The Controlled Synthesis of Metastable Oxides Utilizing Epitaxy and Epitaxial Stabilization

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1. Executive Summary

Molecular beam epitaxy (MBE) has achieved unparalleled control in the integration of semiconductors at the nanometer level. Under the support of this DOE grant we have shown that it is possible to structurally engineer oxides with a precision that rivals the structural engineering and customization achieved in semiconductor structures. Two examples of the structural engineering that we have achieved in oxides are shown in Fig. 1 adjacent to a state-of-the-art semiconductor heterostructure. As described in Sec. 2.7, all of these MBE-grown structures are metastable.

It is the broad and greatly unexplored spectrum of electronic and optical properties exhibited by oxides that makes such structural customization exciting. The ability to structurally-engineer oxides opens the door to establishing the fundamental properties of known oxide materials as a function of direction (many are anisotropic), as well as creating and probing the properties of new oxides. We did both in this DOE program. For example, we used epitaxy to establish some of the fundamental dielectric and ferroelectric properties of SrBi$_2$Ta$_2$O$_9$ and SrBi$_2$Nb$_2$O$_9$—materials used in today’s “smart cards” (despite the dearth of knowledge about their physical properties). We also used epitaxy and epitaxial stabilization to synthesize new phases, e.g., Sr$_{n+1}$Ti$_n$O$_{3n+1}$ Ruddlesden-Popper phases for $n = 1$ to 5, and established some of their dielectric properties.

These advances were made through the use of epitaxy, epitaxial stabilization, and a combination of composition-control techniques including adsorption-controlled growth and RHEED-based composition control that we have developed, understood, and utilized for the growth of oxides. Also key was extensive characterization (utilizing RHEED, four-circle x-ray diffraction, AFM, TEM, and electrical characterization techniques) in order to study growth modes, optimize growth conditions, and probe the structural, dielectric, and ferroelectric properties of the materials grown. The materials that we have successfully engineered include titanates (PbTiO$_3$, Bi$_4$Ti$_3$O$_{12}$), tantalates (SrBi$_2$Ta$_2$O$_9$), and niobates (SrBi$_2$Nb$_2$O$_9$); layered combinations of these perovskite-related materials (Bi$_4$Ti$_3$O$_{12}$—SrTiO$_3$ and Bi$_4$Ti$_3$O$_{12}$—PbTiO$_3$ Aurivillius phases and metastable PbTiO$_3$ / SrTiO$_3$ and BaTiO$_3$ / SrTiO$_3$ superlattices), and new metastable phases (Sr$_{n+1}$Ti$_n$O$_{3n+1}$ Ruddlesden-Popper phases). The films were grown by reactive MBE and pulsed laser deposition (PLD). Many of these materials are either new or have been synthesized with the highest perfection ever reported. The controlled synthesis of such layered oxide heterostructures offers great potential for tailoring the superconducting, ferroelectric, and dielectric properties of these materials. These properties are important for energy technologies.
Fig. 1. High-resolution TEM images of GaAs/AlAs [Ref. 1], PbTiO$_3$/SrTiO$_3$ [Ref. 2], and BaTiO$_3$/SrTiO$_3$ [Ref. 3] superlattices grown by MBE. All are shown at the same magnification for comparison. The GaAs/AlAs and PbTiO$_3$/SrTiO$_3$ superlattices have comparable layer thicknesses (∼4 nm), whereas the layer thicknesses of the BaTiO$_3$/SrTiO$_3$ superlattice are half that of the others (∼2 nm).
2. Results from this DOE-Supported Research

2.1. Establishment and Thermodynamic Understanding of Adsorption-Controlled Growth Regime for PbTiO₃ and Bi₄Ti₃O₁₂ by MBE

We have investigated the use of an adsorption-controlled growth mechanism to accurately and reproducibly control film stoichiometry during the growth of oxides by MBE. Adsorption-controlled growth was first utilized for the MBE synthesis of epitaxial GaAs thin films over 30 years ago.²⁻⁷ This growth mechanism relies on the volatility of the group V component and has been explained using thermodynamics.²⁻¹¹ In the growth of oxides, the oxygen incorporation is controlled by an adsorption-controlled growth mechanism, but we have established and understood (using thermodynamics) that in addition to oxygen, the incorporation of lead and bismuth may also be controlled by an adsorption-controlled growth mechanism.¹²,¹³ For example, PbTiO₃ and Bi₄Ti₃O₁₂ can be grown in a regime where it is only necessary to accurately control the titanium flux. Within a wide range of lead, bismuth, and oxygen fluxes (the “growth window” for the adsorption-controlled growth of these phases), phase-pure PbTiO₃ and Bi₄Ti₃O₁₂ films may be realized with the growth rate entirely controlled by the titanium flux. We have demonstrated from measured film thickness, RBS composition measurements, monitoring of RHEED half-order intensity oscillations during growth, and in situ flux measurements using atomic absorption spectroscopy (AA), that at suitable temperature and ozone pressure the titanium sticking coefficient approaches one and the excess lead or bismuth desorbs.¹²,¹³

In Fig. 2 we show the results of our thermodynamic calculations where we contrast the adsorption-controlled growth window for the synthesis of GaAs with that for PbTiO₃ and Bi₄Ti₃O₁₂. Because PbO (and As₂) is the dominant vapor species that exists when PbTiO₃ (or GaAs) is heated in the temperature-pressure region plotted,¹⁴ the axis of the ordinate in Fig. 2(a) can be plotted as simply a function of pressure. However, as many BiₓOᵧ species with comparable partial pressure are created when Bi₄Ti₃O₁₂ is heated, the ordinate axis in Fig. 2(b) is the total flux of bismuth (or arsenic) atoms. Like GaAs, it can be seen that a growth window exists for the adsorption-controlled growth of PbTiO₃ and Bi₄Ti₃O₁₂. In comparison to GaAs, however, the latter growth windows are considerably narrower. Nonetheless, the adsorption-controlled growth windows significantly simplify the phase-pure growth of these multicomponent oxides by MBE.

Fig. 2. The thermodynamics of adsorption-controlled growth. For GaAs growth, the growth window for phase-pure GaAs growth (as a function of reciprocal temperature and As₂ pressure in (a) or as a function of reciprocal temperature and arsenic flux in (b)) exists.
between the two dashed lines. For PbTiO₃, the growth window for phase-pure PbTiO₃ growth as a function of reciprocal temperature and PbO pressure exists between the two solid lines in (a). For Bi₄Ti₅O₁₂, the growth window for phase-pure Bi₄Ti₅O₁₂ growth as a function of reciprocal temperature and bismuth flux (from all of the BiₓOᵧ species in the vapor phase) exists between the two solid lines in (b).

The use of adsorption-controlled growth has proven to be extremely effective for the MBE growth of III-V and II-VI semiconductors, PbTiO₃ and Bi₄Ti₅O₁₂ (our work which has since been confirmed by others), Bi₂Sr₂CuO₆, and to a lesser degree the growth of (Rb,Ba)BiO₃. We anticipate that adsorption-controlled MBE growth will be applicable to many other multicomponent oxide materials containing a volatile metal-oxide constituent.

2.2. Adsorption-Controlled Growth of SrBi₂Ta₂O₉ and SrBi₂Nb₂O₉ by PLD

Like Bi₄Ti₅O₁₂, these structurally-related Aurivillius compounds also grow in an adsorption-controlled growth regime with bismuth oxide species being analogous to arsenic in the GaAs system. In other words, a constant overpressure of the volatile bismuth oxide species must be maintained in the system to stabilize epitaxial, phase-pure growth. To fully exploit this phenomenon, we have explored the use of non-stoichiometric, bismuth-rich targets as source materials for the growth of SrBi₂Ta₂O₉ and SrBi₂Nb₂O₉ by PLD. To maintain this appropriate overpressure, particular attention must be paid to the PLD growth conditions (substrate temperature, oxidant pressure, laser fluence, and laser pulse rate) as they each play a significant role in determining an optimized growth window. We have optimized the growth conditions of SrBi₂Ta₂O₉ and SrBi₂Nb₂O₉ films by PLD by exploring a wide range of bismuth-rich target compositions and corresponding growth conditions. This optimization of adsorption-controlled growth conditions has allowed us to grow epitaxial films of these materials with unparalleled perfection and establish several of their fundamental properties, as described below.

2.3. Growth of SrBi₂Ta₂O₉ and SrBi₂Nb₂O₉ Films with Highest Structural Perfection and Highest Remanent Polarization Ever Reported

Although they are now widely used in “smart cards,” little is known about the fundamental properties of the layered ferroelectric materials SrBi₂Ta₂O₉ and SrBi₂Nb₂O₉. For example, prior to our work the spontaneous polarization of these materials was unknown, as was the anisotropy in the dielectric constants, coercive fields, and fatigue resistance. The critical property that was known about these materials is that polycrystalline SrBi₂Ta₂O₉ and SrBi₂Nb₂O₉ films were capable of withstanding repeated ferroelectric switching cycles (in excess of 10¹² in polycrystalline films) without degradation. The layered structure of SrBi₂Ta₂O₉, SrBi₂Nb₂O₉, and other Aurivillius phases that show similar fatigue-resistance, was argued to be responsible for this advantageous property. To get a more detailed understanding of what makes these materials fatigue resistant, it is desirable to measure the anisotropy in the properties of SrBi₂Ta₂O₉ and SrBi₂Nb₂O₉ films. For example, are these materials fatigue resistant in all directions, e.g., perpendicular to as well as parallel to their Bi₂O₂ planes? In addition, spontaneous polarization is a key parameter of all ferroelectrics.

To investigate the anisotropy in the dielectric and ferroelectric properties of SrBi₂Ta₂O₉ and SrBi₂Nb₂O₉ films, we have grown epitaxial films of these materials on (001), (110), and (111) SrTiO₃ substrates and studied their orientation, perfection, and electrical properties with four-
circle x-ray diffraction, AFM, RBS, TEM (both planar view and cross-sectional views), polarization-electric field (P-E), and capacitance-voltage (C-V) measurements. The epitaxial orientation relationship on all substrates can be described as one involving a local continuation of the perovskite sublattice and is schematically shown in Fig. 3. Four-circle x-ray diffraction,\textsuperscript{26,29,30} RBS ($\chi_{\text{min}} = 12\%$ for SrBi$_2$Ta$_2$O$_9$ and $\chi_{\text{min}} = 5\%$ for SrBi$_2$Nb$_2$O$_9$),\textsuperscript{26,31} and TEM\textsuperscript{32,33} analyses indicate that the epitaxial films grown under our optimized adsorption-controlled conditions have the highest structural perfection and phase purity reported to date for these materials.

The three orientations of epitaxial SrBi$_2$Ta$_2$O$_9$ and SrBi$_2$Nb$_2$O$_9$ films have been used for three different purposes. The SrBi$_2$Ta$_2$O$_9$ and SrBi$_2$Nb$_2$O$_9$ films on (001) SrTiO$_3$ substrates are free of growth twins (see Fig. 3), making them ideal for the study of two types of domains in these films using TEM: (1) out-of-phase domains\textsuperscript{32,33} and (2) ferroelectric domains.\textsuperscript{34} We recently reported the first observation of ferroelectric domains in SrBi$_2$Nb$_2$O$_9$ films.\textsuperscript{34} The ferroelectric domains are unusual in these films both in their small size, ~50 nm, and in the non-faceted nature of the ferroelectric domain walls. We believe that the latter results from the incredibly small anisotropy (<0.02\%) in the $a$ and $b$ lattice constants of SrBi$_2$Nb$_2$O$_9$, as $a$ and $b$ are equal to five significant digits ($a = b = 5.5094$ Å).\textsuperscript{35} This is in considerable contrast to the widely studied ferroelectrics BaTiO$_3$ and Pb(Zr,Ti)O$_3$, where the difference in lattice constants is 1.1\% and up to 6.4\%, respectively, and the domain walls are high faceted. With the miniscule anisotropy in its $a$ and $b$ lattice parameters, the ferroelastic strain energy associated with 90° ferroelectric domain boundaries in SrBi$_2$Nb$_2$O$_9$ is much smaller than in more conventional ferroelectrics and we believe that this is why the domain walls curve to such a degree.\textsuperscript{34}

By growing SrBi$_2$Ta$_2$O$_9$ and SrBi$_2$Nb$_2$O$_9$ films on (111) SrTiO$_3$ substrates (with an underlying epitaxial SrRuO$_3$ electrode), we achieved what at the time was the highest remanent polarization reported for SrBi$_2$Nb$_2$O$_9$ or SrBi$_2$Ta$_2$O$_9$ films,\textsuperscript{29} 15.7 μC/cm$^2$. Because the spontaneous polarization of SrBi$_2$Ta$_2$O$_9$ and SrBi$_2$Nb$_2$O$_9$ exists entirely along its $a$ axis, an increase in remanent polarization is associated with film orientations in which a larger component of the $a$ axis lies parallel to the direction in which the electric field is applied. From Fig. 3 it is evident that of the three orientations studied, growth on (111) SrTiO$_3$ will have the largest remanent polarization for the standard parallel plate capacitor geometry, and it does.
Fig. 3. SrBi$_2$Nb$_2$O$_9$ and SrBi$_2$Ta$_2$O$_9$ grow epitaxially on (001) SrTiO$_3$ with the c-axis parallel to the substrate surface normal, on (110) SrTiO$_3$ in a two-fold twin structure with the c-axes tilted by ±45° from the surface normal, and on (111) SrTiO$_3$ in a three-fold twin structure with the c-axes tilted by 57° away from the surface normal.

Finally, the SrBi$_2$Ta$_2$O$_9$ and SrBi$_2$Nb$_2$O$_9$ films grown on (110) SrTiO$_3$ have been used to establish the spontaneous polarization in these compounds, as described below.

2.4. Establishment of Lower-Bound of Spontaneous Polarization of SrBi$_2$Nb$_2$O$_9$

A lower-bound for the spontaneous polarization, $P_s$, of SrBi$_2$Nb$_2$O$_9$ was established by epitaxially growing SrBi$_2$Nb$_2$O$_9$ on (110) SrTiO$_3$ substrates. Unlike other potentially interesting epitaxial orientations, this orientation is special because of the specific angular relationship between the $P_s$ and remanent polarization, $P_r$, vectors. Here, the four types of twins (the two growth twins shown in Fig. 3 and an additional two twins generated within each of those during cooling through the Curie temperature (transformation twins) due to a-b twinning) are equivalent in terms of their contributions to the remanent polarization because the projection of the $P_s$ vector along the direction of the applied electric field is identical for all four twins (i.e., always involves two rotations of 45°). This is a key simplification, since quantification of the a-b twinning (at least in this orientation) is not required to estimate $P_s$. Additionally, details concerning the switching nature (through either 90° or 180° reorientation of the polar axis) of the spontaneous polarization can be ignored since both a 90° or a 180° reorientation would result in the same effect on the remanent polarization. Thus, this orientation is special because many of these still unanswered fundamental questions are rendered immaterial to the establishment of $P_s$. From the measured remanent polarization and an understanding of the epitaxial geometry, a lower bound of 22.8 $\mu$C/cm$^2$ was determined for $P_s$. This is a lower bound for this fundamental value, since our
calculation assumes that the entire film is switching and that the film is entirely phase-pure. That the film is free of second phases and fully crystalline is supported by TEM (performed on the same film) and x-ray diffraction results. However, although the \( P \), value is taken from a fully-saturated hysteresis loop, it cannot be concluded that 100% of the film is actually switching. For this reason, our value of 22.8 \( \mu \text{C/cm}^2 \) is a lower bound on the \( P \), of SrBi\(_2\)Nb\(_2\)O\(_9\).

2.5. Observation of Spiral Growth in c-axis Oriented Bi\(_4\)Ti\(_3\)O\(_{12}\), SrBi\(_2\)Ta\(_2\)O\(_9\), and SrBi\(_2\)Nb\(_2\)O\(_9\) Films Grown by MBE and PLD

AFM images of the surfaces of (001) Bi\(_4\)Ti\(_3\)O\(_{12}\) films grown by MBE\(^{36}\) on (001) SrTiO\(_3\) as well as of (001) SrBi\(_2\)Ta\(_2\)O\(_9\) and (001) SrBi\(_2\)Nb\(_2\)O\(_9\) films grown by PLD\(^{26,31}\) on (001) SrTiO\(_3\) reveal the presence of a high density (10\(^8\) to 10\(^9\) per cm\(^2\)) of growth spirals emanating from dislocations with screw component. Such growth spirals also occur in the growth of other layered perovskite thin films, e.g., (001) YBa\(_2\)Cu\(_3\)O\(_7\)-\(\delta\)\(^{37-39}\) and indicate that growth occurs by the incorporation of the deposited species at the steps that emanate from dislocations having a screw component, i.e., spiral growth.\(^{40-42}\) Unfortunately, the surfaces of oxide films that grow by spiral growth tend not to be smooth because the growth spirals contain several winds, making the peak-to-valley roughness over a square micron region typically at least 10 nm. As smooth surfaces are a prerequisite to the growth of high quality superlattices, we have investigated the growth of c-axis oriented Bi\(_4\)Ti\(_3\)O\(_{12}\), SrBi\(_2\)Ta\(_2\)O\(_9\), and SrBi\(_2\)Nb\(_2\)O\(_9\) films on substrates of varying lattice mismatch. By growing on substrates better lattice-matched to Bi\(_4\)Ti\(_3\)O\(_{12}\) than (001) SrTiO\(_3\), e.g., (001) LaAlO\(_3\)-Sr\(_2\)AlTaO\(_6\) (LSAT) or (110) NdGaO\(_3\), we have been able to grow films free of growth spirals.\(^{36}\) This avoidance of spiral growth enabled us to grow smooth Bi\(_4\)Ti\(_3\)O\(_{12}\) films and subsequently higher \( n \) Bi\(_2\)(Bi,Pb,Sr)\(_{n-1}\)Ti\(_n\)O\(_{3n+3}\) Aurivillius phases (which can be considered as a superlattice of alternating formula units of Bi\(_4\)Ti\(_3\)O\(_{12}\) and SrTiO\(_3\) or PbTiO\(_3\)).\(^{43}\)

2.6. Establishment of RHEED-Based Composition Control Method with Absolute Accuracy of Better than 1%

The growth of high quality multicomponent oxide thin films by reactive MBE requires precise composition control. In some cases, e.g., the growth of PbTiO\(_3\) or Bi\(_4\)Ti\(_3\)O\(_{12}\) described above, it is possible to use adsorption-controlled growth conditions to automatically limit the incorporation of volatile constituents. In many other cases, however, such fortuitous automatic composition control is not possible. SrTiO\(_3\) and BaTiO\(_3\) are examples where adsorption-controlled growth conditions are not possible for practical substrate temperatures. Although we use the best of today’s commercially-available techniques for \textit{in situ} composition control, i.e., atomic absorption spectroscopy (AA) and a quartz crystal microbalance (QCM), one of the major obstacles to the controlled synthesis of metastable oxides is the lack of adequate composition control. To this end we have developed an \textit{in situ} RHEED-based composition control method for the stoichiometric deposition of SrTiO\(_3\) (100) from independent strontium and titanium sources.\(^{44}\) By monitoring changes in the RHEED intensity oscillations as monolayer doses of strontium and titanium are sequentially deposited, the Sr:Ti ratio can be adjusted to within 1% of stoichiometry. These shuttered RHEED oscillations differ from the conventional RHEED oscillations that occur when species are codeposited; they are analogous to the RHEED oscillations that occur during the growth of GaAs films at low temperatures by the sequential deposition of gallium and arsenic,\(^{45}\) where fractional coverage results in a modulation of the RHEED intensity oscillation envelope.\(^{46}\) Furthermore, the presence of a beat frequency in the intensity oscillation envelope allows the
adjustment of the strontium and titanium fluxes so that a full monolayer of coverage is obtained with each shuttered dose of strontium or titanium. We have found this technique to have an absolute accuracy of better than 1%. Its use, coupled with epitaxy and epitaxial stabilization, has allowed us to grow the new and metastable oxides described below.


Using reactive MBE and the composition control methods described above (adsorption-controlled growth for PbTiO$_3$ and RHEED-based composition control for SrTiO$_3$ and BaTiO$_3$), we have grown PbTiO$_3$/SrTiO$_3$ and BaTiO$_3$/SrTiO$_3$ superlattices on (001) SrTiO$_3$ substrates. Both of these systems form a solid solution over their entire composition range. Thus, PbTiO$_3$/SrTiO$_3$ as well as BaTiO$_3$/SrTiO$_3$ layered heterostructures are metastable; it is energetically favorable for these oxides to dissolve into each other forming (Pb,Sr)TiO$_3$ and (Ba,Sr)TiO$_3$ solid solutions. The metastability of PbTiO$_3$/SrTiO$_3$ and BaTiO$_3$/SrTiO$_3$ heterostructures is analogous to the situation for AlAs/GaAs heterostructures, which also form a solid solution over their entire composition range.

As can be seen in the cross-sectional TEM images in Fig. 1, the interface abruptness and layer thickness control of our PbTiO$_3$/SrTiO$_3$ and BaTiO$_3$/SrTiO$_3$ superlattices are comparable to what has been achieved for AlAs/GaAs superlattices grown by MBE and MOCVD (not shown). The PbTiO$_3$ and BaTiO$_3$ layers in these superlattices were grown to have thicknesses less than the critical thickness for the formation of interfacial misfit dislocations, leaving the entire superlattice fully coherent with the substrate. Indeed TEM revealed that the interfaces in both the PbTiO$_3$/SrTiO$_3$ and BaTiO$_3$/SrTiO$_3$ superlattices are fully-coherent; no misfit dislocations or

Fig. 4. $\theta$-2$\theta$ x-ray diffraction scan of a [((PbTiO$_3$)$_{10}$/(SrTiO$_3$)$_{10}$)$_{15}$ superlattice in which a PbTiO$_3$ layer 10 unit cells thick (in the c-axis direction) is grown on top of a SrTiO$_3$ layer 10 unit cells thick (in the c-axis direction) and this bilayer is repeated 15 times. The 00$\ell$ superlattice reflections, the 001 reflection of the thick PbTiO$_3$ buffer layer and overlayer, and 001 reflection of the SrTiO$_3$ substrate are labeled. The x-ray diffraction data indicate that this superlattice has a periodicity of 8.37 ± 0.02 nm.
other defects were observed in the superlattices by TEM. The PbTiO$_3$ and BaTiO$_3$ layers are oriented with their $c$-axis parallel to the growth direction. The dimensional control and interface abruptness achieved in these oxides indicate that MBE is a viable method for constructing oxide multilayers on a scale where enhanced dielectric effects are expected.

To probe the regularity in the periodicity of these superlattices over macroscopic dimensions, $\theta$-2$\theta$ x-ray diffraction scans were performed. Figure 4 shows the $\theta$-2$\theta$ scan of the same PbTiO$_3$ / SrTiO$_3$ superlattice whose TEM is shown in Fig. 1. The high degree of uniformity in the structural order of the superlattice over macroscopic dimensions is revealed by the presence of all of the superlattice peaks and by the narrowness of these peaks. The full width at half-maximum (FWHM) of these peaks is comparable to the FWHM of the PbTiO$_3$ peaks arising from the 50 nm thick PbTiO$_3$ buffer layer and overlayer that encapsulate the superlattice.

In addition to superlattices, we have also prepared digitally-graded structures in which the average composition is varied by changing the fraction of occurrence of pure layers of the two constituents. Digital grading is commonplace in the growth of compound semiconductors by MBE. Figure 5(a) shows an example of digital grading in oxides on a comparable length scale to that used in advanced semiconductor structures. In the example shown, the composition is digitally graded from pure SrTiO$_3$ to pure BaTiO$_3$ by linearly increasing (in 10% increments) the fraction of BaTiO$_3$ unit-cell-thick layers that occur in each segment of the structure. The grading from pure SrTiO$_3$ begins by depositing a one unit-cell-thick (in the $c$-axis direction) BaTiO$_3$ layer followed by a SrTiO$_3$ layer nine unit cells thick (in the $c$-axis direction). Then comes a two unit-cell-thick BaTiO$_3$ layer followed by a SrTiO$_3$ layer eight unit cells thick. Next a three unit-cell-thick BaTiO$_3$ layer followed by a SrTiO$_3$ layer seven unit cells thick, ..., until a ten unit-cell-thick BaTiO$_3$ layer is deposited, completing the digital grading from pure SrTiO$_3$ to pure BaTiO$_3$.

Just like their oxide superlattice counterparts, these digitally-graded BaTiO$_3$ / SrTiO$_3$ structures are also metastable; the equilibrium state is a (Ba,Sr)TiO$_3$ solid solution. However, the

![HRTEM images](image.png)

Fig. 5. HRTEM images of a digitally-graded BaTiO$_3$ / SrTiO$_3$ layer that goes from pure SrTiO$_3$ to pure BaTiO$_3$ in unit-cell-thick increments. (a) The as-grown sample ($T_{sub} = 660$ °C) and (b) after annealing at 1000 °C for 2 hours in oxygen. The BaO monolayers in each unit-cell-thick layer of BaTiO$_3$ are marked with arrows. As can be seen in (b), the nano-engineered layering is stable to relatively high temperatures.
rate of cation interdiffusion between the Ba-sites and Sr-sites (both A-sites) in these perovskites is slow. This is apparent from Fig. 5(b), which shows an HRTEM image of a piece of the same film shown in Fig. 5(a) after it was annealed for 2 hours at 1000 °C in 1 atm of pure oxygen. Significant interdiffusion is only just beginning to occur under these conditions. Being able to anneal these metastable structures at such high temperatures in oxygen is advantageous in exploring the intrinsic dielectric, ferroelectric, and optical properties of such customized oxide heterostructures. In their as-grown state, the electrical properties of our layered titanate films have significantly higher leakage (and dielectric loss) than after annealing. We attribute this behavior to a reduction in the concentration of oxygen vacancies.

2.8. Growth of $n = 1$ to 5 $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ Phases, Including Metastable Ones, by MBE

We have used reactive MBE to create new materials by atomic-layer engineering. An example is the phase-pure growth of the $n = 1$ to 5 members of the $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ homologous series, whose crystal structures are shown in Fig. 6. These compounds are known as Ruddlesden-Popper phases after the researchers who discovered the $n = 1$ ($\text{Sr}_2\text{TiO}_4$) and $n = 2$ ($\text{Sr}_3\text{Ti}_2\text{O}_7$) members of this series.53,54 $\text{SrTiO}_3$, the $n = \infty$ member of this homologous series, consists of alternating $\text{TiO}_2$ and $\text{SrO}$ layers. The $n = 1$ ($\text{Sr}_2\text{TiO}_4$) compound has a double $\text{SrO}$ layer disrupting the perovskite network along the $c$-axis. Subsequent members of the series have an increasing number ($n$) of perovskite blocks separating the double $\text{SrO}$ layers.

![Fig. 6.](image)

Fig. 6. $n = 1$ ($\text{Sr}_2\text{TiO}_4$), $n = 2$ ($\text{Sr}_3\text{Ti}_2\text{O}_7$), $n = 3$ ($\text{Sr}_4\text{Ti}_3\text{O}_{10}$), $n = 4$ ($\text{Sr}_5\text{Ti}_4\text{O}_{13}$), $n = 5$ ($\text{Sr}_6\text{Ti}_5\text{O}_{16}$), and $n = \infty$ ($\text{SrTiO}_3$) members of the Ruddlesden-Popper homologous series of compounds $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$. $\text{Ti}^{4+}$ ions lie at the center of the oxygen coordination polyhedra (octahedra). The filled circles represent $\text{Sr}^{2+}$ ions.

As the $\theta-2\theta$ x-ray diffraction patterns in Fig. 7 (and cross-sectional TEM images in Fig. 8) show, it is possible to grow single-phase epitaxial films with specific $n$ values, even though nearby phases have similar formation energies. The example shown is the synthesis of the first five members of the $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ Ruddlesden-Popper homologous series.55 These structures, shown in Fig. 6, are analogous with the $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ series. X-ray diffraction is an excellent probe for spotting non-periodicity (i.e., intergrowths) in the stacking sequence in the $c$-direction. Intergrowths cause certain peaks to broaden, shift, or split in $2\theta$.56-58 All of the peaks in Fig. 7
have narrow widths, are at the correct $2\theta$ positions, and are not split. $\phi$ scans of all the $n$ members grown indicate that the films are oriented with the epitaxial relationship $(001) \text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1} \parallel (001) \text{SrTiO}_3$ and $[010] \text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1} \parallel [010] \text{SrTiO}_3$.\(^{55,59}\) Although the $n = 1 - 3$ members of this series have been grown by bulk methods (in polycrystalline form only),\(^{53,54,60-62}\) this is the first thin film growth of these materials and the first report of phase-pure $n = 4$ and $n = 5$ phases in any form. This achievement, made under our DOE-supported program that recently ended, is described further in Sec. 2.8.

![Fig. 7. $\theta-2\theta$ x-ray diffraction spectra of epitaxial films of the first five members ($n = 1$ to 5) of the $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ Ruddlesden-Popper homologous series, i.e., $\text{Sr}_2\text{TiO}_4$ ($n = 1$), $\text{Sr}_3\text{Ti}_2\text{O}_7$ ($n = 2$), $\text{Sr}_4\text{Ti}_3\text{O}_{10}$ ($n = 3$), $\text{Sr}_5\text{Ti}_4\text{O}_{13}$ ($n = 4$), and $\text{Sr}_6\text{Ti}_5\text{O}_{16}$ ($n = 5$). The $00\ell$ $\text{SrTiO}_3$ substrate peaks are marked by asterisks (*). This data (from Ref. 55) demonstrates that epitaxial engineering using a sequential deposition MBE process can produce single-phase films of high $n$ phases that cannot be synthesized by conventional synthesis techniques [Refs. 53,54,56,60-65].](image)

Using reactive MBE and a combination of AA and RHEED-based composition control we have grown the first five members of the $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ Ruddlesden-Popper homologous series: $\text{Sr}_2\text{TiO}_4$, $\text{Sr}_3\text{Ti}_2\text{O}_7$, $\text{Sr}_4\text{Ti}_3\text{O}_{10}$, $\text{Sr}_5\text{Ti}_4\text{O}_{13}$, and $\text{Sr}_6\text{Ti}_5\text{O}_{16}$.\(^{55}\) X-ray diffraction (Fig. 7) and high-resolution TEM images (Fig. 8) confirm that these films are epitaxially oriented and contain relatively few intergrowths. Dielectric measurements indicate that the dielectric constant tensor coefficient $\varepsilon_{13}$ increases from a minimum of $44\pm4$ in the $n = 1$ ($\text{Sr}_2\text{TiO}_4$) film to a maximum of $263\pm2$ in the $n = \infty$ ($\text{SrTiO}_3$) film.\(^{55}\) Detailed investigations using quantitative high-resolution TEM methods reveal that the films have the expected $n = 1$-5 structures of the Ruddlesden-
Popper $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ homologous series. Among these films, $\text{Sr}_2\text{TiO}_4$, $\text{Sr}_3\text{Ti}_2\text{O}_7$, and $\text{Sr}_4\text{Ti}_3\text{O}_{10}$ thin films are nearly free of intergrowths, while $\text{Sr}_5\text{Ti}_4\text{O}_{13}$ and $\text{Sr}_6\text{Ti}_5\text{O}_{16}$ thin films contain noticeably more anti-phase boundaries in their perovskite sheets and intergrowth defects. We have shown that these results are consistent with what is known about the thermodynamics of $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ phases, including the metastability of $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ phases with $3 \leq n < \infty$. 

Fig. 8. Cross-sectional HRTEM images (from left to right) of the $n = 1$ ($\text{Sr}_2\text{TiO}_4$), $n = 2$ ($\text{Sr}_3\text{Ti}_2\text{O}_7$), $n = 3$ ($\text{Sr}_4\text{Ti}_3\text{O}_{10}$), $n = 4$ ($\text{Sr}_5\text{Ti}_4\text{O}_{13}$), and $n = 5$ ($\text{Sr}_6\text{Ti}_5\text{O}_{16}$) films. A model of the crystal structure of the $n = 1$ and $n = 5$ members are adjacent to the corresponding images showing the position of the SrO double layers and perovskite layers. The arrows mark the position of the interface of the films with the homoepitaxial SrTiO$_3$ buffer layer.

2.9. Understanding of why Epitaxial $\text{Sr}_2\text{RuO}_4$ Films are not Superconducting

$\text{Sr}_2\text{RuO}_4$, which is isostructural to the high-$T_c$ cuprate superconductor La$_{1.8}$Sr$_{0.2}$CuO$_4$, is the only known Cu-free layered perovskite superconductor. Rice and Sigrist predicted that the pairing state of $\text{Sr}_2\text{RuO}_4$ is odd-parity, possibly $p$-wave. However, phase-sensitive measurements similar to those carried out on high-$T_c$ cuprates to establish their $d$-wave paring state are lacking for $\text{Sr}_2\text{RuO}_4$. To facilitate such experiments on $\text{Sr}_2\text{RuO}_4$, an important step is the growth of superconducting epitaxial films of this material. Although epitaxial $\text{Sr}_2\text{RuO}_4$ films have been prepared, superconductivity has not been achieved. From single crystal work it is known that both impurities (e.g., as little as 300 ppm of aluminum) and "structural disorder" can quench superconductivity in $\text{Sr}_2\text{RuO}_4$. To date, there has been very little characterization of structural defects in $\text{Sr}_2\text{RuO}_4$ single crystals and films. Consequently, the particular type of structural defects that suppress superconductivity in $\text{Sr}_2\text{RuO}_4$ is not established.

We grew epitaxial $\text{Sr}_2\text{RuO}_4$ thin films by PLD from high-purity (99.98%) $\text{Sr}_2\text{RuO}_4$ targets on (001) LaAlO$_3$ and found them not to be superconducting down to 0.4 K. A correlation was observed between higher resistivity ratios in electrical transport measurements and narrower x-ray diffraction rocking curve widths of the $\text{Sr}_2\text{RuO}_4$ films. This correlation implicated structural disorder as being responsible for the lack of superconductivity in these epitaxial $\text{Sr}_2\text{RuO}_4$ films. High-resolution TEM was used to investigate the structural defects in these films. The dominant structural defects, i.e., the defects leading to the observed variation in rocking curve widths in the films, are (011) planar defects, with a spacing comparable to the in-plane superconducting coherence length of $\text{Sr}_2\text{RuO}_4$ (see Fig. 9). These results imply that minimizing structural disorder is the key remaining challenge to achieving superconducting $\text{Sr}_2\text{RuO}_4$ films.
2.10. Growth of Superconducting Sr$_2$RuO$_4$ Films by MBE

As described in Sec. 2.9, Sr$_2$RuO$_4$ ($T_c = 1.5$ K in single crystals) is unique in several ways, including increasing evidence that it is an unconventional superconductor. To enable phase-sensitive measurements to establish its pairing symmetry, a crucial step is the growth of superconducting films of Sr$_2$RuO$_4$. In Sec. 2.9, we described our identification of crystallographic shear defects as the dominant defects in epitaxial Sr$_2$RuO$_4$ films. A cross-sectional TEM image showing such defects is shown in Fig. 9. Note that the spacing between the planar defects is not significantly greater than the in-plane superconducting coherence length of Sr$_2$RuO$_4$, $\xi_{ab}(0) \approx 66$ nm. In all images covering a sufficiently large area, at least one such defect was observed over any a-b plane interval of $\xi_{ab}(0)$. And, since any lattice defect can be a pair-breaker in an odd-parity superconductor, these planar defects that disrupt the RuO$_2$ planes are very likely responsible for the suppression of superconductivity in these high-purity Sr$_2$RuO$_4$ films. A schematic of how we believe these defects are generated is shown in Fig. 10.

Fig. 9. An HRTEM image of a high-purity c-axis Sr$_2$RuO$_4$ film grown by PLD [Ref. 82]. The arrowed region is a crystallographic shear defect. These planar defects are spaced more closely than the in-plane superconducting coherence length of Sr$_2$RuO$_4$, explaining the lack of superconductivity in these films.

Fig. 10. A schematic showing a nucleation mechanism for the crystallographic shear defects observed in epitaxial Sr$_2$RuO$_4$ films. Two Sr$_2$RuO$_4$ nuclei on adjacent terraces of a (001) LaAlO$_3$ surface will form such a planar defect where they meet due to the
mismatch between the step height of the substrate (3.79 Å for (001) LaAlO₃) and the repeat length in the growth direction of the film (12.75 Å for (001) Sr₂RuO₄). The unit cell of Sr₂RuO₄ is outlined on the right side of the figure.
3. Bibliography


Although the authors do not discuss this aspect, from the lithium-rich growth conditions reported, LiNbO$_3$ may be another example of adsorption-controlled oxide growth by MBE. See R.A. Betts and C.W. Pritt, “Growth of Thin-Film Lithium Niobate by Molecular Beam Epitaxy,” Electron. Lett. 21 (1985) 960-962.

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