Stability of single-stepped epitaxial $SrRuO_3$ films

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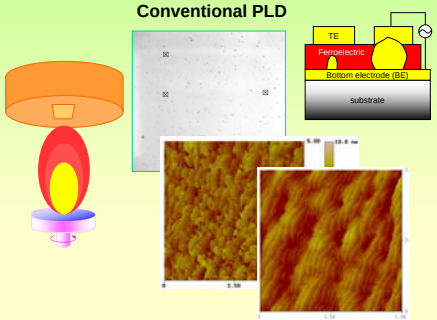
The Emergence of Nanoscale Cooperative Phenomena (ERKCS49)

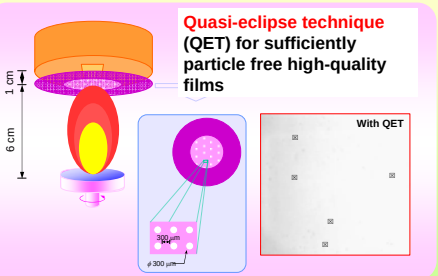
Motivation

- $SrRuO_3$ is a key component in oxide heterostructures and devices including ferroelectrics, ferromagnets, and superconductors.
- Integration with other perovskites requires thermodynamic and chemical stability in the growth environment.
- Growing particle-free oxide films is necessary to fabricate reliable capacitors and to avoid electrical breakdown.
- There have been no systematic studies on the stability of $SrRuO_3$ and its surface, although there is a high demand to apply it within oxide electronics.

Pulsed laser deposition (PLD)

Conventional PLD





Quasi-eclipse technique (QET) for sufficiently particle free high-quality films

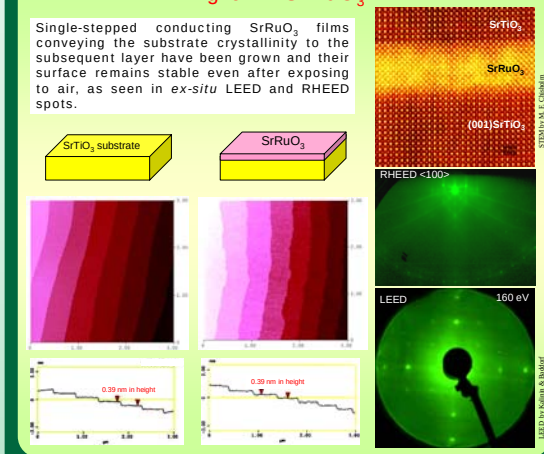
Summary

- Sufficiently particle free, single-stepped epitaxial $SrRuO_3$ films have been successfully grown by PLD with a novel quasi-eclipse technique.
- Decomposition of $SrRuO_3$ (yielding metallic Ru at the surface) is thermally activated with E_a = 63 kJ/mol.
- A stability region was identified for the growth of dielectric materials on top of these electrode layers.
- AFM, TEM, and x-ray diffraction investigations demonstrate the near-perfect transfer of crystalline structure from substrate to dielectric material through these $SrRuO_3$ films.

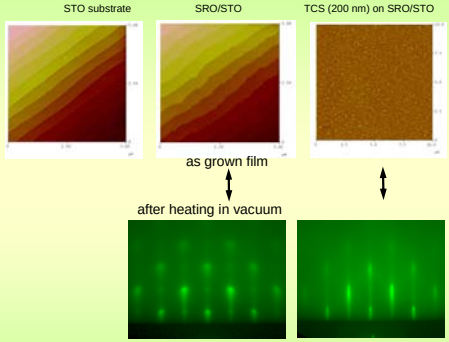
Single-stepped epitaxial $SrRuO_3$ films

A PLD-grown $SrRuO_3$ film

Single-stepped conducting $SrRuO_3$ films conveying the substrate crystallinity to the subsequent layer have been grown and their surface remains stable even after exposing to air, as seen in *ex-situ* LEED and RHEED spots.

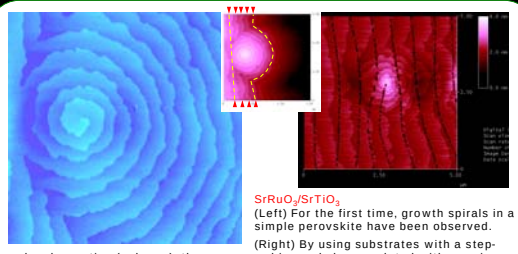


Why is the stability study required?

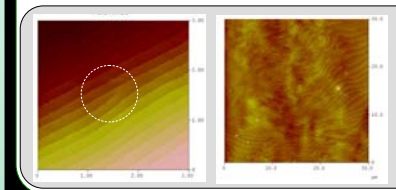


Under reducing conditions, heating $SrRuO_3$ films and growing subsequent layers on them results in the formation of islands on the surface and in poor quality of the subsequently grown films.

Growth spirals in a simple perovskite



$SrRuO_3/SrTiO_3$
(Left) For the first time, growth spirals in a simple perovskite have been observed.
(Right) By using substrates with a step-edge decoration (polymer), they can unambiguously be correlated with merging terraces in the substrate (bulk screw dislocations)

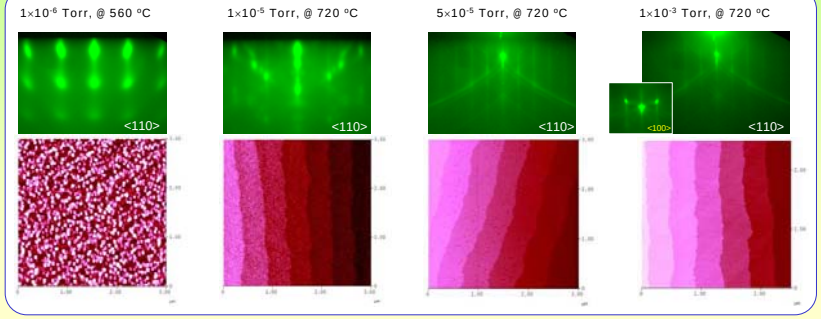


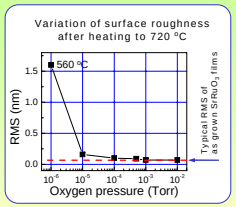
$SrTiO_3$
(Left)
A possible nucleation site for a growth spiral.

(Right)
Bulk defects on a $SrTiO_3$ crystal

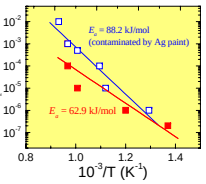
Stability of epitaxial $SrRuO_3$ films

Role of oxygen pressure

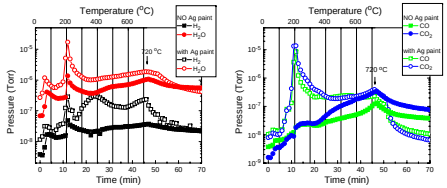




Thermally activated decomposition of $SrRuO_3$ under reducing conditions

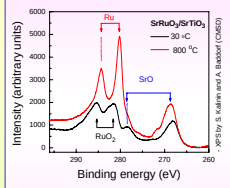


Surface contamination (by Ag paint)



- (Left) The decomposition temperature is determined from the change of RHEED specular spots.
- (Right) The use of Ag paint (for mounting the samples and ensuring good thermal contact) leads to contamination of the vacuum system (H_2, H_2O, CO_2/N_2O, CO, etc., as evidenced by residual gas analysis)
- The intentional introduction of H_2 into the chamber also leads to an accelerated decomposition of $SrRuO_3$ (not shown).

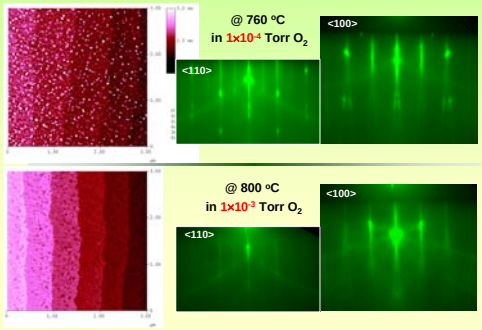
XPS $SrRuO_3/SrTiO_3$

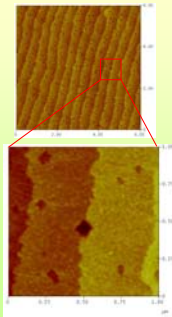


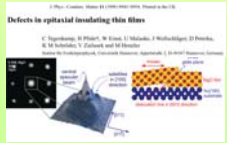
Metallic Ru is clearly observed in XPS data after heating the $SrRuO_3$ sample (500 nm in thickness) in vacuum (taken at RT after heating to 800 °C).

$$SrRuO_3 + 2H_2 \rightarrow Ru + SrO + 2H_2O$$

High temperature behavior: Mosaic grains





The surface of partially decomposed $SrRuO_3$ films exhibit distinct features that coincide with the irreversible appearance of RHEED-spot splitting along the <100> direction.

No splitting is observed along the <110> direction. This strong anisotropy is consistent with an interpretation of mosaic formation, similar to what is observed in MgO/Ag(100) (bottom).