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Title: The Controlled Growth of Perovskite Thin Films:
Opportunities, Challenges, and Synthesis

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THE CONTROLLED GROWTH OF PEROVSKITE THIN FILMS: OPPORTUNITIES, CHALLENGES, AND SYNTHESIS

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ABSTRACT

The broad spectrum of electronic and optical properties exhibited by perovskites offers tremendous opportunities for microelectronic devices, especially when a combination of properties in a single device is desired. Molecular beam epitaxy (MBE) has achieved unparalleled control in the integration of semiconductors at the monolayer-level; its use for the integration of perovskites with similar nanoscale customization appears promising. Composition control and oxidation are often significant challenges to the growth of perovskites by MBE, but we show that these can be met through the use of purified ozone as an oxidant and real-time atomic absorption composition control. The opportunities, challenges, and synthesis of oxide heterostructures by reactive MBE are described, with examples taken from the growth of oxide superconductors and oxide ferroelectrics.

INTRODUCTION

Oxides exhibit the full spectrum of electronic, optical, and magnetic behavior; insulating, semiconducting, metallic, high temperature superconducting, pyroelectric, piezoelectric, ferroelectric, ferromagnetic, and non-linear optical effects are all contained within structurally-compatible oxides (particularly perovskites). Examples are given in Table I and some of their crystal structures are shown in Fig. 1. The electroceramics industry, a more than \$20 billion/year industry, utilizes these electrical properties generally in single devices made primarily by bulk synthesis methods for capacitors, sensors, actuators, night vision and other applications. However, a significant opportunity exists to combine these properties together in oxide heterostructures where multiple properties can be utilized to yield a functional integrated device. Integration of

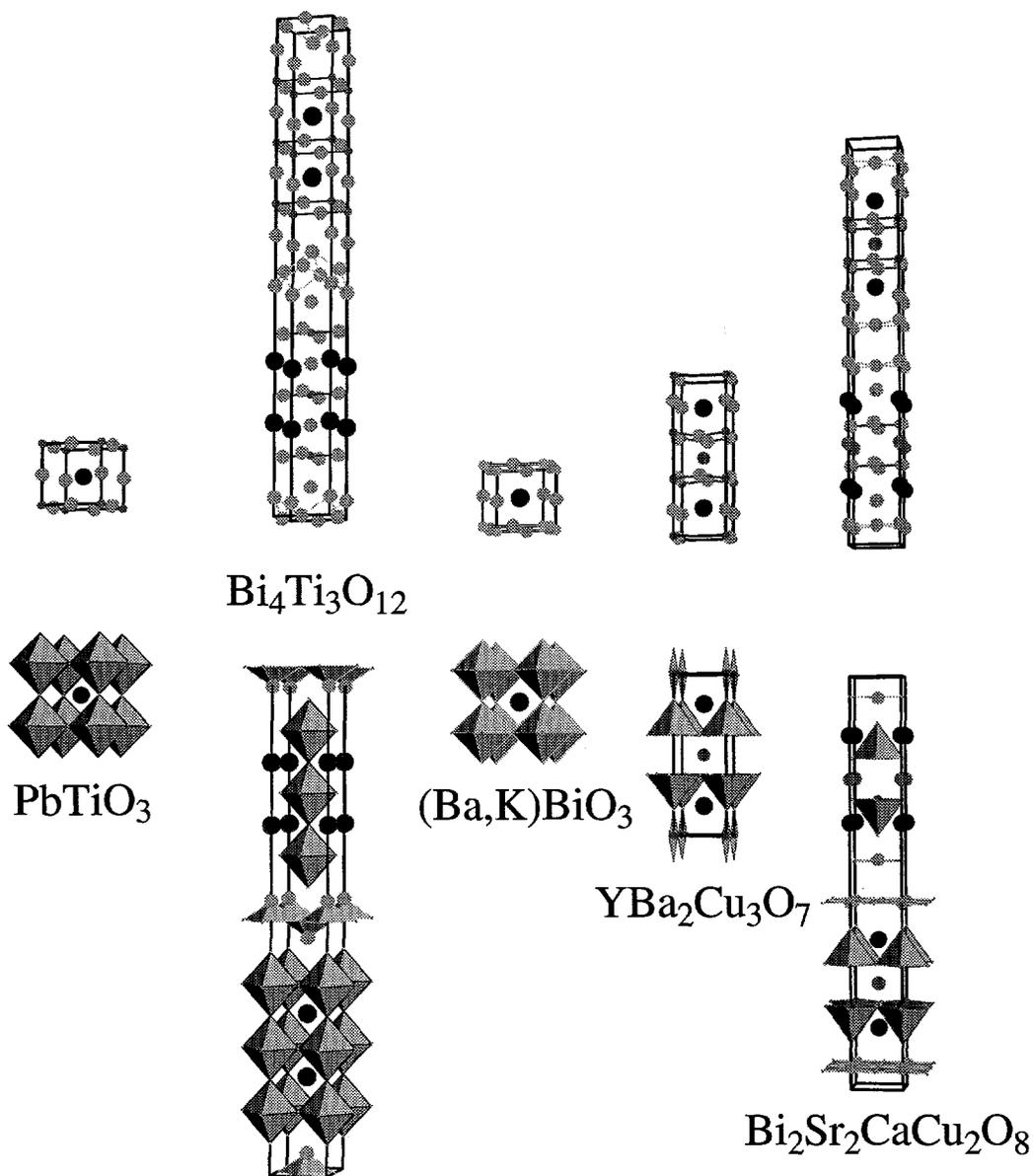


Fig. 1. The crystal structure of some perovskite-related structures exhibiting the properties described in Table I. Two equivalent representations of these crystal structures are shown: the atomic positions (above) and the coordination polyhedra (below). The oxygen atoms occupy the vertices of the coordination polyhedra. The tetragonal subcells of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ structures are shown for clarity and to illustrate the similarities between these perovskite-related phases. The relative sizes of the atoms reflect their relative ionic radii as given by Ref. 1.

Table I: Examples of the properties of compatible (perovskite) oxides.

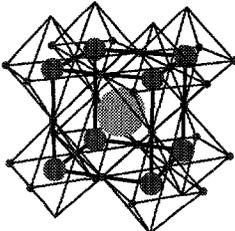
Property	Value	Oxide Material
High ϵ_r Insulators	$\rho \approx 1 \times 10^{11} \Omega\cdot\text{m}$ $\epsilon_r = 20000$ (4 K)	SrTiO ₃
Low ϵ_r Insulators	$\epsilon_r = 16$ (77 K)	LaAlO ₃
Conductors	$\rho \approx 1 \times 10^{-7} \Omega\cdot\text{m}$ (77 K)	Sr ₂ RuO ₄
Superconductors	$\rho \approx 0$	YBa ₂ Cu ₃ O _{7-δ}
Ferroelectrics	$P_r = 0.75 \text{ C/m}^2$	PbTiO ₃
Pyroelectrics	$p_3 = 500 \frac{\mu\text{C}}{\text{m}^2 \text{ K}}$	(Ba,Sr)TiO ₃
Piezoelectrics	$d_{15} = 600 \text{ pC/N}$	BaTiO ₃
Ferromagnets	$M_s = 1.4 \mu_B$	SrRuO ₃
Colossal Magnetoresistance	$\Delta R/R_H > 10^4$ (6 T)	(La,Sr)MnO ₃

epitaxial stacks of these oxide crystals is motivated by the similarity in crystal structure (the perovskite oxides listed in Table I all have perovskite subcell dimensions in the 3.8 Å to 4.0 Å range), the chemical compatibility that exists between many oxides, and the enhanced properties that these materials exhibit in single crystal form. The increase in performance can be by many orders of magnitude for the critical current density (J_c) of a superconductor or the magnetoresistance effect. In addition to synthesizing oxide heterostructures that integrate relatively thick layers of different oxides together, in principle, new oxides can be engineered if structural control can be achieved at the atomic-layer level. Although now commonplace in the growth of semiconductors (i.e., by MBE), such an ability would be new to oxides and would likely result in the discovery/engineering of higher performance materials and possibly the exploitation of new electrical phenomena. Numerous attempts by conventional solid-state techniques to synthesize oxide structures believed to be of significant scientific and technological importance have failed.

Just as MBE made possible the bandgap engineering of semiconductor heterostructures, reactive MBE shows great promise for the growth of oxide heterostructures with control down to the atomic layer level, i.e., atomic layer engineering of oxides.² Using MBE to integrate perovskite heterostructures and even to engineer new perovskites with nanometer control is particularly attractive. The perovskite structure can accommodate the majority of the periodic table, as shown in Fig. 2. Such a malleable structural host offers an opportunity to customize electronic, magnetic, and optical properties in thin films far beyond that possible with conventional semiconductors.

Structure-property relations have been studied for a great many oxides using solid-state synthesis methods. Many cases have been found where the property of a structurally-related family of oxides (i.e., a homologous series) changes drastically from one end to the other of the series. Examples include the

ABX_3



IA	H	IIA	Li	Be	IIIB	IVB	VB	VIB	VIIB	VIII	IX	X	XI	XII	IIIA	IVA	VA	VIA	VIIA	Noble	He
	Na	Mg	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	Xe
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	Kr	Xe	Rn
	Cs	Ba	†	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	Kr	Xe	Rn
	Fr	Ra	‡	Rf	Ha	Sg	Ns	Hs	Mt	Rn	Xe	Rn	Xe	Rn	Xe	Rn	Xe	Rn	Xe	Rn	Xe

†	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
‡	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Fig. 2. A compilation of which elements of the periodic table can occupy the three sites (A, B, and X) of the perovskite crystal structure (based on the data in Ref. 3).

$Sr_{n+1}Ru_nO_{3n+1}$ Ruddlesden-Popper homologous series shown in Fig. 3. The $n = 1$ (Sr_2RuO_4) member of the series is paramagnetic and superconducting whereas the $n = \infty$ ($SrRuO_3$) member of the series is ferromagnetic. Many other equally fascinating homologous series exist in perovskite-related oxide structures showing interesting variation in ferromagnetic, ferroelectric, superconducting, or metal-insulator behavior. However, when the goal is to study the property variation with changing n in detail, solid-state synthesis methods fall short. Invariably researchers have only been able to find conditions of temperature and pressure yielding single-phase products for low values of n and for $n = \infty$. Attempts to make intermediate n values result in uncontrolled intergrowths.⁴¹¹ Calculation of the energy of formation of several homologous series of layered oxide phases indicates the reason for this difficulty—differences in formation energy become smaller and smaller as more building layers are inserted into the parent structure

(i.e., with increasing n).^{*,12} Thus, apart from theoretical calculations, little is known about how the properties of a series of structures vary with n as the dimensionality of the structure changes. A key advantage of the use of MBE for the preparation of oxide heterostructures is that single-phase epitaxial films with intermediate n values can often be synthesized even though nearby phases have similar formation energies.² This is made possible by the ability to supply incident species in any desired sequence with submonolayer composition control. A particular phase can often be grown by supplying the constituents in an ordered sequence corresponding to the atomic arrangement of these constituents in the desired phase.

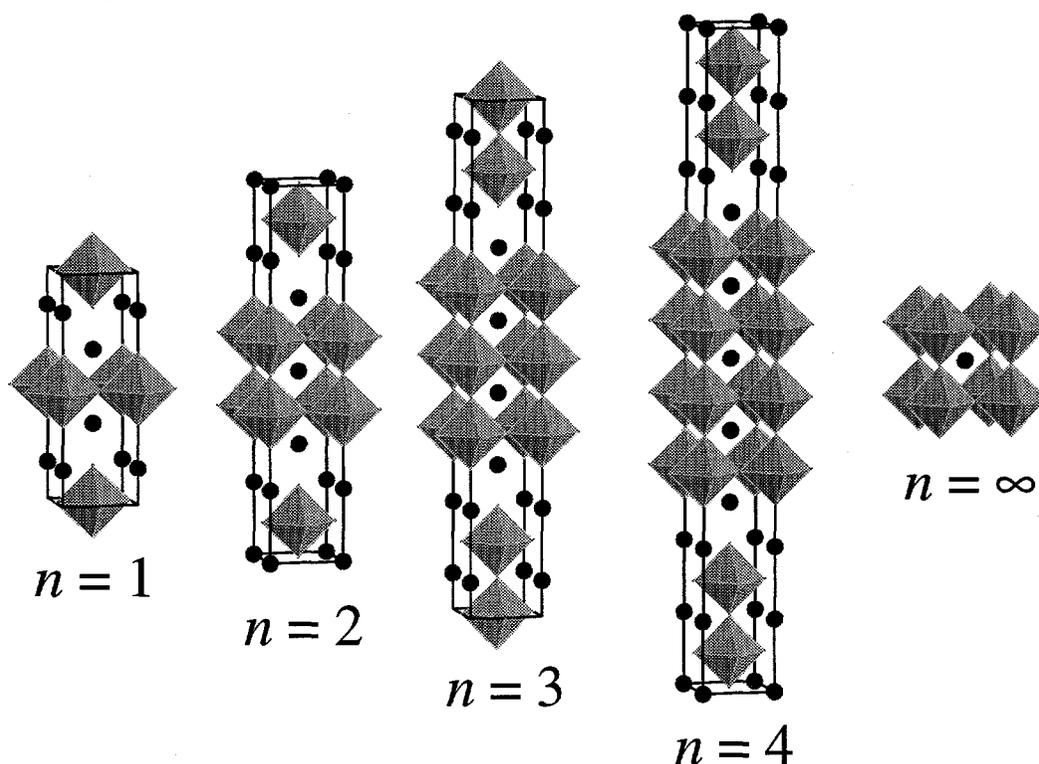


Fig. 3. $n = 1$ (Sr_2RuO_4), $n = 2$ ($\text{Sr}_3\text{Ru}_2\text{O}_7$), $n = 3$ ($\text{Sr}_4\text{Ru}_3\text{O}_{10}$), $n = 4$ ($\text{Sr}_5\text{Ru}_4\text{O}_{13}$), and $n = \infty$ (SrRuO_3) members of the homologous Ruddlesden-Popper series of compounds $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$.

* For example, in the $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ homologous series of compounds (another perovskite-related series of compounds), calculations indicate that the formation enthalpy remains essentially constant for $n > 2$.¹² Since there is insufficient enthalpic driving force for forming a low entropy phase-pure compound, disordered intergrowths are to be expected in the synthesis of these compounds by bulk methods. Indeed, TEM images of these $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ phases⁵ show disordered syntactic intergrowths where n ranges from 2 to 8, as would be expected for the bulk preparation of essentially energetically degenerate phases.

MBE even allows metastable phases to be formed by utilizing interfacial strain energies to favor the desired metastable phase over the equilibrium phase (epitaxial stabilization).¹³ In contrast to bulk synthesis, in epitaxial growth, interfacial energies play a significant role. Specifically, strain energies due to interfacial mismatch are often sufficient to shift the energetics of which phase is most stable. In cases where the equilibrium structure has significantly different lattice spacing than a desired metastable structure, the formation of the metastable structure may be made favorable by selecting a substrate that is lattice matched to it rather than to the equilibrium structure. Numerous examples of epitaxially-stabilized phases exist in semiconductor, metal, and alkali halide systems.¹³⁻¹⁵ Many of these examples have been grown by MBE.

Below the road to the controlled synthesis of oxide heterostructures is first described, followed by examples indicating the promise and current capabilities of reactive MBE. The low growth temperature and atomic layering capability of MBE, widely utilized for the growth of metastable layered semiconductor superlattices, have enabled the *controlled* customized layering of high T_c phases whose phase-pure growth is unattainable by bulk synthesis methods.² These results demonstrate the capability of MBE to grow customized layered structures and metastable phases within *oxide* systems.

MBE GROWTH APPARATUS

MBE machines for the growth of semiconductors (e.g., IV-IV, III-V, and II-VI materials systems) are present in many laboratories and the technique has enjoyed significant success in the preparation of semiconductor microstructures with nanoscale thickness control and exceptional device characteristics. The use of MBE for the controlled growth of multi-component oxides is relatively new.²

A schematic diagram of the growth chamber of the MBE machine¹⁶ used by the authors is shown in Fig. 4. Eight independent shutters, controlled by a computer, supply elemental fluxes to the substrate either at the same time (codeposition) or separately (sequential deposition), as described below. Purified ozone is used to provide sufficient oxidation, while maintaining the long mean free path necessary for MBE.² A titanium sublimation pump, powered by a precision current supply, is used as a stable (flux variation of less than 1% per hour)¹⁷ and economical titanium source.

The lack of adequate composition control has been a major problem for previous oxide MBE work.² The use of atomic absorption spectroscopy (AA) for oxide MBE composition control has allowed flux stability of better than 1% to be achieved.¹⁸ The MBE system also contains a retractable quartz crystal microbalance to provide an absolute *in situ* flux measurement at the position of the wafer (prior to growth) for calibration of the AA signals. The depositing fluxes of *all* the sources (up to eight different elements simultaneously) are monitored during growth by AA.¹⁹ The measured AA signal is fed into the MBE computer control system, which integrates the AA fluxes and closes the appropriate shutters after the desired dose has been delivered to the substrate.²⁰ In addition, the system also contains the standard features found in MBE systems: *in situ* reflection high energy electron diffraction (RHEED), a mass spectrometer, computer-controlled shutters and furnaces for eight elemental sources, and a load-locked wafer introduction chamber.

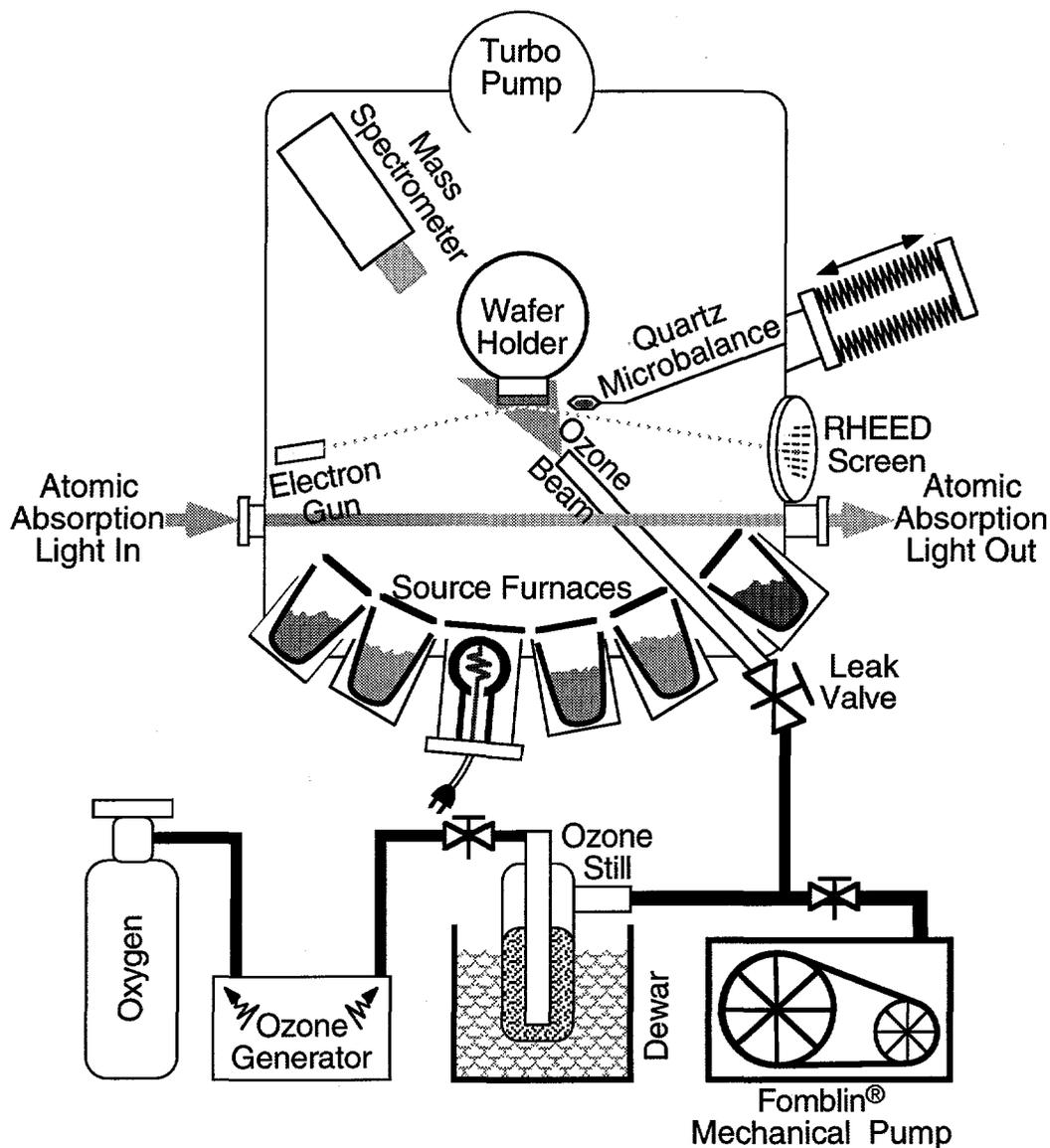


Fig. 4: A schematic diagram of the growth chamber of an MBE system dedicated to the controlled synthesis of oxide heterostructures.

The MBE method of thin film growth may be thought of as atomic spray painting, as shown in Fig. 5 in which an oxide heterostructure consisting of the superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ is schematically assembled layer-by-layer. The flux of spray from each atomic or molecular beam is controlled by the temperature (and thus vapor pressure) of the effusion cell in which each species is contained. The duration of spray is individually controlled for each beam by shutters, which control not only the open time (and thus dose), but also the sequence in which species reach the growth surface. By controlling the shutters

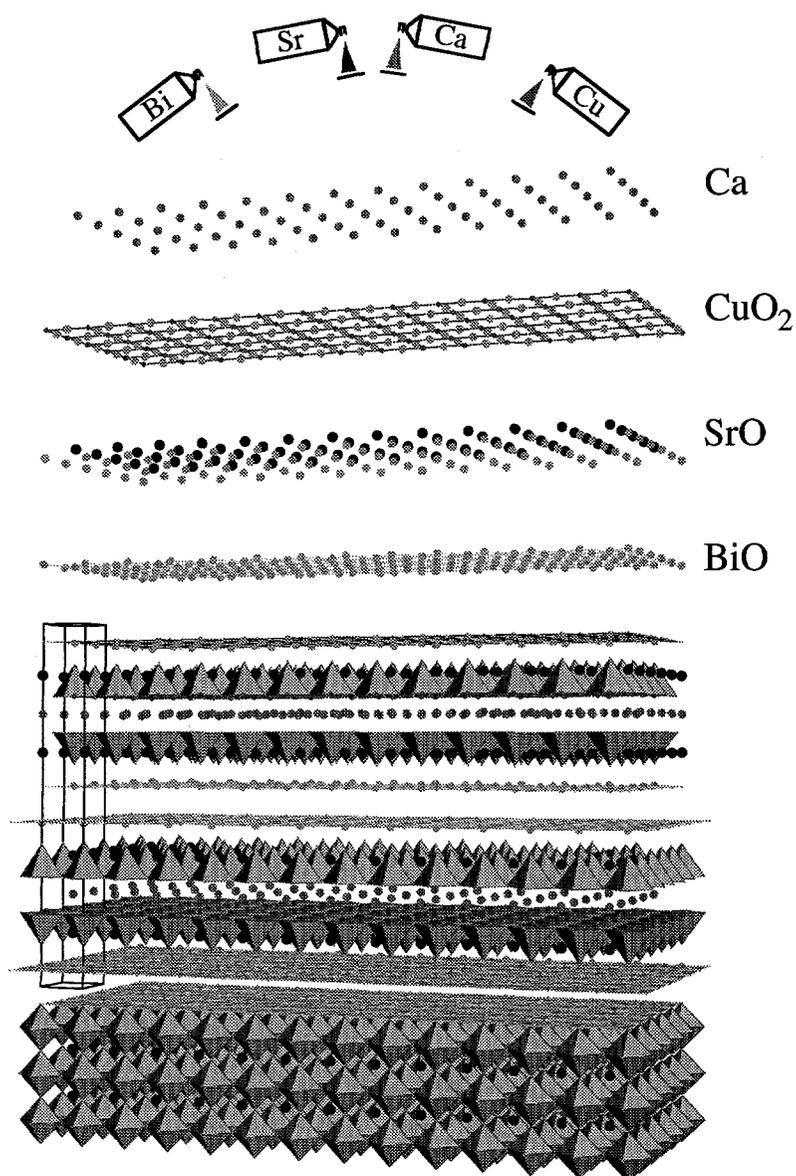


Fig. 5. A highly schematic representation of the MBE growth of a $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ film on a SrTiO_3 substrate by reactive MBE.

and temperature of the evaporant (which control dose and flux, respectively) the layering sequence of the desired structure can be customized. This technique has been used to control the layering of oxides on a unit cell level, allowing the preparation of single phase films of nearly energetically degenerate compounds, including cuprate superconductors.^{2, 21-25} A low growth temperature is frequently used to kinetically minimize subsequent bulk reordering and minimize the loss of the customized (and metastable) layered structures. A unique advantage of MBE

is *in situ* characterization of the growing surface using RHEED, which allows the process to be closely monitored. The sensitivity of this grazing angle diffraction technique to surface structure is ideal for monitoring the evolution of growth from initial nucleation to the deposition of each subsequent layer. The formation of intermediate reaction products or impurity phases can be readily monitored and the growth conditions adjusted *during growth* accordingly. Epitaxial growth, a clean UHV deposition environment, *in situ* RHEED characterization during growth, AA composition control, and the notable absence of highly energetic species are distinct advantages of this MBE approach. These capabilities are key to the customized growth of metastable oxides.

EXAMPLES OF MBE-GROWN OXIDE HETEROSTRUCTURES

To date oxide MBE has been most widely applied to the growth of high T_c superconductors. For such oxide heterostructures, MBE has been extremely successful and demonstrated atomic-scale layering control that parallels its achievements for semiconductor growth. Several notable examples are: (1) the use of MBE to prepare single phase $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ films, for $n = 1$ to 11,^{22,26,27} demonstrating the ability of this technique to select between nearly energetically-degenerate phases; (2) the synthesis of metastable superlattices, e.g., $[\text{Bi}_2\text{Sr}_2\text{CuO}_6 / \text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}]_n$,²¹ and metastable phases, e.g., $\text{Bi}_2\text{Sr}_2\text{SrCu}_2\text{O}_8$,²¹ and (3) the synthesis of superconductor-insulator-superconductor (SIS) Josephson junctions by atomic-layer engineering of the barrier layer between two superconducting layers.²⁸

Although first used for the growth of LiNbO_3 over ten years ago,^{29,30} the use of reactive MBE to grow oxide ferroelectric heterostructures has recently intensified.^{31,32} Here we describe the growth of PbTiO_3 and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ by MBE. A more detailed description is given elsewhere.³³

PbTiO_3 has the largest remanent polarization ($75 \mu\text{C}/\text{cm}^2$) of any known ferroelectric.^{34,35} $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has lower remanent polarization ($\sim 50 \mu\text{C}/\text{cm}^2$ of which the component along the c -axis is $\sim 4 \mu\text{C}/\text{cm}^2$),³⁶ but can withstand far more polarization reversals before it fatigues.³⁷ PbTiO_3 and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ are both members of the $(\text{Bi,Pb})_{n+1}\text{Ti}_n\text{O}_{3n+3}$ Aurivillius homologous series^{38,42} shown in Fig. 6. PbTiO_3 is the $n = \infty$ member of this series and contains a network of TiO_6 octahedra connected in three dimensions. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ lies at the other end of this homologous series, $n = 3$, and is highly layered with a two-dimensionally connected network of TiO_6 octahedra. Its structure consists of Bi_2O_2 layers separated by $\text{Bi}_2\text{Ti}_3\text{O}_{10}$ perovskite sheets. The resistance to fatigue of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and other Aurivillius phases make these materials of interest for use in non-volatile ferroelectric random access memories (FRAMs).⁴³ On the other hand, the high P_r of PbTiO_3 makes it of interest for superconducting field-effect transistors (SuFETs).⁴⁴ We are interested in the variation of properties that occur in the $(\text{Bi,Pb})_{n+1}\text{Ti}_n\text{O}_{3n+3}$ homologous series and describe below the preparation of the two end members of this series by adsorption-controlled MBE.

PbTiO_3 and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ are both grown under conditions where the titanium flux determines the growth rate, and ozone, lead, and bismuth are supplied in excess (2-100 times greater than the titanium flux). The excess ozone, lead, and

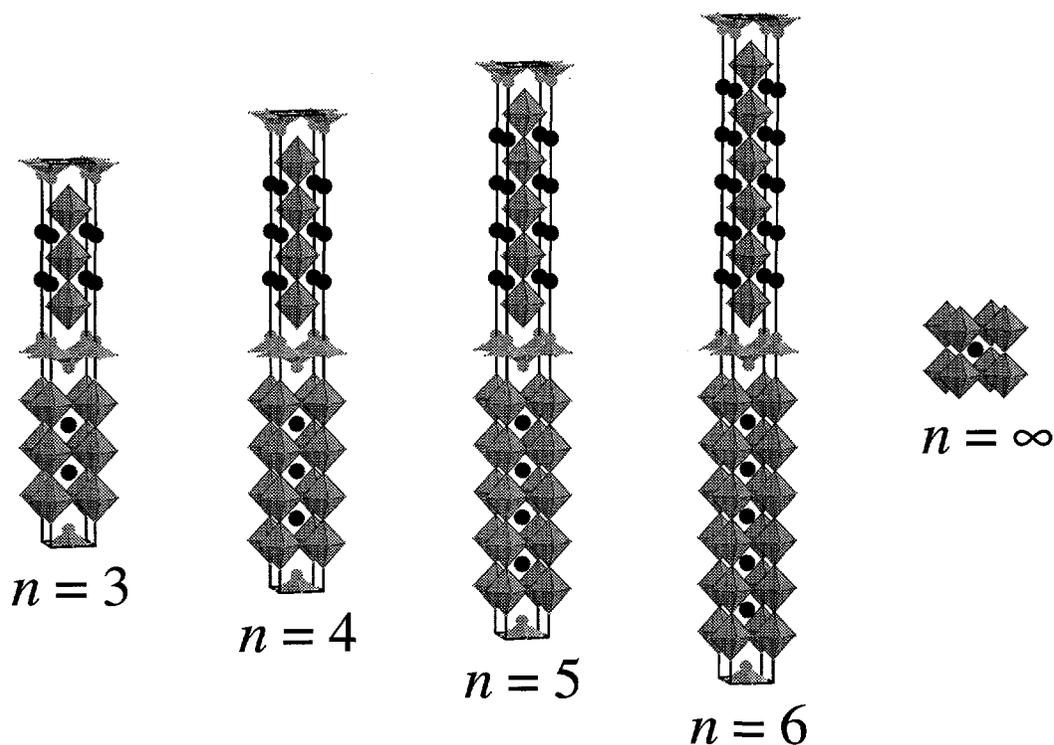


Fig. 6. The Aurivillius phases: $n = 3$ $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $n = 4$ $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$, $n = 5$ $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, $n = 6$ $\text{Pb}_3\text{Bi}_4\text{Ti}_6\text{O}_{21}$, and $n = \infty$ PbTiO_3 .

bismuth desorb leading to the growth of PbTiO_3 and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films that are stoichiometric within the measurement error of Rutherford backscattering spectrometry (RBS). A similar adsorption-controlled mechanism was shown to be operative by de Keijser and Dormans⁴⁵ for organometallic chemical vapor deposited $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ thin films. The growth of PbTiO_3 and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ by reactive MBE is thus quite similar to the MBE growth of III-V semiconductors where the group V species is supplied in overabundance and the group III species determines the growth rate.

Four-circle x-ray diffraction scans indicate that these ferroelectric films are epitaxial and have bulk lattice constants. In Fig. 7 the θ - 2θ and ϕ -scans of a 1000 Å thick film of PbTiO_3 grown on (100) SrTiO_3 are shown. Intense $00l$ peaks indicate that the c -axis of the film is oriented perpendicular to the substrate (c -axis oriented); additional scans showed no evidence of a -axis oriented domains. The ϕ -scan demonstrates that the film is also oriented in the plane of the substrate, with a cube-on-cube epitaxial orientation relationship. The widths of the x-ray diffraction peaks are all approaching the instrumental resolution of our diffractometer.

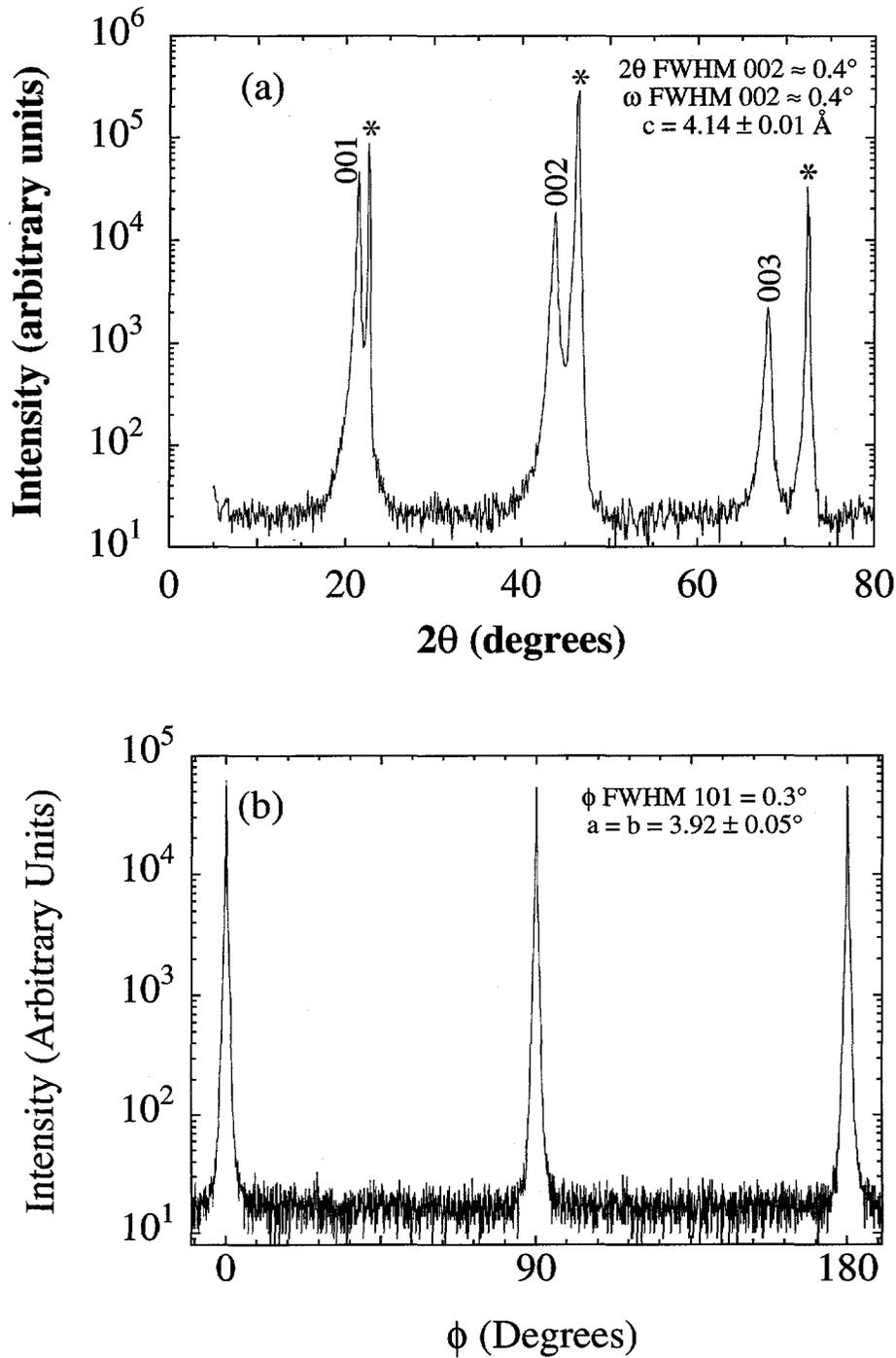


Fig. 7. (a) θ - 2θ scan and (b) ϕ -scan of 101 reflections of a 1000 \AA thick PbTiO_3 film grown on a (100) SrTiO_3 substrate (* indicates substrate reflections).

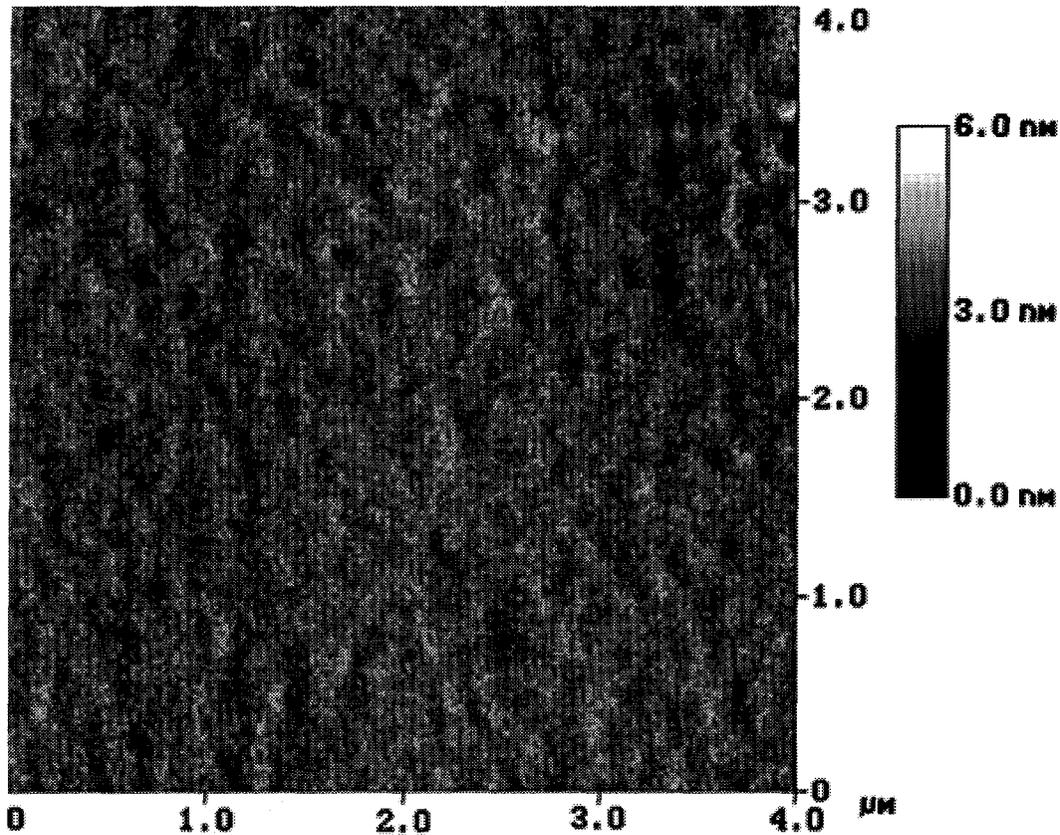


Fig. 8. AFM image of the surface of a 1000 Å thick PbTiO_3 film grown on (100) SrTiO_3 .

Atomic force microscopy (AFM) images of the surface of this same PbTiO_3 film, Fig. 8, show extremely smooth morphologies with a root mean square (RMS) roughness of $< 5 \text{ \AA}$. This surface structure is indicative of a layer-by-layer growth mechanism.

The θ - 2θ and ϕ -scans of a 1000 Å thick film of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ grown on (100) SrTiO_3 are shown in Fig. 9. The intense 00ℓ peaks indicate that the film is entirely c -axis oriented. The ϕ -scan demonstrates that the film is also oriented in the plane of the substrate, with a $\text{Bi}_4\text{Ti}_3\text{O}_{12} [110] \parallel \text{SrTiO}_3 [010]$ orientation relationship. Again the peak widths are all comparable to the instrument resolution of our Picker 4-circle diffractometer. RBS channeling results for this film showed a minimum channeling yield (χ_{\min}) of 0.2, which is the lowest reported value for epitaxial $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

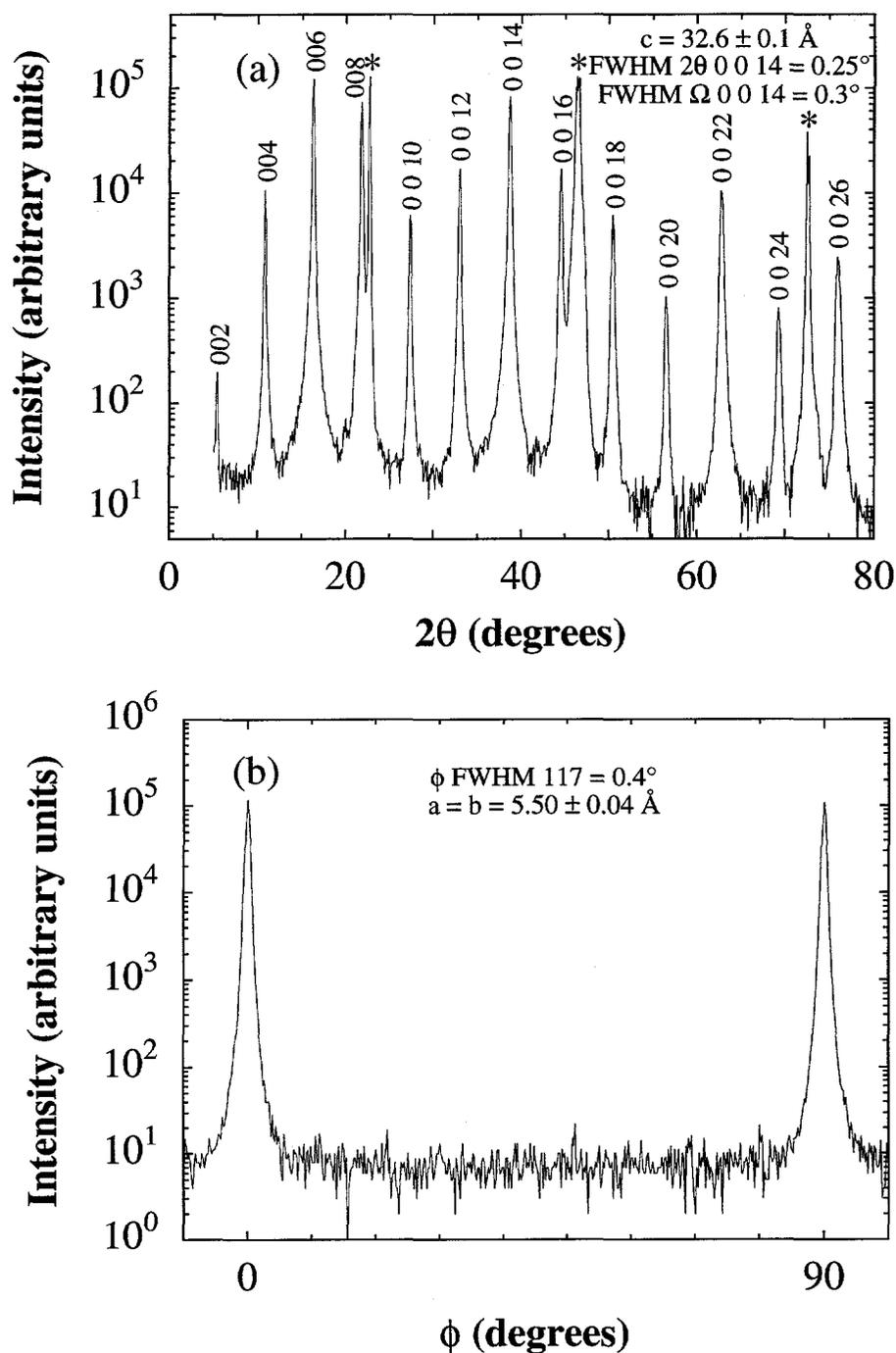


Fig. 9. (a) θ - 2θ scan and (b) ϕ -scan of 117 reflections of a 1000 \AA thick $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ film grown on a (100) SrTiO_3 substrate (* indicates substrate reflections).

In Fig. 10 an AFM image of the surface of this same $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ film is shown. Clearly visible on the surface are micron-sized islands that protrude $\sim 100 - 200 \text{ \AA}$ above the film surface. The terraces making up these islands have step heights that are integral multiples of a half unit cell.* This surface morphology is reminiscent of that of layered perovskite superconductor films,^{46,47} although it is unclear if oppositely-signed screw dislocations are present within each mound or if the mounds are free of screw dislocations and arise due to limited surface diffusion.

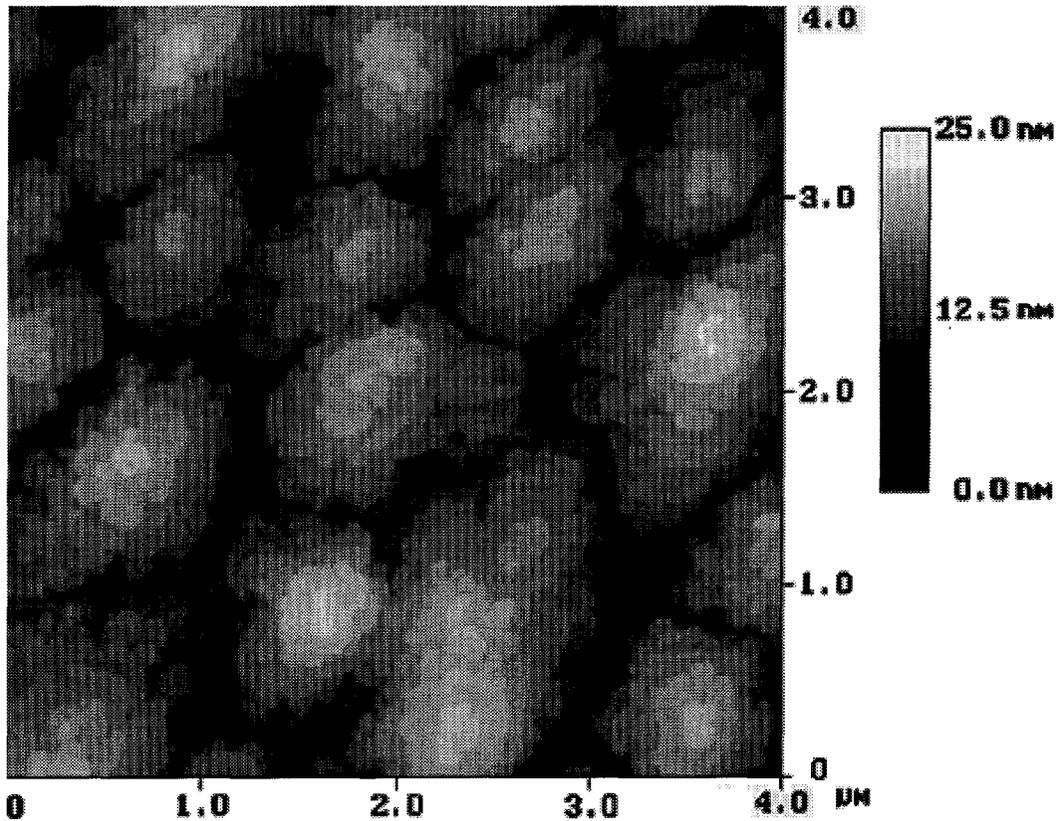


Fig. 10. AFM image of the surface of a 1000 \AA thick $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ film grown on $(100) \text{ SrTiO}_3$.

CHALLENGES

There are three major challenges that must be overcome before reactive MBE is a useful technique for the growth of oxide heterostructures: (1) achieving sufficient oxidation of the growing film without compromising the long mean free path necessary for MBE, (2) achieving accurate composition control during

* A $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ formula unit is contained within each half unit cell as can be seen from Fig. 6.

growth, and (3) maintaining flat surfaces during growth. The pressure of oxidant needed to achieve sufficient oxidation depends on the phase being grown as well as the oxidant and growth temperature used. If the oxidant is restricted to molecular oxygen, the growth of most oxide superconductors would not be possible by MBE. The use of more reactive oxidants, e.g., ozone, NO₂, or the reactive species in an oxygen plasma, have been key to the realization of oxide superconductor films by MBE.² Composition control is also crucial; the inherent flexibility of the MBE technique is only advantageous when it is accompanied by adequate composition control. Without it, the user will be unable to control the formation of the desired custom-made structures and controllably dope them. For the growth of heterostructures containing oxide superconductors, composition control at or better than about ± 1 atomic percent is necessary to produce films with good transport properties.^{48,49} Controlling each monolayer with 1% accuracy requires a resolution in whatever composition monitoring method is used of about 7×10^{12} atoms or about one nanogram for a typical perovskite (e.g., those oxides in Table I). For many elements AA has such sensitivity and has thus become the composition control method of choice for many oxide MBE groups. Finally, even if the growth environment provides sufficient oxidation and sufficient composition control, it is almost always desired to have flat interfaces in oxide heterostructures. To this end it is clearly important to begin with a flat and relatively defect-free substrate. Oxide substrate preparation for MBE growth is an important area of research.^{50,51} *In situ* monitoring techniques like RHEED and spectroscopic ellipsometry can be quite helpful in monitoring surface roughness *in situ* and optimizing growth conditions so that flat surfaces are maintained during growth.⁵²

Once these three major challenges are met, MBE offers an incredibly flexible growth environment with independent control of a large parameter space. For example, the deposition rate of each constituent, the order in which the constituent fluxes (including the oxidant) are sequentially or simultaneously supplied to the growth surface, the duration of dosing, the introduction of periodic growth interruptions, and the substrate temperature are all independently controllable in the MBE process. A timing diagram of a few significantly different ways in which YBa₂Cu₃O_{7- δ} films could be deposited is shown in Fig. 11. However, this tremendous inherent flexibility of the MBE technique brings up a crucial challenge. *What is the best way of navigating this large parameter space to achieve the desired oxide heterostructure?* The improvements that oxide MBE can offer in our ability to customize the structure of oxides on an atomic-level challenges would be greatly enhanced if we had a better microscopic understanding of how oxides grow, e.g., what the diffusing species are and their rates as a function of oxidant pressure and temperature, how nucleation occurs on different substrates, which layer bonds to the substrate, which layer terminates the growing surface, surface reconstructions, the influence of vicinal substrates on growth, etc. With such knowledge, reactive MBE could be used to intelligently navigate this large parameter space to produce the desired phase or heterostructure in short order.

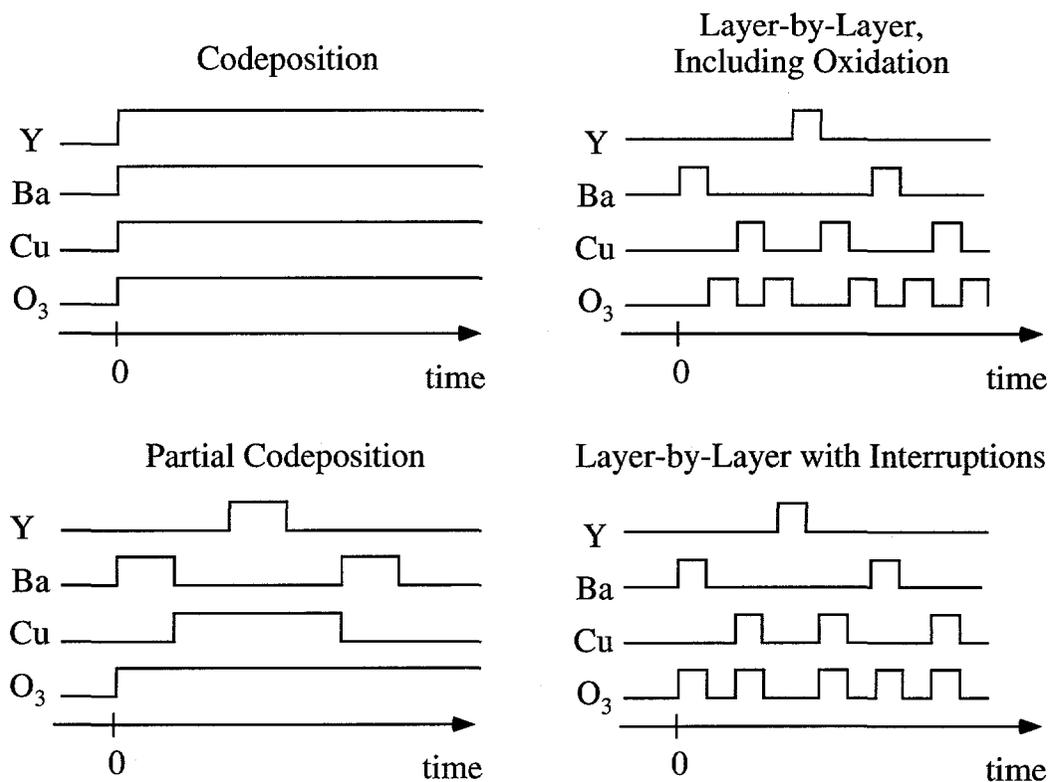


Fig. 11. A few examples of shutter timing diagrams for the growth of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ by MBE.

CONCLUSIONS

The use of reactive MBE for the growth of oxide heterostructures is still in its infancy and many hurdles, in particular accurate composition control, remain to be overcome for this technique to develop greater structural and doping control at the atomic layer level, as well as reproducibility. Nonetheless, reactive MBE has become established as the premiere synthesis technique for epitaxial oxide heterostructures when customized layering control is needed. As the complexity and metastability of desired oxide heterostructures increases, the requirement for a controlled synthesis environment capable of atomic layer engineering of new materials and device heterostructures will become all the more important. MBE appears to be the most likely technique to meet this challenge.

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