes, respectively. The TiO$_x$ layer was prepared by the reactive sputtering followed by the post-oxidation. By increasing the oxygen partial pressure during the post-oxidation process, we doped the larger amount of oxygen vacancies ($V_O$) at the PtBE/TiO$_x$ interface than the TiO$_x$/PtTE interface. Accordingly, the marked rectification was observed in the virgin state of Pt/TiO$_x$/Pt. The current-voltage ($I$-$V$) curves were measured by contacting W probes on PtBE and PtTE. Shown in Fig. 1 is the demonstration of the rectification switching in Pt/TiO$_x$/Pt. The direct current (DC) $I$-$V$ curve was measured after applying a voltage pulse. When the polarity of the voltage pulse is positive, the forward current is observed under the positive voltage in the subsequent DC $I$-$V$ curve measurement. On the other hands, when the polarity of the voltage pulse is negative, the forward current is observed under the negative voltage in the DC $I$-$V$ curve. It is reasonably considered that this rectification switching is caused by the migration of $V_O$ by applying voltage because $V_O$ can act as a charged donor in TiO$_x$. Figures 2(a) and 2(b) are the output signal $V_{out}$ from Pt/TiO$_x$/Pt monitored with an oscilloscope connected in series with Pt/TiO$_x$/Pt for the input sine voltage wave signal. The frequency and amplitude of the input signal are, respectively, 4 Hz and 6 V. The value of the DC offset voltage $V_{DC}$ is 0 V for Fig. 2(a), while $V_{DC} = -9$ V for Fig. 2(b). As expected form the results in Fig. 1, the polarity of $V_{out}$ is successfully switched.

![Fig. 1 Rectification switching in Pt/TiO$_x$/Pt by applying voltage pulse.](image1)

![Fig. 2 Control of the polarity for the output signal $V_{out}$ with the offset voltage $V_{DC}$ of (a) 0 V and (b) -9 V.](image2)
Amorphous Semiconducting Oxides for Thin Film Transistors

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Thin film transistors (TFTs) permeate large area electronic technologies, such as flat panel displays and flexible electronics, with the most prevalent application being in liquid crystal displays where pixels are controlled by a thin film transistor array. In recent years, there has been increasing interest in using TFTs to “transistorize” arbitrary non-crystalline surfaces, thus adding smart surface functionality to arbitrary objects. For thin film transistors, amorphous semiconducting oxides are remarkably attractive in comparison to amorphous Si thin-film transistors. This talk will focus on the processing and properties of both n- and p-type amorphous semiconducting oxides, addressing issues related to device fabrication, device stability. Efforts to realize TFTs with p-type channels will be discussed. Specific materials issues will include doping effects in the n-type Zn-In-O system, as well as p-type conduction in Zn-Co-O.
LaAlO$_3$ as high-$k$ gate dielectric on III-V semiconductors

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The identification of high dielectric constant (high-$k$) gate insulators for III-V semiconductor metal-oxide-semiconductor field-effect transistors (MOSFETs) is of considerable interest, since such a device would combine a high carrier mobility (compared to Si-based transistors) and low gate leakage currents. A basic requirement for suitable dielectrics is its thermodynamic stability in contact with the III-V semiconductor at the expected processing temperatures. Although there is insufficient thermodynamic data available for a complete analysis, the existing data suggests that the same binary oxides (and combinations thereof) which are stable on silicon are also stable on III-V-semiconductors as GaAs, AlAs, AlP, AlSb, GaP, GaSb, InAs, InP, and InSb, and thus could be used as epitaxial or amorphous gate dielectrics, if they also match other important key parameters, such as interface state density, high $k$, and low leakage current. We will focus our presentation on LaAlO$_3$ films on GaAs and Si-capped GaAs. After deposition of the GaAs (or Si/GaAs) layer using molecular beam epitaxy, the samples were capped with an approx. 20 nm thick arsenic layer prior to air exposure and transfer for dielectric deposition. Subsequently, the As cap was removed at 300°C in UHV and the sample cooled to below 100°C, then the LaAlO$_3$ dielectric was deposited at this low temperature by molecular-beam deposition using an oxygen background pressure of 2·10$^{-6}$ Torr. After the film deposition, the samples were annealed at 340°C in O$_2$/O$_3$. TaN was used as gate electrode, and an additional post-deposition or post-metal anneal was performed. The resulting MOS capacitors show promising electrical properties: EOT of 5.4 nm for a 20 nm LaAlO$_3$ layer, interface state density $21\times10^{11}$/cm$^2$eV, low leakage $< 1mA/cm^2$ at $V_{fb}+1V$. Results of the structural and electrical characterization of the devices will be presented.
Low-temperature carrier accumulation of high-density electrons in ionic-liquid/ZnO electric-double-layer transistor

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In metal-insulator-semiconductor field-effect transistors (MISFETs), attaining high capacitance (>1 μF cm⁻²) is extremely difficult for most dielectric insulators due to their relatively low dielectric constants and the voltage limitation of the dielectric breakdown. Electric double layer (EDL) at ionic-liquid/semiconductor interface, working as a nano-gap capacitor with large capacitance, can accumulate high-density charges (carriers) at the semiconductor surface. Using this method, we have realized charge accumulation of high electron density of 6.0×10¹⁴ cm⁻² in ionic-liquid gated EDL transistors (IL-EDLTs) on ZnO at room temperature. Carrier accumulation in IL-EDLTs at low temperature, where the chemical reactivity of IL were greatly suppressed, was reported here for the first time.

The IL-EDLTs were fabricated by sandwiching an ionic liquid (DEME-(CF₃SO₂)₂N) between a platinum-coil gate electrode and a ZnO single crystal with a Hall bar pattern. Field-effect and Hall-effect measurements were carried out at low temperatures for studying the field-effect induced carrier accumulation of high-density electrons in EDLTs.

The measured effective capacitance of EDL was 34 μF/cm², which played a crucial role in the carrier accumulation and insulator-metal transition. Hall effect measurements revealed that due to the extended electrochemical potential window and weaker chemical activity of IL, as well as the low leakage of EDLTs, high-density carriers can be accumulated in a more reliable and reproducible manner via a higher applicable gate bias. The high carrier density of 5.3×10¹⁴ cm⁻², accumulated at 220K by a gate voltage of 5.5 V, showed a temperature-independent behavior as the temperature lowered.

Figure (a) Temperature depended transfer characteristics of IL/ZnO EDLTs. (b) Sheet carrier density of IL/ZnO EDLTs as a function of gate voltage at 300K and 220K. The insert is the temperature dependence of carrier density accumulated by a gate voltage of 5.5V

Please indicate your preference for presentation type: Oral () / Poster (√ )
Electric double layer transistor on NiO and Nd$_2$CuO$_4$

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Field-effect transistors (FETs) using an electrolyte as a gate have attracted a growing interest, because this kind of FETs can control carriers on a surface of semiconductors in a much wider range by a much smaller gate voltage than those of conventional FETs. In such FETs, ions in an electrolyte and carriers on a surface of a semiconductor induced by gate voltage form an electric double layer, and it serves as a gate capacitor (Fig. 1). Therefore, this kind of FETs is called electric double layer transistors (EDLTs). Recently, it has reported that a phase transition between insulating and metallic states was induced by field-effect with EDLT on InO$_x$ and ZnO.2 Because both materials studied with this method were band insulator, it is interesting to expand the application range to oxides having a strong electron correlation. Here, we report EDLTs using NiO and Nd$_2$CuO$_4$ as channels. Besides an electronic structure, NiO is also an important p-type semiconductor for transparent electronics, and there have been few reports on p-type FETs on transparent oxides.

Transfer curves of NiO and Nd$_2$CuO$_4$ EDLT are shown in Fig. 2 and 3. In both devices, KCLO$_4$ dissolved in poly(ethylene oxide) was employed as an electrolyte. The conductance of NiO and Nd$_2$CuO$_4$ were increased by applying a negative and positive gate voltage, respectively, and the modulations of the conductivity were reversible. This means the devices showed a p-type and n-type FET characteristics. The results have demonstrated that EDLT technique can be applied not only to band insulators but also oxides having a strong electron correlation and is useful in future investigation on electronic properties of this kind of oxides.

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Infrared spectroscopy of interface charge in ZnO field-effect transistor

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We used infrared (IR) Spectroscopy to probe voltage-induced interface charge in nanometer-thick accumulation layers in a bottom contact ZnO based field-effect transistor (FET). In these bottom-contact device, source and drain Al electrodes were deposited on top layer of ZnO / SiO2 / p-Si and ground contact at the bottom layer by In. IDT mask with 200µm spacing was used. Infrared transmission in far-IR region 100cm⁻¹ ~700cm⁻¹ was measured for the V_DS = 40V and with varying V_DG = 30V~80V. The Drude absorption exhibits highly localized FIR conductivity σ₁(ω) for gate voltage VGS < 40V. As VGS increases the localization effect decreases and σ₁(ω) involves progressively toward the free carrier behavior. The 2-d electron density of N_{2d} \gg 10^{13}cm^{-2} is estimated from the plasma frequency which is in fair agreement with the dc-capacitance analysis.
Crossover from 180-to-90 degree domains in ferroelectric thin films

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We have grown thin films of the classical tetragonal perovskite ferroelectric PbTiO₃ on DyScO₃ substrates. Due to the minuscule mismatch between PbTiO₃ and DyScO₃ at the growth temperature (< 0.4% at 570°C), high-quality paraelectric thin films can be grown, in which periodic ferroelectric domains form upon cooling down. The thinnest of these films (d< 8 nm) display 180° periodic domains due to the large depolarizing fields, whereas the thicker films (d> 28 nm) consist of 90° domain patterns determined by the elastic energy. For intermediate thicknesses, we have observed for the first time the crossover from 180°-to-90° domain walls. For this crossover, we propose a model that combines the elastic and electrical boundary conditions, giving rise to ferroelectric closure-like domains.

The observed domain periodicity (Λ) versus film thickness (d) correlation, has revealed the energetics of domain wall formation. For d< 8 nm, 180° domains form with periodicity in accordance with Kittel’s Law applied to ferroelectric domains (Λ~d⁷). Taking into account that during the cooling process, the domain walls can ‘freeze in’ [2], we have measured up to T=200°C and did not observe any changes, showing that the 180° domain ‘freezing’ occurs above this temperature. Fitting the vs. d data provides domain wall energy between 120 and 132 mJ/m² for freezing temperatures (Tf) between 200° and 440°C, respectively, which is in good agreement with ab initio calculations for free-standing PbTiO₃ [1].

The 90° domains in thicker films (d> 28 nm), obey Roytburd’s Law for 90° domains, with the same d⁷ dependence and domain wall formation energy between 10 (Tf = 440°C) and 65 mJ/m² (Tf = 25°C). Therefore, 90° domain walls are likely to be mobile down to room temperature [4]. This result, which is in good agreement with ab initio calculations [1] for freestanding PbTiO₃, is somewhat surprising for epitaxially grown films and is most likely due to the elastic properties of DyScO₃ [3].

Tunneling across a ferroelectric barrier: a first-principles study
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Ferroelectric tunnel junctions (FTJ), including a ferroelectric as the barrier material, have recently attracted a lot of interest since they are potentially interesting for technological applications such as data storage. In such system, the barrier has to be sufficiently thin to allow for tunneling but must at the same time remain ferroelectric, a property that tends to be suppressed in ultrathin films. Up to now, the modeling of FTJ has remained at the semi-empirical level. Here, we consider a prototypical system made of a ferroelectric oxide film between two gold electrodes and compute the I-V curve of the system using density functional theory and Non-Equilibrium Green's Function (NEGF+DFT) formalism. Our atomic-scale approach allows for the first time accurate and self-consistent description of the screening at the metal ferroelectric interface and of the atomic relaxation. It predicts that the asymmetry in the I-V curve for up and down polarizations is sufficiently large to be detected experimentally, therefore opening the door to applications in which the tunneling current allows the reading of the polarization state. Work supported by FAME-EMMI.
Effects of thickness and light exposure on ferroelectric properties of ultrathin PbTiO$_3$ films at room temperature

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Due to its collective nature, ferroelectric polarization is expected to change below a critical film thickness. Measurements of the unit cell's tetragonality, which is an indirect measure of the spontaneous polarization, can be used to probe such effects in ultrathin ferroelectric films. Recent synchrotron x-ray scattering studies, which utilized the existence of 180° polar domains as direct evidence of ferroelectricity in ultrathin PbTiO$_3$ (PTO) films, have demonstrated that, at elevated temperatures, layers are ferroelectric down to 3 unit cells' thickness. While it has been suggested that a variation in the domain periodicity at elevated temperatures originates from a change from an unscreened to a screened ferroelectric surface, it yet remains unclear why 180° stripe domains are not observed at room temperature using synchrotron radiation.

We demonstrate that the laboratory x-ray sources allow the study of ferroelectric stripe domains in ultra-thin PTO films. In contrast to the results for reported synchrotron experiments, we observe 180° stripe domains, rather than a mono-domain state, at room temperature for film thicknesses of 1.6 nm to 25 nm. A change in the domain period versus film thickness scaling relation is correlated with a distinct reduction in PTO tetragonality, suggesting that the polarization is constant for films thicker than 10 nm and decays for film thicknesses below 10 nm.

The stripe domain periodicity in thin PTO films displays a dependence on synchrotron radiation and ultraviolet light exposure. A comparative study of the ferroelectric domain behavior at room temperature under illumination by a laboratory x-ray source and by synchrotron light with different exposure times suggests that previous reports of a mono-domain state in ultrathin PTO films at low temperatures may have been caused by a prolonged exposure to synchrotron radiation, which appears to alter the domain configuration in this temperature range.
Film Thickness-Misfit Strain Phase Diagrams and Phase Transitions in Epitaxial PbZr$_{1-x}$Ti$_x$O$_3$ Ultra-thin Ferroelectric Films

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The question of size-effect in ultra-thin ferroelectrics and strain-engineering of ferroelectric thin films has now become an intensely debated topic. Despite the various contradicting results and theoretical approaches, there is unanimous consent that that mechanical and electrical boundary conditions control the ultimate phase stability in epitaxial ferroelectric thin films. Distinctly, the theoretical models reported so far treat these boundary and the system’s geometric conditions as almost independent parameters with no one work that takes into account the entire possible parameters. We present a full-scale non-linear thermodynamic model based on a Landau-Ginzburg-Devonshire formalism and the theory of dense polydomain structures in a multi-parameter space to predict the phase stability of (001) oriented PbZr$_{1-x}$Ti$_x$O$_3$ epitaxial thin films as a function of film thickness and epitaxial strain.\(^1\) The developed methodology, which accounts for electrostatic boundary conditions as well as the formation of misfit dislocations and polydomain structures, produces a thickness-strain phase stability diagram where it finds that the rotational phases (the so called $r$- and $ac$-phases) in epitaxial PZT films are possible only in a much smaller window than the previous predictions. Subsequently the high dielectric and piezoelectric coefficients that are associated with the rotational polar domains exist only in this very small window of phase stability. We find that for experimentally used thickness or strains (or both) that often fall outside this window, the film is in the $c$ or $c/a/c/a$ polydomain state. This work was supported by ARC Discovery Project DP0666231. We thank Dr Javier Junquera, Dr. Catalan and Prof. Noheda for useful discussions.

Figure 1: (a) Film thickness - strain phase diagram for epitaxial [001] PTO as a function of numerical misfit strain. The y-axis is the relative thickness, i.e., the ratio of the real thickness and the critical correlation length. For this particular case, the critical correlation length was taken as 1.4 nm. The x-axis is the numerical misfit strain calculated based on the paraelectric effective cubic lattice parameter of the ferroelectric and the substrate lattice parameter at growth temperature ($T_G=873$ K); the inset shows a contour map displaying the variation of the \( c \)-domain fraction $\phi_c^0$ in the stability area of the $c/a/c/a$ polydomain pattern at RT in the same parameter space; (b) film thickness - strain phase diagram at 473 K; (c) at 673 K; and (d) at 873 K.
Combinatorial growth of Ba(Sr)TiO$_3$ thin films using Pulsed Laser Deposition: Structural, dielectric and ferroelectric investigations

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The Ba$_x$Sr$_{1-x}$TiO$_3$ (BST-x) solid solution is a promising candidate for microelectronics applications in thin film form due to its intrinsic ferroelectric and dielectric properties. Applications rely on the high dielectric constant and the high tunability observed in bulk for certain compositions. However BST shows lower performances when deposited in thin film form. The decrease of the dielectric and tunability properties is explained by the microstructure and the defects present in the film and induced during the growth. A clear understanding of the impact of defects and the structure-properties relationship is needed to optimize the dielectric performance. In this work we grew BST thin films by Pulsed Laser Deposition using the combinatorial method. The development of such a method enabled us to grow in a very short time a library of samples with x spanning the whole phase diagram of the BST system. The thin films were characterized by RHEED, Raman spectroscopy and X-ray diffraction. Electrical properties of capacitors were also studied. We probed and optimized the composition gradient over a 10*10 mm$^2$ area. The X-rays and dielectric measurements show a clear trend from a STO-like to BTO-like response when varying the probed position on the sample. Coherent correlations are revealed between the microstructure and the dielectric and ferroelectric properties. In particular evidences are found for a critical concentration of Ba inducing elastic relaxations and therefore reduction of dielectric performances. In parallel observation of underdamped soft mode suggests stress-induced artificially ordering of Ti ions for high content of Ba. Such a result open the way to use stress engineering for controlling order-disorder interplay in the (Ba,Sr)TiO$_3$ system.
Piezoelectric properties of PbTiO$_3$/SrTiO$_3$ ferroelectric superlattices

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A key attraction of artificial ferroelectric superlattices is the potential to be able to tailor the properties of a material to a particular application. Here we study the piezoelectric properties of a series of PbTiO$_3$/SrTiO$_3$ superlattices [1] as a function of the volume fraction $x$ of PbTiO$_3$ in the structure. It has been demonstrated experimentally that samples with low $x$ and large density of interfaces exhibit improper ferroelectricity due to the coupling of antiferrodistortive and ferroelectric modes, as predicted by $ab$-initio calculations [2]. In order to determine the $d_{33}$ coefficient of the samples, we use a scanning tunneling microscope (STM) [3] in constant tunneling current mode. We have also implemented within the setup a Sawyer-Tower circuit which allows a simultaneous measurement of the polarization as a function of the applied electric field. It was found that the coercive fields decrease and vanish at low $x$ and the STM technique has clear advantages over the usual AFM technique. We investigated the origin of these low coercive fields which is partly linked to the choice of the electrodes.

References:

Dielectric and ferroelectric properties of PbTiO3/SrTiO3 superlattices

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Two-component superlattices, fabricated by epitaxial growth of alternating layers of the constituent compounds, provide an attractive way of generating new artificial materials with highly tuneable properties. In the case of PbTiO3/SrTrO3 superlattices, an elegantly simple recipe for achieving the desired characteristics can be obtained from Landau-Devonshire theory, where the free energy of the structure is given by a simple sum of the two components’ bulk energies, weighted by their relative volume fractions and taking account of the strain [1]. If the individual layers are made sufficiently thin however, another factor becomes dominant – the properties of the interfaces. Our experiments and ab-initio calculations show that when the interface density is high enough, the behaviour of the superlattices becomes drastically different and their structural and electrical properties are better described by treating the polarisation as a secondary order parameter, i.e. they behave as improper ferroelectrics [2].

Here we present new low-temperature electrical measurements aimed at better understanding the dielectric and ferroelectric properties of these fascinating new materials, and at elucidating the effect of different top and bottom electrodes on the stability of the polarisation.

A Ferroelectric Oxide Directly on Silicon

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Silicon and silicon dioxide form what is arguably the most important technological interface. With the end of Moore’s-law scaling for silicon fast approaching, alternatives to silicon dioxide are being pursued that may enable new device architectures and added functionality. The high reactivity of silicon with many elements and their oxides and the tendency of a pristine silicon surface to rapidly form its own oxide, however, present formidable challenges to the integration of functional materials with silicon. Here we demonstrate, for the first time, ferroelectric functionality in intimate contact with silicon. Using piezo-force microscopy we observe ferroelectricity in ultra-thin, strained, SrTiO$_3$ layers grown by oxide molecular-beam epitaxy in direct contact with silicon with no interfacial silicon dioxide. Stable ferroelectric nanodomains created in SrTiO$_3$ and observed at temperatures as high as 400 K, may form the basis for a new class of ferroelectric memories, bistable field-effect transistor devices and low power dissipation devices operating at room temperature.

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Ferroelectric lead strontium titanate films grown above and below $T_C$ using Molecular Beam Epitaxy

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Epitaxial strain can have a large impact on the properties of ferroelectric thin films\(^1\). For the classic ferroelectric perovskite of lead titanate (\(\text{PbTiO}_3\)) the transition is predicted to increase by up to hundreds of degrees by as little as a percent of epitaxial strain\(^2,3\). Moreover, if \(\text{PbTiO}_3\) is grown on (100)-\(\text{SrTiO}_3\) substrates this can lead to the extraordinary situation in which the ferroelectric-to-paraelectric phase transition is raised above the growth temperature. In this scenario, the grown ferroelectric phase is, strictly speaking, not the result of a distortion from a cubic paraelectric phase. How this affects the film properties has, to the best of our knowledge, not been investigated yet.

We have grown epitaxial thin films of \(\text{PbTiO}_3\) and strontium substituted \(\text{PbTiO}_3\) (\(\text{Pb}_x\text{Sr}_{1-x}\text{O}_3\)) on \(\text{SrTiO}_3\) using Molecular Beam Epitaxy\(^4\). This technique allows for an excellent control, at the atomic level, as well as continuous tuning of the Sr-doping. The temperature evolution of the films tetragonality, directly related to the ferroelectric order parameter, was investigated using X-ray diffraction. For pure \(\text{PbTiO}_3\) thin films the transition temperature, $T_C$, was indeed raised over the growth temperature (~650°C). The as-grown films underwent an irreversible transformation when taken to the paraelectric phase for the first time. Taking the films to the paraelectric phase a second time did not result in further change. To investigate the nature of this transformation, the $T_C$ was tuned using strontium substitution.

The temperature dependence of the ferroelectric order parameter was modeled using a Landau approach, including the effect of misfit strain and depolarization field. It has been found that the strain state of the films does not change upon heating to the paraelectric phase and that changes in the effective depolarization field alone account for the differences observed between as-grown \(\text{PbTiO}_3\) films and films cooled from the paraelectric phase.

MEMS Fabrication based on Epitaxial Piezoelectric Thin Films on Silicon

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This contribution will describe the realization of micro-electro-mechanical systems (MEMS) based on epitaxial piezoelectric thin films grown onto (100) silicon substrates. The all-epitaxial approach should provide superior piezoelectric coefficients over conventional polycrystalline films. Using SrTiO$_3$-buffered 2” silicon substrates, we grow by magnetron sputtering epitaxial thin films of Pb(Zr$_{0.2}$Ti$_{0.8}$)O$_3$ (PZT) and Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ onto SrRuO$_3$ electrode. Structural and piezoelectric characterizations of these stacks reveal epitaxial growth and high crystalline quality with piezoelectric coefficients $d_{33}$ of the order of 80 pm/V.

The influence of the microfabrication processing on the piezoelectric layer will be described and alternative routes for reducing their effects will be proposed. Preliminary results on the microfabrication of piezo cantilevers will be discussed.
Electrical properties of epitaxial trilayer heterostructures with ferroelectric BaTiO$_3$ barriers

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We studied the influence of the polarization on the electrical properties of epitaxial trilayer heterostructures with SrRuO$_3$ metallic oxide electrodes and ferroelectric BaTiO$_3$ barriers on SrTiO$_3$ substrates. The heterostructures were grown using atomic-layer controlled pulsed laser deposition, with barrier thickness ranging from 50 nm to 1.6 nm. We discuss the frequency, thickness, and temperature dependence of the remanent polarization and the coercive field of the P-E loops. We examine the current-voltage (I-V) characteristics of the thinner barriers to determine the conductance dependence on the polarization. By correcting for the leakage current through the thin barriers, we find evidence that the BaTiO$_3$ barrier remains ferroelectric down to 3.2 nm. These thin ferroelectric junctions may be used in nonvolatile memory applications.
Synchrotron x-ray scattering determination of interface structure and the ferroelectric ground state

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Heterostructures consisting of complex oxides and silicon, formed by molecular beam epitaxy through a layer-sequencing capability deposition procedure, allow for control of film properties through interface structure engineering. Exploiting the relationship between interfacial structural and oxide electrical properties requires precise synthesis control and detailed structural determination. We show how sub-angstrom structural details can have a substantial influence on film properties. Using synchrotron x-ray scattering, we have measured the polarization of SrTiO₃ thin films grown commensurately on silicon (001) with thicknesses ranging from 2.5 to 5 unit cells. Synchrotron x-ray measurements of the SrTiO₃ structure factor show that the thin films are polarized out-of-plane. This polarization has been reported to be a signature for ferroelectric SrTiO₃ with an in-plane compressive strain. However, we did not observe a displacive phase transition of this measured polarization between 20 and 380 K. First principles density functional theory calculations show that the polar interface couples to the SrTiO₃ thin film to create a polar lattice without a ferroelectric ground state.
Competition between interface stability and ferroelectricity in ultrathin SrTiO$_3$ films on silicon


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The successful growth of SrTiO$_3$ on silicon, made possible by the deposition of an interfacial layer of Sr atoms, opens up numerous possibilities for the integration of functional oxide properties such as ferroelectricity into field effect transistors and other electronics devices. Due to the epitaxial strain in Si-SrTiO$_3$ thin film structures, it has been suggested that SrTiO$_3$ itself may become ferroelectric on silicon substrates. Using density functional theory calculations, we demonstrate that the formation of strong ionic bonds between the interfacial Sr and the oxygen in the bottom oxide layer prevents the existence of ferroelectricity (i.e., a switchable polar state) in films of less than 6 unit cells. This effect is expected to persist into the region of film thickness in which SrTiO$_3$ begins to relax back into the cubic, non-ferroelectric phase. Changes in the atomic structure and the Sr-Ti-O ratio of the interfacial region are shown to affect the magnitude and direction of the interface polarity, but we demonstrate that the lack of ferroelectricity is independent of interface composition over a wide range of structures. Our results provide insight into the nature of the abrupt transition between a covalently bonded material and an ionically bonded material. Furthermore, they suggest several mechanisms for decreasing the intrinsic stability of the interface in order to successfully integrate a ferroelectric oxide with silicon.
Effects of substrate polarity, strain, and chemical boundary conditions on ferroelectricity in PbTiO$_3$ on DyScO$_3$


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Novel substrate materials such as DyScO$_3$ have recently been used to control the epitaxial strain imposed on ferroelectric films such as PbTiO$_3$, since epitaxial strain effects are predicted to strongly modify the phase transition temperature and domain structure. In addition, the polar nature of these substrates can be expected to impose a different electrical boundary condition than would arise at a traditional non-polar substrate surface such as SrTiO$_3$ (001). Chemical conditions at the free surface can also affect polarization in ultrathin films. Here we report in situ synchrotron x-ray investigations of the domain structure and polarization as a function of temperature and oxygen partial pressure for 10nm-thick films of PbTiO$_3$ grown on DyScO$_3$ by metalorganic chemical vapor deposition. While room temperature measurements on this system have been performed by Catalan et al. [1], we find a domain architecture that is very temperature dependent. At high temperatures (T<710K), we find a fine-scale domain structure with little net polarization, that transforms at an intermediate temperature (T<440K) to a domain structure with polarization that increases as temperature is lowered. We also observe that the substrate surface charge imposes a strong bias on the polarization of the film, inducing the film to be polar even above the experimentally determined Curie point. This bias can be overcome at low temperatures by the chemical effect of the oxidizing environment.


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Atomic-scale Imaging and Simulations of Interface Effects in Ferroelectric Thin Films

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The promise of revolutionary technologies based on complex oxide thin films require breakthrough advances in the science, integration and scaling of these materials. New capabilities to directly image the cation-anion dipoles in ferroelectrics and multiferroics is one such breakthrough that will allow quantification of the atomic displacements and the corresponding polarization of these materials at the atomic scale. We will present atomic-level maps of ferroelectricity in the interfaces between PbTiO\textsubscript{3}-based ferroelectrics and paraelectric substrates or metallic electrodes. These measurements are made using aberration-corrected scanning transmission electron microscopes which provide sub-Å electron probes. The oxygen column displacements are found to drop from a PZT matrix value of 0.04 nm to zero at the interface with SrTiO\textsubscript{3}. No appreciable oxygen column displacements are seen in the SrTiO\textsubscript{3}. It is known that the choice of the contact material will affect the properties of thin film ferroelectrics. The depolarizing field can be reduced either through compensation by free charge carriers at the interface or by the formation of oppositely polarized domains. When ferroelectric films are grown on insulating substrates it is expected that 180° domains will form. Interestingly, we find that 180° domains in a PZT film grown on a conducting SrRuO\textsubscript{3} layer and a monodomain PZT structure on what should have been an insulating SrTiO\textsubscript{3} substrate. Actual electrical boundary conditions can be very different than their idealized forms. The results demonstrate the importance of the electrical boundary conditions in determining the properties of very thin ferroelectric films. First principle density functional theory calculations were used to look for the charge-compensation mechanisms at ferroelectric interfaces. Two scenarios that explain/duplicate the observed behaviors at ferroelectric/ SrRuO\textsubscript{3} and ferroelectric/ SrTiO\textsubscript{3} interfaces will be presented.

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Relaxor behavior and ferroelectric switching in single crystal SrTiO$_3$ thin films


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By the virtue of their extraordinary piezoelectric and dielectric properties, relaxor ferroelectrics (relaxor) are a special class of materials that show enormous potential for applications including next-generation sensors, actuators and transducers that convert between mechanical and electrical forms of energy. Enormous electrochemical responses and nanostructures of the relaxor ferroelectrics have been intensively studied in many lead-based, perovskite materials and especially in the prototypical relaxors Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$ and Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ and their solid solutions with the conventional ferroelectric PbTiO$_3$. However, the difficult in achieving materials of the morphotropic-phase-boundary due to the complex composition as well as the volatility and toxicity of lead still hinder the industrial applications of the materials.

In this work, we report that prototype and simple perovskite SrTiO$_3$ thin films are relaxor when grown on (110) NdGaO$_3$ substrate which imposes compressive in-plane strains on the SrTiO$_3$ films. Temperature-dependent measurements of dielectric constants confirm the room-temperature relaxor behavior of the strained SrTiO$_3$ films. Using piezoelectric force microscopy (PFM) and second harmonic generation studies, it is found that the ferroelectric transition occurs around 400 K, which is in good agreement with thermodynamic calculations. PFM shows that nonvolatile ferroelectric switching could be achieved from nanoscale local regions probably due to the polarization build-up in nanopolar domains. These results open the promising potential of SrTiO$_3$ thin films for sensing and actuation in nanoelectromechanical systems and terabit nonvolatile memories for the first time. Details of the growth, crystal structure, relaxor behavior, and nanoscale polarization build-up of the single crystal SrTiO$_3$ films will be discussed. In addition, the convincing explanation of the nanoscale ferroelectricity in the SrTiO$_3$ films will be presented with thermodynamic calculations.
Growth of ZnO Epitaxial Films in Water at 90°C

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Epitaxial n-ZnO can be synthesized on (111) MgAl$_2$O$_4$ and both basal and m-plane GaN substrates, in water at 90°C, using soluble Zn-Nitrate. [1] The discovery that wurtzite ZnO can epi on (111) spinel lead to a new concept that explains the epitaxial growth of dissimilar structures based on Pauling’s rules of crystal chemistry. [1,2] Transparent, epi ZnO top electrodes on commercial GaN LEDs have been tested. [3]

Photoresist masks are used to produce growth windows. At high pH, the negatively charged soluble ZnOH$_3^-$ ion is attracted to the positive basal plane of piezoelectric ZnO to rapidly condense and form sharp, periodic needles with aspect ratios up to 50. The introduction of citrate ions decreases the growth rate in the ‘c’ direction by a factor of 3 to enable lateral epitaxial overgrowth (LEO). [4] The negatively charged citrate ions compete with the negatively charged soluble Zn species, to enable thick, ZnO epitaxial films with smooth surfaces. [4]

Calibrated Rama spectroscopy is used to determine stresses in epitaxial ZnO. Very recent work [5] that combines Rama spectroscopy and finite element analysis shows that the stresses within LEO films can be dramatically reduced by increasing the spacing between the periodic, circular growth windows. The large reduction in growth stresses, primarily due to the lattice mismatch between ZnO and GaN, results in thick (80 µm), crack free films.

Growth of oxide nanostructures on a templated SrTiO$_3$ surface

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The surface preparation techniques and the reconstruction structures of SrTiO$_3$ (STO) have been the considerable subjects to the scientists and engineers engaged in the field of oxide technology. However, one can hardly access the literatures dealing with the growth structures and size-limited characteristics of the initial growth stage of oxide on STO although the numerous reports for the bare surface can be found elsewhere. In this study, we performed the scanning tunneling microscopy (STM) on the initial growth structures of the STO submonolayers homoepitaxially grown on (2x1) reconstructed STO (001) surfaces by the pulsed laser deposition (PLD). STM images obtained from the submonolayers showed the perfect layer by layer growth. The submonolayers grown after one or two laser pulses at 600°C revealed that the minimum size of the thermally equilibrated STO island is 4x4 unit cell (u.c.) square and this size determination is followed by the change of the underlying surface reconstruction into a defective (4x4) one. STM images also showed one dimensional (1D) STO islands having the width of 4 u.c. and the length up to several nanometers, which can be defined by 4x2n u.c.$^2$ (n > 2). We suggest that the island of 4x4 u.c.$^2$ act as a minimum nucleation seed and the addition of 4x2 u.c.$^2$ STO molecular species to the nucleation seed is the most primary and dominant process in STO homoepitaxy. In addition, we observed that the layer by layer growth of STO is prohibited onto the surface of c(6x2) reconstruction, which can’t be described by the simple multiple of (2x1) reconstruction. This fact confirms the deterministic nature of the island formation to the surface reconstruction and reflects that the PLD process is not too destructive to remove the role of surface state in the growth of thin film on STO substrate.
Influence of orthorhombic distortion on the growth of single crystal CaRuO$_3$ metallic oxide thin films

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Development of metallic oxide electrodes is needed for systems containing strain engineered multiferroic materials. CaRuO$_3$, with a pseudo-cubic lattice parameter of 3.84 Å, is a promising electrode material due to its lack of magnetic properties and low resistivity, but previous work shows little progress in the growth of single domain films with smooth surfaces. In this work, the factors affecting growth of this orthorhombic films were investigated by growing epitaxial thin films of (110) CaRuO$_3$ on orthorhombic (110) NdGaO$_3$ and cubic (001) (LaAlO$_3$)$_{0.3}$-(Sr$_2$AlTaO$_6$)$_{0.7}$ (LSAT) substrates using pulsed laser deposition with *in-situ* high pressure reflection high energy electron diffraction. Despite equivalent lattice mismatch and stoichiometry on both substrates, CaRuO$_3$ on NdGaO$_3$ grows as a coherent single crystal with an atomically smooth surface whereas CaRuO$_3$ on LSAT grows as a multi-domain film with a rough surface. This work suggests that the orthorhombic distortion of the substrate plays an important role in heteroepitaxy.

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Dependence of growth directions on the electrical properties of perovskite oxide

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Perovskite oxides exhibit a wide variety of physical properties including superconductivity, ferroelectricity, and magnetism. The possibility of coherent integration of the functions present in their rich ground states has prompted to explore growth of artificial superlattices that may exhibit even wider variety of the properties with tremendous technological and academic interest. Most of the previous attempts have been made with (001) orientated films, whereas an (111)-oriented superlattice provides more enhanced configuration of B-site cations interaction as is the case of naturally formed double perovskites. It is not necessarily guaranteed that the properties of epitaxial films grown along the (111) direction are same as those of bulks and the (001) films, which is a key point to explore this new class of superlattices. Here we compare the physical properties of SrFeO$_{3-x}$ films grown on atomically flat (001) and (111) SrTiO$_3$ substrates. Resistivity of SrFeO$_{3-x}$ bulk crystals is known to be decrease with lowering $x$ [1].

We have grown a number of films in oxygen partial pressure ranging from 0.08 to 53 mTorr and at growth temperatures ranging from 730 to 950°C. Clear RHEED oscillations, of which periods correspond to pseudo-cubic unit cell, and atomically flat film surface were observed for all the conditions. The (001) films showed strong dependence of the oxygen partial pressure on their resistivity in addition to weak growth temperature dependence (Fig. 1). Based on these observations, we have prepared SrFeO$_{3-x}$ films on the (111) substrates at 830°C in two different oxygen partial pressures. We have seen a remarkable difference in the electrical properties between two different growth directions inspite of same growth conditions. This implies that careful study is necessary to elucidate the physical properties of perovskite oxides films grown in different orientations.

Formation of metal oxide nanoparticles from mist sources in a hot fine channel

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Nano-particles (NPs) whose sizes are 1-100 nm in diameter are attracting considerable interest for a variety of applications, for example, electronics via ceramics, catalysts, and even cosmetics, due to their unique or improved properties primarily determined by size, composition, and structure. Various growth methods of NPs have ever been developed, for example, spray pyrolysis, inert gas condensation, sputtering, microwave plasma synthesis, and chemical vapor deposition. However, because NPs heavily cohere by their own electrostatic force or van der Waals' force, agglomerated NPs have tended to be grown with the conventional process.

Recently we succeeded in growing uniformly-sized non-agglomerated metal oxide NPs by mist method. The mist method, which is similar to a spray method, consists of three processes; (1) the raw material solution is made into mist by the ultrasonic wave in the mist generation unit, (2) the mist is transferred to a reaction area by a carrier gas, and (3) the particles are formed by the heat decomposition. In order for effective formation of NPs, we designed the system so that the material solution mist carried into the hot “Fine Channel”. In the experiment we chose zinc acetate as a starting raw material. By using the system we have successfully obtained ZnO particles which are several nanosize in diameter. It should be noted that by conventional spray pyrolysis it has been quite difficult to obtain the NPs of their diameter smaller than several tens nm, in contrast to our mist method. For ZnO NPs, the blue shift of band gap was seen and it was ascertained that this shift was due to the quantum size effect. The luminescence lifetime was significantly increased compared to the ZnO thin films, and from this result the quantum confinement was firmly confirmed.

At the workshop we discuss the detailed advantages of the mist method for the formation of metal oxide NPs.
Tetragonal CuO: A new end member of the 3d transition metal monoxides

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The transition metal monoxides are a classic example of highly correlated materials. The systematic trends in the properties of these materials as one traverses the periodic table from MnO to CuO are well studied. CuO is the exceptional member of this series, however, as it deviates substantially from the trends exhibited by the members with lower atomic number. All the others have the cubic rock salt structure and all are correlated antiferromagnetic insulators. CuO differs in having a monoclinic structure as opposed to the rock salt structure of the other monoxides, and it also has a substantially lower N´eel temperature than a simple extrapolation of the trend across the periodic table would suggest. Presumably, this exceptional behavior is a consequence of its lower symmetry structure.

Clearly, the properties of CuO in higher symmetry structures would be of great fundamental interest in understanding correlated materials. Here we report the synthesis and preliminary electronic property determination of a tetragonal (elongated rock salt) form of CuO created for the first time using an epitaxial thin film deposition approach. The results demonstrate that higher symmetry forms of this important correlated oxide are possible and now available for physical study. Looking ahead, the N´eel temperature of rock salt CuO would be very high (700 to 800 K), as would be its associated exchange coupling J. If such a high-J CuO could be doped, its properties would be of great interest in the context of the high-\(T_c\) cuprate superconductors.
Lithium-Metal Oxides including LiNbO$_3$ and LiTaO$_3$ represent a unique material class as they are inherently multifunctional. Multifunctionalites including ferro/piezo/pyroelectricity, photo-refractivity, and strong non-linear optical and acoustical properties have long been known and exploited in these materials. However, the use of vacuum-restricted oxidation – resulting in incomplete Nb oxidation – has facilitated newly developed Li-based semiconducting derivatives such as LiNbO$_2$. This hexagonal crystal structure semiconductor is epitaxially grown on hexagonal SiC with small lattice mismatch and structural quality, as determined by x-ray diffraction figures of merit, similar to the SiC substrate. This new semiconductor has an optical bandgap of ~2 eV and is photoconductive, indicating material quality sufficient to allow minority carrier lifetimes large enough to modulate conductivity. The addition of an oxide semiconductor to the already multifunctional LiNbO$_3$ family offers tantalizing possibilities for superlattices consisting of semiconductor/ferroelectric materials for memory applications among other potential uses.

While the vacuum restricted oxidation of metals in Li-Metal Oxides facilitates epitaxy of otherwise unstable sub-oxides such as LiNbO$_2$, this form of growth also sets an upper limit on the ultimate growth rate of fully oxidized Li-Metal Oxides grown in vacuum. Thick films resultant from high growth rates such as those needed for optical or acoustic applications will require environments of substantially higher oxygen partial pressures than found in traditional MBE and will likely be provided via CVD or low pressure (as opposed to UHV) evaporative technologies. Efforts in this regard will be detailed.

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The epitaxial integration of complex oxides with semiconductors is a key requirement for many emerging technologies. In the short term, the scaling down of the SiO2 dielectric layer in current CMOS technology will soon result in unacceptable quantum mechanical leakage currents, requiring new materials with higher dielectric constants and defect free interfaces with silicon. More generally, the epitaxial integration of complex oxides with semiconductors would allow new devices which take advantage of the wide range of oxide properties, including ferroelectric, ferromagnetic, and multiferroic behavior.

To date, the only known method to grow complex oxides on silicon epitaxially has required 1/2 ML of an alkaline earth metal, usually Sr, to be deposited as a first step. When the Sr is deposited under normal experimental conditions, transitions from a 2x1 silicon reconstruction to a 2x3 and then to a 1x2 phase are observed. These transitions were thought to be required to achieve good epitaxy, but their origin and significance has not been understood.

Using first-principles density functional theory calculations, we examine the growth of sub-monolayer coverages of Sr on Si (100) and explain the unusual phase diagram observed experimentally. In particular, we report on a novel class of low energy 1/6 ML structures which require the replacement of 2/3 of the surface silicon dimers. These structures explain both the reconstructions seen at 1/6 ML as well as the rotation of the surface silicon dimers which is observed during high-temperature Sr deposition. This model predicts the successful growth of oxides under low-temperature conditions with the same interface structure as in the high-temperature case, but rotated 90 degrees. This low temperature growth path has been experimentally verified and produces epitaxial oxides of the same quality as the high temperature procedure.
Nanoscale depth-resolved study of point defects at chemically etched SrTiO$_3$ crystal surfaces

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The nature of surface electronic states and native point defects are central to exploring quantum phenomena and multifunctionality at complex oxide interfaces. Heterostructural perfection relies on chemically-etched, atomically flat substrate surfaces, while electronic quality depends on low point defect densities. We used nanoscale depth-resolved cathodoluminescence spectroscopy (DRCLS) to observe how chemical etching and annealing create, transform, and remove oxygen vacancies (V$_O$) and Ti$^{3+}$-related defects at SrTiO$_3$ single crystal surfaces etched by conventional buffered HF (BHF) and a new HCl-HNO$_3$ (HCLNO) alternative. Atomic force microscopy shows that both produce atomically flat TiO$_2$-terminated surfaces with similar morphology. DRCLS spectra acquired at ~ 42 K in ultrahigh vacuum with 1-5 kV incident beam voltages corresponding to 20-210 nm excitation depths respectively display 3.2 eV band gap emission, ~2.1 eV V$_O$ emission, and weak 1.6 eV emission from Ti$^{3+}$ defects before etching with V$_O$ emission increasing within the outer 20 nm. BHF treatment increases V$_O$ emission dramatically by ~12x, while HCLNO etching increases it only 2-3-fold, primarily within 20 nm of the surface. BHF-treated SrTiO$_3$ shows no emission from Ti$^{3+}$ defects, versus pronounced Ti$^{3+}$ emission from HCLNO etching. Thus BHF treatment creates significant concentrations of oxygen vacancies but very few defects involving Ti$^{3+}$ charge states, while HCLNO etching produces much fewer oxygen vacancies but more Ti$^{3+}$ defect states. However, annealing HCLNO-treated SrTiO$_3$ crystals at high temperature in oxygen removes Ti$^{3+}$ defects completely and reduces the density of oxygen vacancies as well, so both defect densities become comparable to those before etching. Our results demonstrate that HCLNO etching with O annealing produces both an atomically-flat SrTiO$_3$ surface morphology as well as low electronically-active defect densities. Furthermore, DRCLS is effective in determining the chemical and electronic nature as well as the spatial distribution of native point defects in this complex oxide.
Environmental Impact on the Polarization and Structure of 4 and 10 Layer Epitaxial BaTiO₃ Films

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Film environment and interfaces play a critical role in ferroelectric properties, dictating properties as films become thin through uncompensated surface charge or compensating structure or adsorption. We report the polarization and structure of 4 and 10 layer epitaxial BaTiO₃ films in a controlled ultrahigh vacuum environment and after exposure to water using low energy electron diffraction intensity vs. voltage (LEED I-V). BaTiO₃ ultra-thin films were grown on SrRuO₃/SrTiO₃ using laser-MBE in high oxygen pressures (10 mTorr). Despite the 2.3% lattice mismatch, reflection high energy electron diffraction (RHEED) oscillations and patterns during growth and subsequent atomic force microscopy (AFM) images show that layer-by-layer growth of flat, highly strained films is possible in ultrathin films. Films yield sharp (1x1) LEED patterns, indicating a well-ordered tetragonal phase structure. Comparison of observed diffraction intensities for 4 and 10 layer films with calculated intensities reveals a single BaO dead layer and a mono-domain vertically polarized state below. The single orientation is attributed to the intrinsic imprint asymmetry and the stability of a polarized phase to compensation of depolarizing charges by dipoles induced by surface stress. Exposure to water preserves the LEED pattern, but modifies diffraction intensities. LEED-IV analysis indicates water adsorption introduces significant oxygen vacancies in the top BaO layer and that the polarity of the film is reversed.

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