Molecular Beam Epitaxy of Oxides

Susanne Stemmer
Materials Department, University of California, Santa Barbara

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Overview

• Why oxide MBE?
• Growth of stoichiometric oxide films
• Case study I: perovskite titanates
• Case study II: perovskite stannates
Why Oxide Molecular Beam Epitaxy?

Three main sources of point defects in oxide films:

• Impurities
• Energetic deposition: pulsed laser deposition, sputtering
• Poor stoichiometry control during deposition, resulting in intrinsic point defects, such as vacancies and interstitials
Why Oxide Molecular Beam Epitaxy?

Three main sources of **point defects** in oxide films:

- Impurities

<table>
<thead>
<tr>
<th>Impurities</th>
<th>Content (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>30</td>
</tr>
<tr>
<td>Zn</td>
<td>10</td>
</tr>
<tr>
<td>Fe</td>
<td>30</td>
</tr>
<tr>
<td>Mg</td>
<td>20</td>
</tr>
<tr>
<td>Al</td>
<td>40</td>
</tr>
</tbody>
</table>

Impurity content in commercial SrTiO$_3$ single crystals (Toplent)

Compare with semiconductor standards: ppb or better
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Oxide Molecular Beam Epitaxy

☑ High purity
☑ Layer-by-layer control
☑ Low energetic deposition

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Before you begin: the MBE system

- There is no point in investing in MBE if you then allow cross-contamination
- Some/many elements will stay in the system forever
- Typically, one MBE system for one class of materials
- An MBE is not a multi-user facility
Before you begin: the MBE system

The growth of high-purity homoepitaxial InSb layers in a molecular-beam epitaxy reactor previously used for CdTe growth

G. M. Williams, C. R. Whitehouse, J. J. Ward, D. Brumhead, and T. Ashley
Royal Signals and Radar Establishment, St Andrews Road, Malvern, Worcs WR14 3PS United Kingdom

(Received 6 July 1989; accepted 12 September 1989)

Cross contamination problems can, in certain circumstances, impose a serious limitation for a molecular-beam epitaxy (MBE) system that is utilized to perform the growth of different high-purity semiconductors. Due to the very high capital cost associated with MBE technology it is essential that cross contamination be eliminated to allow continued use of the apparatus. In this paper we provide full details of a major vacuum-system cleaning exercise performed on an MBE reactor, previously used for cadmium telluride growth, which has allowed it to be subsequently and successfully used for the growth of state of the art high-purity InSb epilayers. Secondary ion mass spectroscopy (SIMS) and electrical measurements performed on InSb layers grown prior to the full cleaning process showed them to be heavily contaminated with tellurium. However, corresponding data obtained following the decontamination exercise indicated the successful removal of the previously observed impurities to below the SIMS detection limit. The cleaning process described should be suitable for any laboratory requiring to change the usage of an existing MBE reactor to the growth of alternative materials.

Estimated cost of cleaning: 20 – 25% of the purchase price of a new system
Before you begin: vapor pressures
Before you begin: the phase diagram

GaAs, like SrTiO$_3$, is a **line compound** (except at high temperatures) and can be grown stoichiometric.  

Bi$_2$Te$_3$ is **not** a line compound and cannot be grown stoichiometric, resulting in huge defect concentrations.

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Oxide Molecular Beam Epitaxy

- High purity
- Layer-by-layer control
- Low energetic deposition

What about stoichiometry control?

- Without a MBE growth window, stoichiometry control requires precise flux control → only possible to 0.1 - 1%
- Corresponds to defect concentrations of $10^{20}$-$10^{21}$ cm$^{-3}$
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Before you begin: vapor pressures
A wide MBE growth window is largely responsible for the ease and success of III-V MBE.

- No need for precise flux control.
- Also sometimes called “adsorption controlled growth.”

J. Tsao, Materials Fundamentals of Molecular Beam Epitaxy.
**Stoichiometry Control: Growth Window**

No practical growth window in MBE of SrTiO$_3$ using only solid sources

Rely on flux control?

Alternate solution: supply one constituent from a more volatile source

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Hybrid MBE = use metal-organic and solid sources to supply the metals

Oxide MBE with a Growth Window – Hybrid MBE

\[
\text{Ti(OC}_3\text{H}_7)_4 \rightarrow \text{TiO}_2 + 2 \text{C}_3\text{H}_7\text{OH} + 2 \text{C}_3\text{H}_6 @ T = 350\degree C
\]

- TTIP has orders of magnitude higher vapor pressures than solid Ti
- Scalable growth rate and stable flux
- No flux instabilities in presence of oxygen: higher oxygen pressure can be used
- Ti already comes bonded to four oxygens → improved oxygen stoichiometry

Oxide MBE with a Growth Window – Hybrid MBE

Growth Modes

Oxide MBE with a Growth Window – Hybrid MBE

- Use of a metalorganic Ti source (TTIP) leads to a growth window at practical substrate temperatures and fluxes.
- Excellent stoichiometry control
- Supplies extra oxygen
- High growth rates

Stoichiometry Control: RHEED

- c(4×4) reconstruction corresponds to a completely Ti-terminated surface.
- The boundary between c(2×1) and c(4×4) marks the truly adsorption controlled regime.
- Highest mobility films are grown in regime where XRD growth window and c(4×4) reconstruction overlap.

Stoichiometry Control: RHEED

Within the XRD growth window, surface reconstructions indicate transition to complete TiO$_2$ coverage with increasing TTIP/Sr flux ratio.

Properties of MBE Films

Electron Mobilities in SrTiO$_3$

- SrTiO$_3$ films doped with La
- Mobilities > 50,000 cm$^2$V$^{-1}$s$^{-1}$
- Higher than single crystals
- Strained films have mobilities > 130,000 cm$^2$V$^{-1}$s$^{-1}$

J. Son, P. Moetakef, B. Jalan, O. Bierwagen, N. J. Wright, R. Engel-Herbert, S. Stemmer, Nat. Mater. 9, 482 (2010).
Properties of MBE Films

(Ba,Sr)TiO$_3$ films have a tunable dielectric constant that is of interest for microwave applications.

- High dielectric losses have prevented wide-spread application.
- $Q = (\tan \delta)^{-1}$ of MBE-grown films is higher than single crystals.


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Sheet charge carrier density corresponds to the theoretical expected density of \( \sim 3 \times 10^{14} \text{ cm}^{-2} \)

Thank you!