# LECTURE #4—

# NUTS AND BOLTS OF OXIDE MBE: EPITAXY, SUBSTRATES, AND CRYSTAL GROWTH

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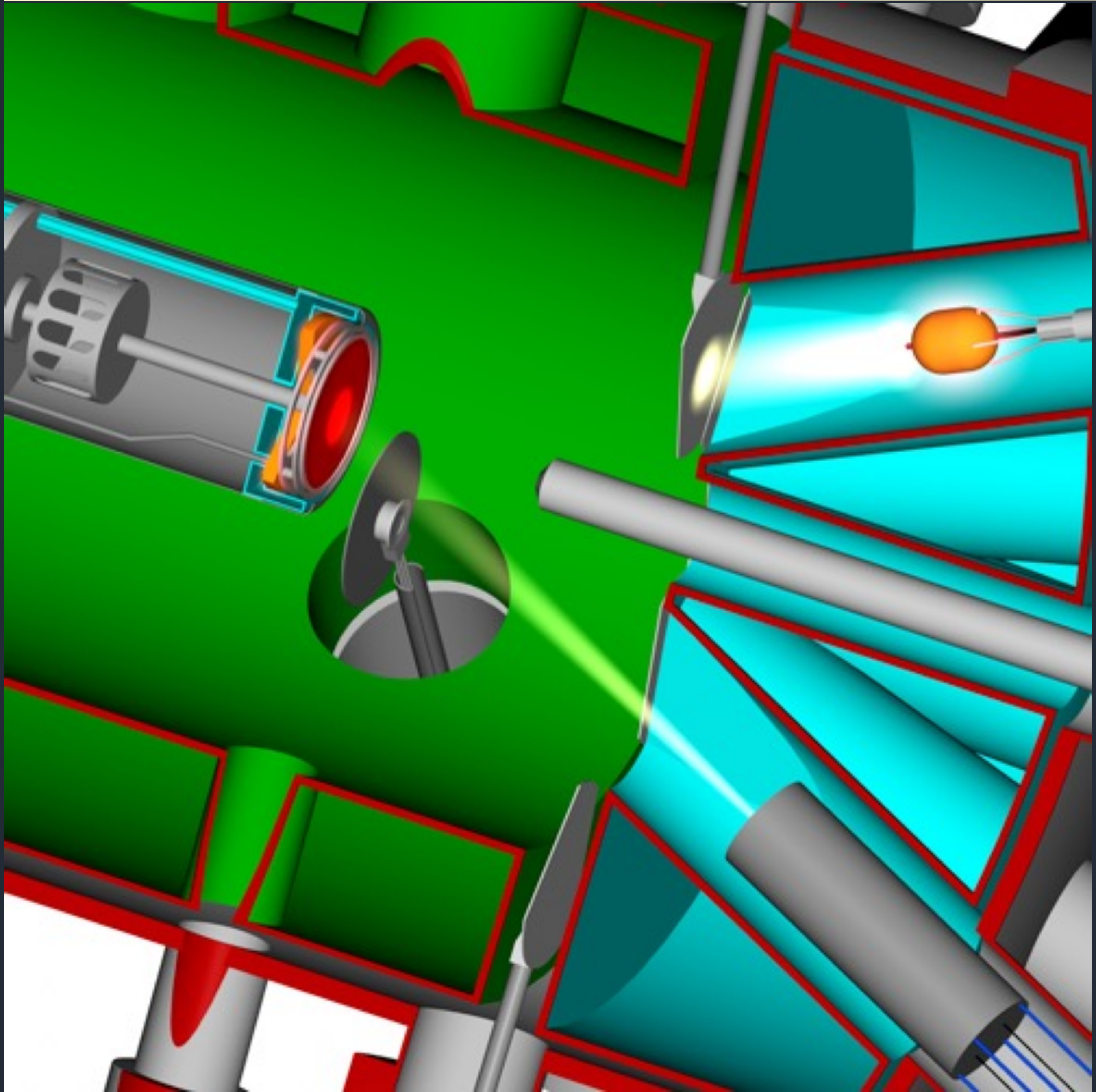
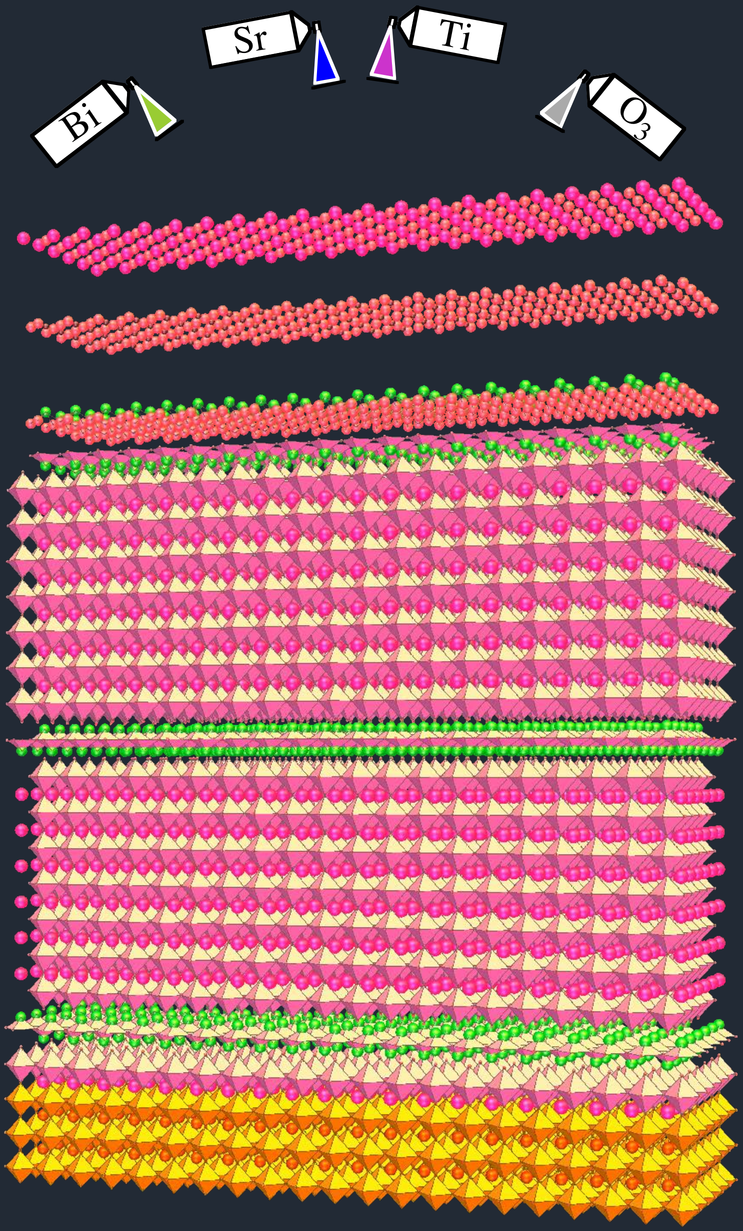
# Nuts and Bolts of Oxide MBE

## How to grow your favorite oxide by MBE?

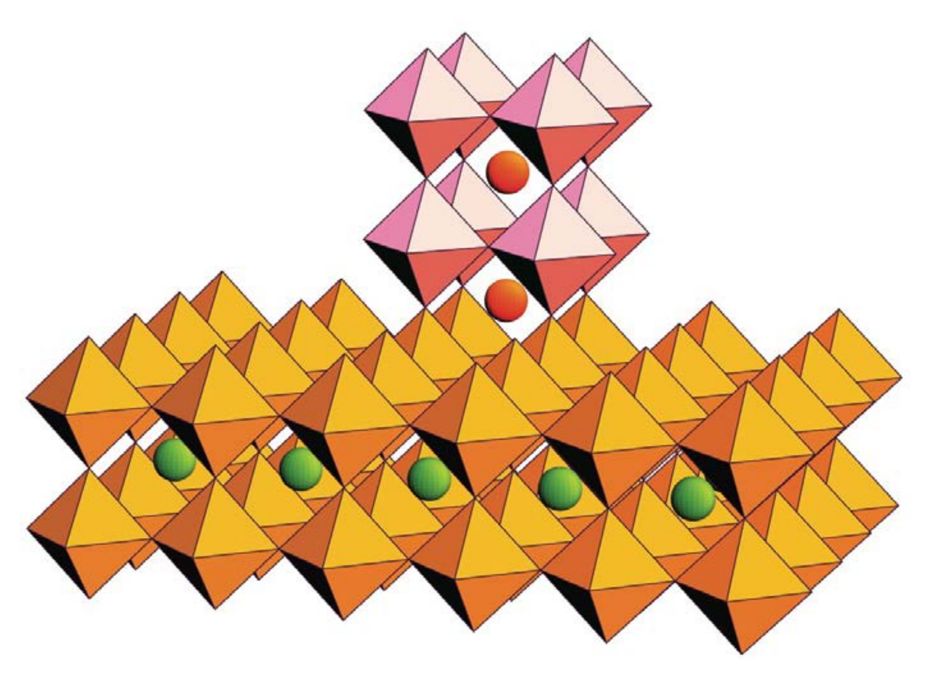
- Lecture #2—Growth Conditions, Sources, and Crucibles
- Lecture #3—Composition Control and Calibration
- Lecture #4—Epitaxy, Substrates, and Crystal Growth

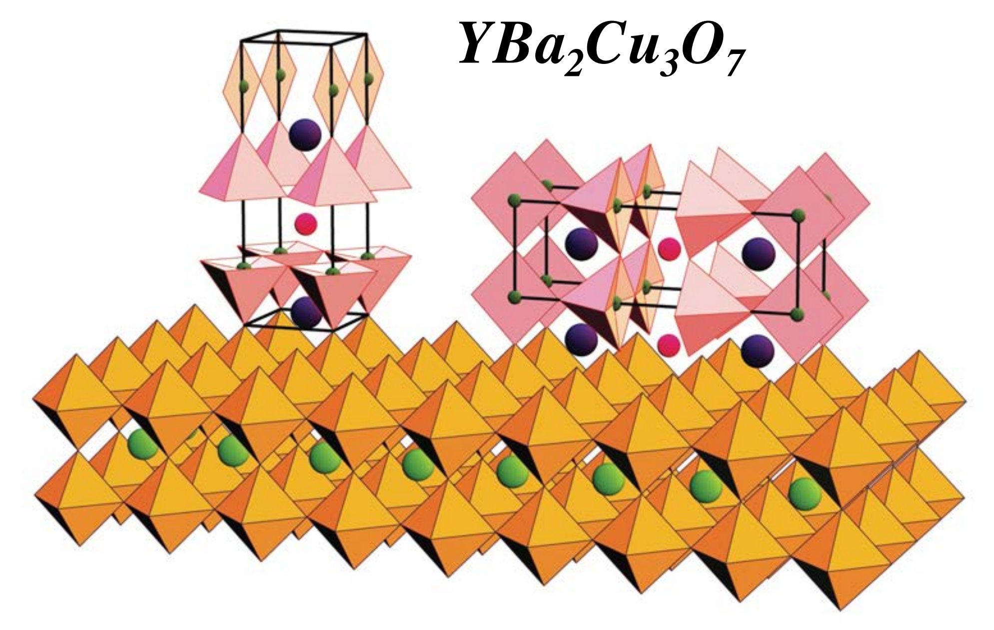
# MBE ≈ Atomic Spray Painting

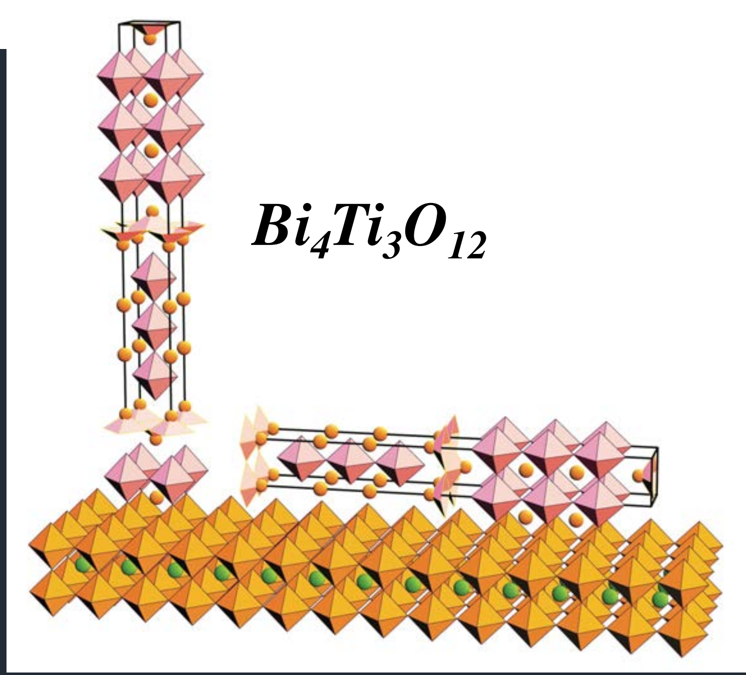




# Epitaxial Growth





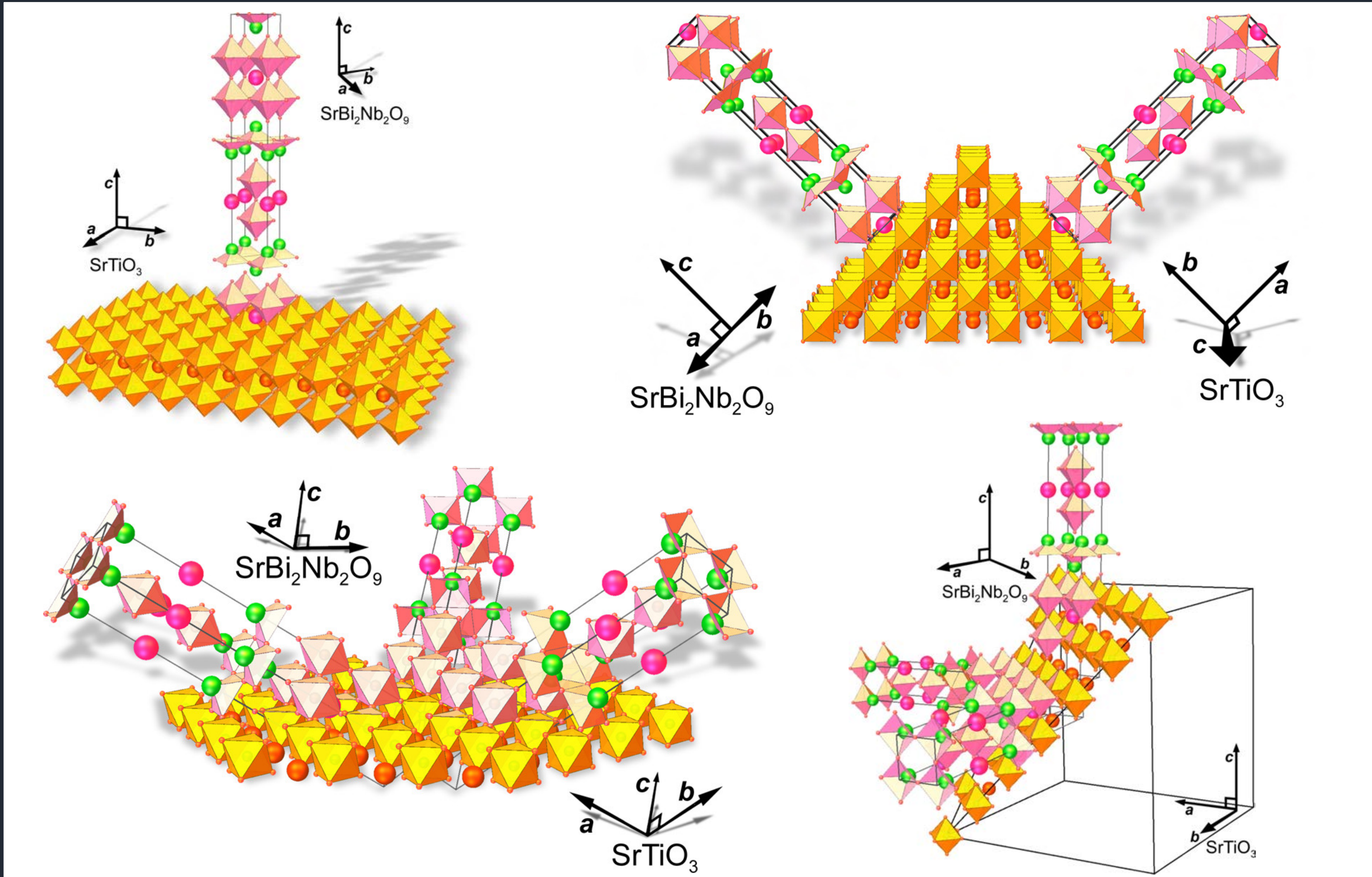




$ABO_3$ / $A'B'O_3$

"Cube-on-Cube"

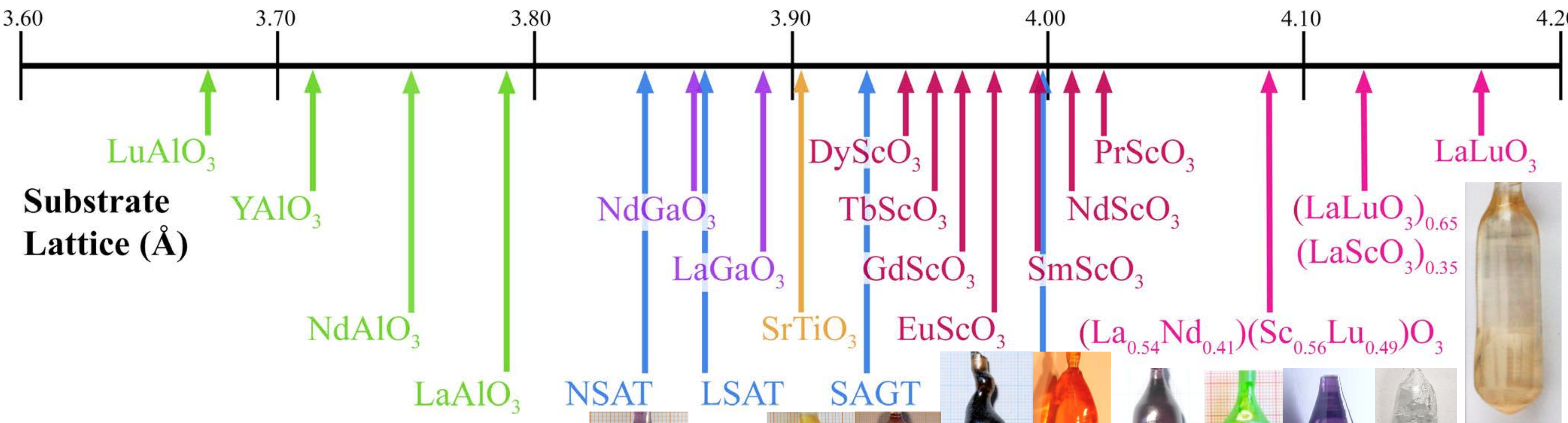
R. Ramesh and D.G. Schlom, *Science* **296** (2002) 1975–1976.

# Epitaxial Growth




D.G. Schlom, L.Q. Chen, X.Q. Pan, A. Schmehl, and M.A. Zurbuchen, *Journal of the American Ceramic Society* **91** (2008) 2429-2454.

# Perovskite Substrates to Impose Strain





Images courtesy of
**Christo Guguschev**
**Institut für Kristallzüchtung (IKZ)**

# How $SrTiO_3$ Single Crystals are Grown

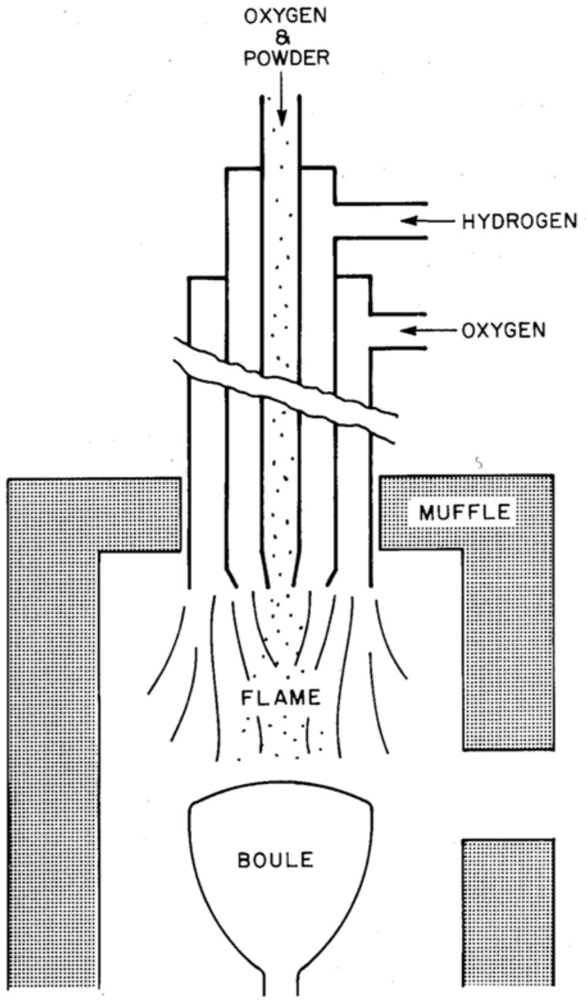



FIG. 18–1. The tricone modification of the Verneuil flame-fusion apparatus used for the growth of synthetic rutile and strontium titanate. The water-cooling arrangement is not shown.

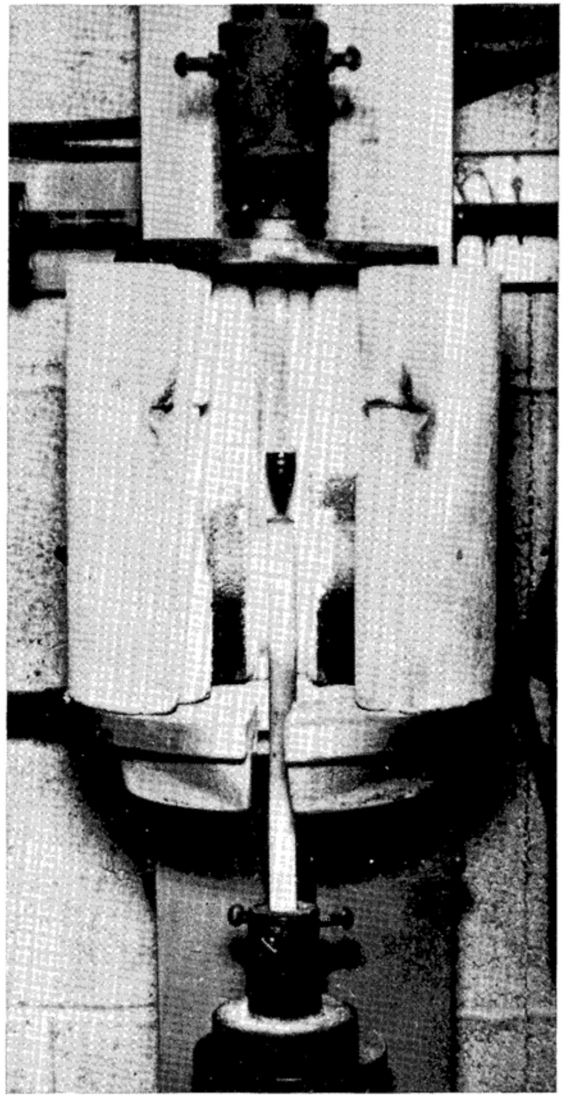


FIG. 18–2. An as-grown black synthetic rutile boule, this will turn a pale yellow after annealing. *Courtesy of N. L. Industries.*

N. Nassau, *Gems Made by Man* (Chilton Books, 1980).

# How “Real Crystals” are Grown

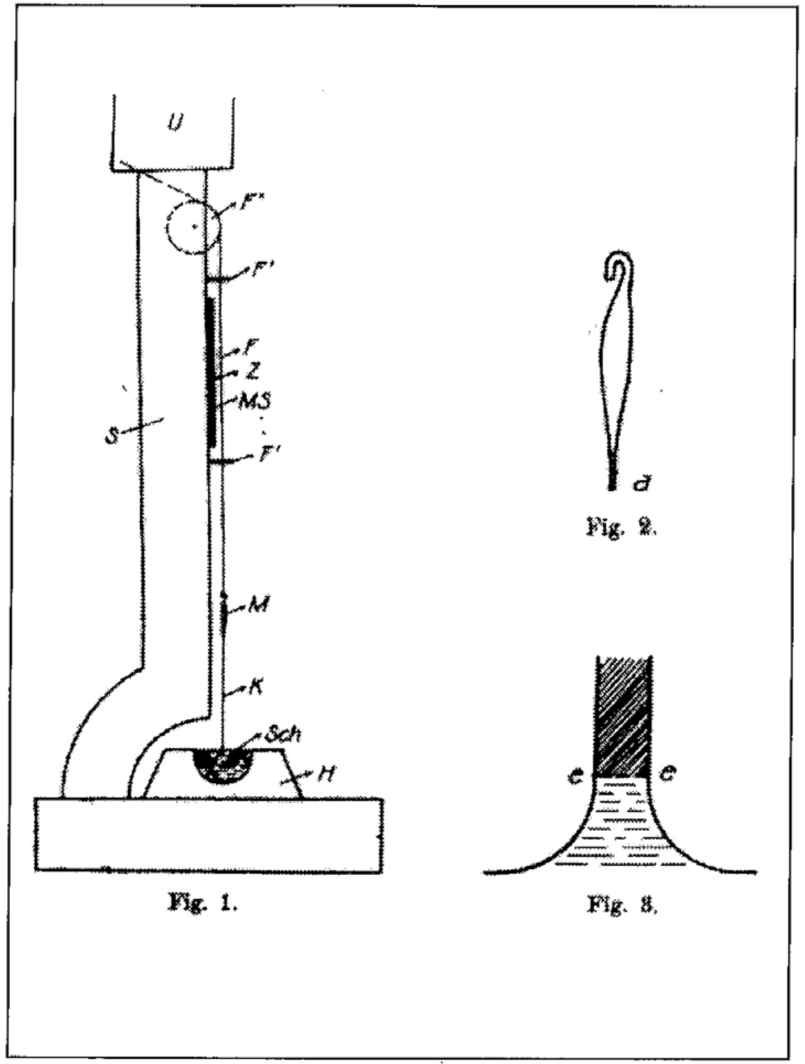



Figure 1. *Schematic illustration of Czochralski’s method, published in* Zeitschrift für physikalische Chemie ***92*** *(1918) p. 220.*

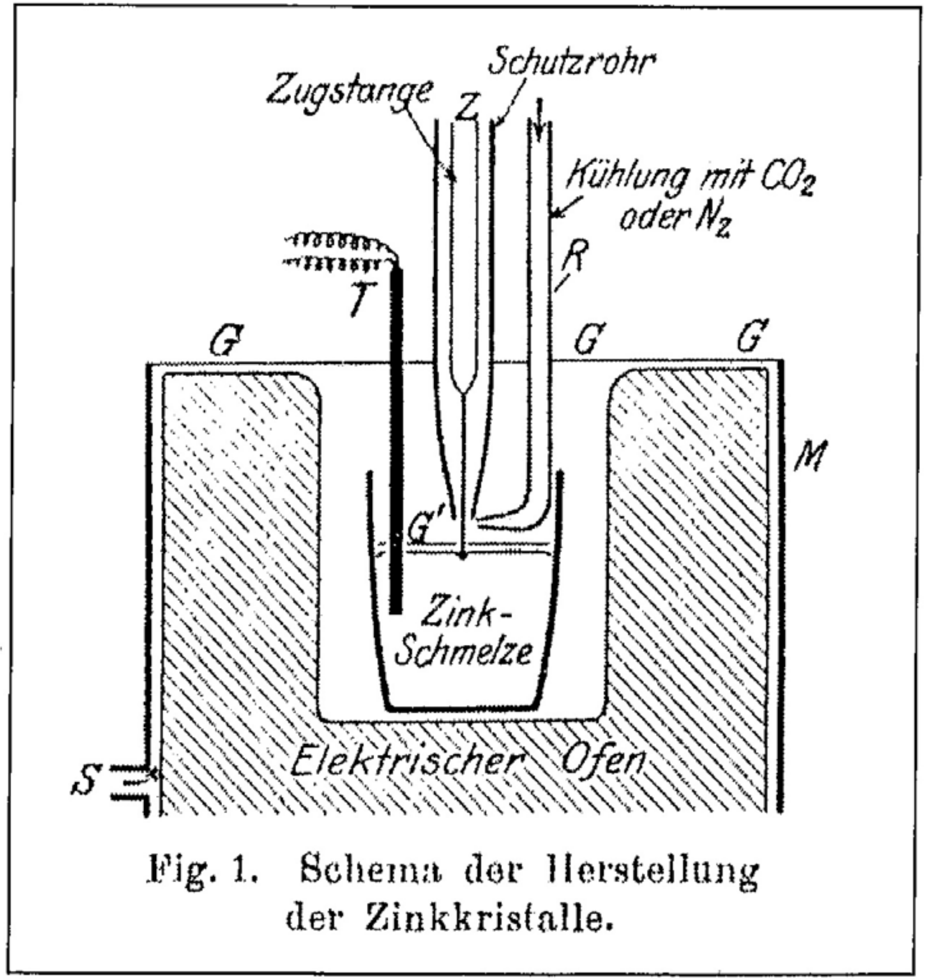
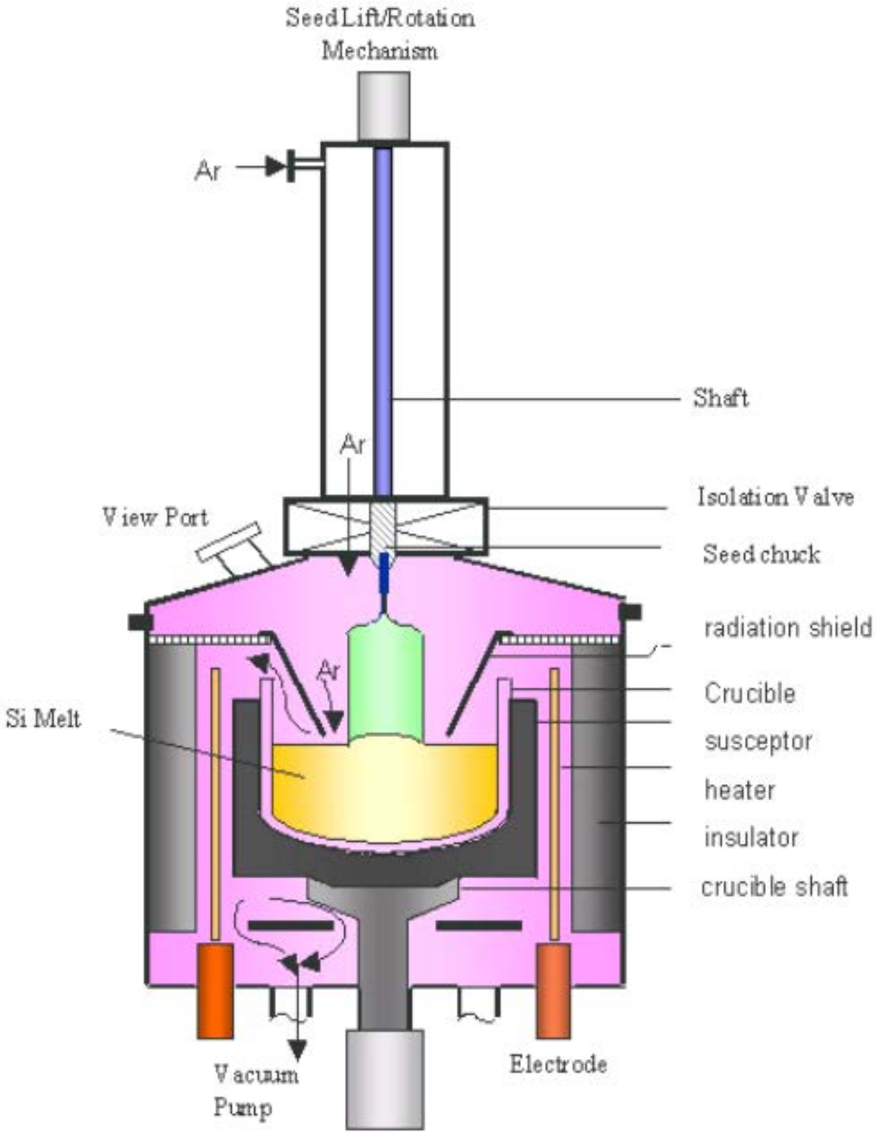
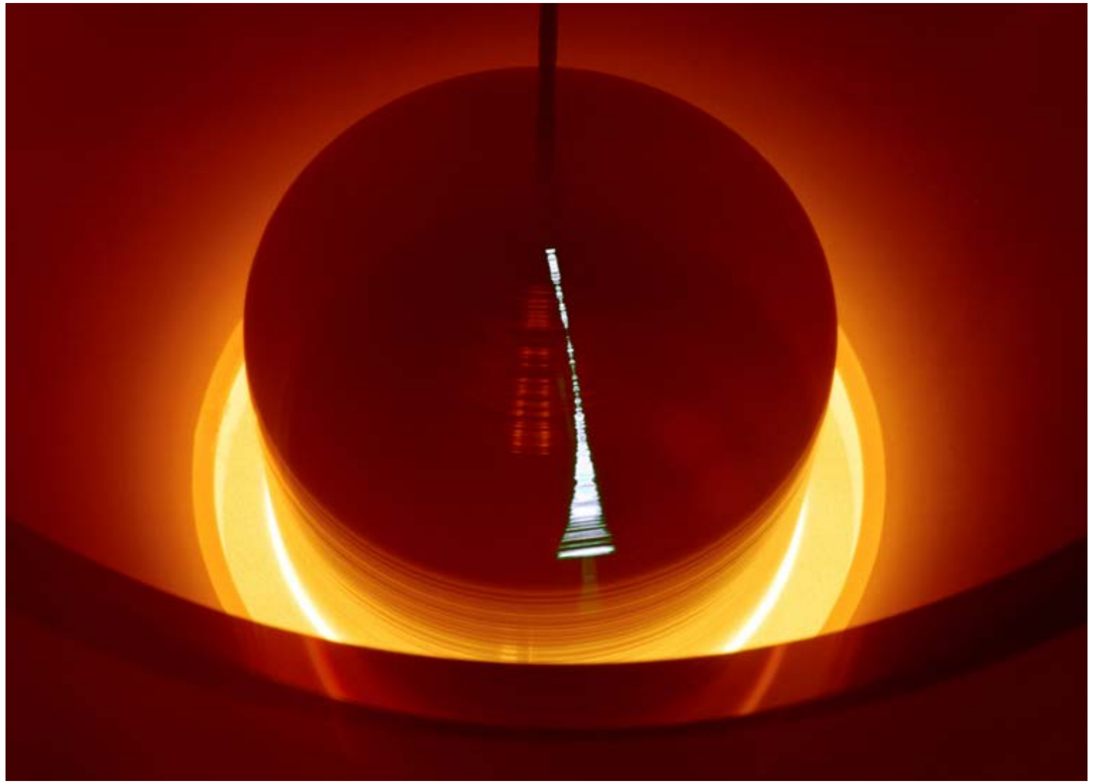



*Figure 2. Schematic illustration of Czochralski’s method as modified by Mark, Polanyi, and Schmid; published in* Zeitschrift für Physik **12** *(1923) p. 58.*

# How "Real Crystals" are Grown

## CZOCHRALSKI CRYSTAL GROWTH



J.Czochralski, 1916

# Surface Termination of Substrates is Important

## (100) and (111) $SrTiO_3$

G. Koster, B.L. Kropman, G.J.H.M. Rijnders, D.H.A. Blank, H. Rogalla,
"Quasi-Ideal Strontium Titanate Crystal Surfaces through Formation of Strontium Hydroxide,"
*Applied Physics Letters* **73** (1998) 2920-2922.

M. Kawasaki, K. Takahashi, T. Maeda, R. Tsuchiya, M. Shinohara,
O. Ishiyama, T. Yonezawa, M. Yoshimoto, and H. Koinuma,
"Atomic Control of the $SrTiO_3$ Crystal Surface,"
*Science* **266** (1994) 1540-1542.

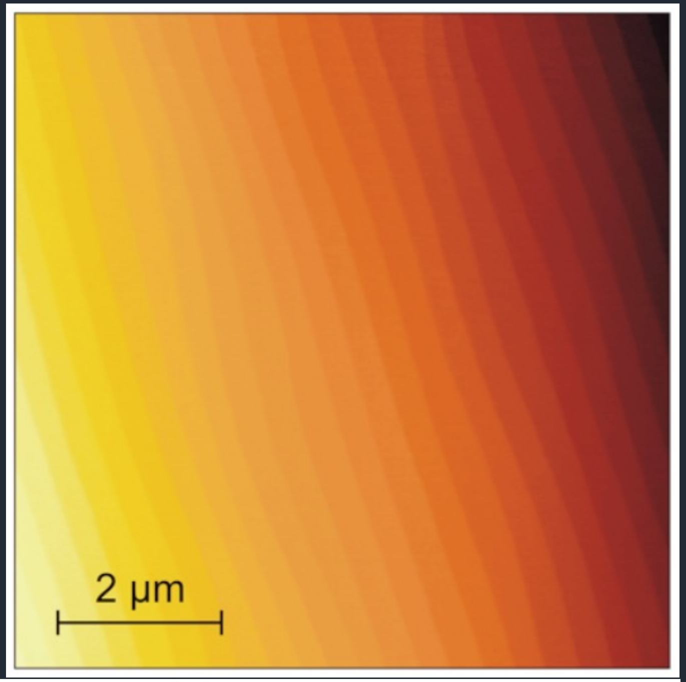
## (110) *RE*$ScO_3$

J.E. Kleibeuker, G. Koster, W. Siemons, D. Dubbink, B. Kuiper, J.L. Blok, C-H. Yang,
J. Ravichandran, R. Ramesh, J.E. ten Elshof, D.H.A. Blank, and G. Rijnders,
"Atomically Defined Rare-Earth Scandate Crystal Surfaces,"
*Advanced Materials* **20** (2010) 3490-3496.

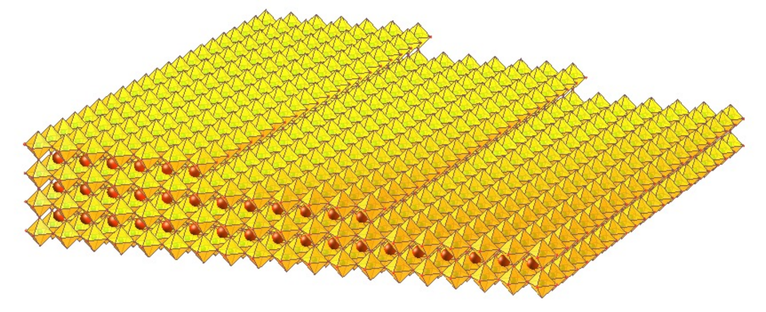
## $(100)_p$ and $(111)_p$ $LaAlO_3$

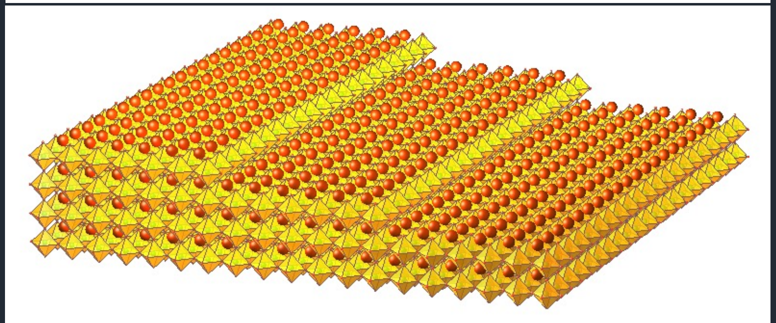
J.L. Blok, X. Wan, G. Koster, D.H.A. Blank, and G. Rijnders,
"Epitaxial Oxide Growth on Polar (111) Surfaces,"
*Applied Physics Letters* **99** (2011) 151917.

**Nice review →** A. Biswas, C.-H. Yang, R. Ramesh, and Y.H. Jeong,
"Atomically Flat Single Terminated Oxide Substrate Surfaces,"
*Progress in Surface Science* **92** (2017) 117-141.



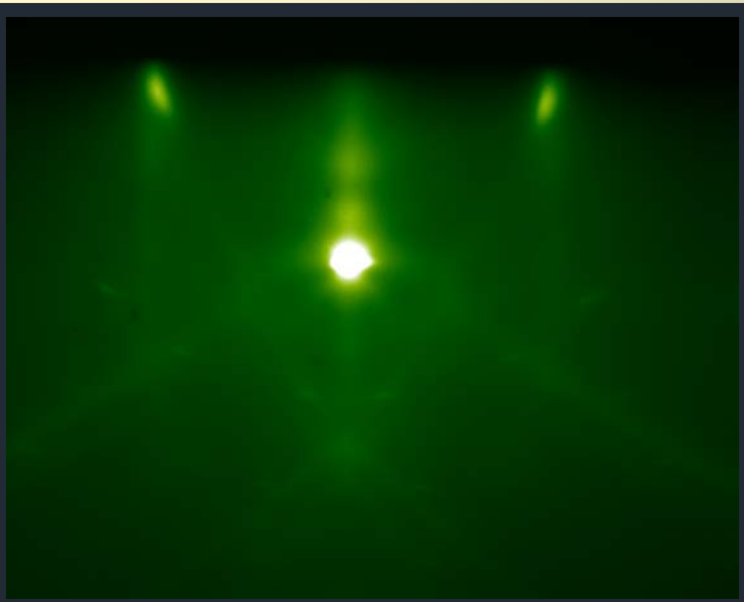

AFM (100) $SrTiO_3$—Jochen Mannhart

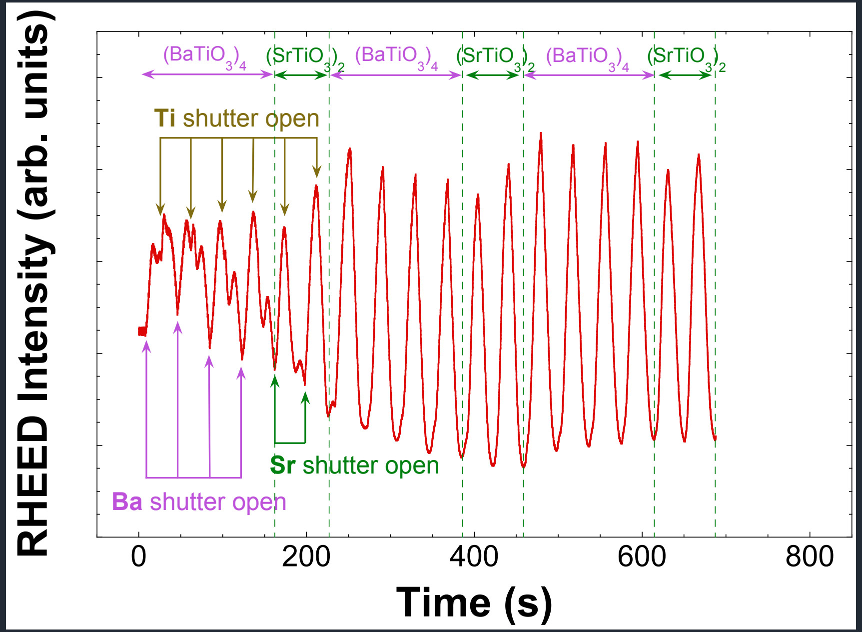




# Not Terminated vs. Terminated $SrTiO_3$

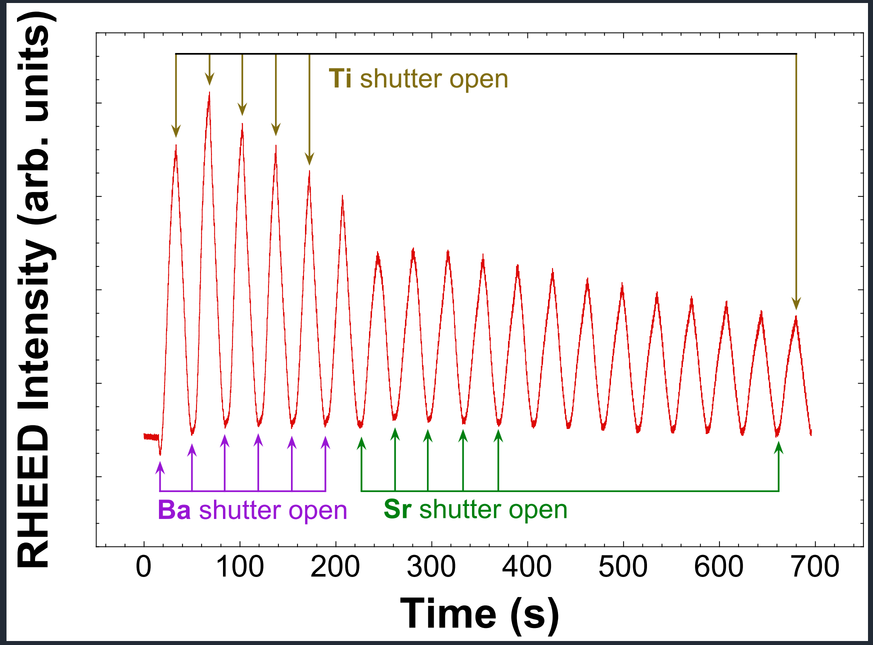
[110] azimuth






Not Terminated

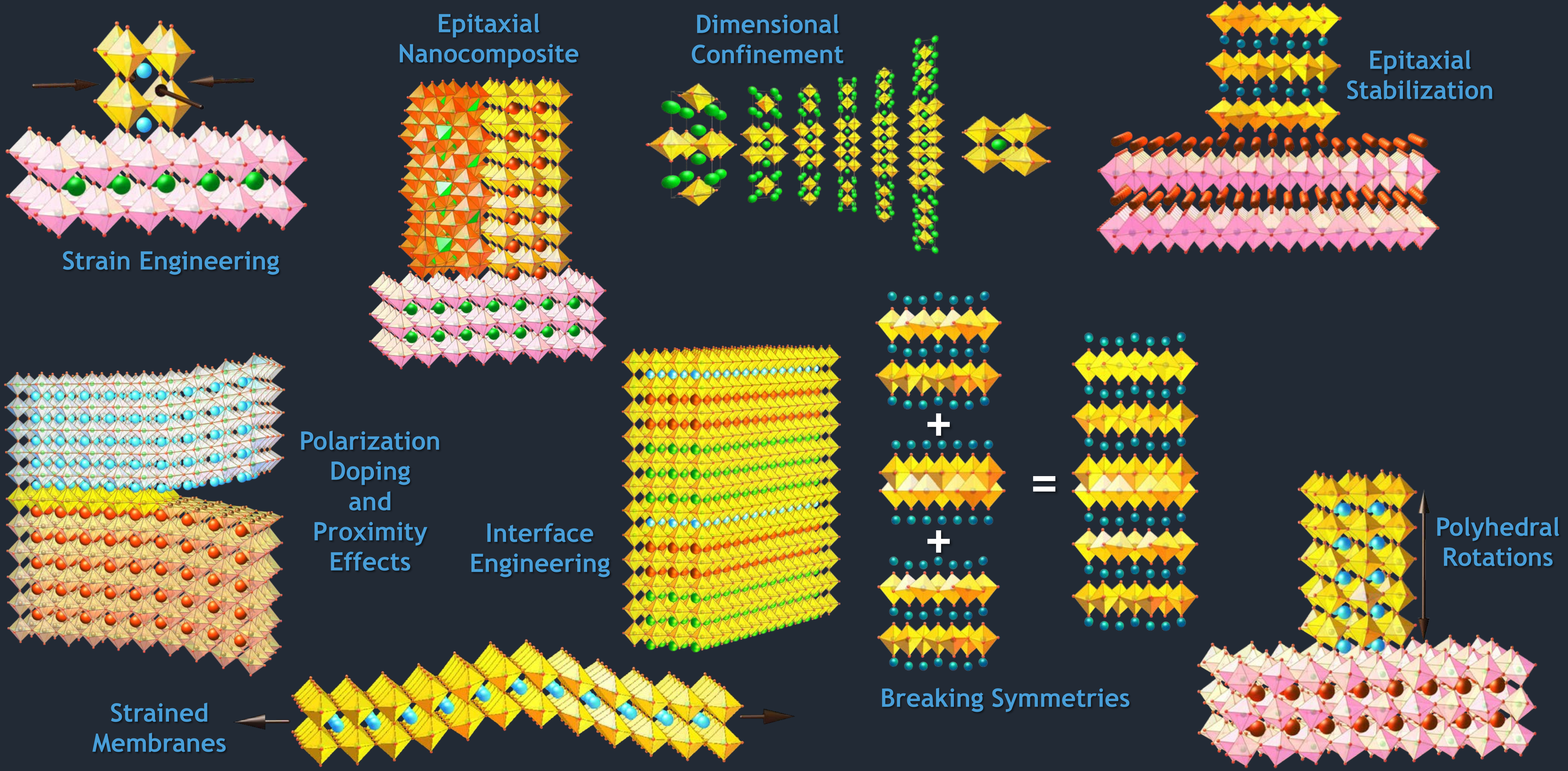
[100] azimuth



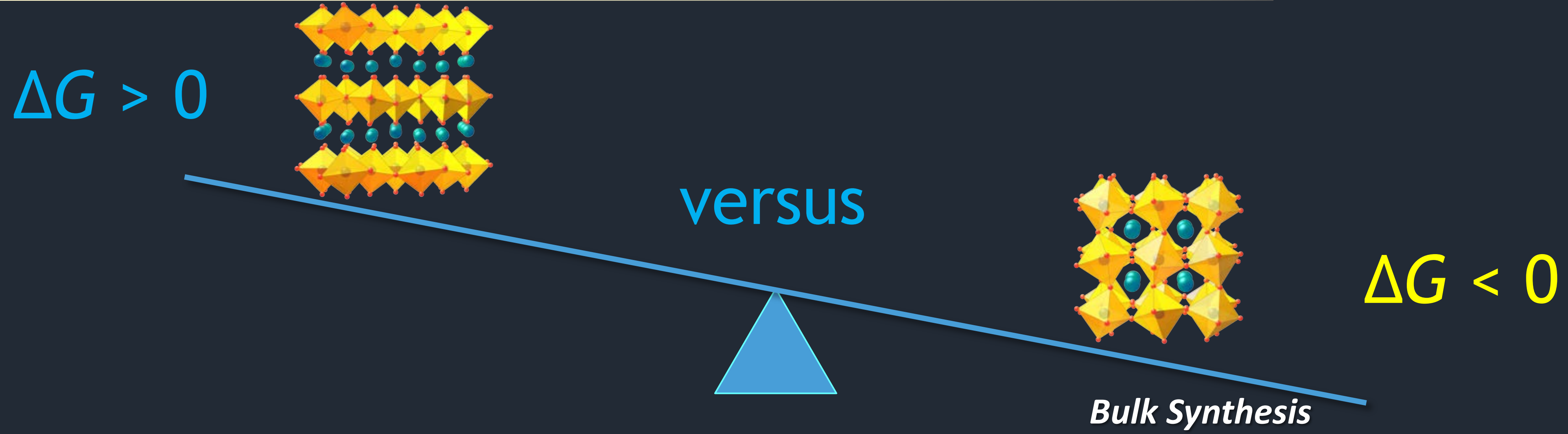

Terminated

A. Soukiassian, W. Tian, V. Vaithyanathan, J.H. Haeni, L.Q. Chen, X.X. Xi, D.G. Schlom, D.A. Tenne, H.P. Sun, X.Q. Pan, K.J. Choi, C.B. Eom, Y.L. Li, Q.X. Jia, C. Constantin, R.M. Feenstra, M. Bernhagen, P. Reiche, and R. Uecker, *Journal of Materials Research* **23** (2008) 1417–1432.

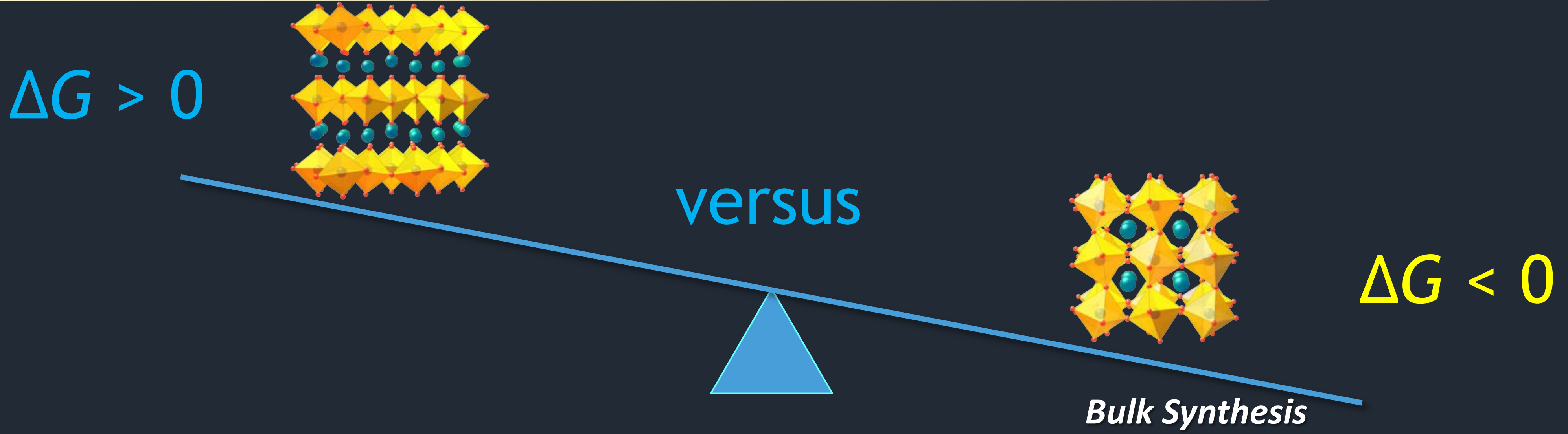
# Epitaxial Routes to Engineer Properties



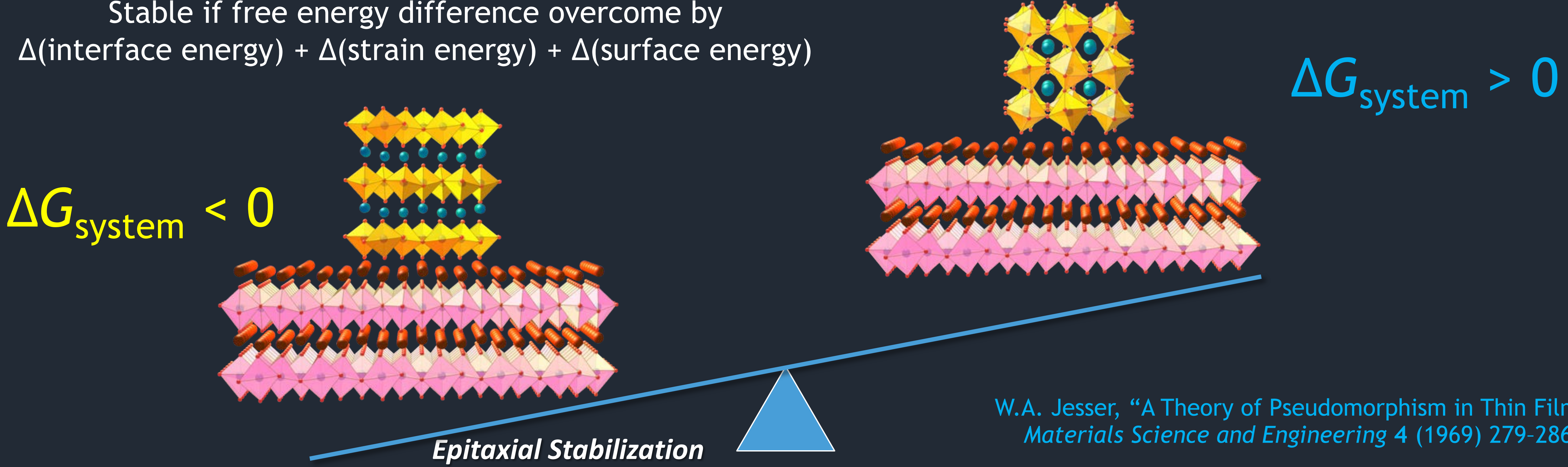
# Bulk Thermodynamics



# Thin-Film Thermodynamics




Stable if free energy difference overcome by
Δ(interface energy) + Δ(strain energy) + Δ(surface energy)




W.A. Jesser, "A Theory of Pseudomorphism in Thin Films," *Materials Science and Engineering* 4 (1969) 279-286.

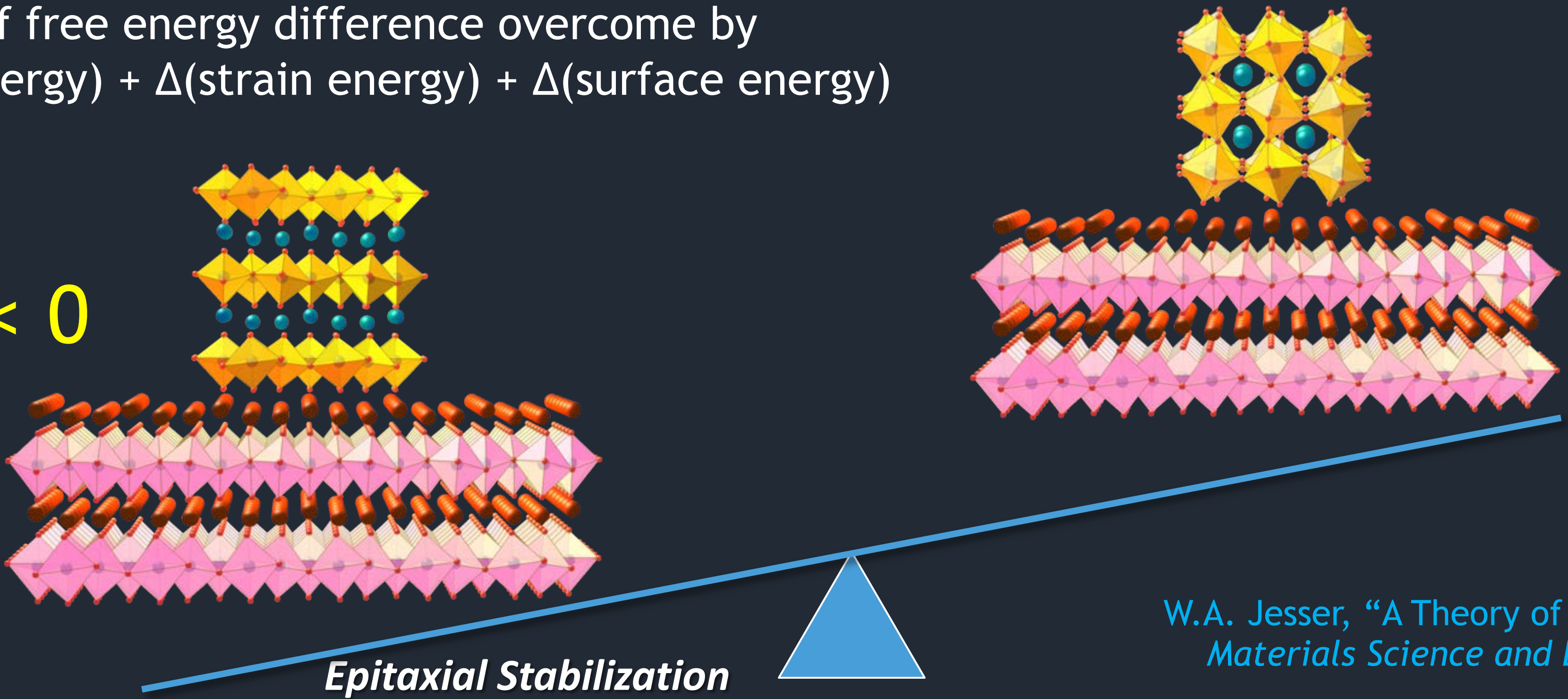
# Substrates are Key

"… the large interface-to-volume ratio found in thin bicrystal films can stabilize the overgrowth in the structure of the substrate rather than its normal bulk structure."

**William A. Jesser**

Stable if free energy difference overcome by
Δ(interface energy) + Δ(strain energy) + Δ(surface energy)

$\Delta G_{system} < 0$




$\Delta G_{system} > 0$


W.A. Jesser, "A Theory of Pseudomorphism in Thin Films," *Materials Science and Engineering* 4 (1969) 279-286.