Lecture #3—
NUTS AND BOLTS OF OXIDE MBE:
Composition Control and Calibration

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Nuts and Bolts of Oxide MBE

How to grow your favorite oxide by MBE?

• Lecture #2—*Growth Conditions, Sources, and Crucibles*

• Lecture #3—*Composition Control and Calibration*

• Lecture #4—*Epitaxy, Substrates, and Crystal Growth*
How to Calibrate Growth Rate

- Shadow Mask and Surface Profilometer
- Quartz Crystal Microbalance
- Ion Gauge
- RHEED Oscillations
- Shuttered RHEED Oscillations
- Rutherford Backscattering Spectrometry
- Mass Spectrometer
- Atomic Absorption Spectroscopy
- Atomic Emission Spectroscopy
- X-Ray Reflectivity, Ellipsometry, …
Composition Control

- Adsorption-Controlled Growth
- Flux-Controlled Growth
Adsorption-Controlled Growth of GaAs

Adsorption-Controlled Growth of PbTiO₃

C.D. Theis, J. Yeh, D.G. Schlom, M.E. Hawley, and G.W. Brown,
Adsorption-Controlled Growth of PbTiO$_3$

$T_{\text{sub}} = 630 \, ^\circ\text{C}$

$T_{\text{sub}} = 650 \, ^\circ\text{C}$

* = Substrate Peaks
Adsorption-Controlled Growth of

- **Plumbites**
  - PbZrO$_3$ — (unpublished)

- **Bismuthates**
  - Bi$_2$Sn$_2$O$_7$ and Bi$_2$Ru$_2$O$_7$ — (unpublished)

- **Ferrites**
Adsorption-Controlled Growth of

- **Ruthenates**
  - Ca$_2$RuO$_4$ — (unpublished)

- **Iridates**

- **Stannates**

- **Other**
Adsorption-Controlled Growth of

- **Titanates by MOMBE**

- **Vanadates by MOMBE**

- **Stannates by MOMBE**
Growth of Bi$_4$Ti$_3$O$_{12}$ by MBE

\[
\Phi_{\text{Bi}_x\text{O}_y(g)} \quad \Phi_{\text{Bi}_4\text{Ti}_3\text{O}_{12}(s) + \text{TiO}_2(s)}
\]

\[
\Phi_{\text{As}_4(g)} \quad 4\text{As}_4(s) \rightleftharpoons \text{As}_4(g)
\]

\[
\Phi_{\text{Ga}_2\text{As}_2(g)} \quad 2\text{GaAs}(s) \rightleftharpoons 2\text{Ga}(l) + \text{As}_2(g)
\]
Adsorption-Controlled Growth of Bi$_4$Ti$_3$O$_{12}$

Intensity (Arbitrary Units)

$T_{\text{sub}} = 660$ °C

$T_{\text{sub}} = 700$ °C

* = Substrate Peaks
Adsorption-Controlled Growth of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$
Adsorption-Controlled Growth of BaSnO$_3$

Eu Flux = $1.1 \times 10^{14}$ Eu atoms/(cm$^2$ s), $T_{\text{sub}} = 590$ °C
EuO film thickness (from RBS) after 30 min

Adsorption-Controlled SrTiO$_3$

FIG. 3. (Color online) Out-of-plane lattice parameter as a function of TTIP/Sr BEP ratio for epitaxial SrTiO$_3$ films grown on (001)SrTiO$_3$ at (a) 800 °C, (b) 725 °C, and (c) 700 °C. All films were grown using an oxygen BEP of $8 \times 10^{-6}$ torr. The darker gray-shaded region shows the growth window for stoichiometric films with a lattice parameter that is equivalent to that of the substrate at each temperature.

MOMBE Sources
Sr
Ti(OC$_3$H$_7$)$_4$
Oxygen Plasma

Single-Phase Field of GaAs vs. PbTiO$_3$


PbTiO$_3$

Single-phase film does not imply stoichiometric film

On the As-rich side both density and lattice parameter were recorded, their data cannot be used to plot the solidus in the vicinity of their MPs vs atom fraction of Group V element in the melt.

It is not sufficient to consider just a single native point defect. The above information alone is insufficient to permit deductions on the density/lattice parameter pair assuming only VP to be present. From that iterative process.

The calculated solidus of gallium arsenide showing the catastrophic deviation from stoichiometry at low temperature under arsenic-rich conditions. Arrow marks the congruent point.

FIG. 2. The calculated solidus of gallium arsenide showing the catastrophic deviation from stoichiometry at low temperature under arsenic-rich conditions. Arrow marks the congruent point.

FIG. 3. Calculated GaP solidus. Arrow marks the congruent point. Experimental data: Jordan et al. (○); Morozov et al. (□).

FIG. 4. Density of GaSb vs atom fraction of Sb in the melt at 80 atm. We further know that the range of density observed in GaSb, i.e., down to approximately 0.6 K below the MP.

FIG. 5. Calculated GaSb solidus. Arrow marks the congruent point.

FIG. 7. Calculated InAs solidus. Arrow marks the congruent point. Data points: Bublik et al. (○).

FIG. 8. Calculated InP solidus. Arrow marks the congruent point. Data points: Morozov et al. (Ref. 34) (○).

FIG. 9. Calculated InSb solidus. Arrow marks the congruent point.
Challenge

What if the oxide you desire cannot be grown by adsorption-control?
Composition Control

- Adsorption-Controlled Growth
- Flux-Controlled Growth
Reflection High-Energy Electron Diffraction (RHEED) Oscillations

B. Bölger and P. K. Larsen

Conventional RHEED Oscillations

Conventional RHEED Oscillations

BaTiO$_3$

La$_2$CuO$_4$

YBa$_2$Cu$_3$O$_7$

Figure 3. Schematical illustrations for the deposition and growth process of (a) BaTiO$_3$(001), (b) La$_2$CuO$_4$(001), and (c) YBa$_2$Cu$_3$O$_7$-(001) on SrTiO$_3$(100). Insets: The stacking sequences of the atomic layers in each crystal, with the growth units indicated. Note that the stacking sequences in the growth units shown in the figures have no specific meaning; the top layer cannot be specified.
Y. Horikoshi, M. Kawashima, and H. Yamaguchi

Migration-Enhanced Epitaxy of GaAs and AlGaAs


Migration-Enhanced Epitaxy

GaAs or (Al,Ga)As

Migration-Enhanced Epitaxy

GaAs

or

(Al,Ga)As
Shuttered RHEED to get Sr:Ti = 1:1

Oscillations of the central diffracted rod as the Sr and Ti are deposited in a sequential manner.

J.H. Haeni, C.D. Theis, and D.G. Schlom

Beat Frequency for Sr:Ti = 1:1 Absolute

J.H. Haeni, C.D. Theis, and D.G. Schlom


SrTiO$_3$

Sequential Deposition of SrTiO$_3$ (Sr : Ti Ratio = 1)

RHEED Intensity from First Diffracted Rod
SrTiO$_3$ [011] Azimuth

- 1.15 monolayers of each cation (beat frequency $\approx$ 7 oscillations)
- 1.1 monolayers of each cation (beat frequency $\approx$ 10 oscillations)
- 1.0 monolayers of each cation
- 0.9 monolayers of each cation (beat frequency $\approx$ 10 oscillations)
- 0.85 monolayers of each cation (beat frequency $\approx$ 7 oscillations)
How we do it

- Use Quartz Crystal Microbalance to Get Fluxes Close (~10% accuracy)
- Use Shuttered RHEED Oscillations (analogous to MEE of GaAs)
- Yields Sr:Ti Relative Incorporation Ratio (~1% accuracy)
- Yields Absolute Monolayer Dose for SrO and TiO$_2$ (~1% accuracy)
- Works for many Perovskites

J.H. Haeni, C.D. Theis, and D.G. Schlom
Shuttered RHEED Oscillations
Shuttered RHEED Oscillations

A-Site Rich

B-Site Rich
Deposition of superlattices and layered structures requires precise control to achieve perfect layer termination.

Calibration of beam flux with quartz crystal monitor not precise enough.

Intensity variation of electron diffraction (RHEED) pattern during deposition of one unit cell can be used for flux calibration.

Very time-consuming process, calibration can easily take 8 hours.
Examples of Oxides we Grow

- **BaSnO₃**
  - today’s record transparent transistors

- **LuFe₂O₄**
  - today’s record room-temperature multiferroic (superlattices)

- **LuFeO₃**

- **α-Bi₂Sn₂O₇**
  - (352 atoms/unit cell)

- **Sr₇Ti₆O₁₉**
  - leading candidate odd-parity topological superconductor

- **Sr₂RuO₄**
  - tunable microwave dielectric

- **BaSr₆Ti₆O₁₉**
  - today’s record transparent transistors

- **LuFe₂O₄**
  - room-temperature multiferroic (superlattices)

- **LuFeO₃**
  - today’s record room-temperature multiferroic (superlattices)

- **Sr₇Ti₆O₁₉**
  - leading candidate odd-parity topological superconductor

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  - tunable microwave dielectric