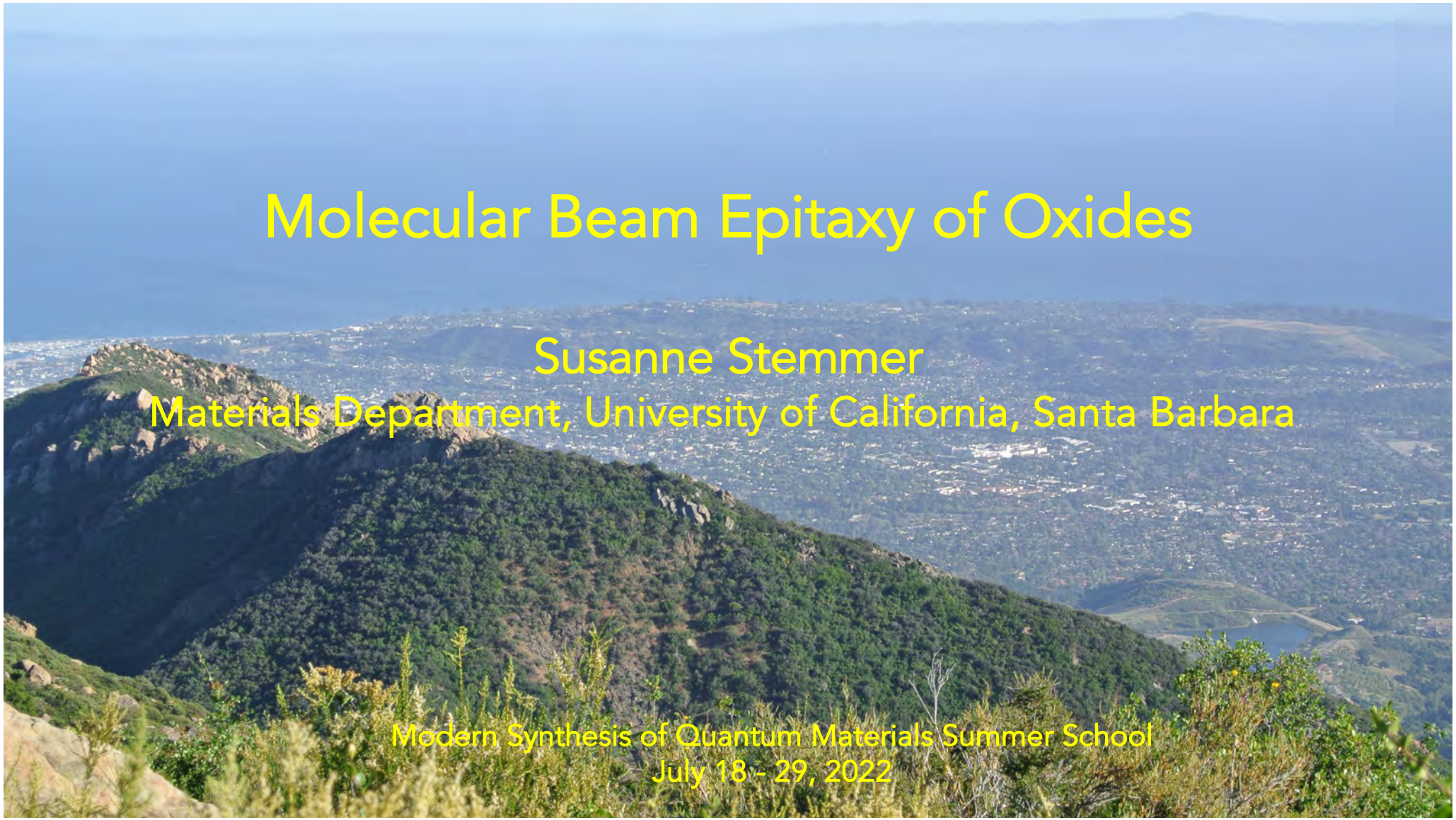


Molecular Beam Epitaxy of Oxides

Susanne Stemmer
Materials Department, University of California, Santa Barbara

Modern Synthesis of Quantum Materials Summer School
July 18 - 29, 2022

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

Impurity content in commercial $SrTiO_3$ single crystals (Toplent)

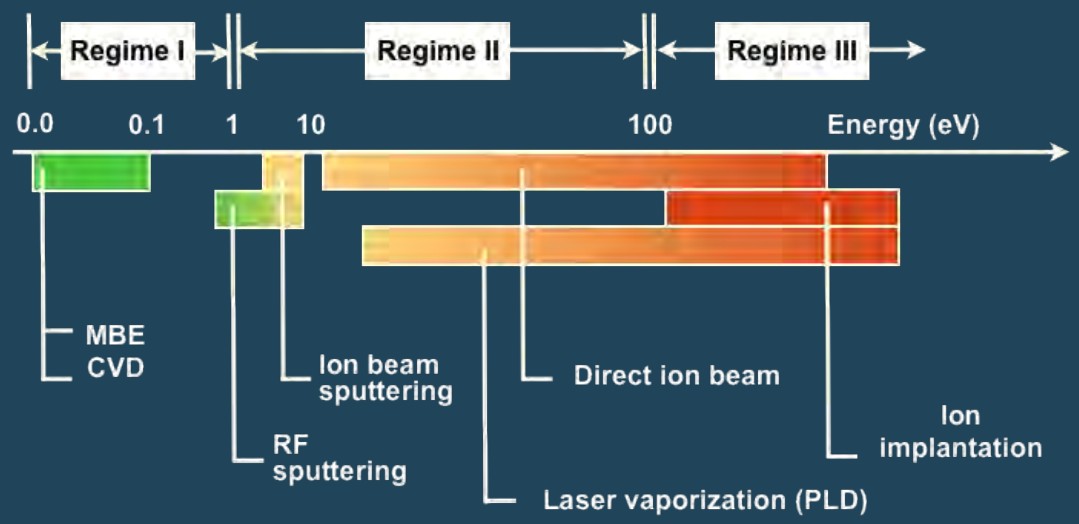
Impurities	Content (ppm)
Ca	30
Zn	10
Fe	30
Mg	20
Al	40

Compare with semiconductor standards: ppb or better

Why Oxide Molecular Beam Epitaxy?

Three main sources of point defects in oxide films:

- Impurities
- Energetic deposition: pulsed laser deposition, sputtering



Cuomo et al., J. Appl. Phys. 70 1706 (1991).

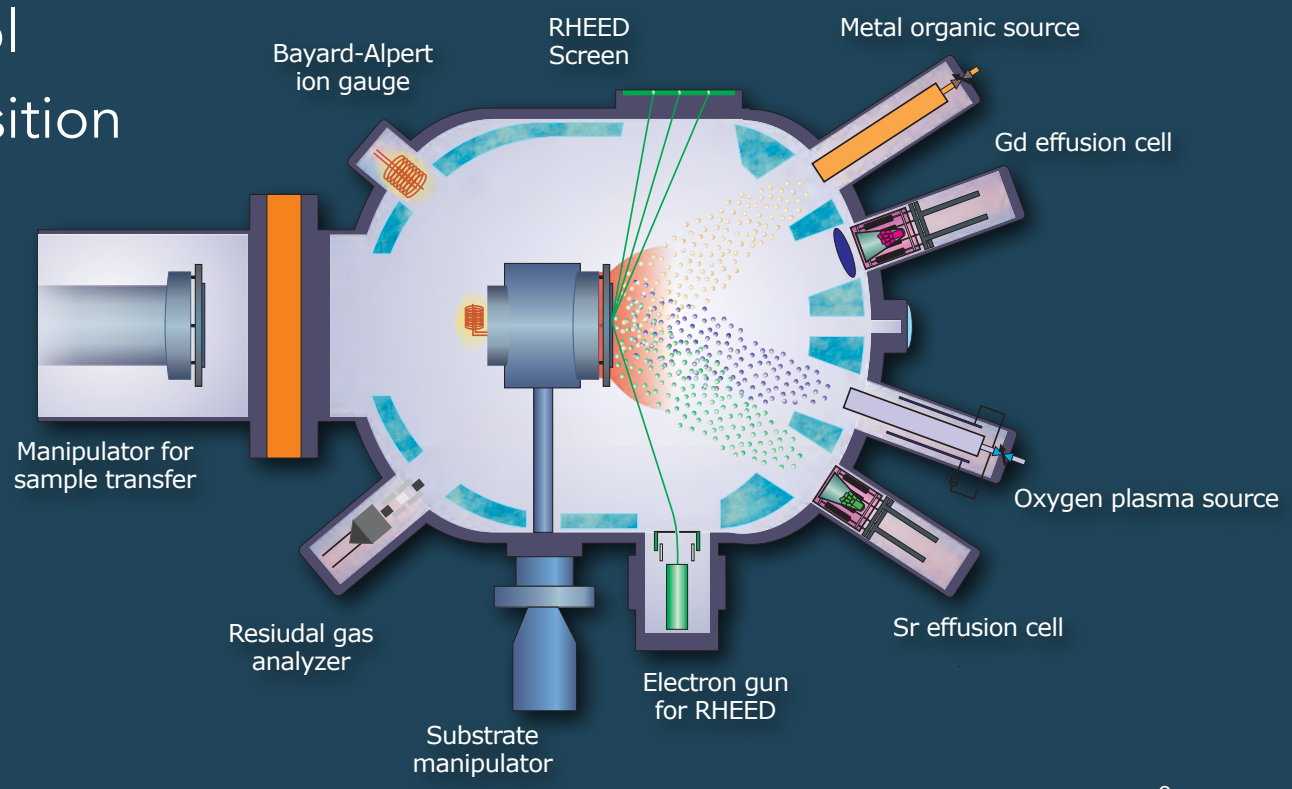
Why Oxide Molecular Beam Epitaxy?

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

Oxide Molecular Beam Epitaxy

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



Before you begin: the MBE system

- There is no point in a 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

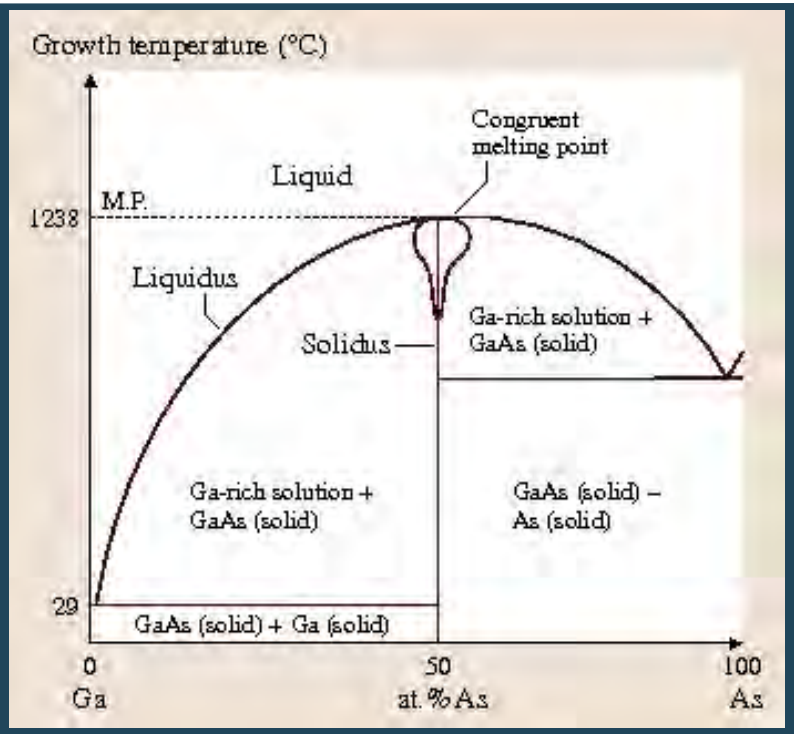
(Received 6 July 1989; accepted 12 September 1989)

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.

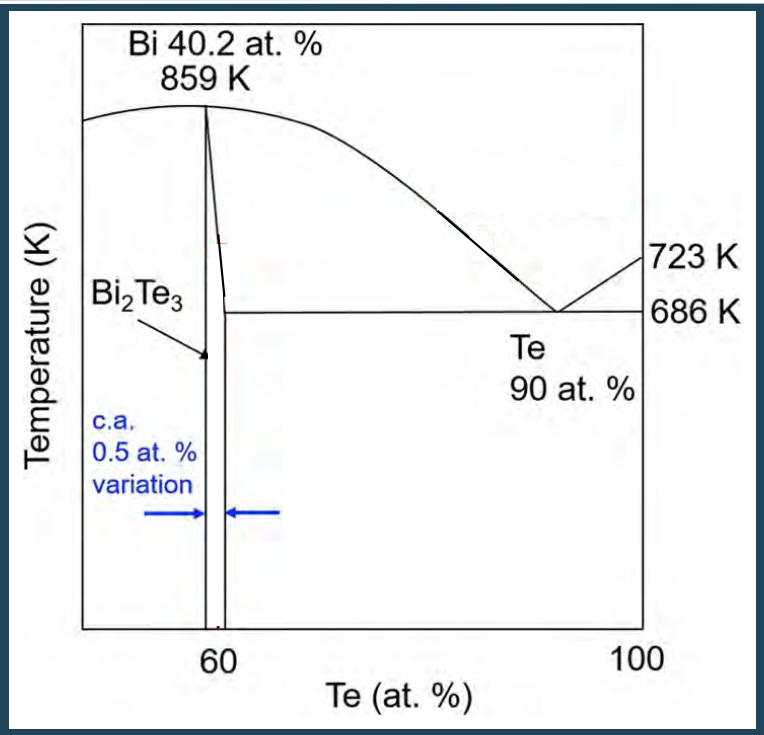
Estimated cost of cleaning: 20 – 25% of the purchase price of a new system

Before you begin: vapor pressures

Before you begin: the phase diagram



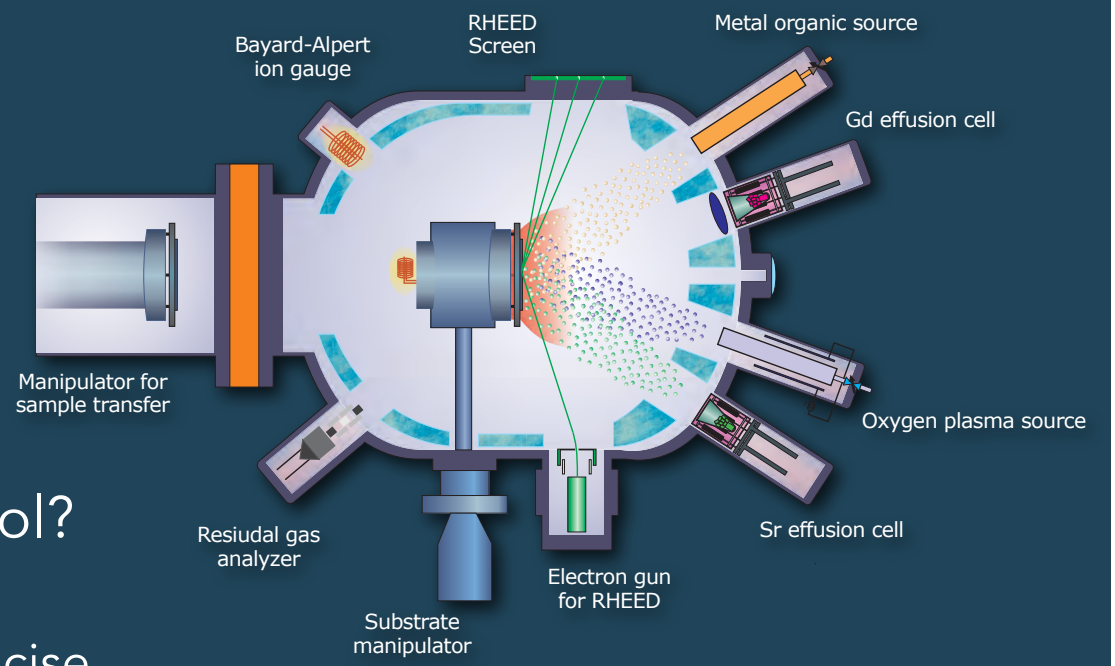
GaAs, like $SrTiO_3$, is a line compound **(except at high temperatures)** and can be grown stoichiometric



Bi_2Te_3 is **not** a line compound and cannot be grown stoichiometric, resulting in huge defect concentrations

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}

Overview

- Why oxide MBE?
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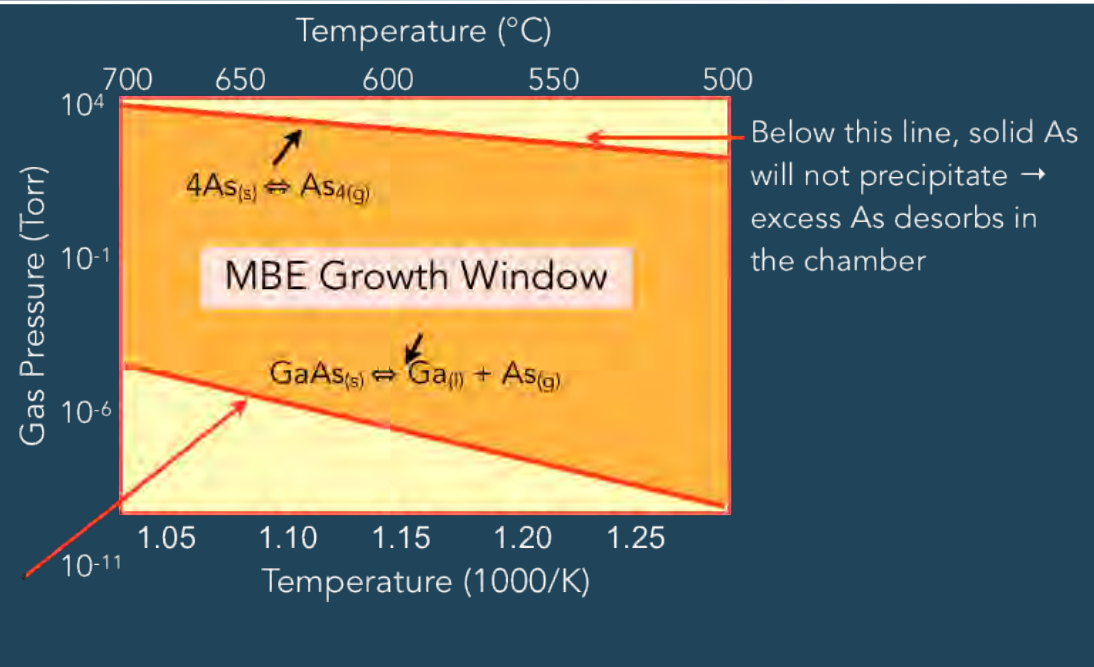
Before you begin: vapor pressures

Stoichiometry Control: Growth Window

GaAs

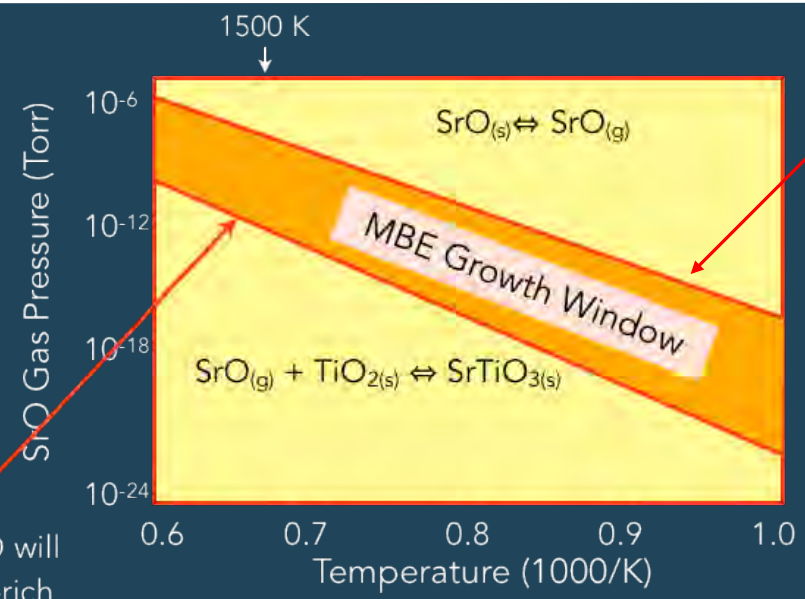


- A wide MBE growth window is largely responsible for the ease and success of III-V MBE
- No need for precise flux control
- Also sometimes called "adsorption controlled growth"

C.D. Theis et al., Thin Solid Films 325, 107 (1998).
J. Tsao, Materials Fundamentals of Molecular Beam Epitaxy.

Stoichiometry Control: Growth Window

$SrTiO_3$



Below this line, solid SrO will not precipitate: SrO will desorb in the chamber*

Ti has a sticking coefficient of 1

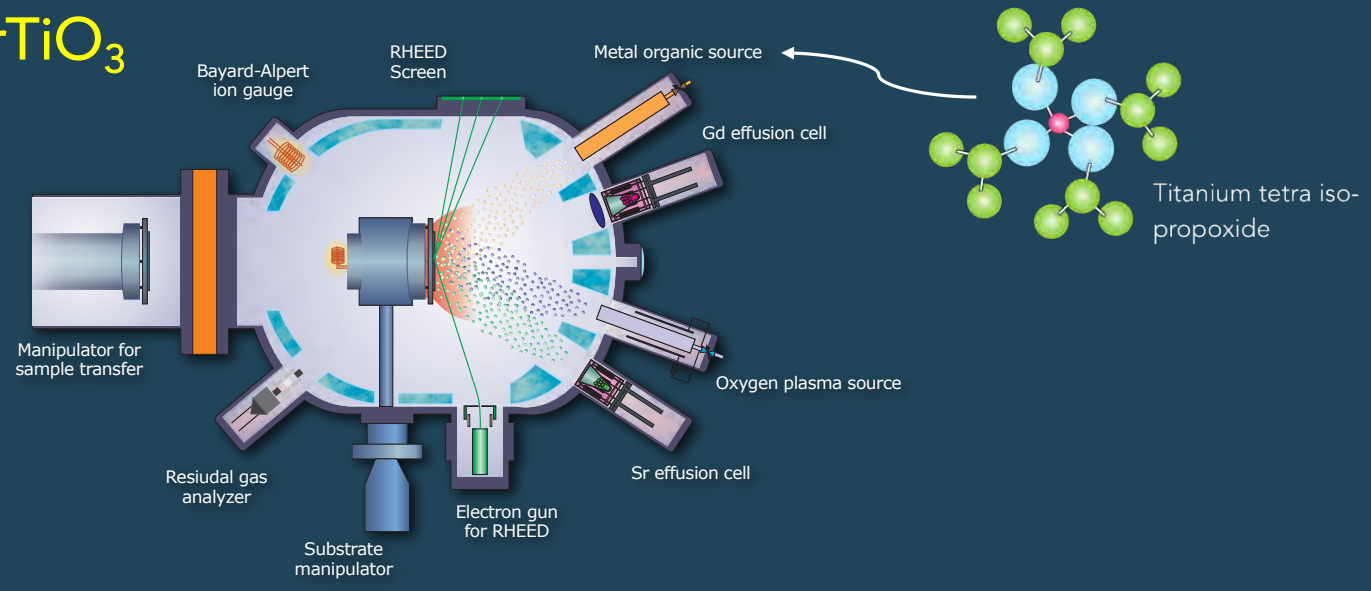
Above this line, SrO will condense on a TiO-rich $SrTiO_3$ surface*

- ❑ 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

C.D. Theis et al., Thin Solid Films 325, 107 (1998).

Oxide MBE with a Growth Window – Hybrid MBE

$SrTiO_3$

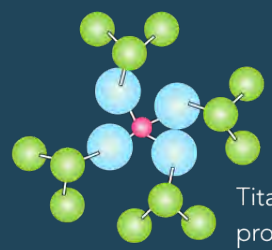


Hybrid MBE = use metal-organic and solid sources to supply the metals

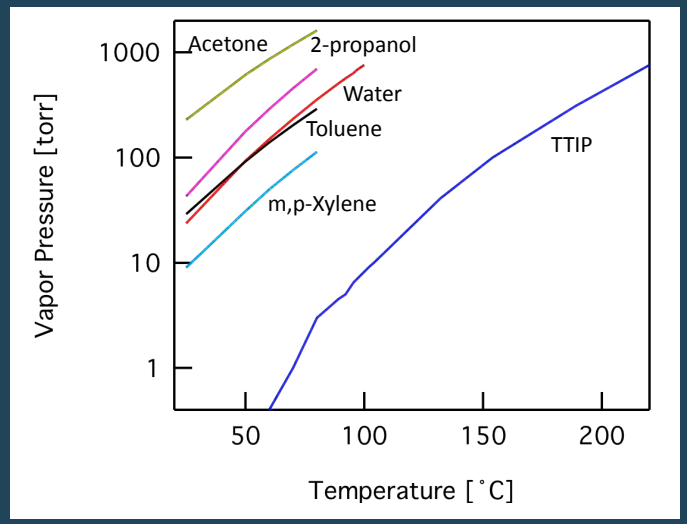
B. Jalan, R. Engel-Herbert, N. J. Wright, S. Stemmer, J. Vac. Sci. and Technol. A 27, 461 (2009).
B. Jalan, P. Moetakef, S. Stemmer, Appl. Phys. Lett. 95, 032906 (2009).

Oxide MBE with a Growth Window – Hybrid MBE

$$Ti(OC_3H_7)_4 \rightarrow TiO_2 + 2\ C_3H_7OH + 2\ C_3H_6$$
@ T = 350˚C



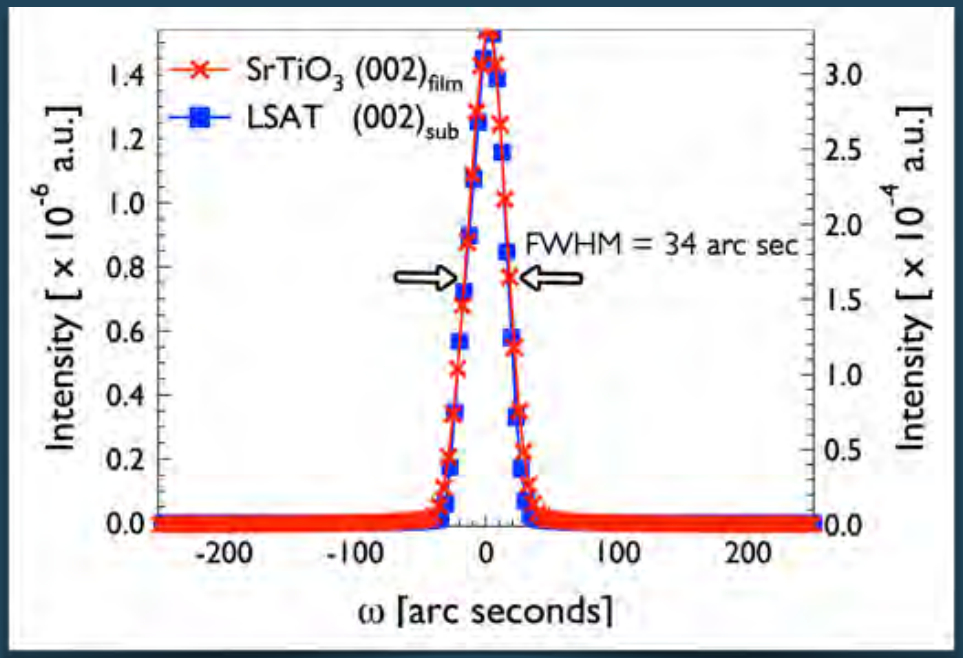
Titanium tetra iso-propoxide

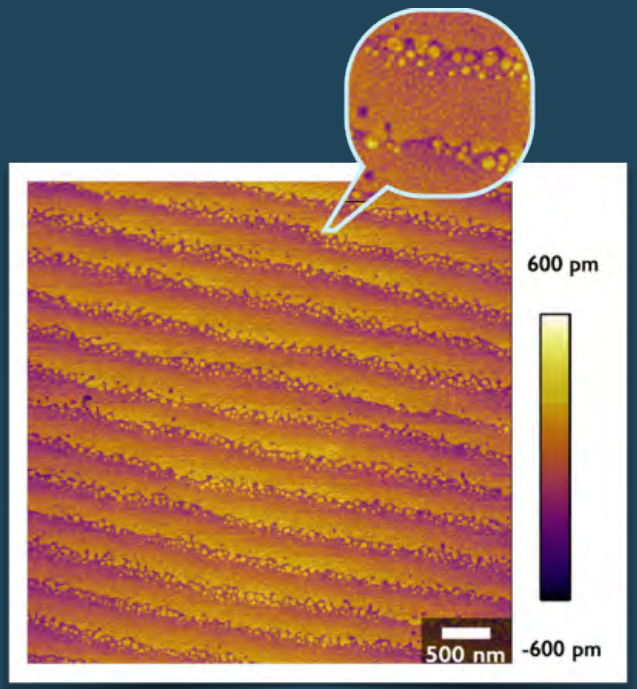


- TTIP has orders of magnitude higher vapor pressures than solid Ti
- Scalable growth rate and stable flux
- No flux instabilities in presence of oxygen: higher oxygen pressure can be used
- Ti already comes bonded to four oxygens → improved oxygen stoichiometry

B. Jalan, R. Engel-Herbert, N. J. Wright, S. Stemmer, J. Vac. Sci. and Technol. A 27, 461 (2009).
B. Jalan, P. Moetakef, S. Stemmer, Appl. Phys. Lett. 95, 032906 (2009).

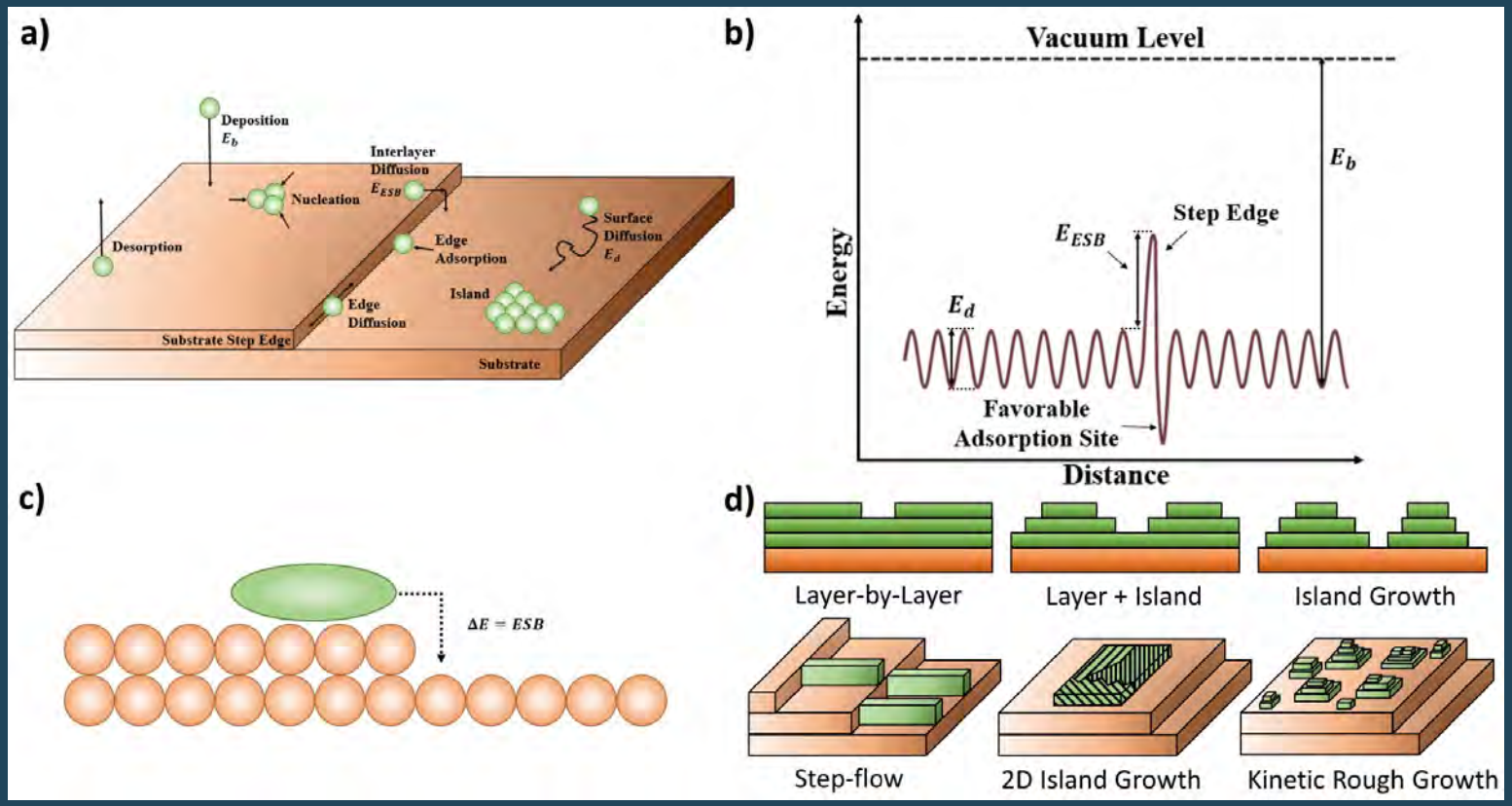
Oxide MBE with a Growth Window – Hybrid MBE





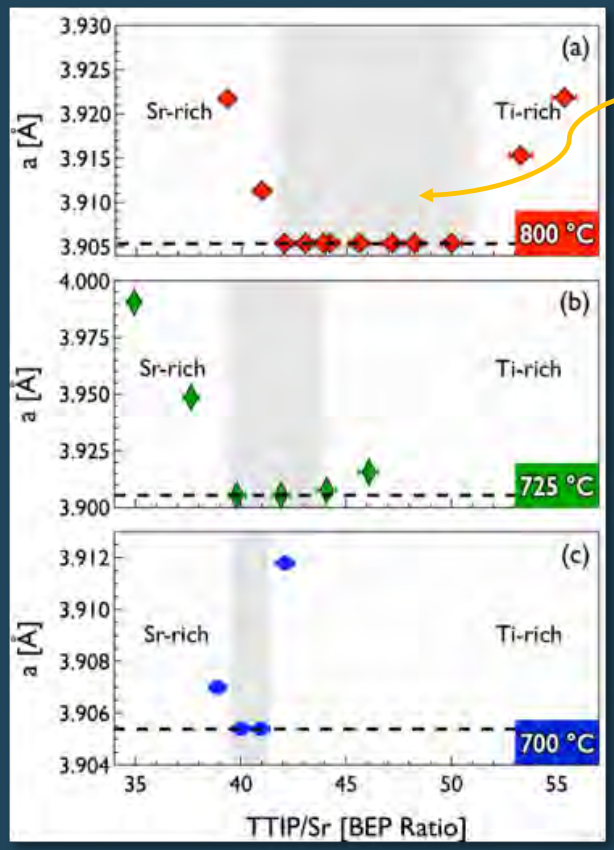
B. Jalan, R. Engel-Herbert, N. J. Wright, S. Stemmer, J. Vac. Sci. and Technol. A 27, 461 (2009).
B. Jalan, P. Moetakef, S. Stemmer, Appl. Phys. Lett. 95, 032906 (2009).

Growth Modes

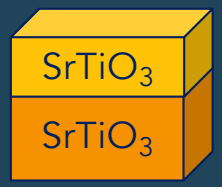


A. Tan and P. Zhang, J. Phys.: Condens. Matter 31 503001 (2019).

Oxide MBE with a Growth Window – Hybrid MBE



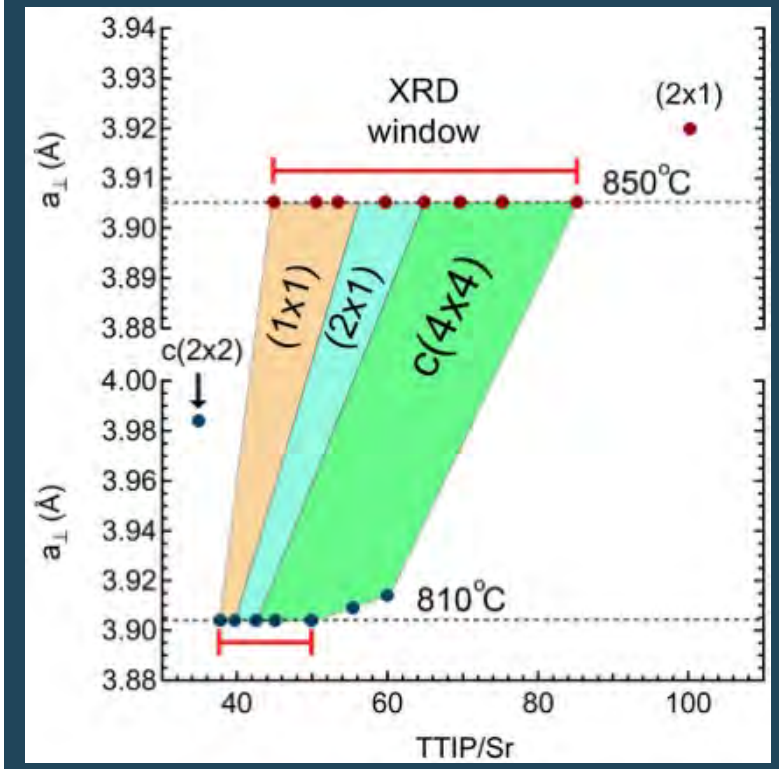
MBE Growth Window

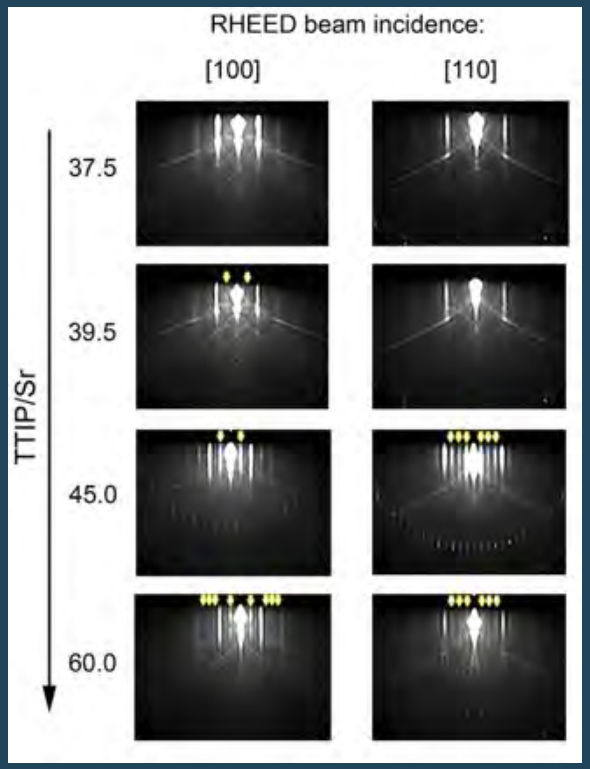


- ❑ Use of a metalorganic Ti source (TTIP) leads to a growth window at practical substrate temperatures and fluxes.
- ❑ Excellent stoichiometry control
- ❑ Supplies extra oxygen
- ❑ High growth rates

B. Jalan, R. Engel-Herbert, N. J. Wright, S. Stemmer, J. Vac. Sci. and Technol. A 27, 461 (2009).
B. Jalan, P. Moetakef, S. Stemmer, Appl. Phys. Lett. 95, 032906 (2009).

Stoichiometry Control: RHEED

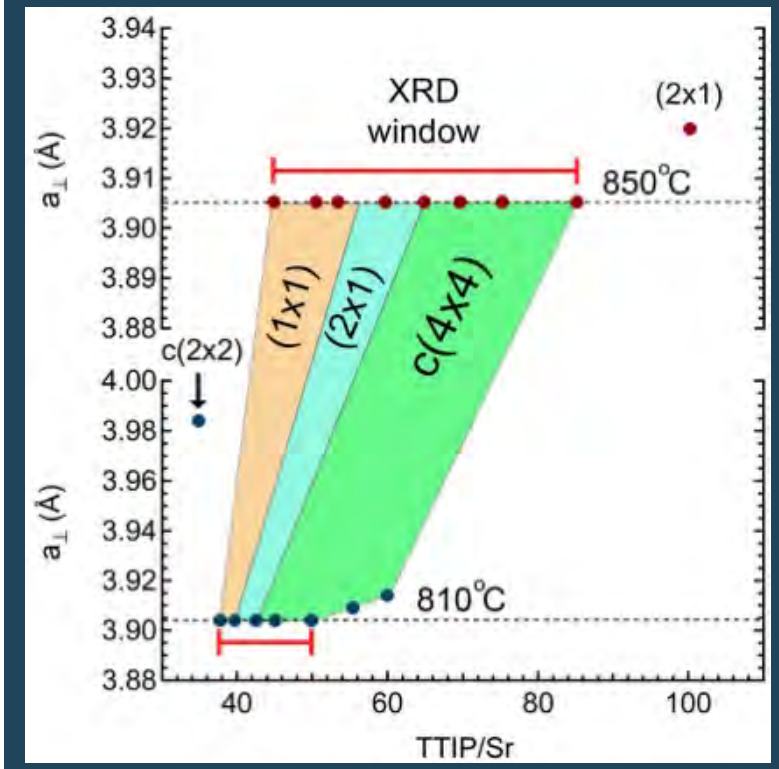


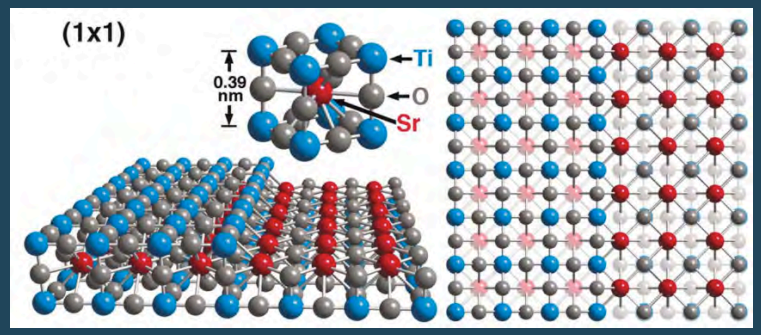


- c(4×4) reconstruction corresponds to a completely Ti-terminated surface
- The boundary between c(2×1) and c(4×4) marks the truly adsorption controlled regime
- Highest mobility films are grown in regime where XRD growth window and c(4×4) reconstruction overlap

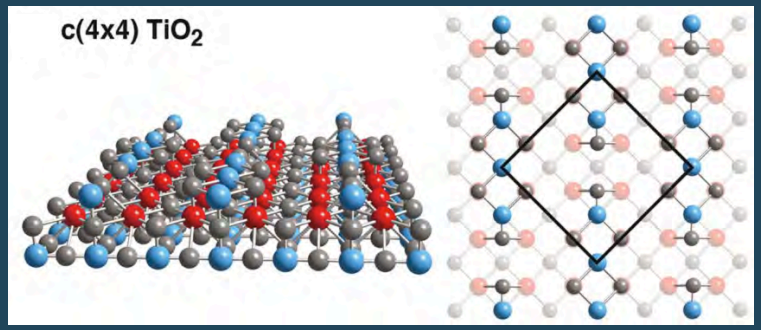
A. P. Kajdos, and S. Stemmer, Appl. Phys. Lett. 105, 191901 (2014).

Stoichiometry Control: RHEED





(1×1)
mixed SrO and TiO_2 termination



(4×4)
TiO_2 termination

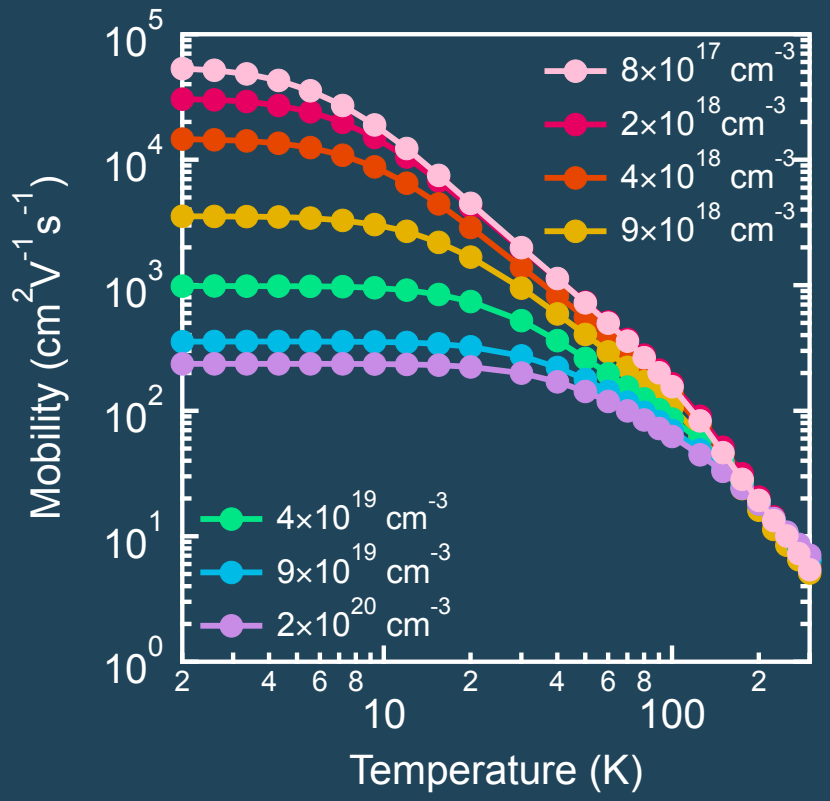
M. Castell, Surf. Sci. 505, 1 (2002).

Within the XRD growth window, surface reconstructions indicate transition to complete TiO_2 coverage with increasing TTIP/Sr flux ratio

A. P. Kajdos, and S. Stemmer, Appl. Phys. Lett. 105, 191901 (2014).

Properties of MBE Films

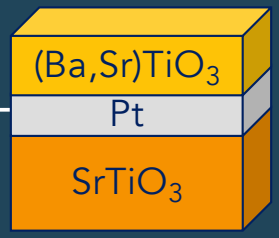
Electron Mobilities in $SrTiO_3$



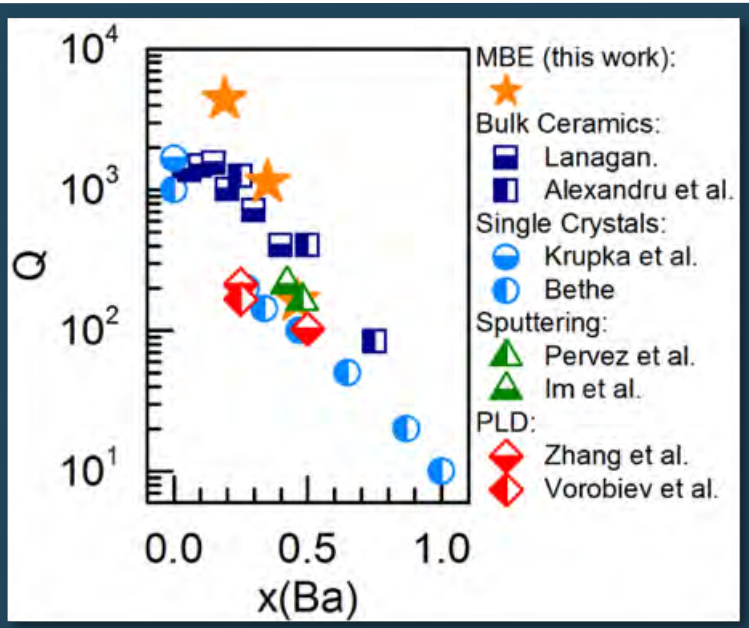
- ❑ $SrTiO_3$ films doped with La
- ❑ Mobilities >50,000 cm^{2}V^{-1}s^{-1}
- ❑ Higher than single crystals
- ❑ Strained films have mobilities > 130,000 cm^{2}V^{-1}s^{-1}

J. Son, P. Moetakef, B. Jalan, O. Bierwagen, N. J. Wright, R. Engel-Herbert, S. Stemmer, Nat. Mater. 9, 482 (2010).
T. A. Cain, A. P. Kajdos, and S. Stemmer, Appl. Phys. Lett. 102, 182101 (2013).
B. Jalan, S. J. Allen, G. E. Beltz, P. Moetakef, S. Stemmer, Appl. Phys. Lett. 98, 132102 (2011).

Properties of MBE Films



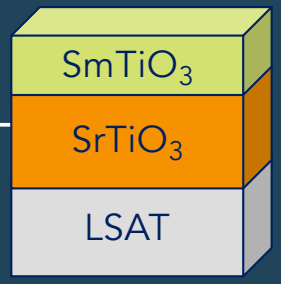
Dielectric quality factor

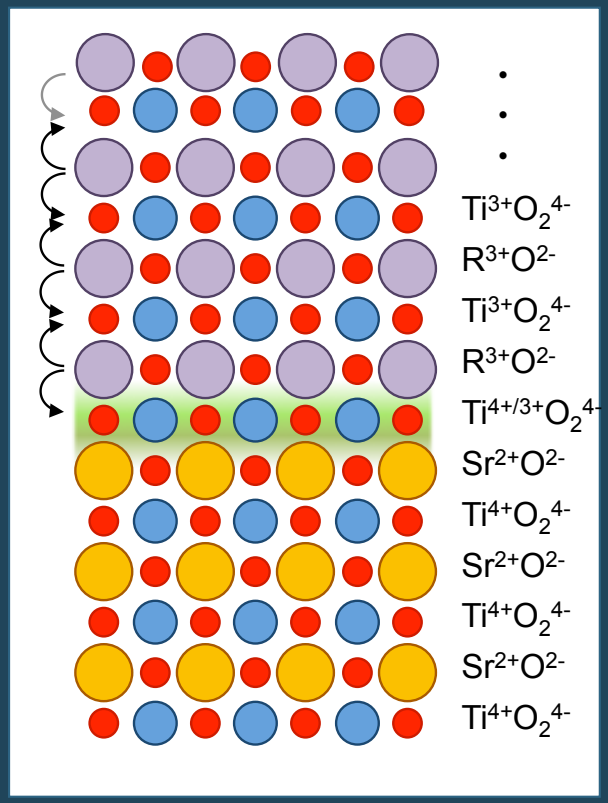


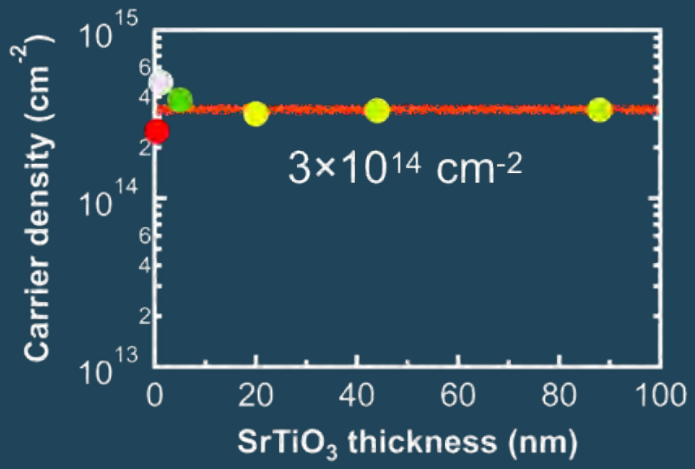
E. Mikheev, A. P. Kajdos, A. J. Hauser, S. Stemmer, Appl. Phys. Lett. 101, 252906 (2012).

- ❑ $(Ba,Sr)TiO_3$ 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

Properties of MBE Heterostructures







Sheet charge carrier density corresponds to the theoretical expected density of ~ 3×10^{14} cm^{-2}

P. Moetakef, et al., Appl. Phys. Lett. 99, 232116 (2011).

Thank you!