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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 $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$—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., $Sr_{n+1}Ti_nO_{3n+1}$ 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 ($PbTiO_3$, $Bi_4Ti_3O_{12}$), tantalates ($SrBi_2Ta_2O_9$), and niobates ($SrBi_2Nb_2O_9$); layered combinations of these perovskite-related materials ($Bi_4Ti_3O_{12}$—$SrTiO_3$ and $Bi_4Ti_3O_{12}$—$PbTiO_3$ Aurivillius phases and metastable $PbTiO_3$ / $SrTiO_3$ and $BaTiO_3$ / $SrTiO_3$ superlattices), and new metastable phases ($Sr_{n+1}Ti_nO_{3n+1}$ 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.

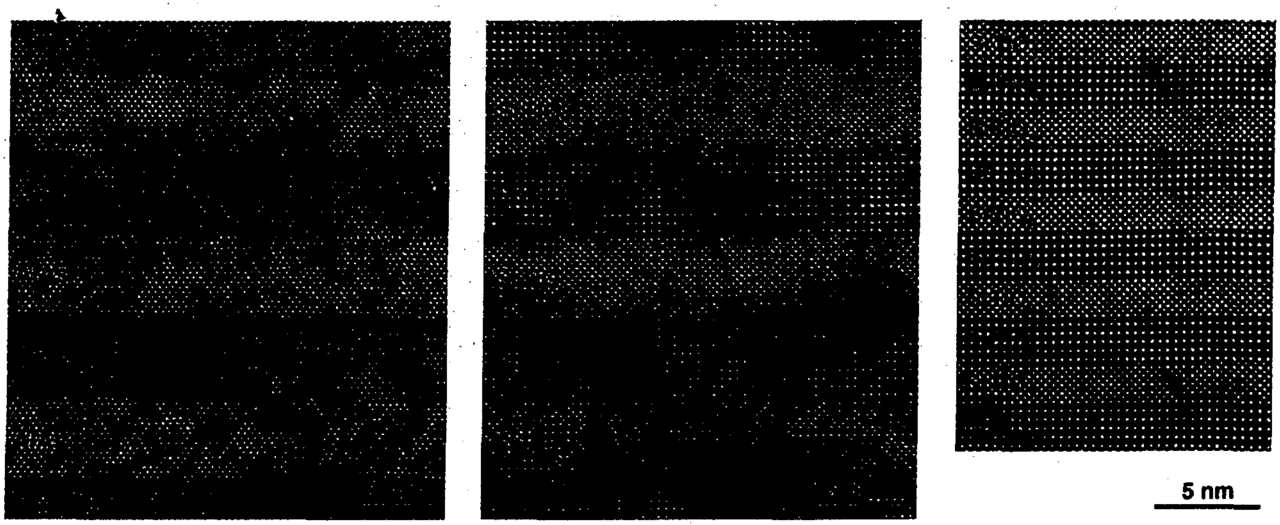

Fig. 1. High-resolution TEM images of GaAs / AlAs [Ref. 1], $PbTiO_3$ / $SrTiO_3$ [Ref. 2], and $BaTiO_3$ / $SrTiO_3$ [Ref. 3] superlattices grown by MBE. All are shown at the same magnification for comparison. The GaAs / AlAs and $PbTiO_3$ / $SrTiO_3$ superlattices have comparable layer thicknesses (~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 $PbTiO_3$ and $Bi_4Ti_3O_{12}$ 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.[4-7] This growth mechanism relies on the volatility of the group V component and has been explained using thermodynamics.[8-11] 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, $PbTiO_3$ and $Bi_4Ti_3O_{12}$ 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 $PbTiO_3$ and $Bi_4Ti_3O_{12}$ 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 $PbTiO_3$ and $Bi_4Ti_3O_{12}$. Because PbO (and As_2) is the dominant vapor species that exists when $PbTiO_3$ (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 Bi_xO_y species with comparable partial pressure are created when $Bi_4Ti_3O_{12}$ 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 $PbTiO_3$ and $Bi_4Ti_3O_{12}$. 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.

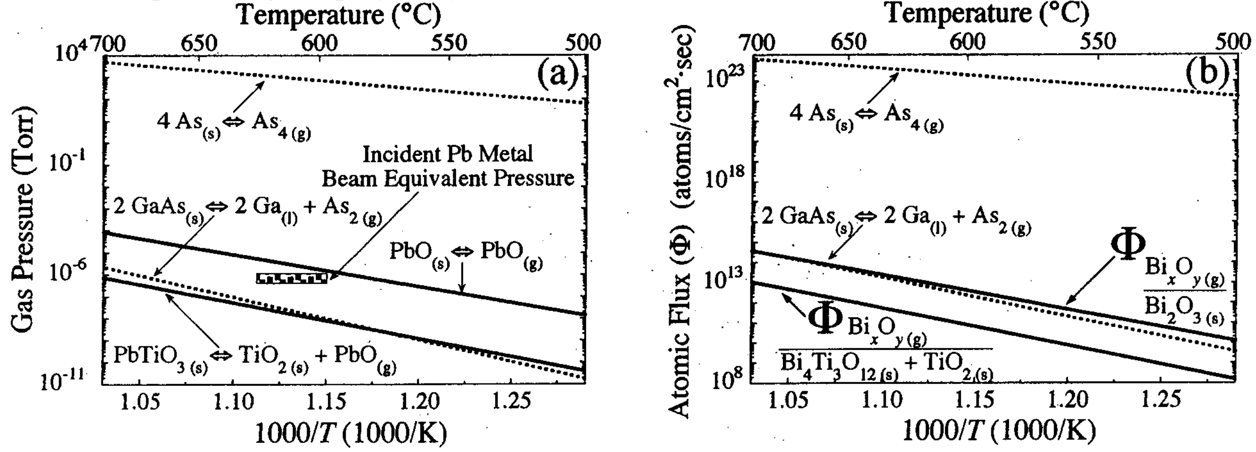

Fig. 2. The thermodynamics of adsorption-controlled growth. For GaAs growth, the growth window for phase-pure GaAs growth (as a function of reciprocal temperature and As_2 pressure in (a) or as a function of reciprocal temperature and arsenic flux in (b)) exists

between the two dashed lines. For $PbTiO_3$, the growth window for phase-pure $PbTiO_3$ growth as a function of reciprocal temperature and PbO pressure exists between the two solid lines in (a). For $Bi_4Ti_3O_{12}$, the growth window for phase-pure $Bi_4Ti_3O_{12}$ growth as a function of reciprocal temperature and bismuth flux (from all of the Bi_xO_y 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,[11,15,16] $PbTiO_3$ and $Bi_4Ti_3O_{12}$ (our work[12,13] which has since been confirmed by others[17]), $Bi_2Sr_2CuO_6$,[18] and to a lesser degree the growth of $(Rb,Ba)BiO_3$.[19] We anticipate that adsorption-controlled MBE growth will be applicable to many other multicomponent oxide materials containing a volatile metal-oxide constituent.[20]

2.2. *Adsorption-Controlled Growth of $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$ by PLD*

Like $Bi_4Ti_3O_{12}$, these structurally-related Aurivillius compounds[21-25] 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 $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$ 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 $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$ films by PLD by exploring a wide range of bismuth-rich target compositions and corresponding growth conditions.[26] 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 $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$ 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 $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$. 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 that has enabled the smart card application is that polycrystalline $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$ films were capable of withstanding repeated ferroelectric switching cycles (in excess of 10^{12} in polycrystalline films) without degradation.[27,28] The layered structure of $SrBi_2Ta_2O_9$, $SrBi_2Nb_2O_9$, and other Aurivillius phases[21-25] 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 $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$ films. For example, are these materials fatigue resistant in all directions, e.g., perpendicular to as well as parallel to their Bi_2O_2 planes? In addition, spontaneous polarization is a key parameter of all ferroelectrics.

To investigate the anisotropy in the dielectric and ferroelectric properties of $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$ films, we have grown epitaxial films of these materials on (001), (110), and (111) $SrTiO_3$ 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,[26,29,30] RBS ($\chi_{min} = 12\%$ for $SrBi_2Ta_2O_9$ and $\chi_{min} = 5\%$ for $SrBi_2Nb_2O_9$),[26,31] and TEM[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 $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$ films have been used for three different purposes. The $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$ 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[32,33] and (2) ferroelectric domains.[34] We recently reported the first observation of ferroelectric domains in $SrBi_2Nb_2O_9$ films.[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 $SrBi_2Nb_2O_9$, as *a* and *b* are equal to five significant digits ($a = b = 5.5094$ Å).[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 $SrBi_2Nb_2O_9$ is much smaller than in more conventional ferroelectrics and we believe that this is why the domain walls curve to such a degree.[34]

By growing $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$ 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 $SrBi_2Nb_2O_9$ or $SrBi_2Ta_2O_9$ films,[29] 15.7 μC/cm^2. Because the spontaneous polarization of $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$ 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.

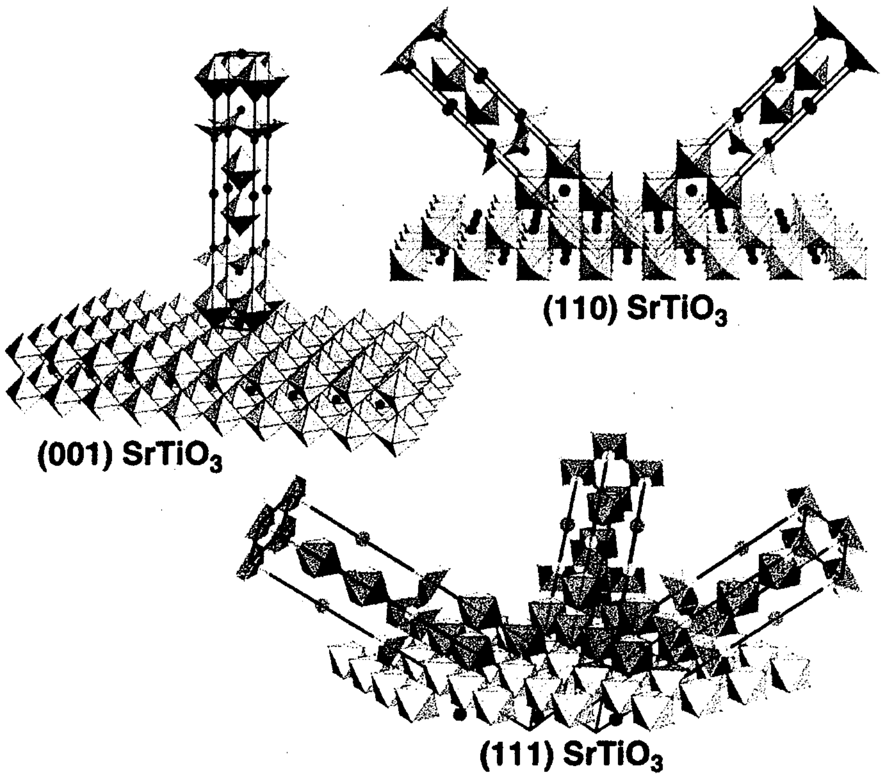

Fig. 3. $SrBi_2Nb_2O_9$ and $SrBi_2Ta_2O_9$ grow epitaxially on (001) $SrTiO_3$ with the *c*-axis parallel to the substrate surface normal, on (110) $SrTiO_3$ in a two-fold twin structure with the *c*-axes tilted by ±45° from the surface normal, and on (111) $SrTiO_3$ in a three-fold twin structure with the *c*-axes tilted by 57° away from the surface normal.

Finally, the $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$ 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 $SrBi_2Nb_2O_9$*

A lower-bound for the spontaneous polarization, P_s, of $SrBi_2Nb_2O_9$ was established by epitaxially growing $SrBi_2Nb_2O_9$ on (110) $SrTiO_3$ substrates.[30] 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.[30] 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_r 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 $\mu C/cm^2$ is a lower bound on the P_s of $SrBi_2Nb_2O_9$.

2.5. *Observation of Spiral Growth in c-axis Oriented $Bi_4Ti_3O_{12}$, $SrBi_2Ta_2O_9$, and $SrBi_2Nb_2O_9$ Films Grown by MBE and PLD*

AFM images of the surfaces of (001) $Bi_4Ti_3O_{12}$ films grown by MBE[36] on (001) $SrTiO_3$ as well as of (001) $SrBi_2Ta_2O_9$ and (001) $SrBi_2Nb_2O_9$ 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) $YBa_2Cu_3O_{7-\delta}$,[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 $Bi_4Ti_3O_{12}$, $SrBi_2Ta_2O_9$, and $SrBi_2Nb_2O_9$ films on substrates of varying lattice mismatch. By growing on substrates better lattice-matched to $Bi_4Ti_3O_{12}$ than (001) $SrTiO_3$, e.g., (001) $LaAlO_3$—Sr_2AlTaO_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 $Bi_4Ti_3O_{12}$ films and subsequently higher n $Bi_2(Bi,Pb,Sr)_{n-1}Ti_nO_{3n+3}$ Aurivillius phases (which can be considered as a superlattice of alternating formula units of $Bi_4Ti_3O_{12}$ 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 $Bi_4Ti_3O_{12}$ 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 *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 *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.[44] We have found this technique to have an absolute accuracy of better than 1%.[44] Its use, coupled with epitaxy and epitaxial stabilization, has allowed us to grow the new and metastable oxides described below.

2.7. Growth of Metastable $PbTiO_3$ / $SrTiO_3$ and $BaTiO_3$ / $SrTiO_3$ Superlattices by MBE with Structural Perfection Comparable to Superlattices of III / V Semiconductors Grown by MBE

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.[2,3] Both of these systems form a solid solution over their entire composition range.[47,48] 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.[49]

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[1] and MOCVD[50] (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

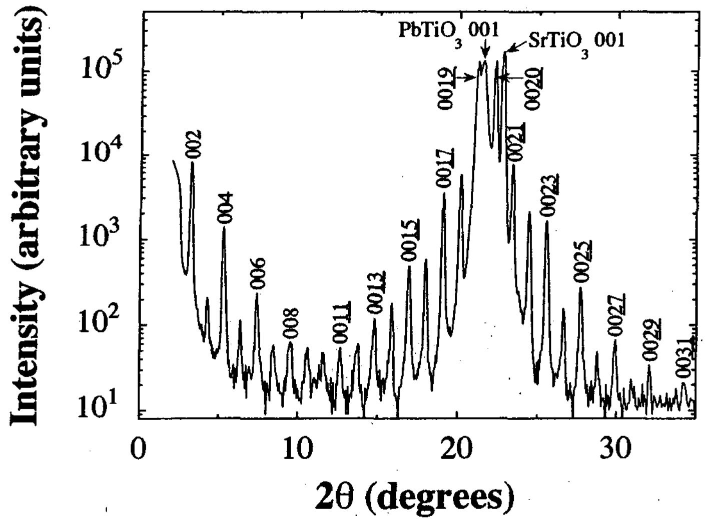

Fig. 4. θ-2θ x-ray diffraction scan of a $[(PbTiO_3)_{10} / (SrTiO_3)_{10}]_{15}$ superlattice in which a $PbTiO_3$ layer 10 unit cells thick (in the *c*-axis direction) is grown on top of a $SrTiO_3$ layer 10 unit cells thick (in the *c*-axis direction) and this bilayer is repeated 15 times. The 00ℓ 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.[2,3] 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.[51]

To probe the regularity in the periodicity of these superlattices over macroscopic dimensions, θ-2θ x-ray diffraction scans were performed. Figure 4 shows the θ-2θ 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.[15] 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.[52] 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

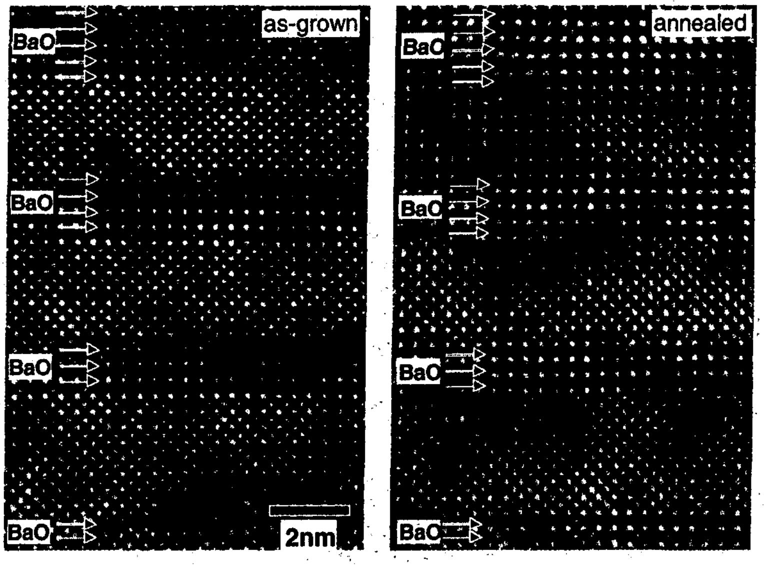

Fig. 5. HRTEM images of a digitally-graded $BaTiO_3$ / $SrTiO_3$ layer that goes from pure $SrTiO_3$ to pure $BaTiO_3$ in unit-cell-thick increments. (a) The as-grown sample (T_{sub} = 660 °C) and (b) after annealing at 1000 °C for 2 hours in oxygen. The BaO monolayers in each unit-cell-thick layer of $BaTiO_3$ 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 $Sr_{n+1}Ti_nO_{3n+1}$ 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 $Sr_{n+1}Ti_nO_{3n+1}$ homologous series, whose crystal structures are shown in Fig. 6. These compounds are known as Ruddlesden-Popper phases after the researchers who discovered the $n = 1$ (Sr_2TiO_4) and $n = 2$ ($Sr_3Ti_2O_7$) members of this series.[53,54] $SrTiO_3$, the $n = \infty$ member of this homologous series, consists of alternating TiO_2 and SrO layers. The $n = 1$ (Sr_2TiO_4) compound has a double 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 SrO layers.

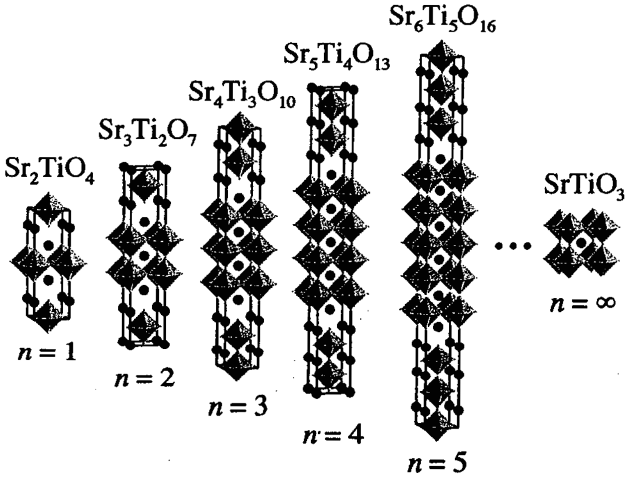

Fig. 6. $n = 1$ (Sr_2TiO_4), $n = 2$ ($Sr_3Ti_2O_7$), $n = 3$ ($Sr_4Ti_3O_{10}$), $n = 4$ ($Sr_5Ti_4O_{13}$), $n = 5$ ($Sr_6Ti_5O_{16}$), and $n = \infty$ ($SrTiO_3$) members of the Ruddlesden-Popper homologous series of compounds $Sr_{n+1}Ti_nO_{3n+1}$. Ti^{4+} ions lie at the center of the oxygen coordination polyhedra (octahedra). The filled circles represent Sr^{2+} ions.

As the θ-2θ 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 $Sr_{n+1}Ti_nO_{3n+1}$ Ruddlesden-Popper homologous series.[55] These structures, shown in Fig. 6, are analogous with the $Sr_{n+1}Ru_nO_{3n+1}$ 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 2θ.[56-58] All of the peaks in Fig. 7

have narrow widths, are at the correct 2θ positions, and are not split. ϕ scans of all the n members grown indicate that the films are oriented with the epitaxial relationship (001) $Sr_{n+1}Ti_nO_{3n+1}$ ‖ (001) $SrTiO_3$ and [010] $Sr_{n+1}Ti_nO_{3n+1}$ ‖ [010] $SrTiO_3$.[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.

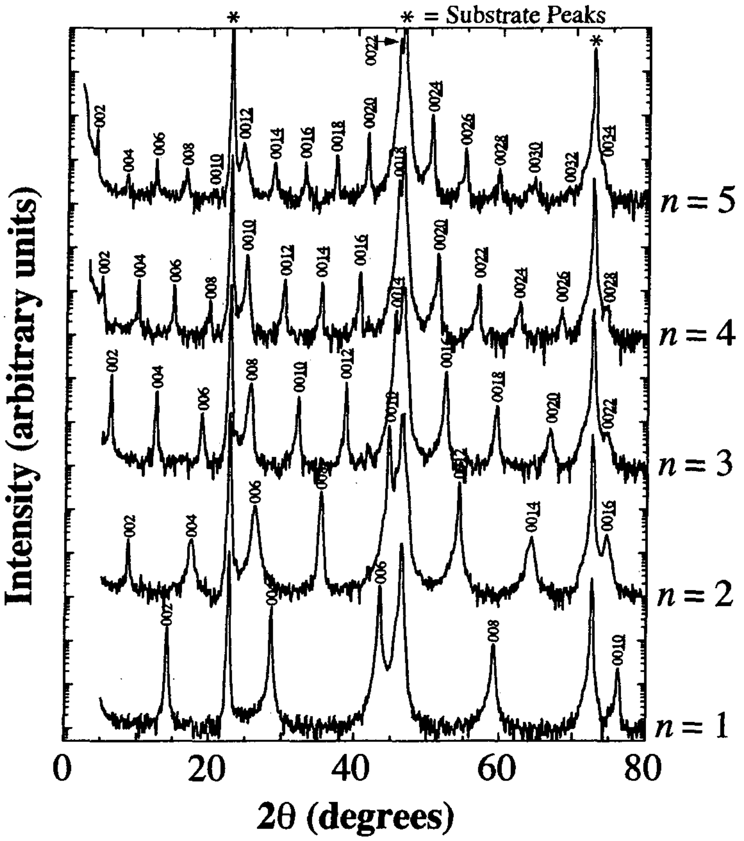

Fig. 7. θ-2θ x-ray diffraction spectra of epitaxial films of the first five members (n = 1 to 5) of the $Sr_{n+1}Ti_nO_{3n+1}$ Ruddlesden-Popper homologous series, i.e., Sr_2TiO_4 (n = 1), $Sr_3Ti_2O_7$ (n = 2), $Sr_4Ti_3O_{10}$ (n = 3), $Sr_5Ti_4O_{13}$ (n = 4), and $Sr_6Ti_5O_{16}$ (n = 5). The 00ℓ $SrTiO_3$ 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].

Using reactive MBE and a combination of AA and RHEED-based composition control we have grown the first five members of the $Sr_{n+1}Ti_nO_{3n+1}$ Ruddlesden-Popper homologous series: Sr_2TiO_4, $Sr_3Ti_2O_7$, $Sr_4Ti_3O_{10}$, $Sr_5Ti_4O_{13}$, and $Sr_6Ti_5O_{16}$.[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 ε_{33} increases from a minimum of 44±4 in the $n = 1$ (Sr_2TiO_4) film to a maximum of 263±2 in the $n = \infty$ ($SrTiO_3$) 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 $Sr_{n+1}Ti_nO_{3n+1}$ homologous series. Among these films, Sr_2TiO_4, $Sr_3Ti_2O_7$, and $Sr_4Ti_3O_{10}$ thin films are nearly free of intergrowths, while $Sr_5Ti_4O_{13}$ and $Sr_6Ti_5O_{16}$ thin films contain noticeably more anti-phase boundaries in their perovskite sheets and intergrowth defects.[59] We have shown that these results are consistent with what is known about the thermodynamics of $Sr_{n+1}Ti_nO_{3n+1}$ phases, including the metastability of $Sr_{n+1}Ti_nO_{3n+1}$ phases with $3 \leq n < \infty$.[59]

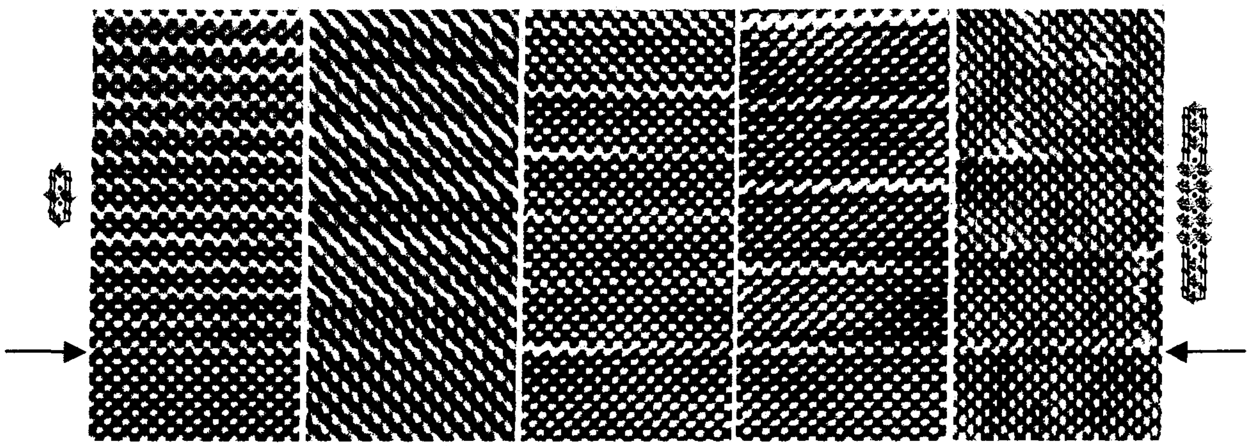

Fig. 8. Cross-sectional HRTEM images (from left to right) of the $n = 1$ (Sr_2TiO_4), $n = 2$ ($Sr_3Ti_2O_7$), $n = 3$ ($Sr_4Ti_3O_{10}$), $n = 4$ ($Sr_5Ti_4O_{13}$), and $n = 5$ ($Sr_6Ti_5O_{16}$) films. A model of the crystal structure of the $n = 1$ and $n = 5$ members are adjacent to the corresponding 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 Sr_2RuO_4 Films are not Superconducting

Sr_2RuO_4, which is isostructural to the high-T_c cuprate superconductor $La_{1-x}Sr_xCuO_4$, is the only known Cu-free layered perovskite superconductor.[66] Rice and Sigrist predicted that the pairing state of Sr_2RuO_4 is odd-parity, possibly *p*-wave.[67] However, phase-sensitive measurements similar to those carried out on high-T_c cuprates to establish their *d*-wave paring state,[68-75] are lacking for Sr_2RuO_4. To facilitate such experiments on Sr_2RuO_4, an important step is the growth of superconducting epitaxial films of this material. Although epitaxial Sr_2RuO_4 films have been prepared,[77-79] superconductivity has not been achieved. From single crystal work it is known that both impurities (e.g., as little as 300 ppm of aluminum)[80] and "structural disorder"[81] can quench superconductivity in Sr_2RuO_4. To date, there has been very little characterization of structural defects in Sr_2RuO_4 single crystals and films. Consequently, the particular type of structural defects that suppress superconductivity in Sr_2RuO_4 is not established.

We grew epitaxial Sr_2RuO_4 thin films by PLD from high-purity (99.98%) Sr_2RuO_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 Sr_2RuO_4 films. This correlation implicated structural disorder as being responsible for the lack of superconductivity in these epitaxial Sr_2RuO_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 Sr_2RuO_4 (see Fig. 9). These results imply that minimizing structural disorder is the key remaining challenge to achieving superconducting Sr_2RuO_4 films.[82]

2.10. Growth of Superconducting Sr_2RuO_4 Films by MBE

As described in Sec. 2.9, Sr_2RuO_4 ($T_c = 1.5$ K in single crystals)[83] is unique in several ways, including increasing evidence that it is an unconventional superconductor.[67,76,80,84-86] To enable phase-sensitive measurements to establish its pairing symmetry, a crucial step is the growth of superconducting films of Sr_2RuO_4. In Sec. 2.9, we described our identification of crystallographic shear defects as the dominant defects in epitaxial Sr_2RuO_4 films.[82] 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_2RuO_4, $\xi_{ab}(0) \approx 66$ nm.[83] 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_2RuO_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_2RuO_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_2RuO_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_2RuO_4 films. Two Sr_2RuO_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) $LaAlO_3$) and the repeat length in the growth direction of the film (12.75 Å for (001) Sr_2RuO_4). The unit cell of Sr_2RuO_4 is outlined on the right side of the figure.

3. Bibliography

[1] A.K. Gutakovskii, L.I. Fedina, and A.L. Aseev, "High Resolution Electron Microscopy of Semiconductor Interfaces," Phys. Status Solidi A **150** (1995) 127-140.

[2] J.C. Jiang, X.Q. Pan, W. Tian, C.D. Theis, and D.G. Schlom, "Abrupt $PbTiO_3/SrTiO_3$ Superlattices Grown by Reactive Molecular Beam Epitaxy," Appl. Phys. Lett. **74** (1999) 2851-2853.

[3] W. Tian, X.Q. Pan, J.H. Haeni, and D.G. Schlom, "Strain-Induced Elevation of the Spontaneous Polarization of $BaTiO_3$ in a Commensurate $BaTiO_3$ / $SrTiO_3$ Superlattice," submitted to Phys. Rev. Lett.

[4] J.R. Arthur, Jr., "Interaction of Ga and As_2 Molecular Beams with GaAs Surfaces," J. Appl. Phys. **39** (1968) 4032-4034.

[5] A.Y. Cho, "Epitaxy by Periodic Annealing," Surf. Sci. **17** (1969) 494-503.

[6] A.Y. Cho, "Morphology of Epitaxial Growth of GaAs by a Molecular Beam Method: The Observation of Surface Structures," J. Appl. Phys. **41** (1970) 2780-2786.

[7] A.Y. Cho, "GaAs Epitaxy by a Molecular Beam Method: Observations of Surface Structure on the (001) Face," J. Appl. Phys. **42** (1971) 2074-2081.

[8] R. Heckingbottom, G.J. Davies, and K.A. Prior, "Growth and Doping of Gallium Arsenide using Molecular Beam Epitaxy (MBE): Thermodynamic and Kinetic Aspects," Surf. Sci. **132**, (1983) 375-389.

[9] H. Seki and A. Koukitu, "Thermodynamic Analysis of Molecular Beam Epitaxy of III-V Semiconductors," J. Cryst. Growth **78** (1986) 342-352.

[10] J.Y. Tsao, "Phase Equilibria during InSb Molecular Beam Epitaxy," J. Cryst. Growth **110** (1991) 595-603.

[11] J.Y. Tsao, *Materials Fundamentals of Molecular Beam Epitaxy* (Academic Press, Boston, 1993) pp. 65-88.

[12] C.D. Theis, J. Yeh, D.G. Schlom, M.E. Hawley, G.W. Brown, J.C. Jiang, and X.Q. Pan "Adsorption-Controlled Growth of $Bi_4Ti_3O_{12}$ by Reactive MBE," Appl. Phys. Lett. **72** (1998) 2817-2819.

[13] C.D. Theis, J. Yeh, D.G. Schlom, M.E. Hawley, and G.W. Brown, "Adsorption-Controlled Growth of $PbTiO_3$ by Reactive Molecular Beam Epitaxy," Thin Solid Films **325** (1998) 107-114.

[14] R.H. Lamoreaux, D.L. Hildenbrand, and L. Brewer, "High-Temperature Vaporization Behavior of Oxides II. Oxides of Be, Mg, Ca, Sr, Ba, B, Al, Ga, In, Tl, Si, Ge, Sn, Pb, Zn, Cd, and Hg," J. Phys. Chem. Ref. Data **16** (1987) 419-443.

[15] M.A. Herman and H. Sitter, *Molecular Beam Epitaxy: Fundamentals and Current Status*, 2nd. ed. (Springer, New York, 1996).

[16] *Molecular Beam Epitaxy: Applications to Key Materials*, edited by R.F.C. Farrow (Noyes, Park Ridge, 1995).

[17] S. Migita, H. Ota, H. Fujino, Y. Kasai, and S. Sakai, "Epitaxial $Bi_4Ti_3O_{12}$ Thin Film Growth using Bi Self-Limiting Function," J. Cryst. Growth **200** (1999) 161-168.

[18] S. Migita, Y. Kasai, H. Ota, and S. Sakai, "Self-Limiting Process for the Bismuth Content in Molecular Beam Epitaxial Growth of $Bi_2Sr_2CuO_y$ Thin Films," Appl. Phys. Lett. **71** (1997) 3712-3714.

[19] E.S. Hellman and E.H. Hartford, "Adsorption Controlled Molecular Beam Epitaxy of Rubidium Barium Bismuth Oxide," J. Vac. Sci. Technol. B **8** (1990) 332-335.

[20] 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.

[21] B. Aurivillius, "Mixed Bismuth Oxides with Layer Lattices I. The Structure Type of $CaNb_2Bi_2O_9$," Arkiv Kemi **1** (1950) 463-480.

[22] B. Aurivillius, "Mixed Bismuth Oxides with Layer Lattices II. Structure of $Bi_4Ti_3O_{12}$," Arkiv Kemi **1** (1950) 499-512.

[23] B. Aurivillius, "Mixed Oxides with Layer Lattices III. Structure of $BaBi_4Ti_4O_{15}$," Arkiv Kemi **2** (1951) 519-527.

[24] B. Aurivillius, "The Structure of Bi_2NbO_5F and Isomorphous Compounds," Arkiv Kemi **5** (1953) 39-47.

[25] B. Aurivillius and P.H. Fang, "Ferroelectricity in the Compound $Ba_2Bi_4Ti_5O_{18}$," Phys. Rev. **126** (1962) 893-896.

[26] J. Lettieri, Y. Jia, S.J. Fulk, D.G. Schlom, M.E. Hawley, and G.W. Brown, "Optimization of the Growth of Epitaxial $SrBi_2Ta_2O_9$ Thin Films by Pulsed Laser Deposition," Thin Solid Films **379** (2000) 64-71.

[27] C.A. Paz de Araujo, J.D. Cuchiaro, L.D. McMillan, M.C. Scott, and J.F. Scott, "Fatigue-Free Ferroelectric Capacitors with Platinum Electrodes," Nature **374** (1995) 627-629.

[28] C.A. Paz de Araujo, J.D. Cuchiaro, M.C. Scott, and L.D. McMillan, "Layered Superlattice Material Applications," International Patent, publication No. WO 93/12542.

[29] J. Lettieri, M.A. Zurbuchen, Y. Jia, D.G. Schlom, S.K. Streiffer, and M.E. Hawley, "Epitaxial Growth of non-*c*-oriented $SrBi_2Nb_2O_9$ on (111) $SrTiO_3$," Appl. Phys. Lett. **76** (2000) 2937-2939.

[30] J. Lettieri, M.A. Zurbuchen, Y. Jia, D.G. Schlom, S.K. Streiffer, and M.E. Hawley, "Epitaxial Growth of $SrBi_2Nb_2O_9$ on (110) $SrTiO_3$ and the Establishment of a Lower Bound on the Spontaneous Polarization of $SrBi_2Nb_2O_9$," Appl. Phys. Lett. **77** (2000) 3090-3092.

[31] J. Lettieri, M.A. Zurbuchen, G.W. Brown, Y. Jia, W. Tian, X.Q. Pan, M.E. Hawley, and D.G. Schlom, "Investigation of Growth Evolution in *c*-Axis $SrBi_2Nb_2O_9$ Epitaxial Thin Films," in: *Multicomponent Oxide Films for Electronics*, edited by M.E. Hawley, D.H.A. Blank, C.B. Eom, D.G. Schlom, and S.K. Streiffer, Vol. 574 (Materials Research Society, Warrendale, 1999), pp. 31-36.

[32] M.A. Zurbuchen, J. Lettieri, S.K. Streiffer, Y. Jia, M.E. Hawley, X.Q. Pan, A.H. Carim, and D.G. Schlom, "Microstructure and Electrical Properties of Epitaxial $SrBi_2Nb_2O_9$ and $SrBi_2Ta_2O_9$ Films," Integr. Ferroelectr. **33** (2001) 27-37.

[33] M.A. Zurbuchen, J. Lettieri, Y. Jia, D.G. Schlom, S.K. Streiffer, and M.E. Hawley, "Transmission Electron Microscopy Study of (103)-Oriented Epitaxial $SrBi_2Nb_2O_9$ Films Grown on (111) $SrTiO_3$ and (111) $SrRuO_3$ / (111) $SrTiO_3$," J. Mater. Res. **16** (2001) 489-502.

[34] M.A. Zurbuchen, J. Lettieri, Y. Jia, G. Asayama, D.G. Schlom, S.K. Streiffer, and M.E. Hawley, "Domains in $SrBi_2Nb_2O_9$ and $SrBi_2Ta_2O_9$ Ferroelectric Films," presented at the *Fall 2000 Materials Research Society Meeting* in Boston, Massachusetts (2000); M.A. Zurbuchen, G. Asayama, D.G. Schlom, and S.K. Streiffer, "Ferroelectric Domain Structure of $SrBi_2Nb_2O_9$ Epitaxial Thin Films," Phys. Rev. Lett. **88** (2002) 107601-1-107601-4.

[35] A.D. Rae, J.G. Thompson, R.L. Withers, and A.C. Willis, "Structure Refinement of Commensurately Modulated Bismuth Titanate, $Bi_4Ti_3O_{12}$," Acta Crystallogr., Sect. B: Struct. Sci. **46** (1990) 474-487.

[36] G.W. Brown, M.E. Hawley, C.D. Theis, J. Yeh, and D.G. Schlom, "Atomic Force Microscopy Examination of the Evolution of the Surface Morphology of $Bi_4Ti_3O_{12}$ grown by Molecular Beam Epitaxy," J. Electroceram. **4** (2000) 351-356.

[37] C. Gerber, D. Anselmetti, J.G. Bednorz, J. Mannhart, and D.G. Schlom, "Screw Dislocations in High-T_c Films," Nature **350** (1991) 279-280.

[38] M. Hawley, I. D. Raistrick, J. G. Beery, and R. J. Houlton, "Growth Mechanism of Sputtered Films of $YBa_2Cu_3O_7$ Studied by Scanning Tunneling Microscopy," Science **251** (1991) 1587-1589.

[39] D.G. Schlom and J. Mannhart, "High-Temperature Superconductors: Thin Films and Multilayers," *in The Encyclopedia of Materials: Science and Technology* (Pergamon, Amsterdam, 2001) pp. 3806-3820.

[40] F.C. Frank, "The Influence of Dislocations on Crystal Growth," Disc. Farad. Soc. **5** (1949) 48-79.

[41] W.K. Burton, N. Cabrera, and F.C. Frank, "The Growth of Crystals and the Equilibrium Structure of Their Surfaces," Philos. Trans. R. Soc. London A **243** (1951) 299-358.

[42] F.C. Frank, "The Theory of Crystal Growth," Adv. Phys. **1** (1952) 91-109.

[43] D.G. Schlom, J.H. Haeni, C.D. Theis, W. Tian, X.Q. Pan, G.W. Brown, and M.E. Hawley, "The Importance of *in situ* Monitors in the Preparation of Layered Oxide Heterostructures by Reactive MBE," in *Recent Developments in Oxide and Metal Epitaxy—Theory and Experiment* edited by M. Yeadon, S. Chiang, R.F.C. Farrow, J.W. Evans, and O. Auciello, Vol. 619 (Materials Research Society, Warrendale, 2000), pp. 105-114.

[44] J.H. Haeni, C.D. Theis, and D.G. Schlom, "RHEED Intensity Oscillations for the Stoichiometric Growth of $SrTiO_3$ Thin Films by Reactive Molecular Beam Epitaxy," J. Electroceram. **4** (2000) 385-391.

[45] Y. Horikoshi, M. Kawashima, and H. Yamaguchi, "Low-Temperature Growth of GaAs and AlAs-GaAs Quantum-Well Layers by Modified Molecular Beam Epitaxy," Jpn. J. Appl. Phys. **25** (1986) L868-L870.

[46] Y. Horikoshi, M. Kawashima, and H. Yamaguchi, "Migration-Enhanced Epitaxy of GaAs and AlGaAs," Jpn. J. Appl. Phys. **27** (1988) 169-179.

[47] T. Ikeda, "A Few Quarternary Systems of Perovskite Type $A^{2+}B^{4+}O_3$ Solid Solutions," J. Phys. Soc. Jpn. **14** (1959) 1286-1294.

[48] *Phase Diagrams for Ceramists*, Vol. 1, edited by E.M. Levin, C.R. Robbins, and H.F. McMurdie (American Ceramic Society, Columbus, 1964), p. 195.

[49] *Phase Equilibria Diagrams*, Vol. 9, edited by G.B. Stringfellow (American Ceramic Society, Westerville, 1992), pp. 126, 130.

[50] S. Thoma and H. Cerva, "Comparison of the Information Content in <110>- and <100>-Projected High-Resolution Transmission Electron Microscope Images for the Quantitative Analysis of AlAs/GaAs Interfaces," Ultramicroscopy **53** (1994) 37-51.

[51] S. Li, J.A. Eastman, J.M. Vetrone, R.E. Newnham, and L.E. Cross, "Dielectric Response in Ferroelectric Superlattices," Philos. Mag. B **76** (1997) 47-57.

[52] D.G. Schlom, J.H. Haeni, J. Lettieri, C.D. Theis, W. Tian, J.C. Jiang, and X.Q. Pan, "Oxide Nano-Engineering using MBE," Mater. Sci. Eng. B **87** (2001) 282-291.

[53] S.N. Ruddlesden and P. Popper, "New Compounds of the K_2NiF_4 Type," Acta Cryst. **10** (1957) 538-539.

[54] S.N. Ruddlesden and P. Popper, "The Compound $Sr_3Ti_2O_7$ and its Structure," Acta Cryst. **11** (1958) 54-55.

[55] J.H. Haeni, C.D. Theis, D.G. Schlom, W. Tian, X.Q. Pan, H. Chang, I. Takeuchi, and X.-D. Xiang, "Epitaxial Growth of the First Five Members of the $Sr_{n+1}Ti_nO_{3n+1}$ Ruddlesden-Popper Homologous Series," Appl. Phys. Lett. **78** (2001) 3292-3294.

[56] R. Seshadri, M. Hervieu, C. Martin, A. Maignan, B. Domenges, B. Raveau, and A.N. Fitch, "Study of the Layered Magnetoresistive Perovskite $La_{1.2}Sr_{1.8}Mn_2O_7$ by High-Resolution Electron Microscopy and Synchrotron X-Ray Powder Diffraction," Chem. Mater. **9** (1997) 1778-1787.

[57] S. Hendricks and E. Teller, "X-Ray Interference in Partially Ordered Layer Lattices," J. Chem Phys. **10** (1942) 147-167.

[58] G. Grzinic, "Calculation of Incommensurate Diffraction Intensities from Disordered Crystals," Philos. Mag. A **52** (1985) 161-187.

[59] W. Tian, X.Q. Pan, J.H. Haeni, and D.G. Schlom, "Transmission Electron Microscopy Study of n = 1-5 $Sr_{n+1}Ti_nO_{3n+1}$ Epitaxial Thin Films," J. Mater. Res. **16** (2001) 2013-2026.

[60] R.J.D. Tilley, "An Electron Microscope Study of Perovskite-Related Oxides in the Sr-Ti-O System," J. Solid State Chem. **21** (1977) 293-301.

[61] G.J. McCarthy, W.B. White, and R. Roy, "Phase Equilibria in the 1375 °C Isotherm of the System Sr-Ti-O," J. Am. Ceram. Soc. **52** (1969) 463-467.

[62] W. Kwestroo and H.A.M. Paping, "The Systems BaO—SrO—TiO_2, BaO—CaO—TiO_2, and SrO—CaO—TiO_2," J. Am. Ceram. Soc. **42** (1959) 292-299.

[63] M.A. McCoy, R.W. Grimes, and W.E. Lee, "Phase Stability and Interfacial Structures in the SrO—$SrTiO_3$ System," Philos. Mag. A **75** (1997) 833-846.

[64] *Phase Diagrams for Ceramists 1969 Supplement*, edited by E.M. Levin, C.R. Robbins, and H.F. McMurdie (American Ceramic Society, Columbus, 1969), p. 93.

[65] C. Noguera, "Theoretical Investigation of the Ruddlesden-Popper Compounds $Sr_{n+1}Ti_nO_{3n+1}$ (n = 1—3)," Philos. Mag. Lett. **80**, 173-180 (2000).

[66] Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J.G. Bednorz, and F. Lichtenberg, "Superconductivity in a Layered Perovskite without Copper," Nature **372** (1994) 532-534.

[67] T.M. Rice and M. Sigrist, "Sr_2RuO_4: An Electronic Analogue of ^{3}He?" J. Phys.: Condens. Matter **7** (1995) L643-L648.

[68] D.A. Wollman, D.J. Van Harlingen, W.C. Lee, D.M. Ginsberg, and A.J. Leggett, "Experimental Determination of the Superconducting Pairing State in YBCO from the Phase Coherence of YBCO-Pb dc SQUIDs," Phys. Rev. Lett. **71** (1993) 2134-2137.

[69] C.C. Tsuei, J.R. Kirtley, C.C. Chi, L.S. Yu-Jahnes, A. Gupta, T. Shaw, J.Z. Sun, and M.B. Ketchen, "Pairing Symmetry and Flux Quantization in a Tricrystal Superconducting Ring of $YBa_2Cu_3O_{7-\delta}$," Phys. Rev. Lett. **73** (1994) 593-596.

[70] D.J. Van Harlingen, "Phase-Sensitive Tests of the Symmetry of the Pairing State in the High-Temperature Superconductors—Evidence for $d_{x^2-y^2}$ Symmetry," Rev. Mod. Phys. **67** (1995) 515-535.

[71] J.R. Kirtley, C.C. Tsuei, J.Z. Sun, C.C. Chi, L.S. Yu-Jahnes, A. Gupta, M. Rupp, and M.B. Ketchen, "Symmetry of the Order Parameter in the High-T_c Superconductor $YBa_2Cu_3O_{7-\delta}$," Nature **373** (1995) 225-228.

[72] C.C. Tsuei and J.R. Kirtley, M. Rupp, J.Z. Sun, A. Gupta, M.B. Ketchen, C.A. Wang, Z.F. Ren, J.H. Wang, M. Bhushan, "Pairing Symmetry in Single-Layer $Tl_2Ba_2CuO_{6+\delta}$ Superconductors," Science **271** (1996) 329-332.

[73] C.C. Tsuei, J.R. Kirtley, Z.F. Ren, J.H. Wang, H. Raffy, and Z.Z. Li, "Pure $d_{x^2-y^2}$ Order-Parameter Symmetry in the Tetragonal Superconductor $Tl_2Ba_2CuO_{6+\delta}$," Nature **387** (1997) 481-483.

[74] J.R. Kirtley, C.C. Tsuei, and K.A. Moler, "Temperature Dependence of the Half-Integer Magnetic Flux Quantum," Science **285** (1999) 1373-1375.

[75] C.C. Tsuei and J.R. Kirtley, "Phase-Sensitive Evidence for *d*-Wave Pairing Symmetry in Electron-Doped Cuprate Superconductors," Phys. Rev. Lett. **85** (2000) 182-185.

[76] Y. Maeno, T.M. Rice, and M. Sigrist, "The Intriguing Superconductivity of Strontium Ruthenate," Phys. Today 54 (January 2001) 42-47.

[77] S. Madhavan, D.G. Schlom, A. Dabkowski, H.A. Dabkowska, and Y. Liu, "Growth of Epitaxial *a*-axis and *c*-axis Oriented Sr_2RuO_4 Films," Appl. Phys. Lett. **68** (1996) 559-561.

[78] D.G. Schlom, Y. Jia, L.-N. Zou, J.H. Haeni, S. Briczinski, M.A. Zurbuchen, C.W. Leitz, S. Madhavan, S. Wozniak, Y. Liu, M.E. Hawley, G.W. Brown, A. Dabkowski, H.A. Dabkowska, R. Uecker, and P. Reiche, "Searching for superconductivity in epitaxial films of copper-free layered oxides with the K_2NiF_4 structure," in: *Superconducting and Related Oxides: Physics and Nanoengineering III*, edited by D. Pavuna and I. Bozovic, SPIE Vol. 3481 (SPIE, Bellingham, 1998), pp. 226-240.

[79] S. Ohashi, M. Lippmaa, N. Nakagawa, H. Nagasawa, H. Koinuma, and M. Kawasaki, "Compact Laser Molecular Beam Epitaxy System using Laser Heating of Substrate for Oxide Film Growth," Rev. Sci. Instrum. **70** (1999) 178-183.

[80] A.P. Mackenzie, R.K.W. Haselwimmer, A.W. Tyler, G.G. Lonzarich, Y. Mori, S. Nishizaki, and Y. Maeno, "Extremely Strong Dependence of Superconductivity on Disorder in Sr_2RuO_4," Phys. Rev. Lett. **80** (1998) 161-164.

[81] Z.Q. Mao, Y. Mori, and Y. Maeno, "Supression of Superconductivity in Sr_2RuO_4 Caused by Defects," Phys. Rev. B **60** (1999) 610-614.

[82] M.A. Zurbuchen, Y. Jia, S. Knapp, A.H. Carim, D.G. Schlom, L.-N. Zou, and Y. Liu, "Suppression of Superconductivity by Crystallographic Defects in Epitaxial Sr_2RuO_4 Films," Appl. Phys. Lett. **78** (2001) 2351-2353.

[83] T. Akima, S. NishiZaki, and Y. Maeno, "Intrinsic Superconducting Parameters of Sr_2RuO_4," J. Phys. Soc. Jpn. **68** (1999) 694-695.

[84] K. Ishida, H. Mukuda, Y. Kitaoka, K. Asayama, Z.Q. Mao, Y. Mori, and Y. Maeno, "Spin-Triplet Superconductivity in Sr_2RuO_4 Identified by ^{17}O Knight Shift," Nature **396** (1998) 658-660.

[85] G.M. Luke, Y. Fudamoto, K.M. Kojima, M.I. Larkin, J. Merrin, B. Nachumi, Y.J. Uemura, Y. Maeno, Z.Q. Mao, Y. Mori, H. Nakamura, and M. Sigrist, "Time-Reversal Symmetry-Breaking Superconductivity in Sr_2RuO_4," Nature **394** (1998) 558-561.

[86] R. Jin, Yu. Zadorozhny, Y. Liu, D.G. Schlom, Y. Mori, and Y. Maeno, "Observation of Anomalous Temperature Dependence of the Critical Current in $Pb/Sr_2RuO_4/Pb$ Junctions," Phys. Rev. B **59** (1999) 4433-4438.

4. Papers Published or Submitted under the Support of this Grant

1. C.D. Theis, J. Yeh, D.G. Schlom, M.E. Hawley, G.W. Brown, J.C. Jiang, and X.Q. Pan "Adsorption-Controlled Growth of $Bi_4Ti_3O_{12}$ by Reactive MBE," *Applied Physics Letters* **72** (1998) 2817-2819.

2. C.D. Theis, J. Yeh, D.G. Schlom, M.E. Hawley, and G.W. Brown, "Adsorption-Controlled Growth of $PbTiO_3$ by Reactive Molecular Beam Epitaxy," *Thin Solid Films* **325** (1998) 107-114.

3. C.D. Theis, J. Yeh, D.G. Schlom, M.E. Hawley, and G.W. Brown "The Influence of Vicinal $SrTiO_3$ Surfaces on the Growth and Ferroelectric Properties of Epitaxial $Bi_4Ti_3O_{12}$ Thin Films," *Materials Science and Engineering B* **56** (1998) 228-233.

4. D.G. Schlom, Y. Jia, L.-N. Zou, J.H. Hanei, S. Briczinski, M.A. Zurbuchen, C.W. Leitz, S. Madhavan, S. Wozniak, Y. Liu, M.E. Hawley, G.W. Brown, A. Dabkowski, H.A. Dabkowska, R. Uecker, and P. Reiche, "Searching for superconductivity in epitaxial films of copper-free layered oxides with the K_2NiF_4 structure," in: *Superconducting and Related Oxides: Physics and Nanoengineering III*, edited by D. Pavuna and I. Bozovic, SPIE Vol. 3481 (SPIE, Bellingham, 1998), pp. 226-240.

5. J.C. Jiang, X.Q. Pan, W. Tian, C.D. Theis, and D.G. Schlom, "Abrupt $PbTiO_3/SrTiO_3$ Superlattices Grown by Reactive Molecular Beam Epitaxy," *Applied Physics Letters* **74** (1999) 2851-2853.

6. J.H. Haeni, C.D. Theis, and D.G. Schlom, "RHEED Intensity Oscillations for the Stoichiometric Growth of $SrTiO_3$ Thin Films by Reactive Molecular Beam Epitaxy," *Journal of Electroceramics* **4** (2000) 385-391.

7. G.W. Brown, M.E. Hawley, C.D. Theis, J. Yeh, and D.G. Schlom, "Atomic Force Microscopy Examination of the Evolution of the Surface Morphology of $Bi_4Ti_3O_{12}$ grown by Molecular Beam Epitaxy," *Journal of Electroceramics* **4** (2000) 351-356.

8. J. Lettieri, M.A. Zurbuchen, Y. Jia, D.G. Schlom, S.K. Streiffer, and M.E. Hawley, "Epitaxial Growth of non-*c*-oriented $SrBi_2Nb_2O_9$ on (111) $SrTiO_3$," *Applied Physics Letters* **76** (2000) 2937-2939.

9. J. Lettieri, M.A. Zurbuchen, Y. Jia, D.G. Schlom, S.K. Streiffer, and M.E. Hawley, "Epitaxial Growth of $SrBi_2Nb_2O_9$ on (110) $SrTiO_3$ and the Establishment of a Lower Bound on the Spontaneous Polarization of $SrBi_2Nb_2O_9$," *Applied Physics Letters* **77** (2000) 3090-3092.

10. J. Lettieri, Y. Jia, S.J. Fulk, D.G. Schlom, M.E. Hawley, and G.W. Brown, "Optimization of the Growth of Epitaxial $SrBi_2Ta_2O_9$ Thin Films by Pulsed Laser Deposition," *Thin Solid Films* **379** (2000) 64-71.

11. J.H. Haeni, C.D. Theis, D.G. Schlom, W. Tian, X.Q. Pan, H. Chang, I. Takeuchi, and X.-D. Xiang, "Epitaxial Growth of the First Five Members of the $Sr_{n+1}Ti_nO_{3n+1}$ Ruddlesden-Popper Homologous Series," *Applied Physics Letters* **78** (2001) 3292-3294.

12. M.A. Zurbuchen, J. Lettieri, S.K. Streiffer, Y. Jia, M.E. Hawley, X.Q. Pan, A.H. Carim, and D.G. Schlom, "Microstructure and Electrical Properties of Epitaxial $SrBi_2Nb_2O_9$ and $SrBi_2Ta_2O_9$ Films," *Integrated Ferroelectrics* **33** (2001) 27-37.

13. D.G. Schlom and J. Mannhart, "High-Temperature Superconductors: Thin Films and Multilayers," in *The Encyclopedia of Materials: Science and Technology* (Pergamon, Amsterdam, 2001) pp. 3806-3820.
Available on-line at http://ww3.elsevier.nl/mrwclus/15/show/.

14. I. Bozovic and D.G. Schlom, "Superconducting Thin Films: Materials, Preparation, and Properties," in *The Encyclopedia of Materials: Science and Technology* (Pergamon, Amsterdam, 2001) pp. 8955-8964.
Available on-line at http://ww3.elsevier.nl/mrwclus/15/show/.

15. M.A. Zurbuchen, J. Lettieri, Y. Jia, D.G. Schlom, S.K. Streiffer, and M.E. Hawley, "Transmission Electron Microscopy Study of (103)-Oriented Epitaxial $SrBi_2Nb_2O_9$ Films Grown on (111) $SrTiO_3$ and (111) $SrRuO_3$ / (111) $SrTiO_3$," *Journal of Materials Research* **16** (2001) 489-502.

16. D.G. Schlom, J.H. Haeni, C.D. Theis, W. Tian, X.Q. Pan, G.W. Brown, and M.E. Hawley, "The Importance of *in situ* Monitors in the Preparation of Layered Oxide Heterostructures by Reactive MBE," in *Recent Developments in Oxide and Metal Epitaxy—Theory and Experiment* edited by M. Yeadon, S. Chiang, R.F.C. Farrow, J.W. Evans, and O. Auciello, Vol. 619 (Materials Research Society, Warrendale, 2000), pp. 105-114.

17. M.A. Zurbuchen, Y. Jia, S. Knapp, A.H. Carim, D.G. Schlom, L.-N. Zou, and Y. Liu, "Suppression of Superconductivity by Crystallographic Defects in Epitaxial Sr_2RuO_4 Films," *Applied Physics Letters* **78** (2001) 2351-2353.

18. Z-K. Liu, D.G. Schlom, Q. Li, and X.X. Xi, "Thermodynamics of the Mg-B System: Implications for the Deposition of MgB_2 Thin Films," *Applied Physics Letters* **78** (2001) 3678-3680.

19. W. Tian, X.Q. Pan, J.H. Haeni, and D.G. Schlom, "Transmission Electron Microscopy Study of $n = 1$-5 $Sr_{n+1}Ti_nO_{3n+1}$ Epitaxial Thin Films," *Journal of Materials Research* **16** (2001) 2013-2026.

20. W. Tian, J.H. Haeni, D.G. Schlom, and X.Q. Pan, "Strain-Induced Elevation of the Spontaneous Polarization in $BaTiO_3$ Thin Films," in *Ferroelectric Thin Films IX* edited by P.C. McIntyre, S.R. Gilbert, Y. Miyasaka, R.W. Schwartz, and D. Wouters, Vol. 655 (Materials Research Society, Warrendale, 2001), pp. CC7.8.1-CC7.8.6.

21. D.G. Schlom, J.H. Haeni, J. Lettieri, C.D. Theis, W. Tian, J.C. Jiang, and X.Q. Pan, "Oxide Nano-Engineering using MBE," *Materials Science & Engineering B* **87** (2001) 282-291.

22. M.A. Zurbuchen, D.G. Schlom, and S.K. Streiffer, "Comment on 'High-resolution electron microscopy investigations on stacking faults in $SrBi_2Ta_2O_9$ ferroelectric thin films' [Appl. Phys. Lett. **78**, 973 (2001)]," *Applied Physics Letters* **79** (2001) 887-888.

23. X.X. Xi, X.H. Zeng, A. Soukiassian, J. Jones, J. Hotchkiss,Y. Zhong, C.O. Brubaker, Z.-K. Liu, J. Lettieri, D.G. Schlom,Y.F. Hu, E. Wertz, Q. Li, W. Tian, H.P. Sun, and X.Q. Pan, "Thermodynamics and Thin Film Deposition of MgB_2 Superconductors," *Superconductor Science and Technology* **15** (2002) 451-457.

24. X.H. Zeng, A. Sukiasyan, X.X. Xi, Y.F. Hu, E. Wertz, Q. Li, W. Tian, H.P. Sun, X.Q. Pan, J. Lettieri, D.G. Schlom, C.O. Brubaker, Z.-K. Liu, and Q. Li, "Superconducting Properties of Nanocrystalline MgB_2 Thin films Made by an *in situ* Annealing Process," *Applied Physics Letters* **79** (2001) 1840-1842.

25. X.H. Zeng, A.V. Pogrebnyakov, A. Kotcharov, J.E. Jones, X.X. Xi, E.M. Lysczek, J.M. Redwing, S.Y. Xu, Q. Li, J. Lettieri, D.G. Schlom, W. Tian, X.Q. Pan, and Z.-K. Liu, "*In Situ* Epitaxial MgB_2 Thin Films for Superconducting Electronics," *Nature Materials* **1** (2002) 35-38.

26. R. Ramesh and D.G. Schlom, "Orienting Ferroelectric Films," *Science* **296** (2002) 1975-1976.

27. X.X. Xi, X.H. Zeng, A.V. Pogrebnyakov, A. Soukiassian, S.Y. Xu, Y.F. Hu, E. Wertz, Q. Li, Y. Zhong, C.O. Brubaker, Z.-K. Liu. E.M. Lysczek, J.M. Redwing, J. Lettieri, D.G. Schlom, W. Tian, H.P. Sun, and X.Q. Pan, "Deposition and Properties of Superconducting MgB_2 Thin Films," submitted to *Journal of Superconductivity.*

28. X.X. Xi, X.H. Zeng, A.V. Pogrebnyakov, S.Y. Xu, Q. Li, Y. Zhong, C.O. Brubaker, Z.-K. Liu, E.M. Lysczek, J.M. Redwing, J. Lettieri, D.G. Schlom, W. Tian, and X.Q. Pan, "*In situ* Growth of MgB_2 Thin Film by Hybrid Physical-Chemical Vapor Deposition," submitted to *IEEE Transactions on Applied Superconductivity.*

29. X.H. Zeng, A.V. Pogrebnyakov, M.H. Zhu, J.E. Jones, X.X. Xi, S.Y. Xu, E. Wertz, Q. Li, J.M. Redwing, J. Lettieri, V. Vaithyanathan, D.G. Schlom , Z.-K. Liu, O. Trithaveesak, and J. Schubert, "Superconducting MgB_2 Thin Films on Silicon Carbide Substrates by Hybrid Physical-Chemical Vapor Deposition," submitted to *Applied Physics Letters.*

5. Presentations under the Support of this Grant

1. C.D. Theis*, D.G. Schlom, M.E. Hawley, and X. Pan, "The Controlled Growth of Ferroelectric Superlattices by MBE;" presented at the *Fall '97 Materials Research Society Meeting* in Boston, Massachusetts (1997).

2. C.D. Theis*, J.C. Jiang, G.W. Brown, M.E. Hawley, X. Pan, and D.G. Schlom, "Growth of Ferroelectric Superlattices with Unit Cell Precision by MBE," presented at the *10th International Symposium on Integrated Ferroelectrics* in Monterey, California (1998).

3. D.G. Schlom*, C.D. Theis, J.H. Haeni, G.W. Brown, M.E. Hawley, J.C. Jiang, and X.Q. Pan, "The Growth of Titanate Perovskites with Unit Cell Precision by MBE," presented at the *40th Electronic Materials Conference* in Charlottesville, Virginia (1998). **(Invited)**

4. C.D. Theis*, D.G. Schlom, G.W. Brown, and M.E. Hawley, "Artifically-Designed Ferroelectric Superlattices: MBE Growth of the Aurivillius Homologous Series $(Bi_2O_2)(A_{n-1}B_nO_{3n+1})$ with Atomic Layer Precision," *The Eastern Regional Conference on Crystal Growth and Epitaxy (ACCGE/east-98)* in Atlantic City, NJ (1998).

5. J.H. Haeni*, D.G. Schlom, and X.Q. Pan, "MBE growth of the $Sr_{n+1}Ti_nO_{3n+1}$ Ruddlesden-Popper Homologous Series: Opening the Door to Synthetic and Metastable Crystal Growth," *The Eastern Regional Conference on Crystal Growth and Epitaxy (ACCGE/east-98)* in Atlantic City, NJ (1998). (Winner of Best Student Paper Award (**1st Prize** and check for $800))

6. C.D. Theis*, J.C. Jiang, G.W. Brown, M.E. Hawley, X.Q. Pan, and D.G. Schlom, "Manmade Ferroelectric Superlattices: MBE Growth of Metastable $PbTiO_3$ / $SrTiO_3$ and High n Members of the Aurivillius Homologous Series," presented at the *17th North American Molecular Beam Epitaxy Conference* in State College, Pennsylvania (1998).

7. D.G. Schlom*, J.H. Haeni, C.D. Theis, J. Lettieri, W. Tian, J.C. Jiang, L-N. Zou, G.W. Brown, M.E. Hawley, Y. Liu, and X.Q. Pan, "The Emergence of Molecular Beam Epitaxy as a Means to Build Smart Oxide Heterostructures with Nanometer Precision," presented at the *56th Annual Pittsburgh Diffraction Conference* in Pittsburgh, Pennsylvania (1998). **(Invited)**

8. D.G. Schlom*, J.H. Haeni, C.D. Theis, J. Lettieri, W. Tian, J.C. Jiang, L-N. Zou, G.W. Brown, M.E. Hawley, Y. Liu, and X.Q. Pan, "Perovskite NanoComposites," presented at the *1st International Symposium on Atomic Scale Processing and Novel Properties in Nanoscopic Materials* in Osaka, Japan (1998).

9. D.G. Schlom*, C.D. Theis, J. Lettieri, J.C. Jiang, X.Q. Pan, G.W. Brown, and M.E. Hawley, "Adsorption-Controlled growth of Bismuth Titanate, Lead Titanate, and their Superlattices," presented at the *International Workshop on Chemical Designing and Processing of High-T_c Superconductors IV (Chem-HTSC IV)* in Tokyo, Japan (1998). **(Invited)**

10. G.W. Brown*, M.E. Hawley, C.D. Theis, J. Yeh, and D.G. Schlom, "Atomic Force Microscopy Examination of the Evolution of the Surface Morphology of $Bi_4Ti_3O_{12}$ Grown by Molecular Beam Epitaxy," presented at the *Fall '98 Materials Research Society Meeting* in Boston, Massachusetts (1998).

11. C.D. Theis*, J. Lettieri, D.G. Schlom, G.W. Brown, M.E. Hawley, J.C. Jiang, and X.Q. Pan, "Growth and Electrical Properties of MBE-Grown Bismuth Titanate," presented at the *Fall '98 Materials Research Society Meeting* in Boston, Massachusetts (1998).

12. J.C. Jiang, X.Q. Pan*, C.D. Theis, and D.G. Schlom, "Transmission Electron Microscopy Study of $Bi_4Ti_3O_{12}$ Grown by Reactive MBE on SrO- and TiO_2-Terminated $SrTiO_3$," presented at the *Fall '98 Materials Research Society Meeting* in Boston, Massachusetts (1998).

13. J.H. Haeni*, L-N. Zou, W. Tian, X.Q. Pan, Y. Liu, and D.G. Schlom, "Searching for Superconductivity in La-Doped Sr_2TiO_4 Films Grown by MBE," presented at the *Fall '98 Materials Research Society Meeting* in Boston, Massachusetts (1998).

14. G.W. Brown*, M.E. Hawley, C.D. Theis, J. Yeh, and D.G. Schlom, "Evolution of the Surface Morphology of *c*-axis $Bi_4Ti_3O_{12}$ Films Grown by Molecular Beam Epitaxy," presented at the *5th International Workshop on Oxide Electronics* in College Park, Maryland (1998).

15. J.H. Haeni*, C.D. Theis, and D.G. Schlom, "RHEED Intensity Oscillations for the Stoichiometric Growth of $SrTiO_3$ Thin Films by Molecular Beam Epitaxy," presented at the *5th International Workshop on Oxide Electronics* in College Park, Maryland (1998).

16. J. Im, O. Auciello*, A.R. Krauss, D.M. Gruen, Y. Gao, E.A. Irene, J. Lettieri, D.G. Schlom, and R.P.H. Chang, "Studies of Growth, Post-Deposition Processes, and Surface Structure of Strontium Bismuth Tantalate Thin Films Using in situ Time-of-Flight Ion Beam Analysis and Spectroscopic Ellipsometry," presented at the *5th International Workshop on Oxide Electronics* in College Park, Maryland (1998).

17. X.Q. Pan*, W. Tian, J.C. Jiang, J.H. Haeni, C.D. Theis, J. Lettieri, and D.G. Schlom, "Graded Ferroelectric Thin Films Grown by Molecular Beam Epitaxy," presented at the *11th International Symposium on Integrated Ferroelectrics (ISIF '99)* in Colorado Springs, Colorado (1999). **(Invited)**

18. D.G. Schlom*, C.D. Theis, J. Lettieri, Y. Jia, W. Si, X.X. Xi, G.W. Brown, M.E. Hawley, J.C. Jiang, X.Q. Pan, H. Li, R. Ramesh, O. Auciello, J. Im, A.R. Krauss, R. Uecker, and P. Reiche, "Epitaxial Growth of Aurivillius Phases by MBE and PLD," presented at the *11th International Symposium on Integrated Ferroelectrics (ISIF '99)* in Colorado Springs, Colorado (1999). **(Invited)**

19. J. Im*, O. Auciello, A.R. Krauss, J. Lettieri, and D.G. Schlom, "*In-Situ* Studies of the Surface Structure of Strontium-Bismuth-Tantalate Films using Time-of-Flight Ion Scattering and Recoil Spectroscopy," presented at the *11th International Symposium on Integrated Ferroelectrics (ISIF '99)* in Colorado Springs, Colorado (1999).

20. J.C. Jiang, X.Q. Pan*, C.D. Theis, and D.G. Schlom, "A TEM Study of Epitaxial $Bi_4Ti_3O_{12}$ Thin Films Grown on (001) $SrTiO_3$ Substrates," presented at the *101st Annual Meeting of the American Ceramics Society* in Indianapolis, Indiana (1999).

21. W. Tian*, J.C. Jiang, X.Q. Pan, J.H. Haeni, and D.G. Schlom, "Atomistic Structure of Interfaces and Crystal Defects in $Sr_{n+1}Ti_nO_{3n+1}$ ($n = 1$–5) Thin Films of Ruddlesden-Popper Series Grown by MBE," presented at the *101st Annual Meeting of the American Ceramics Society* in Indianapolis, Indiana (1999).

22. X.Q. Pan*, W. Tian, J.C. Jiang, C.D. Theis, D.G. Schlom, Q. Gan, R.A. Rao, and C.B. Eom, "Interfacial Atomic Structure of Oxide Thin Films," presented at the *IUMRS International Conference on Advanced Materials* in Beijing, China (1999). **(Invited)**

23. X.Q. Pan*, W. Tian, J.C. Jiang, J.H. Haeni, C.D. Theis, and D.G. Schlom, "Oxide Thin Films and Superlattices Grown by Reactive Molecular Beam Epitaxy," presented at the *IUMRS International Conference on Advanced Materials* in Beijing, China (1999). **(Invited)**

24. D.G. Schlom*, J.H. Haeni, C.D. Theis, J. Lettieri, M.A. Zurbuchen, W. Tian, J.C. Jiang, L-N. Zou, G.W. Brown, M.E. Hawley, Y. Liu, and X.Q. Pan, "Nano-Engineering Perovskites: An Epitaxial Perspective (with examples)," presented at the *3rd STCS-CNRS Workshop* in Evanston, Illinois (1999). **(Invited)**

25. G.W. Brown,* M.E. Hawley, C.D. Theis, J. Yeh, and D.G. Schlom, "Atomic Force Microscopy Study of the Evolution of the Surface Morphology of $Bi_4Ti_3O_{12}$ Grown by Molecular Beam Epitaxy," presented at the *11th American Conference on Crystal Growth & Epitaxy* in Tucson, Arizona (1999). **(Invited)**

26. D.G. Schlom,* J. Lettieri, M.A. Zurbuchen, C.D. Theis, J.H. Haeni, Y. Jia, S. Wozniak, G.W. Brown, M.E. Hawley, W. Tian, J.C. Jiang, X.Q. Pan, A. Dabkowski, H.A. Dabkowska, R. Uecker, and P. Reiche, "Substrates for Epitaxial Oxide Films—A Film Grower's Perspective," presented at the *11th American Conference on Crystal Growth & Epitaxy* in Tucson, Arizona (1999). **(Invited)**

27. W. Tian*, J.H. Haeni, D.G. Schlom, and X.Q. Pan, "Microstructure of Epitaxial $Sr_{n+1}Ti_nO_{3n+1}$ Thin Films of the Ruddlesden-Popper Series," presented at the *Fall '99 Materials Research Society Meeting* in Boston, Massachusetts (1999).

28. J. Lettieri*, M.A. Zurbuchen, Y. Jia, G.W. Brown, W. Tian, A.H. Carim, X.Q. Pan, M.E. Hawley, and D.G. Schlom, "Epitaxial Growth of $SrBi_2Nb_2O_9$ Films on $SrTiO_3$ (110)," presented at the *Fall '99 Materials Research Society Meeting* in Boston, Massachusetts (1999).

29. W. Tian*, J.C. Jiang, J.H. Haeni, D.G. Schlom, and X.Q. Pan, "Microstructure of Ferroelectric Superlattices Grown by Molecular Beam Epitaxy," presented at the *Fall '99 Materials Research Society Meeting* in Boston, Massachusetts (1999).

30. M.A. Zurbuchen*, J. Lettieri, Y. Jia, W. Tian, A.H. Carim, X.Q. Pan, and D.G. Schlom, "Microstructure of $SrBi_2Nb_2O_9$ and $SrBi_2Ta_2O_9$ Epitaxial Thin Films," presented at the *Fall '99 Materials Research Society Meeting* in Boston, Massachusetts (1999).

31. J. Lettieri*, M.A. Zurbuchen, S.K. Streiffer, Y. Jia, G.W. Brown, M.E. Hawley, and D.G. Schlom, "Epitaxial $SrBi_2Nb_2O_9$ Films with (103) Orientation on $SrRuO_3$ Electrodes," presented at the *6th International Workshop on Oxide Electronics* in College Park, Maryland (1999).

32. J. Lettieri*, M.A. Zurbuchen, Y. Jia, D.G. Schlom, S.K. Streiffer, and M.E. Hawley, "Investigation of the Anisotropy of $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$ through Epitaxial Growth," presented at the *Science and Technology of Ferroelectric Materials (7th Frontier Science Research Conference in Materials Science and Technology Series)* in La Jolla, California (2000). **(Invited)**

33. D.G. Schlom*, "Physical Deposition Methods: Sputtering, PLD, and MBE," presented at the *12th International Symposium on Integrated Ferroelectrics (ISIF 2000)* in Aachen, Germany (2000). (**Invited** Tutorial)

34. M.A. Zurbuchen*, J. Lettieri, S.K. Streiffer, Y. Jia, M.E. Hawley, A.H. Carim, and D.G. Schlom, "Morphology and Electrical Properties of Epitaxial $SrBi_2Nb_2O_9$ Films," presented at the *12th International Symposium on Integrated Ferroelectrics (ISIF 2000)* in Aachen, Germany (2000).

35. C.A. Billman*, R.A. McKee, F.J. Walker, M.F. Chisholm, J. Lettieri, and D.G. Schlom, "2" Oxide Substrates with a (100) $SrTiO_3$ Surface and (100) Silicon Foundation," presented at the *12th International Symposium on Integrated Ferroelectrics (ISIF 2000)* in Aachen, Germany (2000).

36. D.G. Schlom*, J.H. Haeni, C.D. Theis, W. Tian, X.Q. Pan, G.W. Brown, and M.E. Hawley "The Importance of *In Situ* Monitors in the Preparation of Layered Oxide Heterostructures by Reactive MBE," presented at the *Spring '00 Materials Research Society Meeting* in San Francisco, California (2000). **(Invited)**

37. J. Lettieri*, M.A. Zurbuchen, Y. Jia, D.G. Schlom, S.K. Streiffer, and M.E. Hawley, "Growth Evolution, Morphology, and Microstructure of Epitaxial $SrBi_2Nb_2O_9$ Films," presented at the Spring '00 Materials Research Society Meeting in San Francisco, California (2000). **(Invited)**

38. J. Lettieri*, M.A. Zurbuchen, D.G. Schlom, S.K. Streiffer, and M.E. Hawley, "Growth Evolution, Morphology, and Microstructure of Epitaxial $SrBi_2Nb_2O_9$ Films," presented at the *12th IEEE International Symposium on the Applications of Ferroelectrics (ISAF 2000)* in Honolulu, Hawaii (2000).

39. D.G. Schlom*, M.A. Zurbuchen, J.H. Haeni, J. Lettieri, C.D. Theis, J. Yeh, A.H. Carim, W. Tian, J.C. Jiang, X.Q. Pan, G.W. Brown, and M.E. Hawley, "The Interrelationship between Interfaces and the Structural Customization on the Nanometer Scale of Oxide Films, Superlattices, and New Compounds," presented at the *Fall 2000 Materials Research Society Meeting* in Boston, Massachusetts (2000). **(Invited)**

40. M.A. Zurbuchen*, J. Lettieri, Y. Jia, G. Asayama, D.G. Schlom, S.K. Streiffer, and M.E. Hawley, "Domains in $SrBi_2Nb_2O_9$ and $SrBi_2Ta_2O_9$ Ferroelectric Films," presented at the *Fall 2000 Materials Research Society Meeting* in Boston, Massachusetts (2000).

41. M.A. Zurbuchen*, Y. Jia, S. Knapp, A.H. Carim, D.G. Schlom, L.-N. Zou, Y. Liu, W. Tian, X.Q. Pan, G.W. Brown, and M.E. Hawley, "Correlation of Structural Disorder with Electrical Transport in Epitaxial Sr_2RuO_4 Films,"presented at the *Fall 2000 Materials Research Society Meeting* in Boston, Massachusetts (2000).

42. D.G. Schlom*, J.H. Haeni, J. Lettieri, C.D. Theis, W. Tian, J.C. Jiang, X.Q. Pan, G.W. Brown and M.E. Hawley "Oxide Nano-Engineering using MBE," presented at the *Lawrence Symposium on Critical Issues in Epitaxy* in Scottsdale, Arizona (2001). **(Invited)**

43. G. Asayama*, J. Lettieri, M.A. Zurbuchen, S. Trolier-McKinstry, D.G. Schlom, S.K. Streiffer, and J.P. Maria, "Growth of (103) Fiber-Textured $SrBi_2Nb_2O_9$ Thin Films on Pt-Coated Si Substrates," presented at the *13th Annual International Symposium on Integrated Ferroelectrics (ISIF)* in Colorado Springs, Colorado (2001).

44. D.G. Schlom*, "Physical Vapor Deposition Techniques—Sputtering, PLD, and MBE," presented at the *13th Annual International Symposium on Integrated Ferroelectrics (ISIF)* in Colorado Springs, Colorado (2001). **(Invited Tutorial)**

45. C.A. Billman*, R.A. McKee, F.J. Walker, and D.G. Schlom "Electrical Properties of Alkaline Earth Oxides on Silicon," presented at the *2001 March Meeting of the American Physical Society* in Seattle, Washington (2001).

46. D.G. Schlom*, "Use of X-Ray Diffraction to Assess the Quality and Crystallographic Orientation of Oxide Thin Films," presented at the *Spring 2001 Materials Research Society Meeting* in San Francisco, California (2001). **(Invited Tutorial)**

47. Z-K. Liu, D.G. Schlom*, Q. Li, and X.X. Xi, "Thermodynamics of the Mg-B System and its Implications for the *in situ* Deposition of MgB_2 Thin Films," presented at the *Spring 2001 Materials Research Society Meeting* in San Francisco, California (2001). **(Invited)**