In-plane orientation control of $SrTiO_3$(111) epitaxy on sapphire(0001)

I. Ohkubo, M. F. Chisholm, H. M. Christen

Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

J. R. Knab, A. Markelz, J. Cerne

Department of Physics, University at Buffalo, The State University of New York, Buffalo, NY 14260-1500

The Emergence of Nanoscale Cooperative Phenomena (ERKCS49)

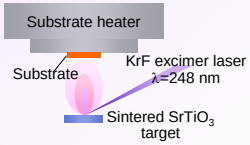
Research Motivation :

Transition metal oxides with perovskite structure attract much interest due to the richness of physical properties that are exhibited in these materials (high-Tc superconductivity, CMR, ferroelecticity, etc.).

IR spectroscopy is powerful tool to investigate the electronic structure of such materials. While $SrTiO_3$ is one of the best substrates for perovskite oxide thin film growth, its absorption in the far-IR region is too high for such measurements in transmission when used as a bulk substrate. However, here we show that (111)-oriented $SrTiO_3$ thin films can be fabricated on sapphire(0001) substrates and act as a template layer for other perovskite oxide thin film growth, especially hexagonal perovskite oxides (AMO_3 : A=Sr, Ba, M=3d and 4d transition metal) with quasi-one dimensional structure.

Experiments:

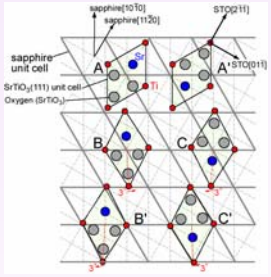
Thin film growth by pulsed laser deposition



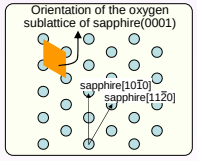
Growth conditions
- Substrate : sapphire(0001) [α-Al_2O_3]
- Target : sintered $SrTiO_3$
- Ablation laser : KrF excimer laser, λ=248 nm
- Laser repetition : 0.5 ~ 10Hz
- Laser fluence : 1 ~ 5 J/cm^2
- Growth temperature : 550 ~750°C
- Deposition rate : 0.01 ~ 0.05 nm/pulse
- Oxygen pressure : 10 ~ 80mTorr
- Background pressure : 1x10^{-8} Torr

In-plane epitaxial relationships between $SrTiO_3$ and the sapphire (0001) substrate :

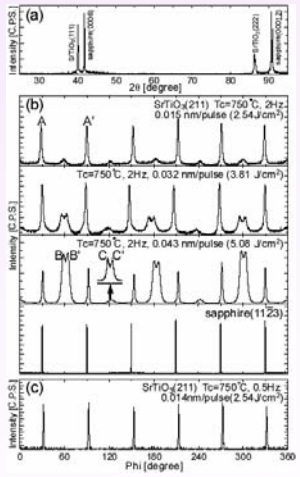
In the conceptually simplest epitaxial relationship (yielding a lattice mismatch of 0.4%), the close-packed oxygen sublattices in (0001)-oriented sapphire and the (111)-oriented $SrTiO_3$ have an identical in-plane orientation. For symmetry reasons, two equivalent orientations (A and A') occur (by rotation of 60º along the sapphire [10$\bar{1}$0] direction . However, XRD phi scan results show that $SrTiO_3$ <0$\bar{1}\bar{1}$> // sapphire <11$\bar{2}$0> relationships (B, B', C, C' domains) are also possible (~30º rotation of oxygen sublattice with respect to that of the sapphire(0001)).



Out of plane:
STO[111]//sapphire[0001]
In-plane:
STO[2$\bar{1}\bar{1}$]//sapphire[11$\bar{2}$0] - A
STO[2$\bar{1}$1]//sapphire[11$\bar{2}$0] - A
STO[011]//sapphire[11$\bar{2}$0] - B,B'
STO[01$\bar{1}$]//sapphire[11$\bar{2}$0] - C,C'

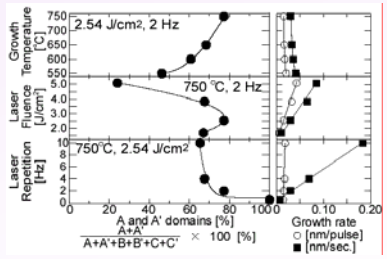


In-plane orientation control of $SrTiO_3$ layer on sapphire(0001) → obtain films containing only A, A'



The relative abundance of the different in-plane orientations depends strongly on the deposition parameters (substrate temperature, laser energy and repetition rate)

As determined from the intensities of the XRD phi-scan peaks, the A/A' domains increased in abundance with increasing substrate temperature.
Furthermore, their abundance also increased with decreasing growth rate.
These results indicate that the preferential growth of the 30º rotated domains (B, B', C, C') at low temperature is due to kinetic factors and that the A and A' in-plane oriented domains are thermodynamically more stable than the 30º rotated domains.

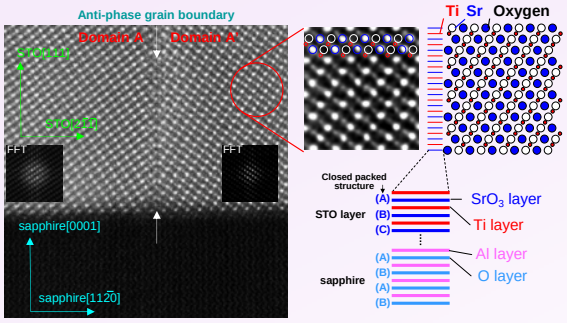


Two domains structures
STO[2$\bar{1}\bar{1}$]//sapphire[11$\bar{2}$0]
STO[2$\bar{1}$1]//sapphire[11$\bar{2}$0]

A and A' domains --- thermodynamically favorable orientations
B, B', C, C' domains --- kinetically favorable orientations

Z-contrast STEM images of two in-plane orientations $SrTiO_3$ layer on sapphire(0001) :

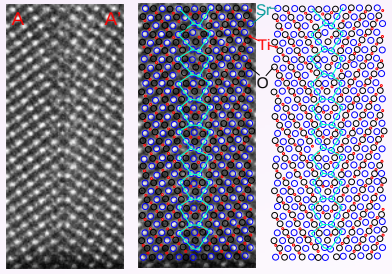
Atomic-resolution Z-contrast Scanning Transmission Electron Microscopy (Z-STEM) images provide the valuable information about the local crystalling structure of $SrTiO_3$. Anti-phase grain boundary between A and A' type domains were clearly observed.



With a lattice mismatch of less than 0.5%, the growth of (111)-oriented $SrTiO_3$ onto (0001)-oriented sapphire is expected to yield good crystallinity.
Note that the oxygen sublattice in $SrTiO_3$ has a fcc closed packed structure (ABCABC…) along the [111] direction, whereas that in sapphire exhibits a hcp closed packed structure (ABABAB…).

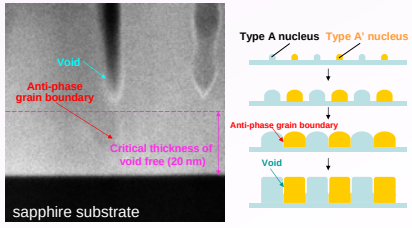
The interface structure between the (111)-oriented $SrTiO_3$ film and the sapphire (0001) substrate is currently being investigated.

Anti-phase grain boundary structure in two in-plane orientations $SrTiO_3$ layer :



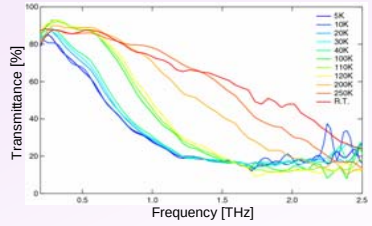
Z-STEM images provide information regarding the atomic structure of the A/A' interface (currently being analyzed in more detail).

Void formation mechanism in two in-plane orientations $SrTiO_3$ layer :



Two in-plane orientations $SrTiO_3$ thin films exhibit columnar growth and the formation of voids (see micrograph on left). The images appear to suggest a critical thickness of 20 nm before voids are formed. As template layer for other perovskite or related materials, a void-free $SrTiO_3$ film is required. Conditions under which the growth of such continuous films can be achieved are currently being investigated.

Far-IR transmittance of two in-plane orientations $SrTiO_3$ thin films:



Far-IR transmittance data (from time-domain measurements performed at SUNY-Buffalo) show that at the lowest energies (below 1 THz (30 cm^{-1}), i.e. in the range of a few meV), the samples are sufficiently transparent (even at a thickness of 120 nm) for use as buffer layers in samples to be analyzed by transmission IR spectroscopy.
Note that the observed temperature-dependence of the absorption is consistent with the well-known phonon softening in $SrTiO_3$.

Summary:

We have prepared (111)-oriented $SrTiO_3$ thin films on sapphire(0001) substrates under various growth conditions by pulsed laser deposition and identified the various types of in-plane orientation occurring in these films.
At high growth temperatures and low growth rates (near-equilibrium conditions), only two in-plane orientations (i.e. the minimum allowed by symmetry) are observed. The anti-phase grain boundaries between these two in-plane orientations were analyzed by Z-contrast STEM.
Time-domain far-IR spectroscopy was employed to determine these films' transparency to IR radiation in the sub-1THz region, demonstrating that such layers will be useful as buffers for film growth of samples to be studied by IR transmission spectroscopy.
The feasibility of void free films is currently being investigated.

Significance and impact :

This thin film growth investigation will contribute to IR optical spectroscopy of transition metal oxide having unusual physical properties (to investigate their electronic structure).
Furthermore, the detailed observation of the competition between the thermodynamically favored domain structure with that occurring at higher growth rates and/or lower substrate temperatures sheds light onto broader issues of complex heteroepitaxy.