Compositionally Asymmetric Tri-Color Superlattices Grown by High-Pressure Pulsed Laser Deposition

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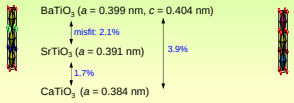
The Emergence of Nanoscale Cooperative Phenomena (ERKCS49)

Motivation

- Synthesis of new functional materials that do not exist in nature.
- Discovery of new physical phenomena at the nanoscale in complex materials.
- Artificially layered heterostructures: Ideal materials for exploring the unprecedented nature of man-made materials.
- Utilizing the freedom of materials design for manipulating the resulting properties.

Compositionally-broken inversion symmetry : Tri-color superlattice (TCS)

A-site modulation | B-site modulation

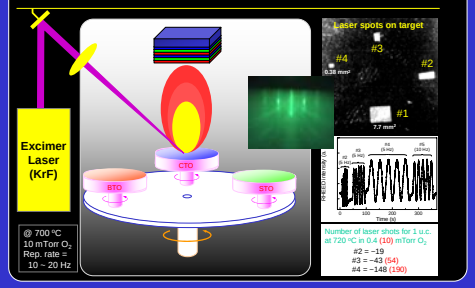


- Modulation of composition on the near-*atomic scale*.
- Control of *elastic and electrostatic interactions* via *ionic size and valence* (Sai *et al*., PRL **84**, 5636 (2000)).
- Design a locally asymmetric thermodynamic potential
- Anomalous FE properties (strong self-poling, enhanced piezoelectricity, etc.)

Keys to success

- Near-lattice-matched layers
- Thermodynamically stable electrode layers
- Atomically flat substrate surface (single-stepped)
- Controlled growth of single unit-cell units – flat surfaces and abrupt interfaces

Multi-target PLD for growing oxide heterostructures



Summary

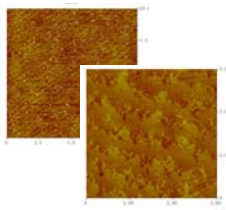
- Atomically flat single-stepped $SrTiO_3$ substrates have been successfully prepared by a chemical treatment followed by a thermal annealing at 1100~1200 °C.
- Thermodynamically and chemically stable, single-stepped conducting $SrRuO_3$ layers with an atomically flat interface with the $SrTiO_3$ substrates were grown for electrical characterization.
- A-site isovalent artificial tri-color superlattices using $CaTiO_3$, $SrTiO_3$, and $BaTiO_3$ have been synthesized under precisely controlled growth conditions (especially at high oxygen pressure, 10 mTorr) on single-stepped $SrTiO_3$ substrates covered with $SrRuO_3$ bottom electrodes.
- RHEED, AFM, and XRD investigations reveal nearly perfect superlattices, even up to 1 μm in thickness.
- Artificial mutilayers give unprecedented freedom for materials design.
- Artificial mutilayers are attractive for developing new materials and exploring new physical phenomena.

Preparing atomically flat substrates

Single-stepped $SrTiO_3$

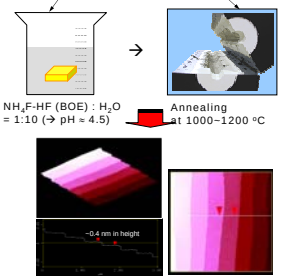
As-purchased $SrTiO_3$ substrates

- Rough surface.
- Chemically non-uniform (acidic TiO_2 and basic SrO coexist at the surface).



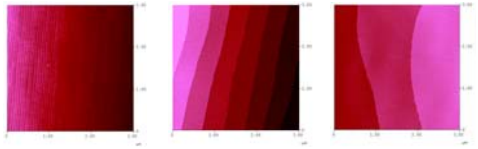
Approach:

dissolve SrO and recrystallize surface

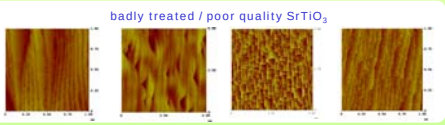


- Atomically flat terraces have been obtained with widths from 50 nm to 1 μm
- Parameters depend on substrate miscut angle

image size: 3 × 3 μm²



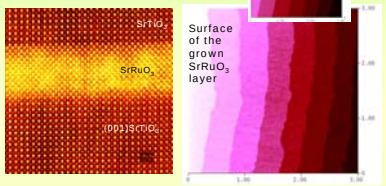
badly treated / poor quality $SrTiO_3$



Growth of particle-free, single-stepped conducting $SrRuO_3$ films

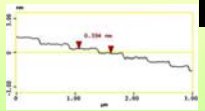
$SrRuO_3$ / $SrTiO_3$(001)

Surface of the $SrTiO_3$ (001) substrate→



LEED by S. Kalinin (CMSD, ORNL)

Importance: Grow high quality conducting films that serve as buffer layer for epitaxial growth and as bottom electrode for electrical characterization of subsequent oxide films.

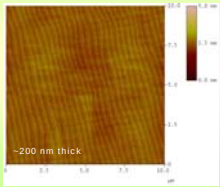


Our single-stepped $SrRuO_3$ electrode layer with a particle-free surface perfectly transfers the high crystallinity to the subsequent layer and remains stable even after air exposure (e.g., both *ex-situ* RHEED and LEED show no chemical contamination).

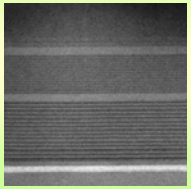
Nanoscale control of artificial heterostructures

Optimization

$[(BTO)_1/(STO)_1/(CTO)_1]_{165}$ on STO(001)

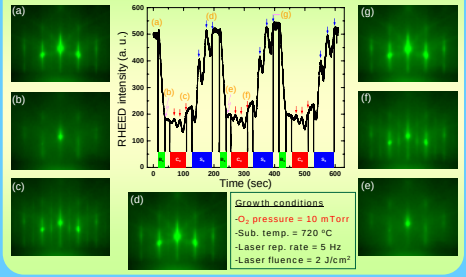


Z-STEM of $[(BTO)_1/(STO)_1/(CTO)_k]_n$



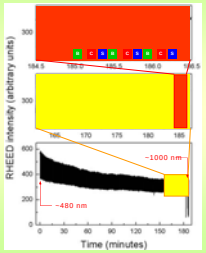
Controlled surfaces at each step:

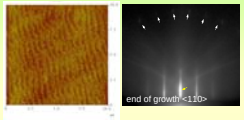
$(BTO)_1/(STO)_3/(CTO)_3$ on $SrRuO_3/SrTiO_3$(001)



The ultimate control:

thousands of layers, $(BTO)_1/(STO)_1/(CTO)_1$



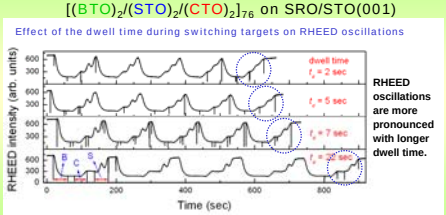


RHEED oscillations and AFM image demonstrating the ability to grow atomically-flat superlattices with complete reproducibility for thousands of unit cells. Pronounced RHEED oscillations and single-steps on the surface were clearly observed from a one-micron-thick TCS.

Different growth behavior of each layer:

$[(BTO)_2/(STO)_2/(CTO)_2]_{76}$ on SRO/STO(001)

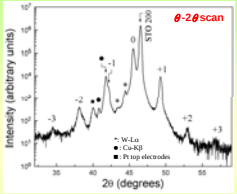
Effect of the dwell time during switching targets on RHEED oscillations



RHEED oscillations are more pronounced with longer dwell time.

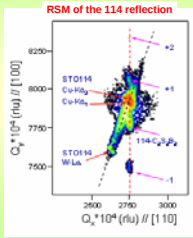
Fully strained superlattices

ex: $[(BTO)_2/(STO)_2/(CTO)_2]_{76}$/SRO/STO(001)

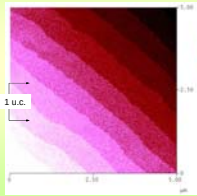


- (top) Diffraction peaks in an XRD θ-2θ scan confirm the quality and periodicity of a superlattice.
- (right) Reciprocal space map of the 114 reflection shows no evidence of relaxation of the film and reconfirms the superlattice peaks.

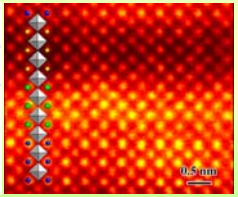
RSM of the 114 reflection



AFM topography with single steps from a ~180 nm-thick film.



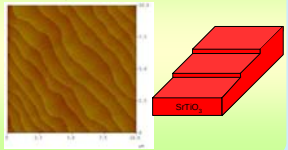
Cross sectional Z-STEM (B/C/S = 3/3/3)



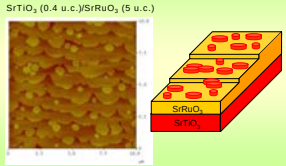
An example of materials-by-design:

Developing fractional-layer superlattices (FLS)

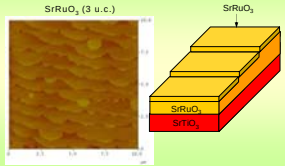
STEP 1: Prepare single-stepped substrate



STEP 2: Grow islands with 1 u.c. height by interrupting the *layer-by-layer growth*



STEP 3: Cover with 2D layers that have step-flow growth



- Precise control of the growth mode in perovskites enables us to form perovskite-type islands (unit-cell height, sub-micron diameter) onto a layer of a dissimilar material, and subsequently to embed these islands into an atomically flat matrix layer of the first or a third material
  - $SrTiO_3$ islands are formed by interrupting the growth before making a flat surface (step 2) during the layer-by-layer growth, and 2D layers of $SrRuO_3$ then cover the $SrTiO_3$ islands by the step-flow growth (step 3).
- The periodic stacking of such embedded-island layers (so called FLS) will allow us to investigate, manipulate, and utilize interlayer coupling effects in "designer materials".