PARADIM
AN NSF MATERIALS INNOVATION PLATFORM

Lecture #5—Suboxide MBE

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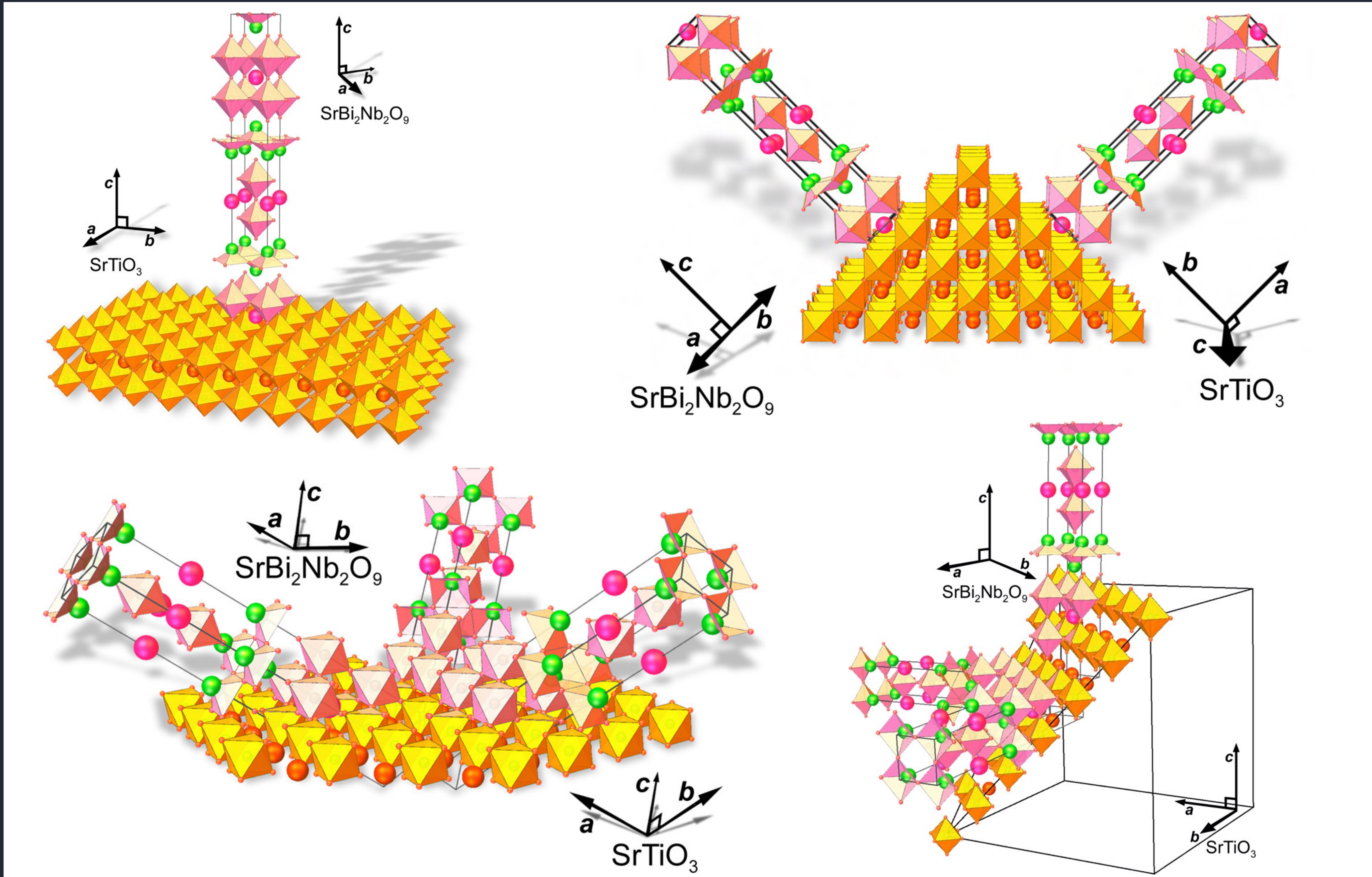
Department of Materials Science and Engineering
Cornell University

Kavli Institute at Cornell for Nanoscale Science

Leibniz-Institut für Kristallzüchtung

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.

RHEED of $YBa_2Cu_3O_7$

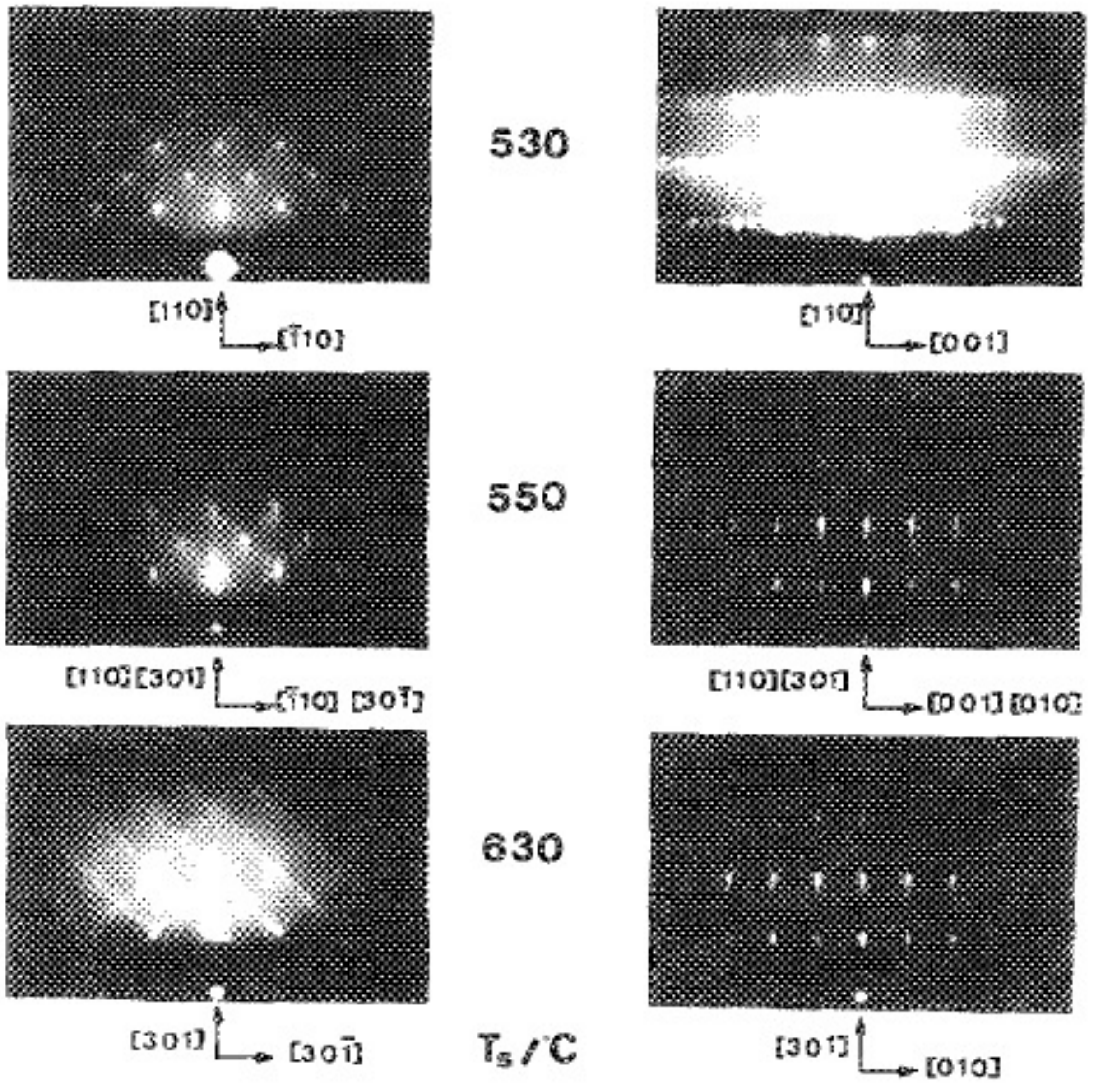
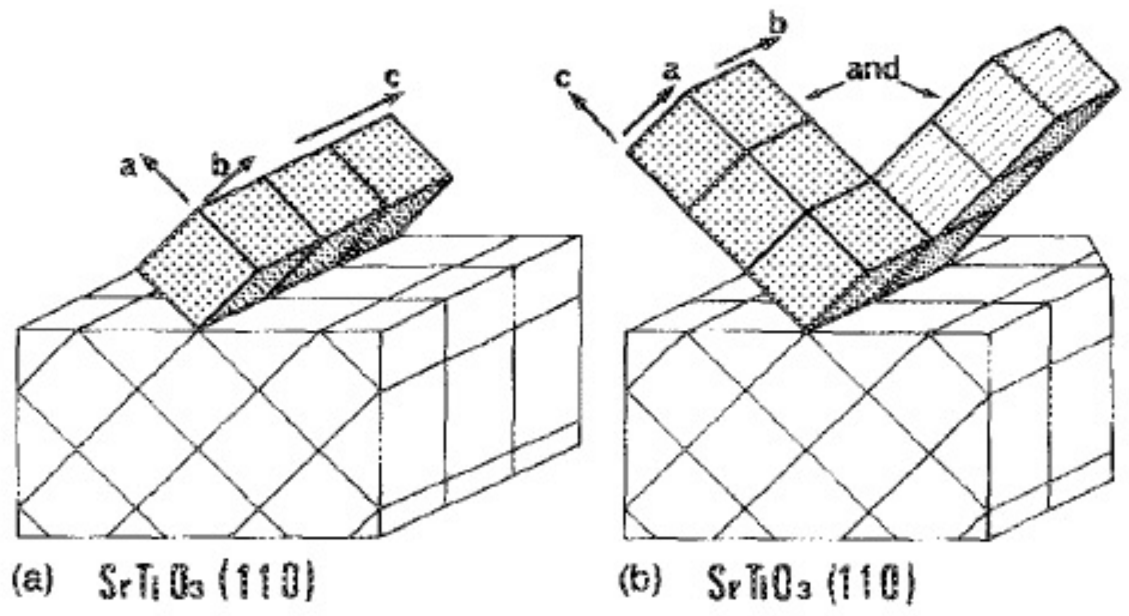
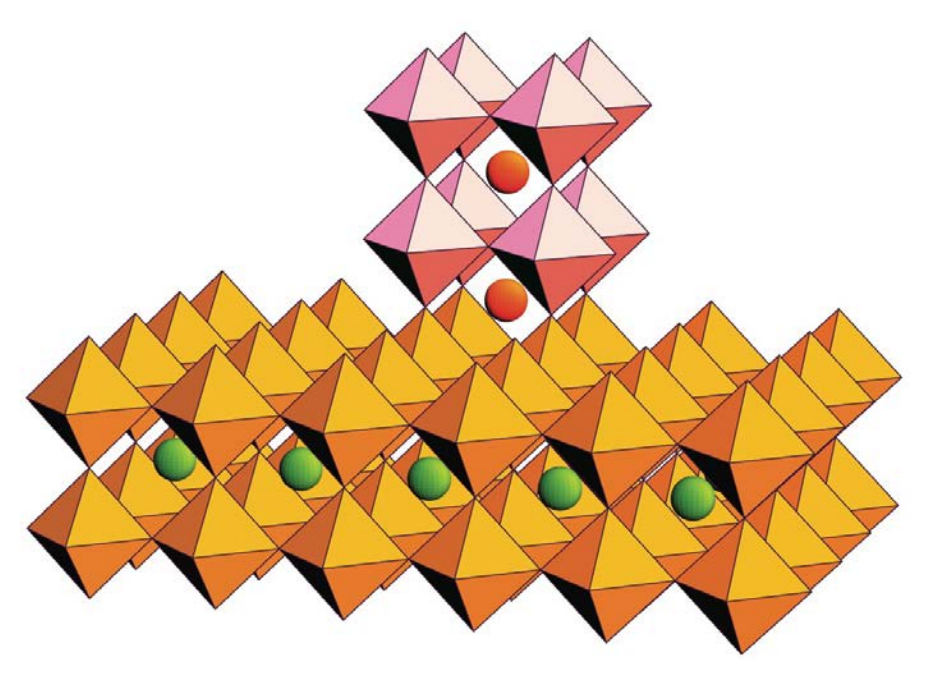


FIG. 1. Reflection high-energy electron diffraction (RHEED) patterns for the YBCO films grown at various temperatures.



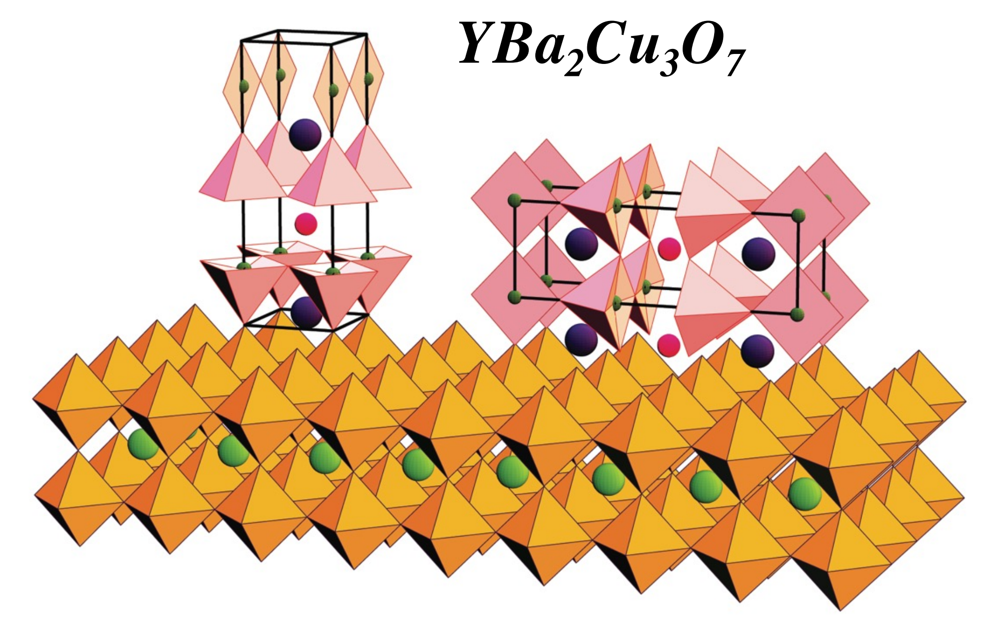
T. Terashima, Y. Bando, K. Iijima, K. Yamamoto, K. Hirata, "Epitaxial Growth of $YBa_2Cu_3O_{7-x}$ Thin Films on (110) $SrTiO_3$ Single Crystals by Activated Reactive Evaporation," *Appl Phys Lett*. **53** (1988) 2232–2234.

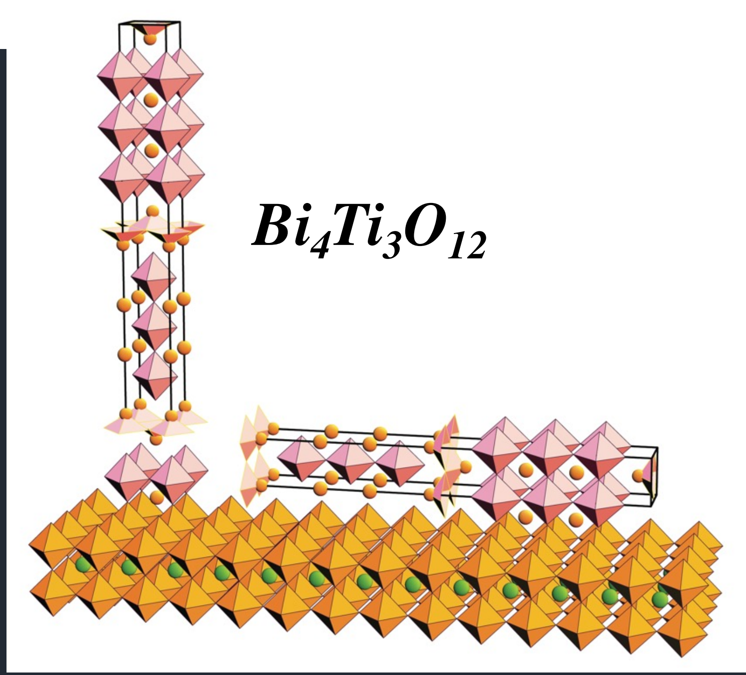
Epitaxial Growth



ABO_3 / $A'B'O_3$

“Cube-on-Cube”

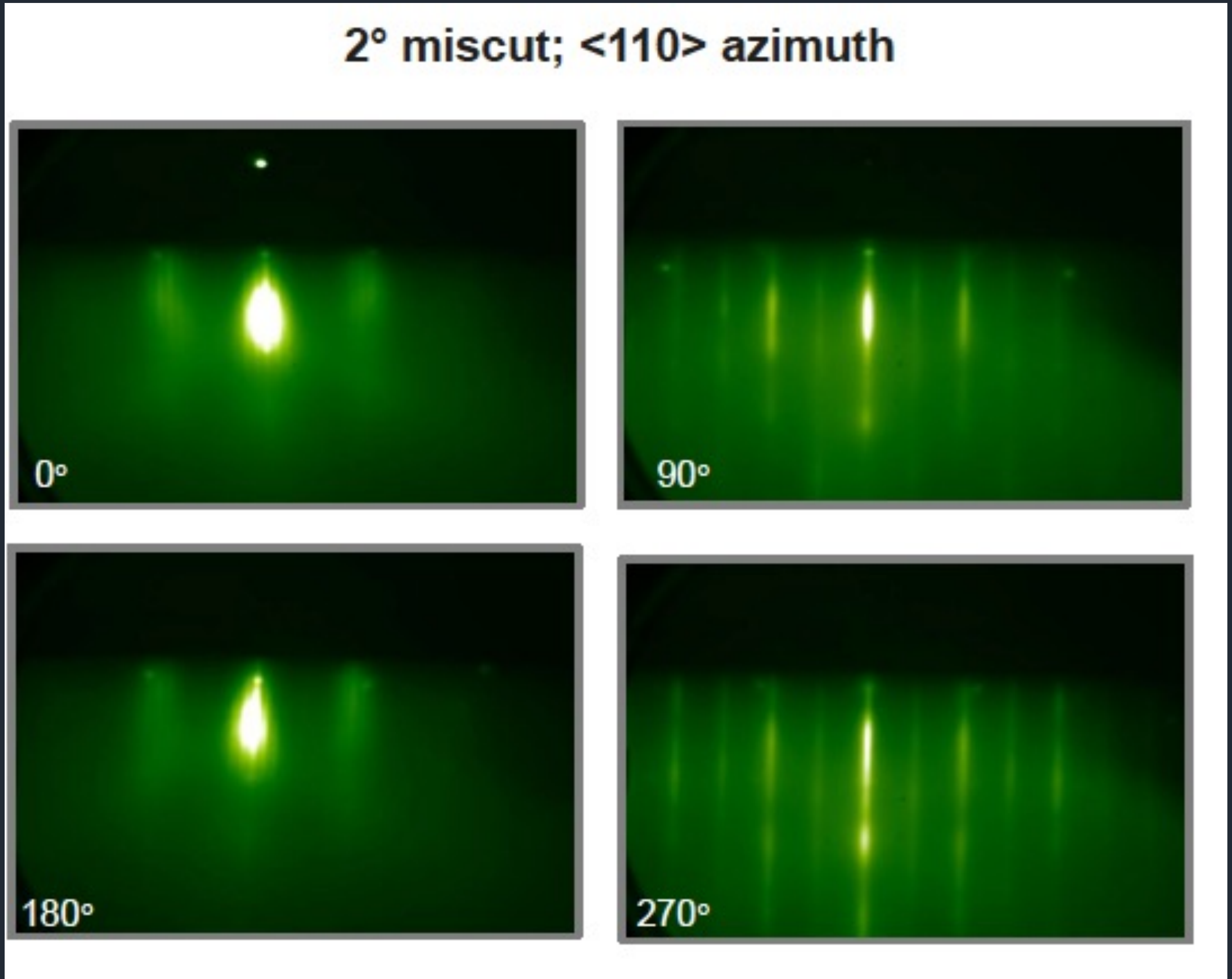


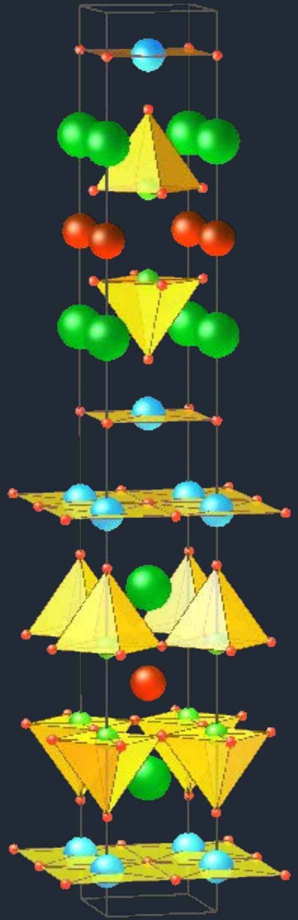


R. Ramesh and D.G. Schlom, *Science* **296** (2002) 1975–1976.

RHEED of $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212)

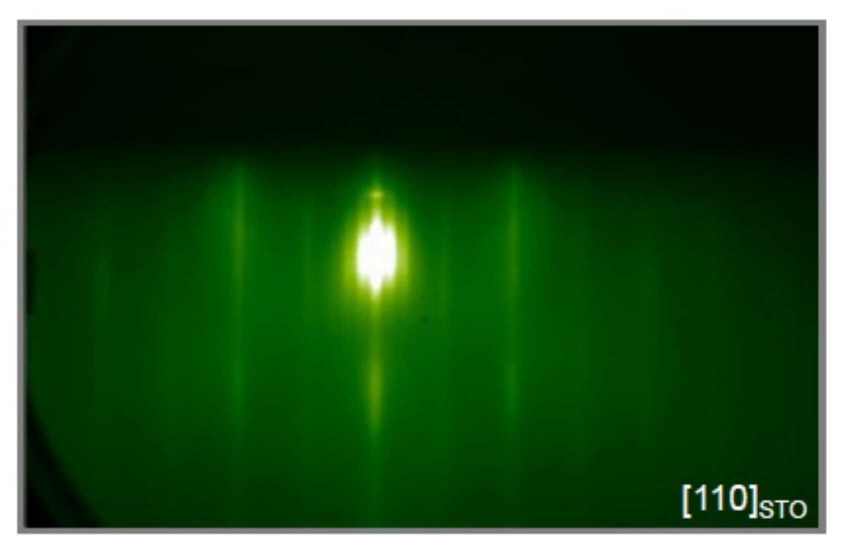
untwinned film





twinned film

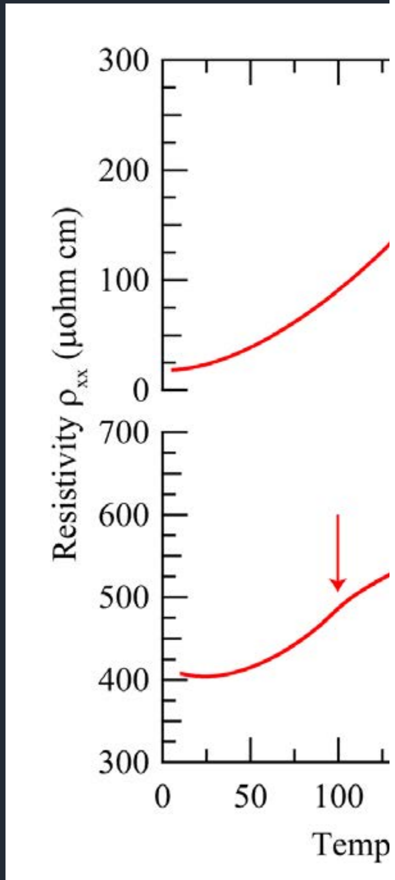
(90° in-plane rotation twins)



Benc… …s

Best PL… …e Crystal

$\rho_{300\ K}$ / $\rho_{1…}$ … $_{…0\ K}$ = 192



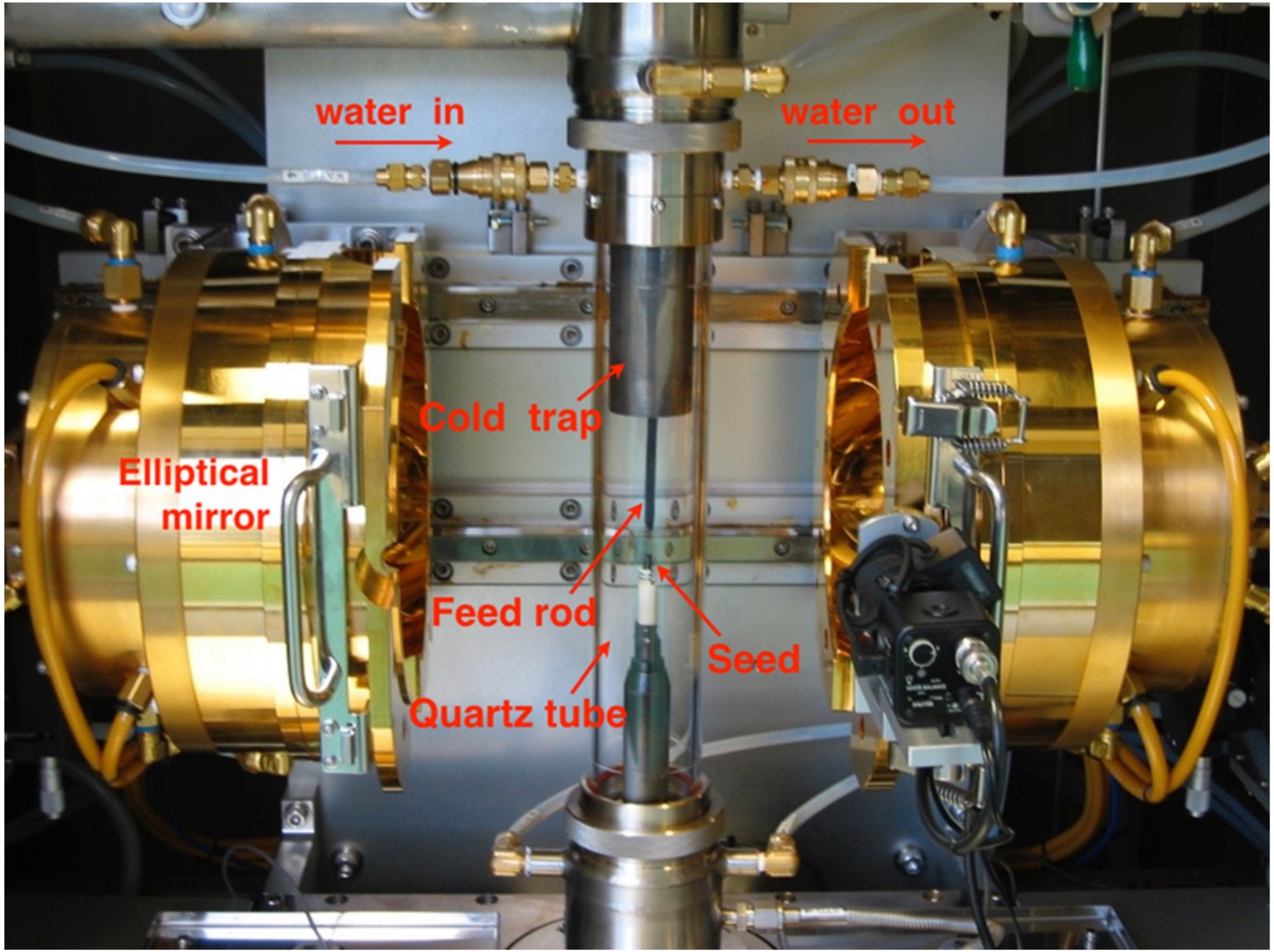
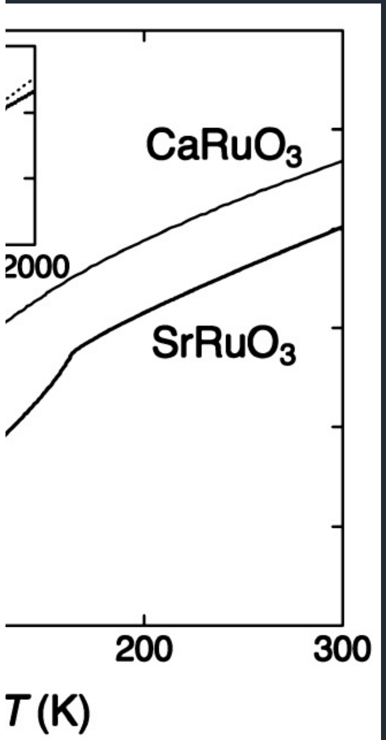


Figure 1. Photograph of an infrared image furnace. In this study, we employed a cold trap in which water is circulating during the growth.



~20 nm $SrRuO_3$ …

…gle crystal

D. Kan, R. Aso, H. Kura…
J. Appl. Phys. **113**…

…mbach, J.S. Brooks,
…ji, and Y. Maeno,
…n **15** (2015) 5573-5577.

Outline of MBE Lectures

- What is MBE and what is it good for?
  Lecture #1 — Greatest hits of MBE
- How to grow your favorite oxide by MBE?
  Lectures #2-4 — Nuts and bolts of oxide MBE
- Detailed Examples of Oxide MBE
  Lectures #5,6 — Suboxide MBE
  High Purity Synthesis of Binary Oxides
- How can I gain access to an oxide MBE if I don't have one?
  Use PARADIM's oxide MBE (+ ARPES + ...)

Why Ga_2O_3?

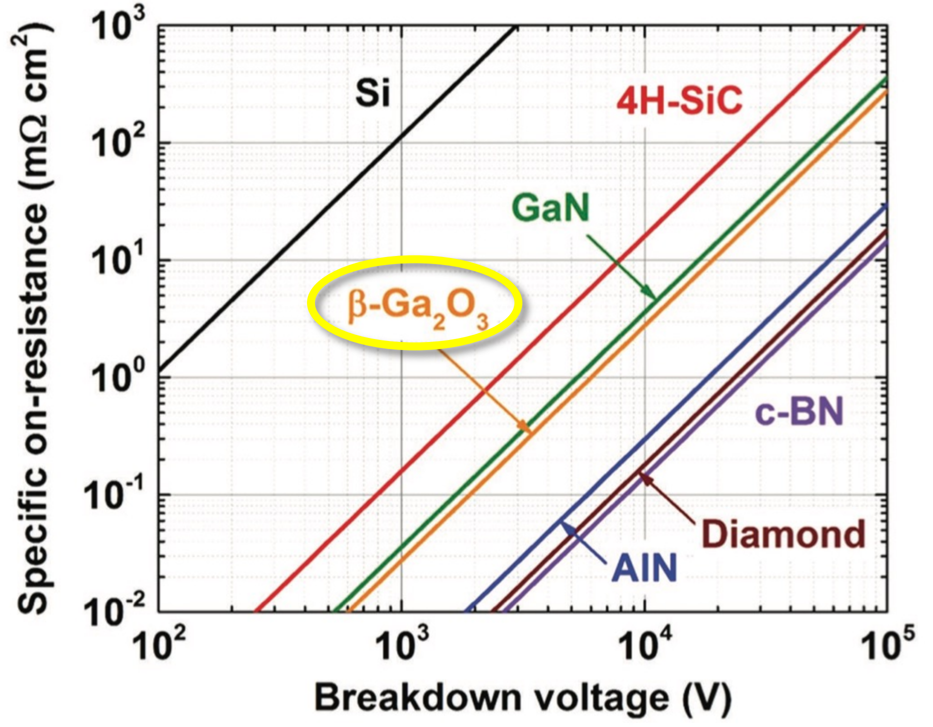


Figure 1. Contours of constant Baliga figure-of-merit (BFOM) for various conventional, WBG and UWBG semiconductors, drawn on a log-log specific on-resistance versus breakdown voltage plot. This is the figure-of-merit of interest for low-frequency unipolar vertical power switches; the lower right region represents higher BFOM, hence higher performance.

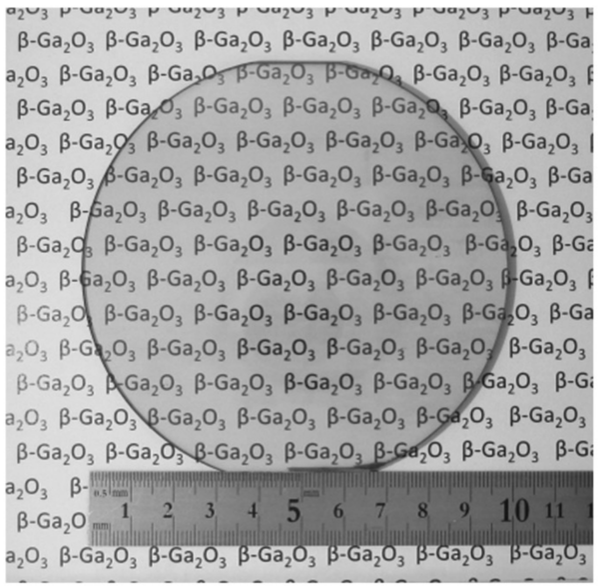


Figure 6. Photograph of transparent 4″-diameter single-crystal Ga_2O_3 wafer. Copyright Tamura Corporation via Masataka Higashiwaki, National Institute of Information and Communications Technology.

4" β-Ga_2O_3 Single-Crystal Substrate

J.Y. Tsao, S. Chowdhury, M.A. Hollis, D. Jena, N.M. Johnson, K.A. Jones, R.J. Kaplar, S. Rajan, C.G.V. de Walle, E. Bellotti, C.L. Chua, R. Collazo, M.E. Coltrin, J.A. Cooper, K.R. Evans, S. Graham, T.A. Grotjohn, E.R. Heller, M. Higashiwaki, M.S. Islam, P.W. Juodawlkis, M.A. Khan, A.D. Koehler, J.H. Leach, U.K. Mishra, R.J. Nemanich, R.C.N. Pilawa-Podgurski, J.B. Shealy, Z. Sitar, M.J. Tadjer, A.F. Witulski, M. Wraback, and J.A. Simmons, "Ultrawide-Bandgap Semiconductors: Research Opportunities and Challenges," *Advanced Electronic Materials* 4 (2018) 1600501.

β-Ga_2O_3 has High Bandgap

E_g = 4.7 eV

High Breakdown Field

E_{max} ≈ 5 MV/cm

High Baliga Figure of Merit

Dopable *n*-Type with good mobility

E_D ≈ 0.02 eV (Si)

μ ≈ 200 cm^2/(V·s)

Thermal Conductivity

k = 11-29 W/(m K)

Conventional (Ga) MBE of β-Ga_2O_3

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Low Growth Rate

- Growth Rate: **0.2 µm/hr** (maximum reported is 0.7 µm/hr)
- Peak Mobility at this Growth Rate: **120 $cm^2/(V \cdot s)$** at room temperature

E. Ahmadi, O.S. Koksaldi, S.W. Kaun, Y. Oshima, D.B. Short, U.K. Mishra, and J.S. Speck, "Ge Doping of β-Ga_2O_3 Films Grown by Plasma-Assisted Molecular Beam Epitaxy," *Applied Physics Express* **10** (2017) 041102.

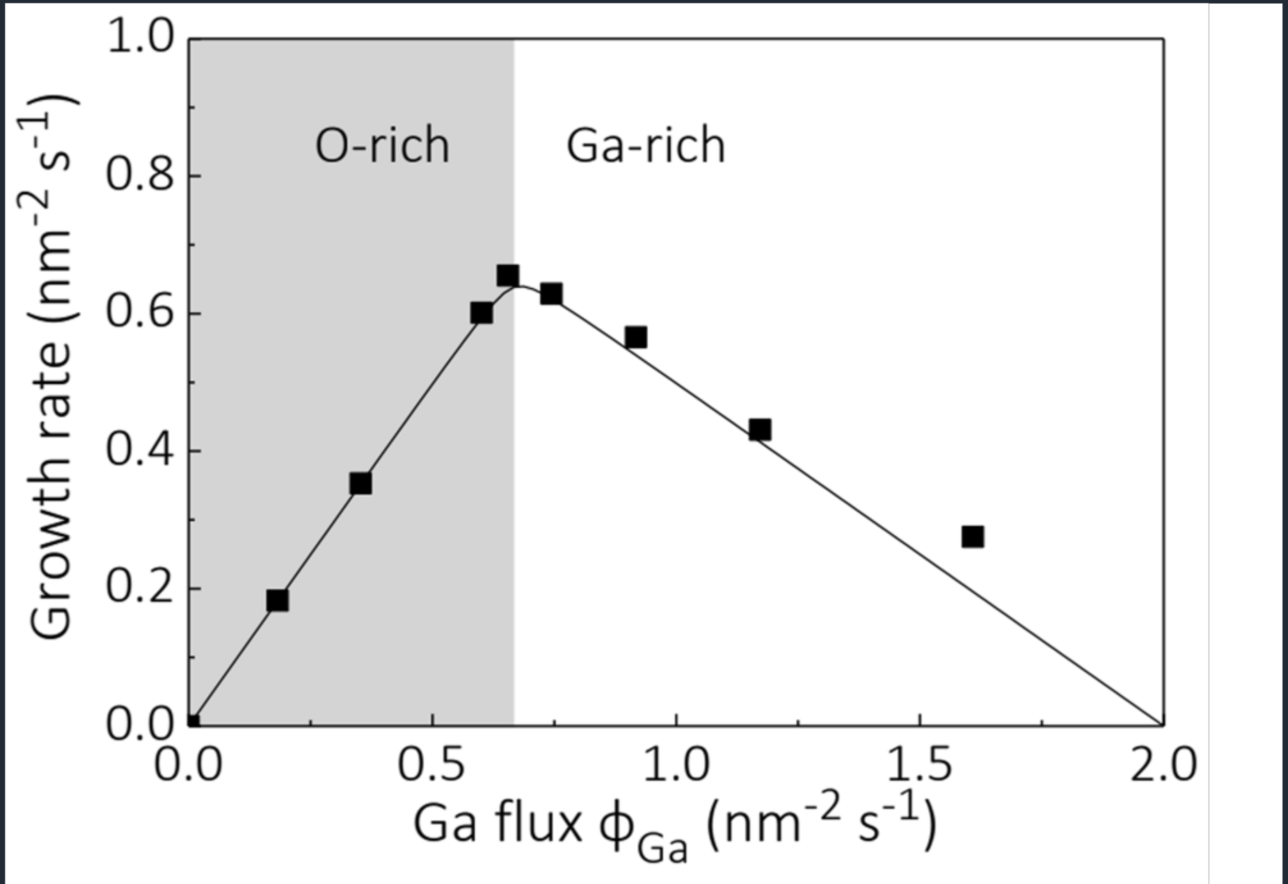
MOCVD is considerably better

- Growth Rate: ~**0.5 µm/hr** (up to 10 µm/hr reported)
- Peak Mobility at this Growth Rate: **194 $cm^2/(V \cdot s)$** at room temperature

Z. Feng, A.F.M.A.U. Bhuiyan, Z. Xia, W. Moore, Z. Chen, J.F. McGlone, D.R. Daughton, A.R. Arehart, S.A. Ringel, S. Rajan, and H. Zhao, "Probing Charge Transport and Background Doping in Metal-Organic Chemical Vapor Deposition-Grown (010) β-Ga_2O_3," *Physica Status Solidi RRL* **14** (2020) 2000145.

Can MBE be improved for the growth of *β*-Ga_2O_3?

Conventional (Ga) MBE of β-Ga_2O_3



P. Vogt and O. Bierwagen,
"The Competing Oxide and Sub-Oxide Formation in Metal-Oxide Molecular Beam Epitaxy,"
Applied Physics Letters **106** (2015) 081910.

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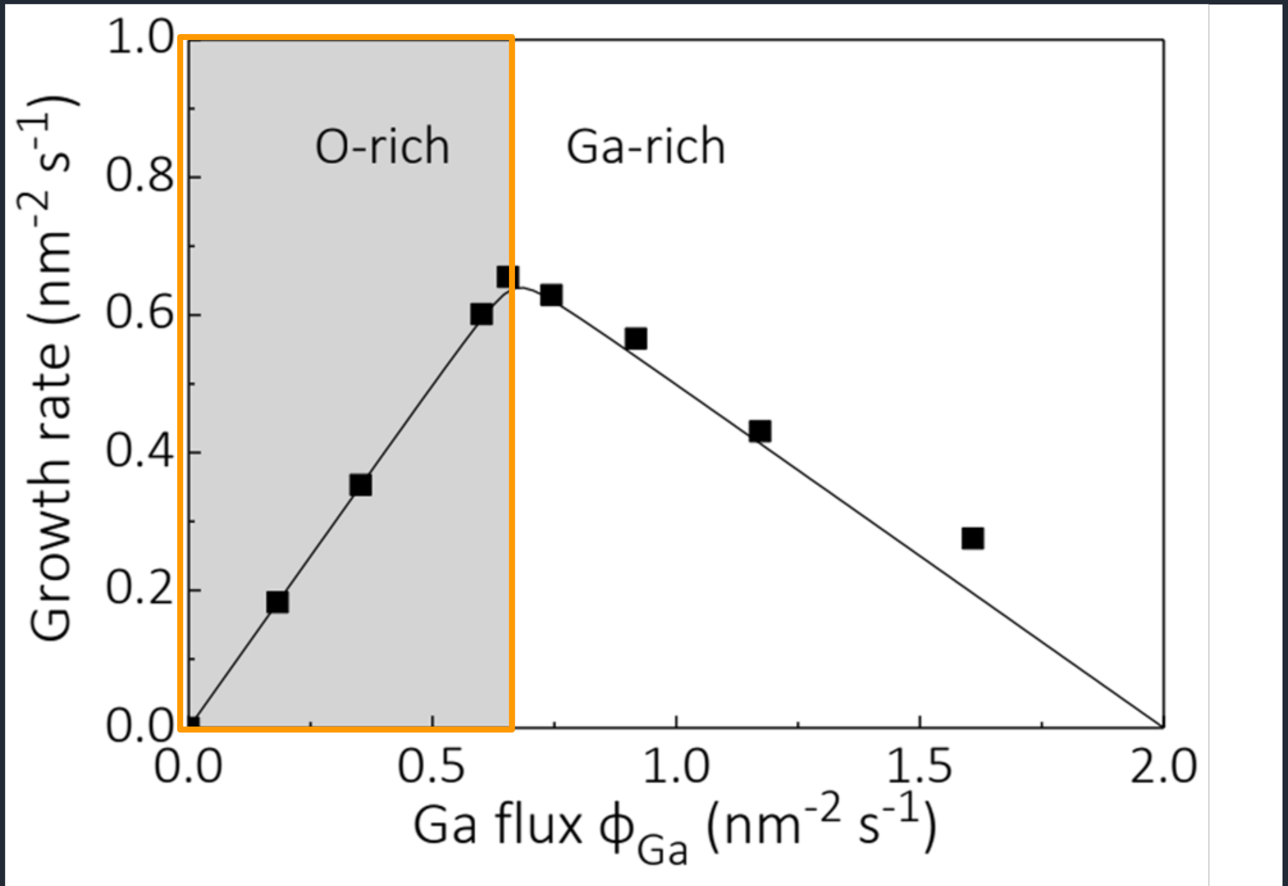

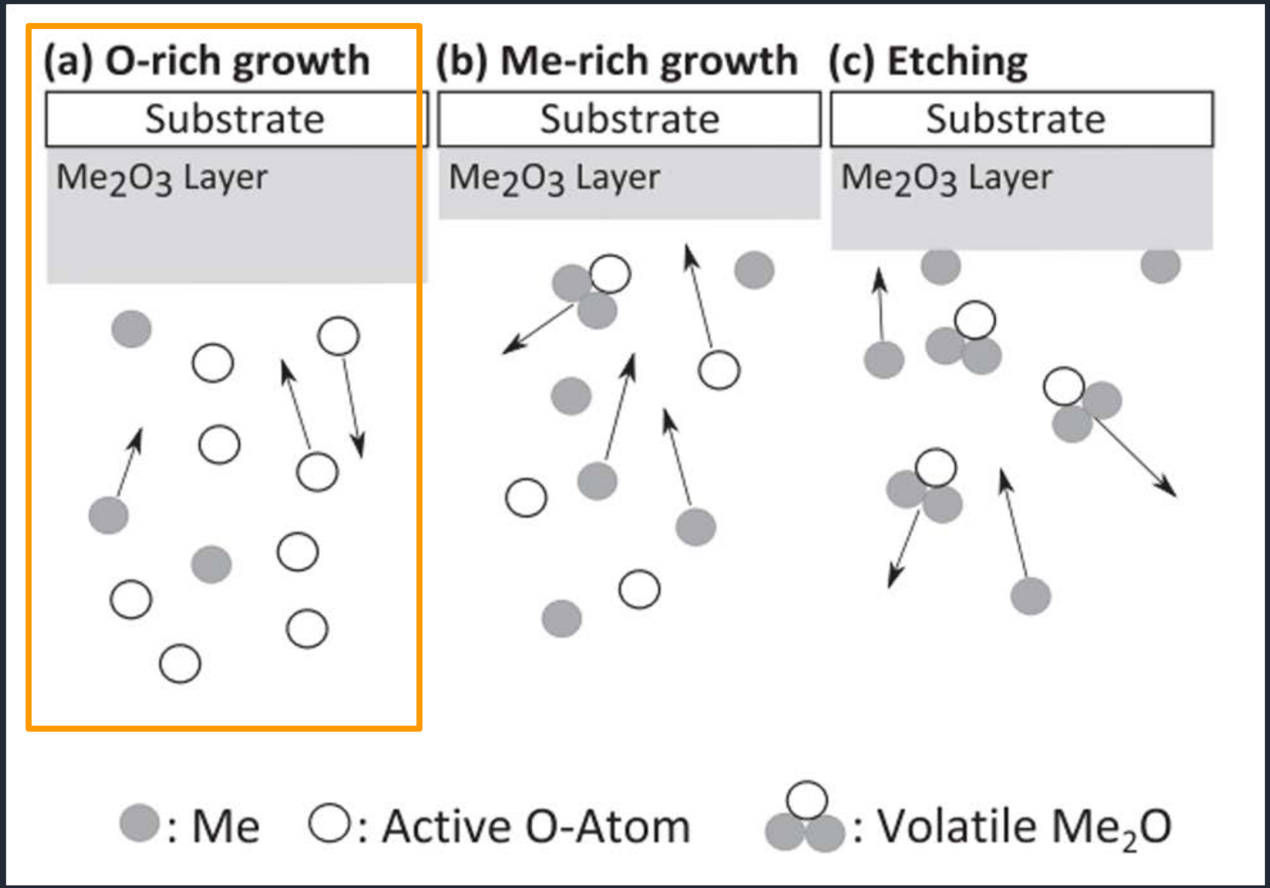

<u>2-step reaction mechanism explains:</u>

$\phi_{Ga} = 2/3\ \phi_O$: 2 Ga(g) + 3 O(g) → Ga_2O + 2 O → Ga_2O_3 (s) (full Ga incorporation)

$\phi_{Ga} = 2\phi_O$: 6 Ga(g) + 3 O(g) → 3 Ga_2O … no oxygen → no Ga_2O_3(s) formation

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"The Competing Oxide and Sub-Oxide Formation in Metal-Oxide Molecular Beam Epitaxy,"
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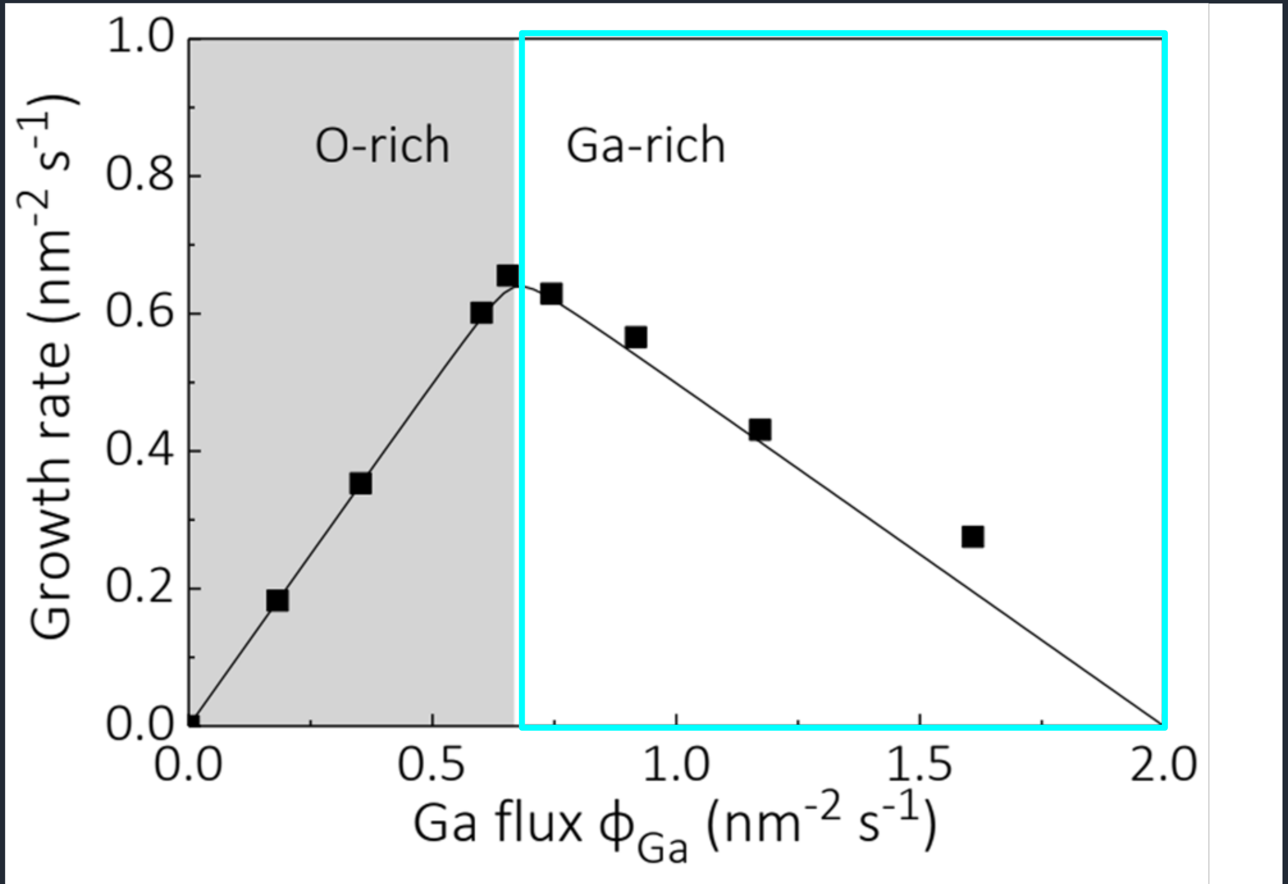
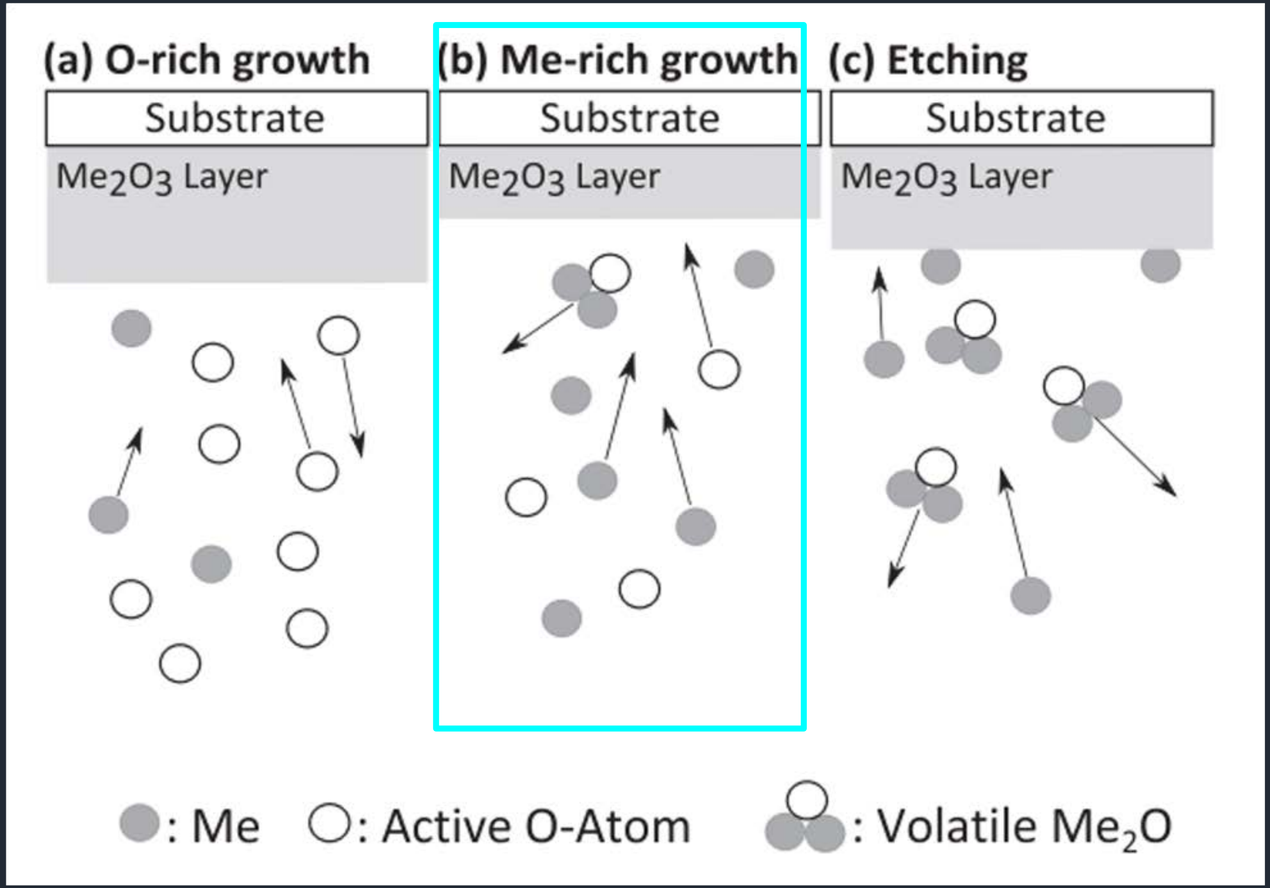
P. Vogt and O. Bierwagen,
"Quantitative Subcompound-Mediated Reaction Model for the Molecular Beam Epitaxy of III-VI and IV-VI Thin Films: Applied to Ga_2O_3, In_2O_3, and SnO_2,"
Physical Review Materials **2** (2018) 120401.

Conventional (Ga) MBE of β-Ga_2O_3





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Conventional (Ga) MBE of β-Ga_2O_3

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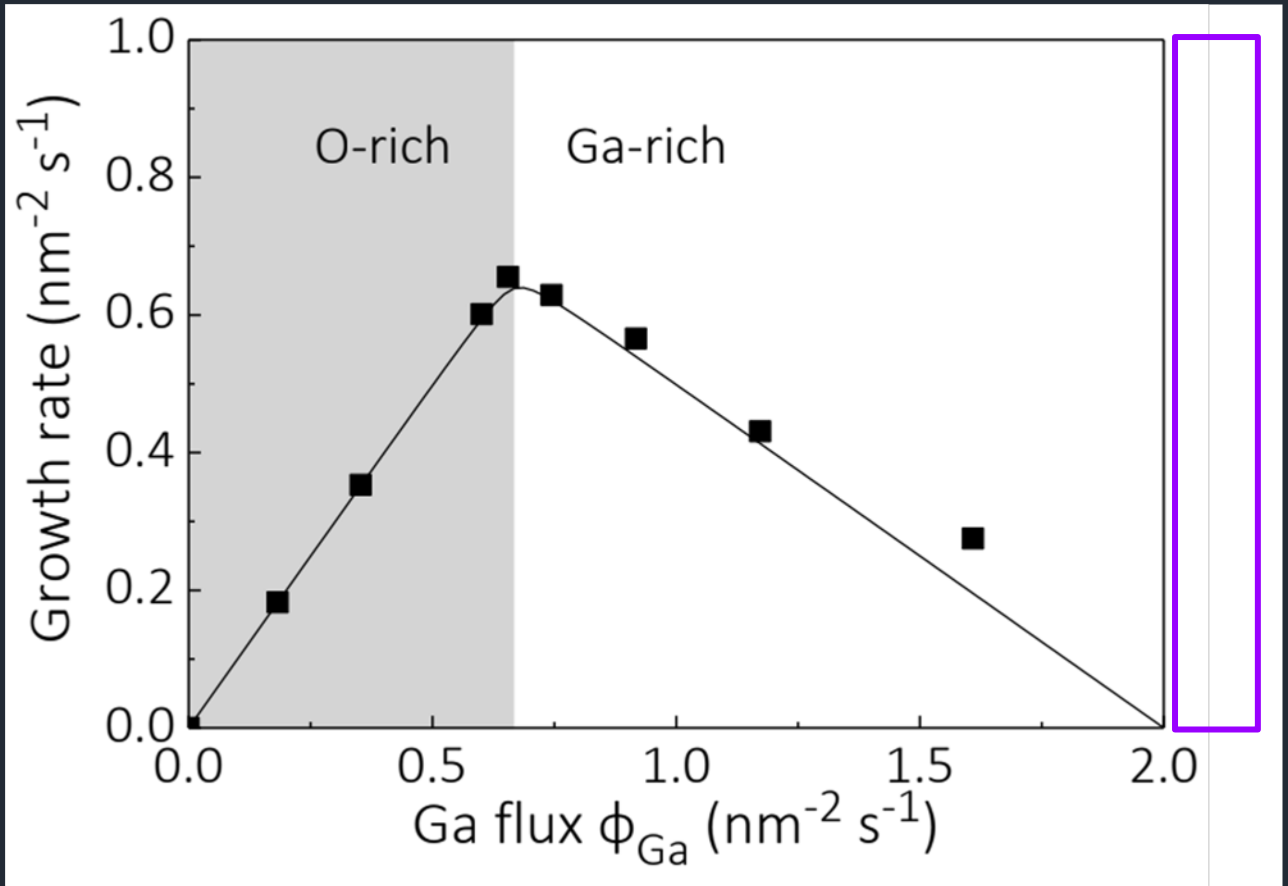

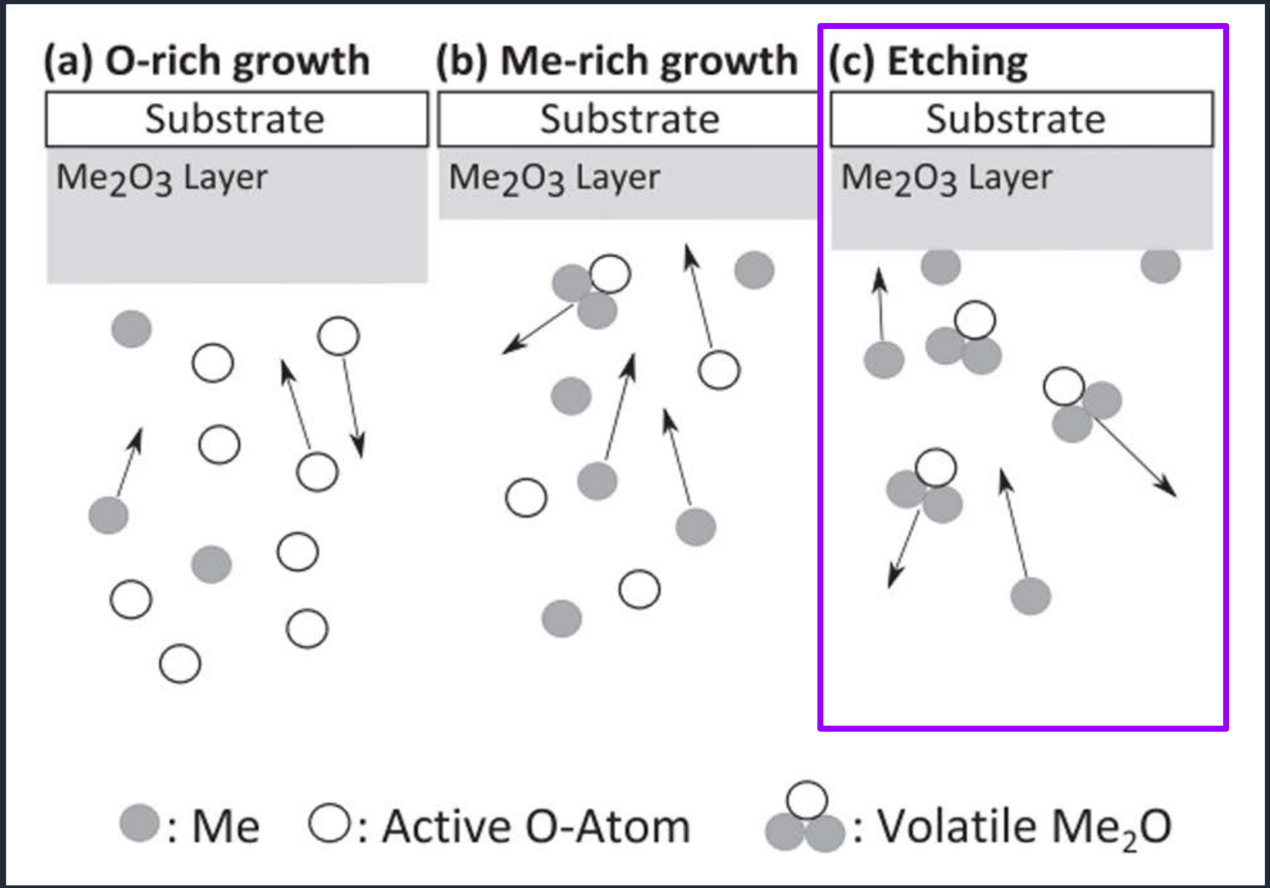

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Applied Physics Letters **106** (2015) 081910.

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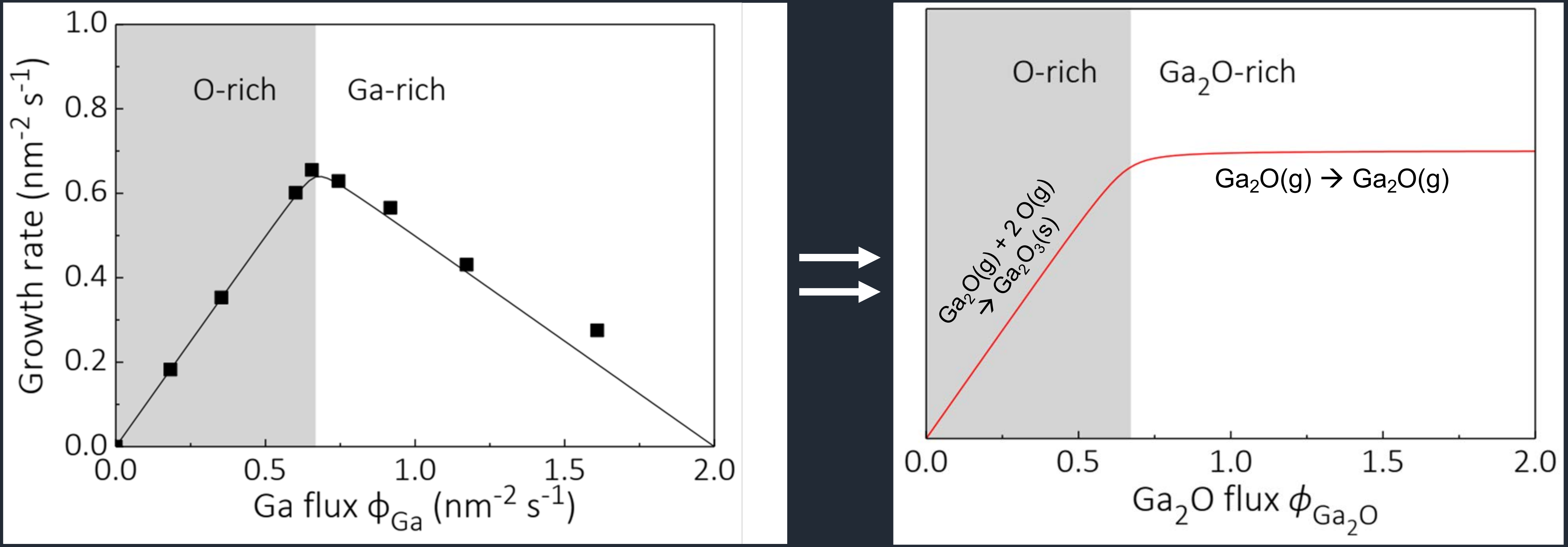
"Quantitative Subcompound-Mediated Reaction Model for the Molecular Beam Epitaxy of III-VI and IV-VI Thin Films: Applied to Ga_2O_3, In_2O_3, and SnO_2,"
Physical Review Materials **2** (2018) 120401.

Suboxide (Ga_2O) MBE of β-Ga_2O_3



2-step reaction mechanism explains:

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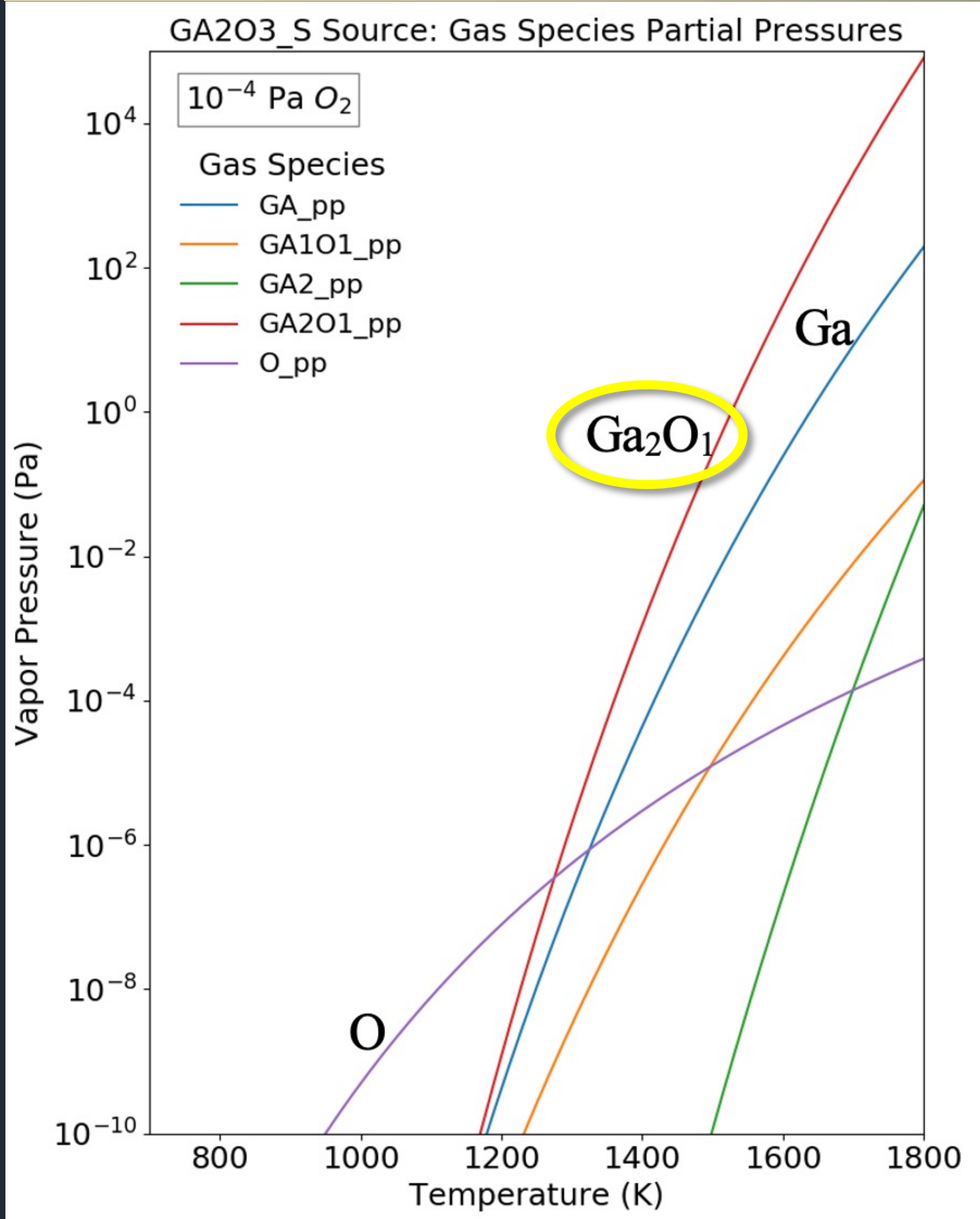
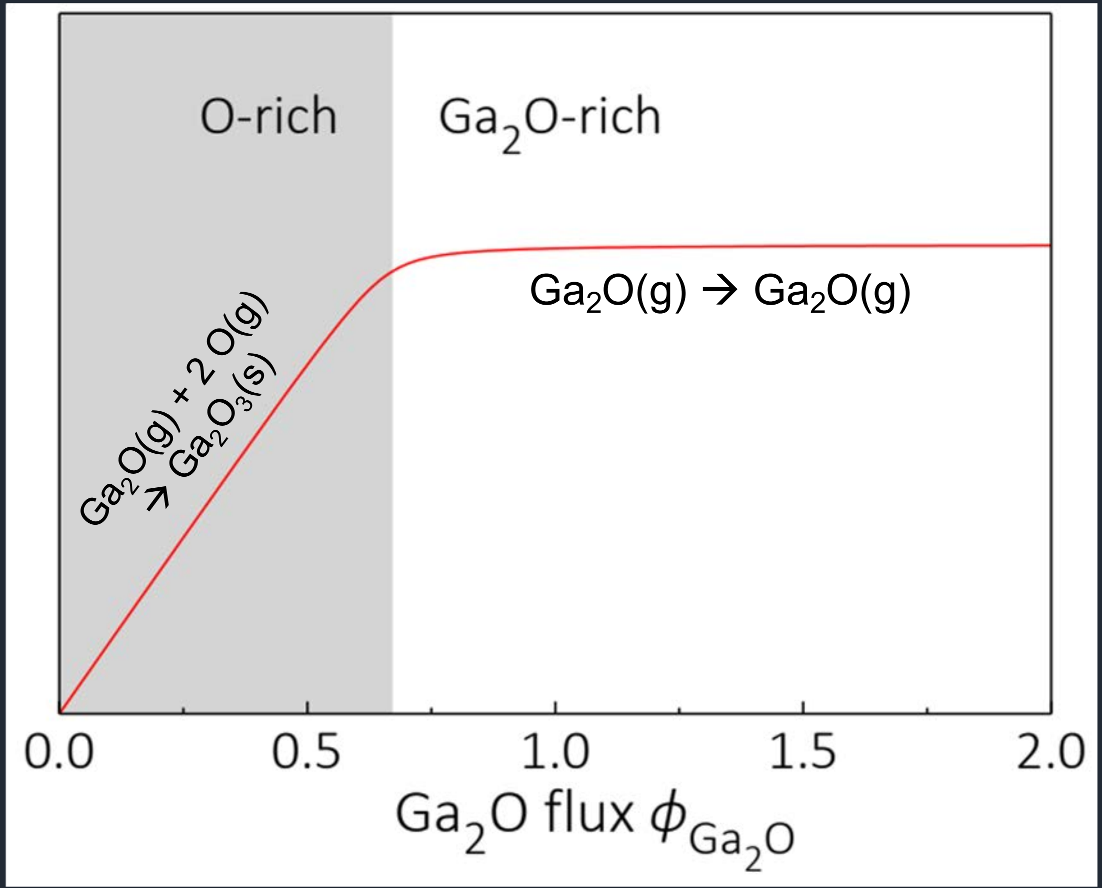
$\phi_{Ga} = 2\phi_O$: ~~6 Ga(g) + 3 O(g)~~ → 3 Ga_2O … no oxygen → no Ga_2O_3(s) formation

Use Ga_2O_3(s) rather than Ga(ℓ)?





K.M. Adkison, S-L. Shang, B.J. Bocklund, D. Klimm, D.G. Schlom, and Z.K. Liu, "Suitability of Binary Oxides for Molecular-Beam Epitaxy Source Materials: A Comprehensive Thermodynamic Analysis," *APL Materials* **8** (2020) 081110.

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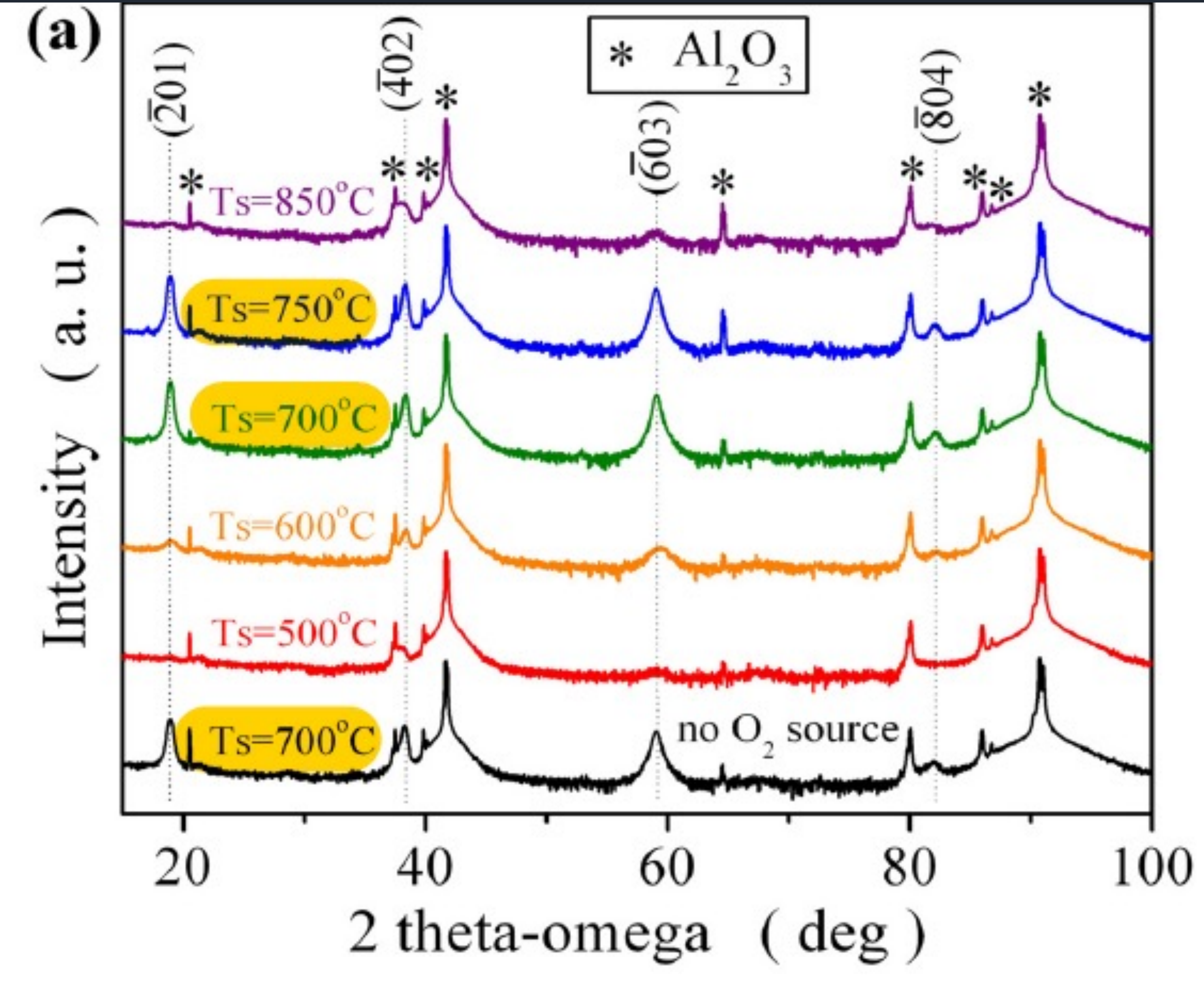

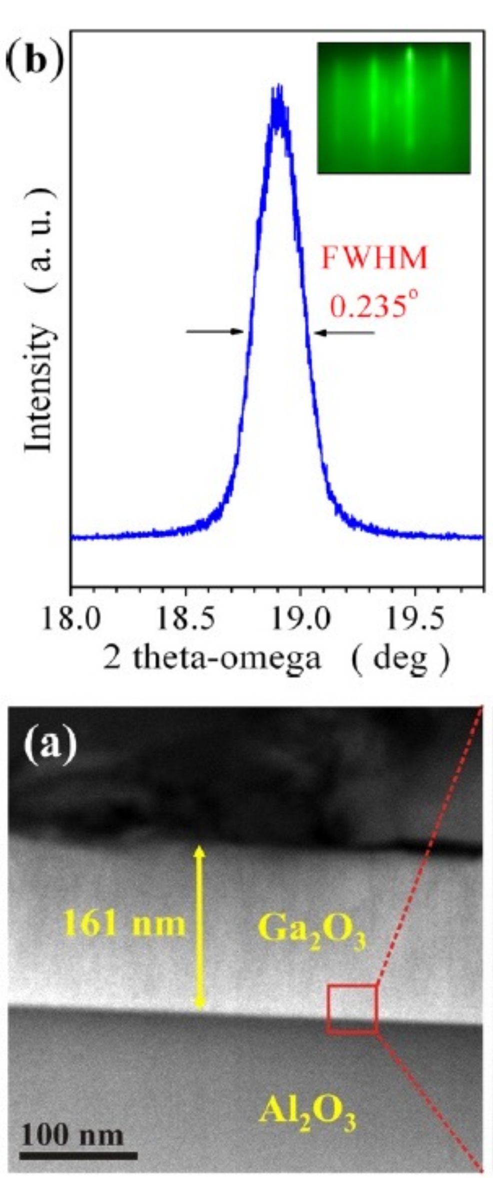

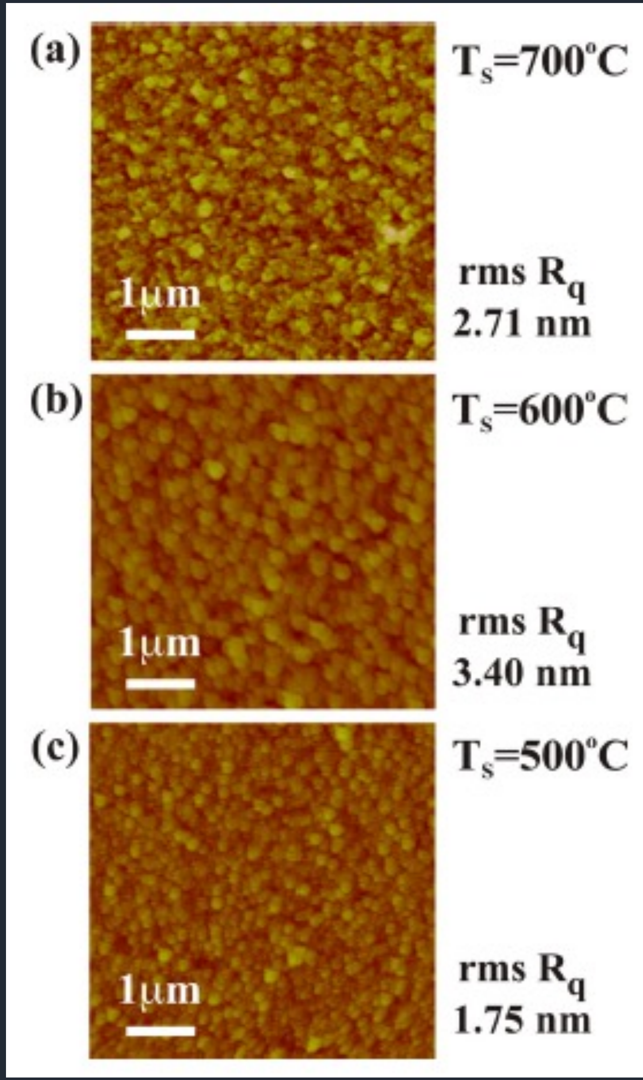

S. Ghose, S. Rahman, L. Hong, J.S. Rojas-Ramirez, H. Jin, K. Park, R. Klie, and R. Droopad, "Growth and Characterization of β-Ga_2O_3 Thin Films by Molecular Beam Epitaxy for Deep-UV Photodetectors," *Journal of Applied Physics* **122** (2017) 095302.

Use Ga_2O_3(s) rather than Ga(ℓ)?

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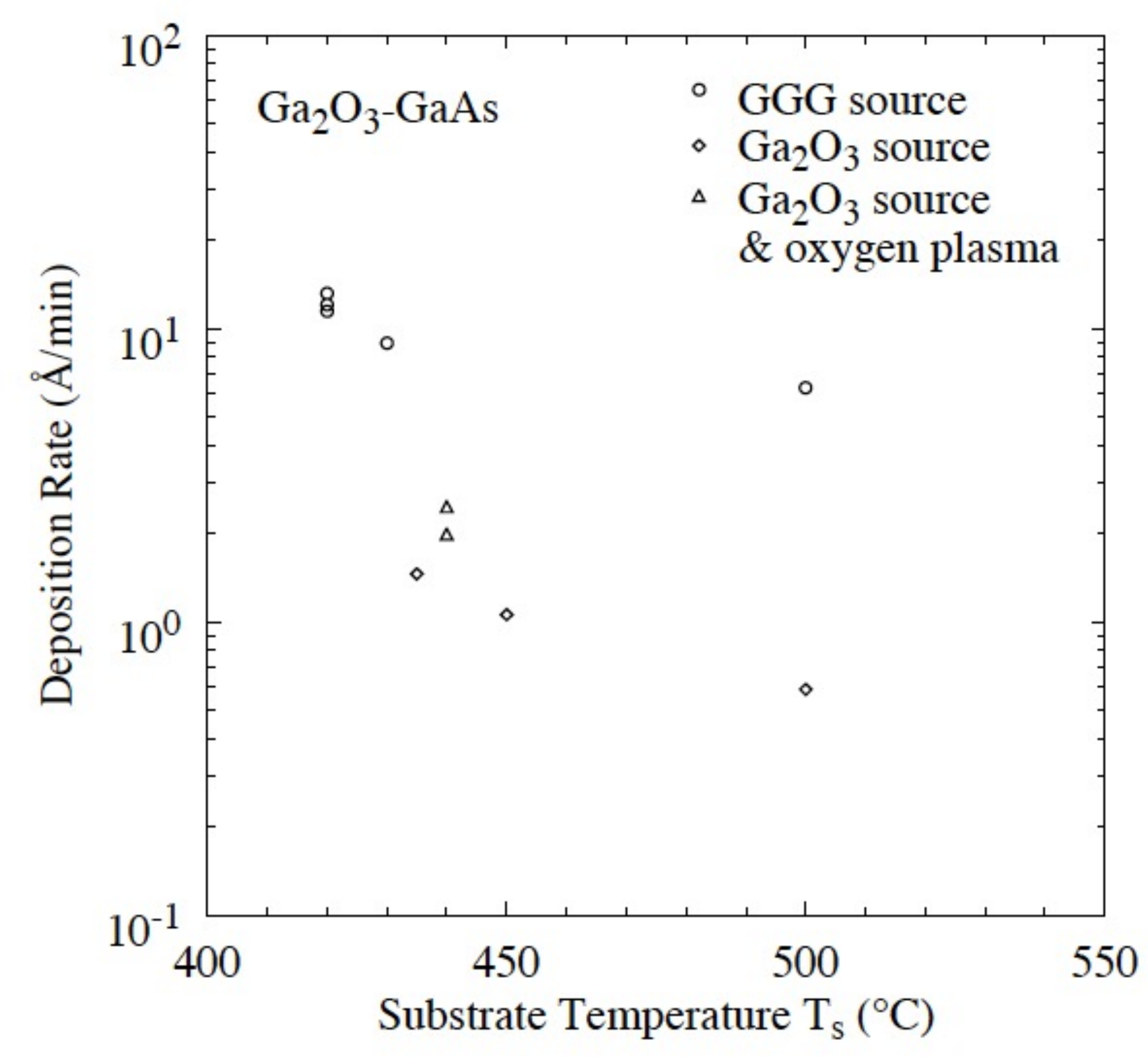


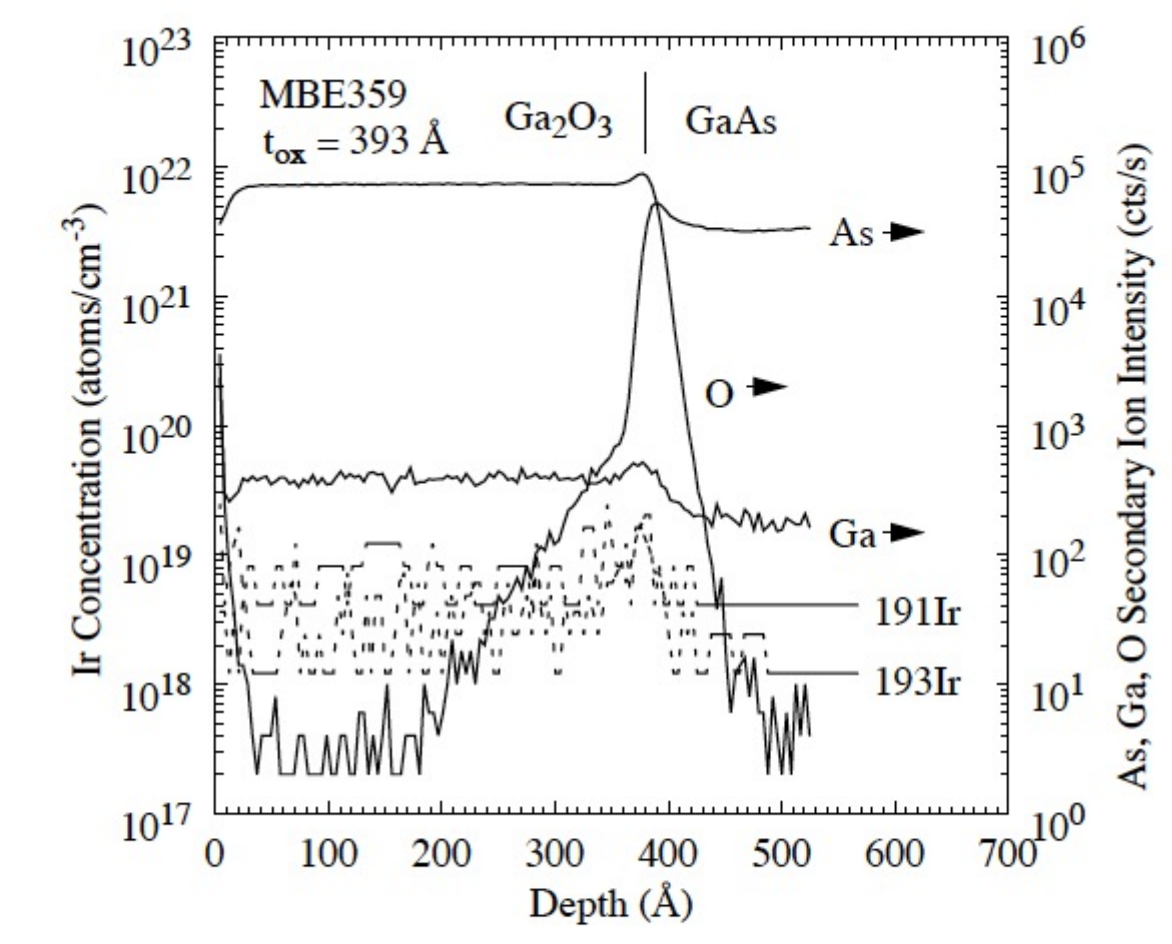


Fig. 9 *SIMS depth profile of MBE359. The Ir concentration is in a range of mid 10^{18} cm^{-3}.*

Maximum Growth Rate = 0.008 µm/hr

Ga_2O_3 in Ir crucible at T = 1800–1980 ° C

Matthias Passlack (private communication).

Use Ga(ℓ) + Ga_2O_3(s) Mixture?

THE PRESSURE OF Ga_2O OVER GALLIUM–Ga_2O_3 MIXTURES

BY C. J. FROSCH AND C. D. THURMOND
Bell Telephone Laboratories, Inc., Murray Hill, New Jersey

Received October 28, 1961

Mixture with $Ga:Ga_2O_3$ = 5:1

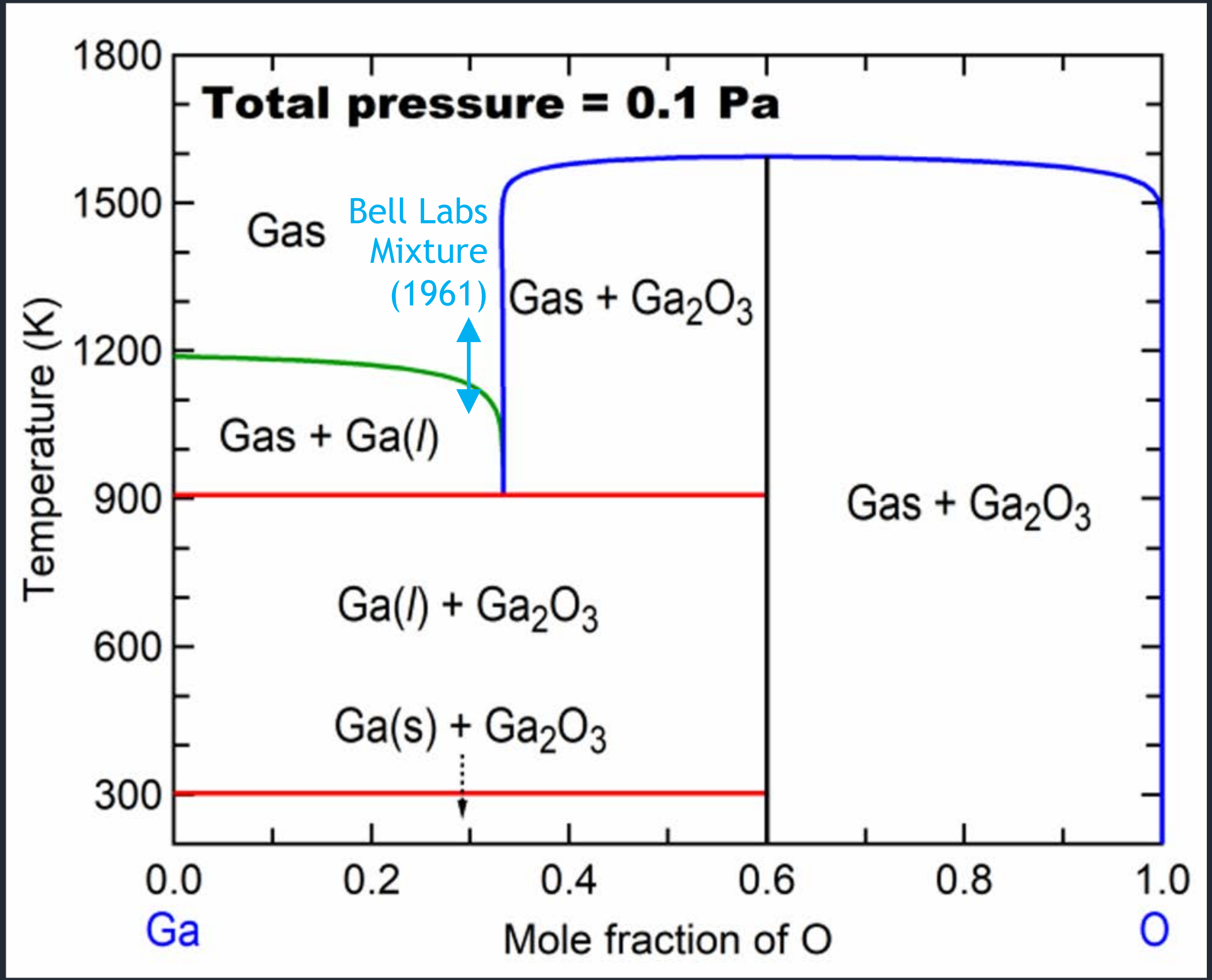
TABLE I

T°,K.	P_{Ga_2O}, atm.	ΔH^0_{298}
1073	1.56×10^{-4}	65.7
1173	1.49×10^{-3}	66.3
1223	3.48×10^{-3}	66.7
1273	9.90×10^{-3}	66.6

$$(\Delta H^0_{298}) = 66.3 \text{ kcal./mole}$$
$$(\Delta H^0_{Ga_2O})_{298} = -20.7 \text{ kcal./mole}$$

C.J. Frosch and C.D. Thurmond, "The Pressure of Ga_2O over Gallium-Ga_2O_3 Mixtures," *Journal of Physical Chemistry* **66** (1962) 877–878.

Use Ga(ℓ) + Ga_2O_3(s) Mixture?



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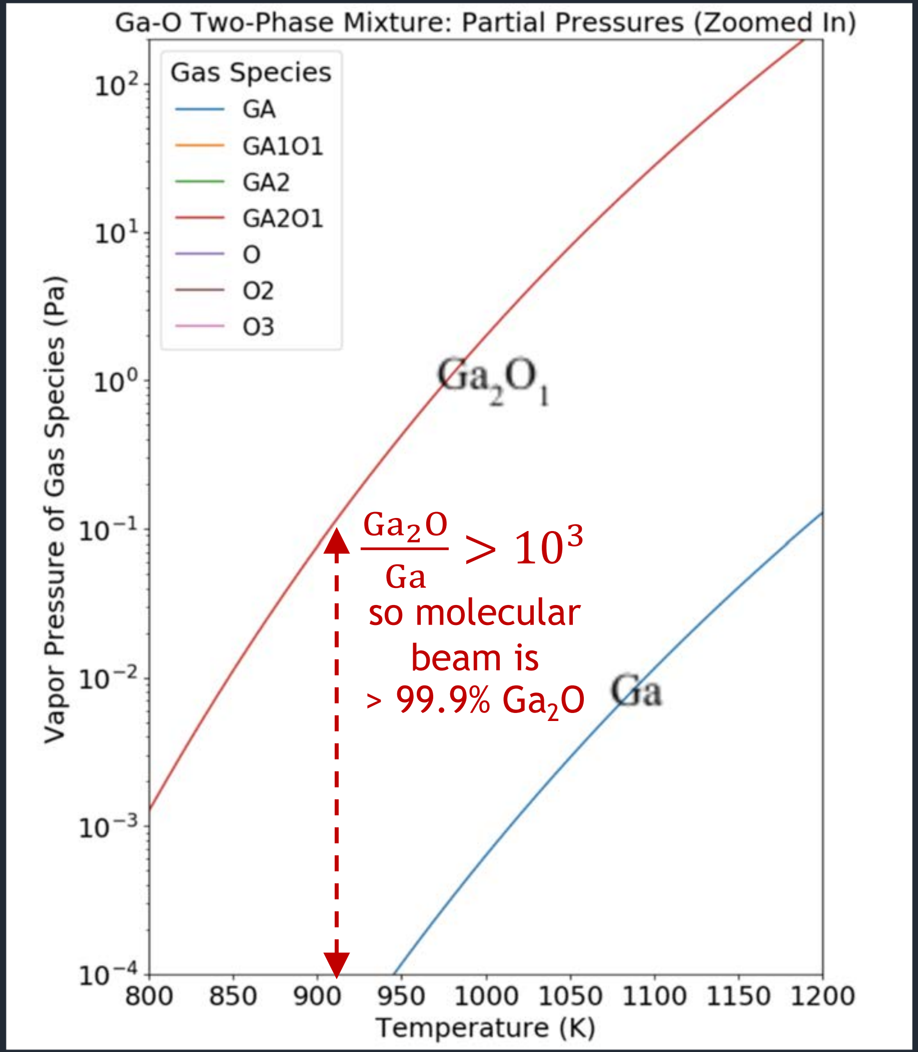

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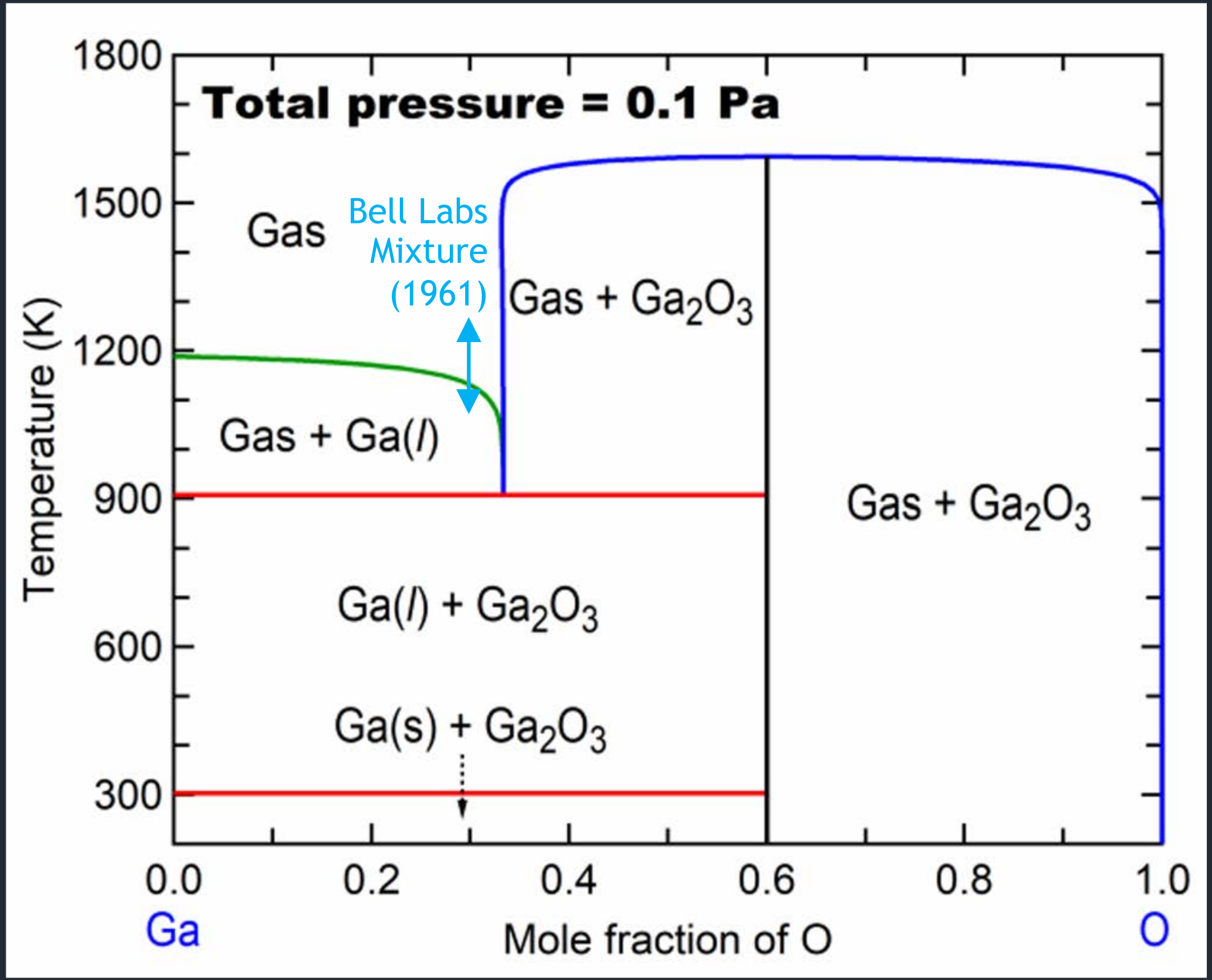
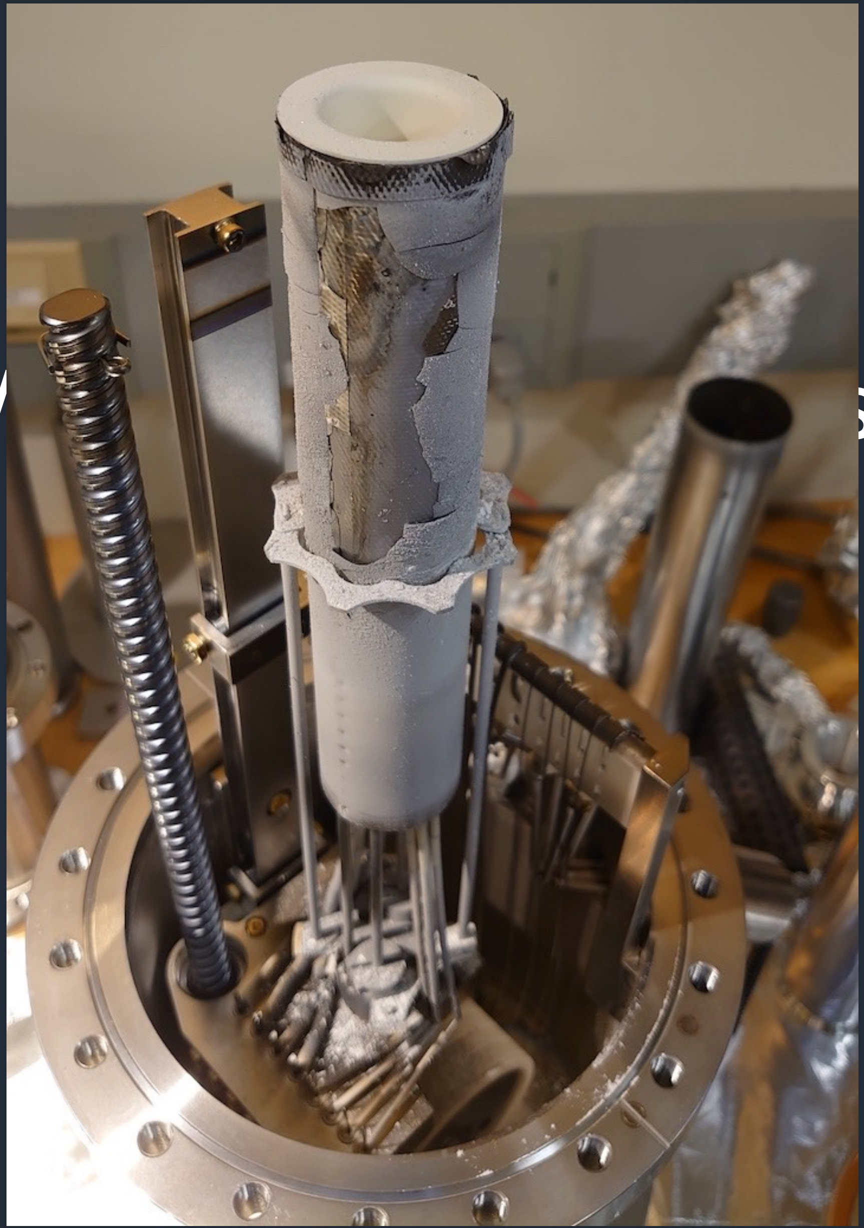
Use Ga(ℓ) + Ga_2O_3(s) Mixture?





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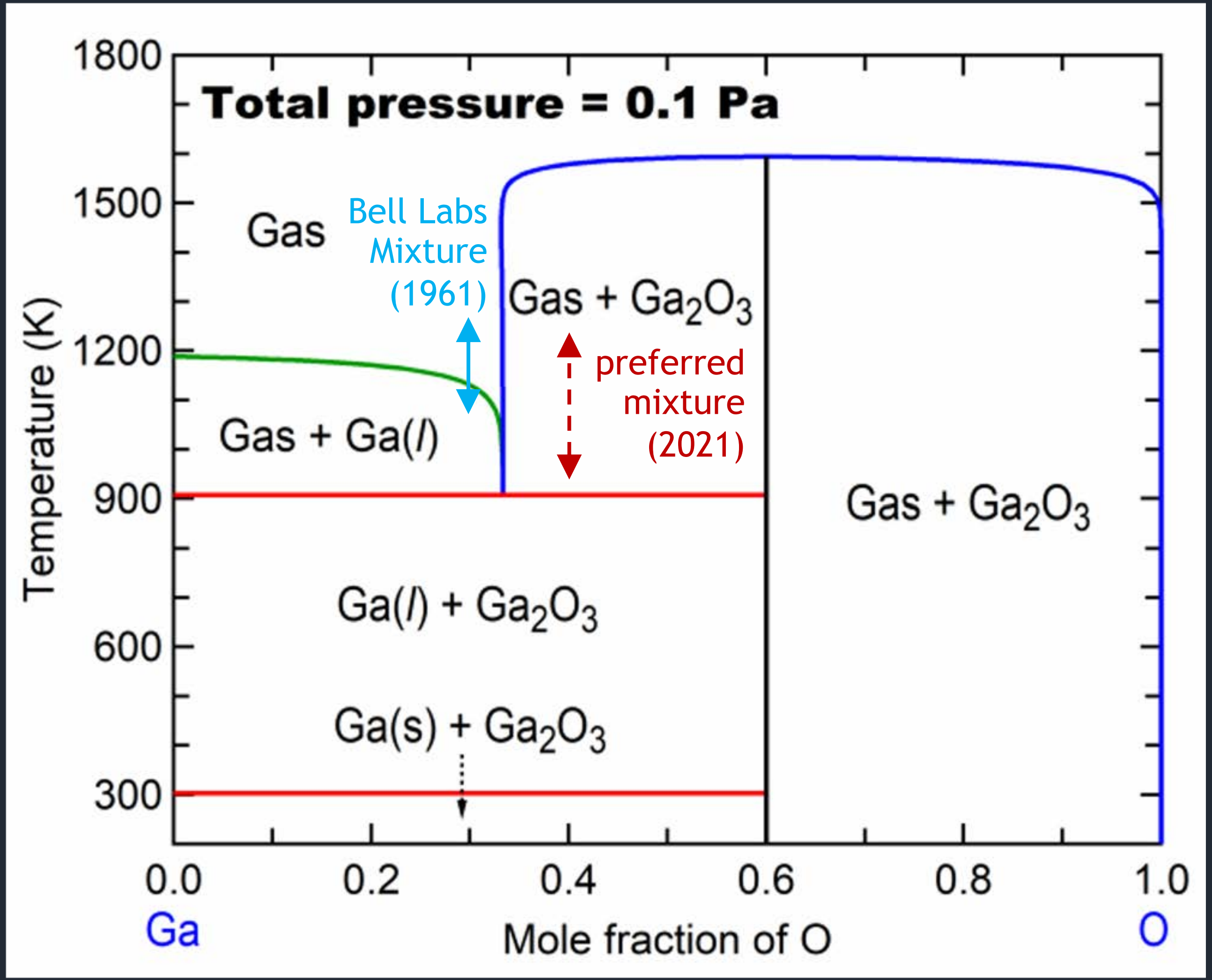

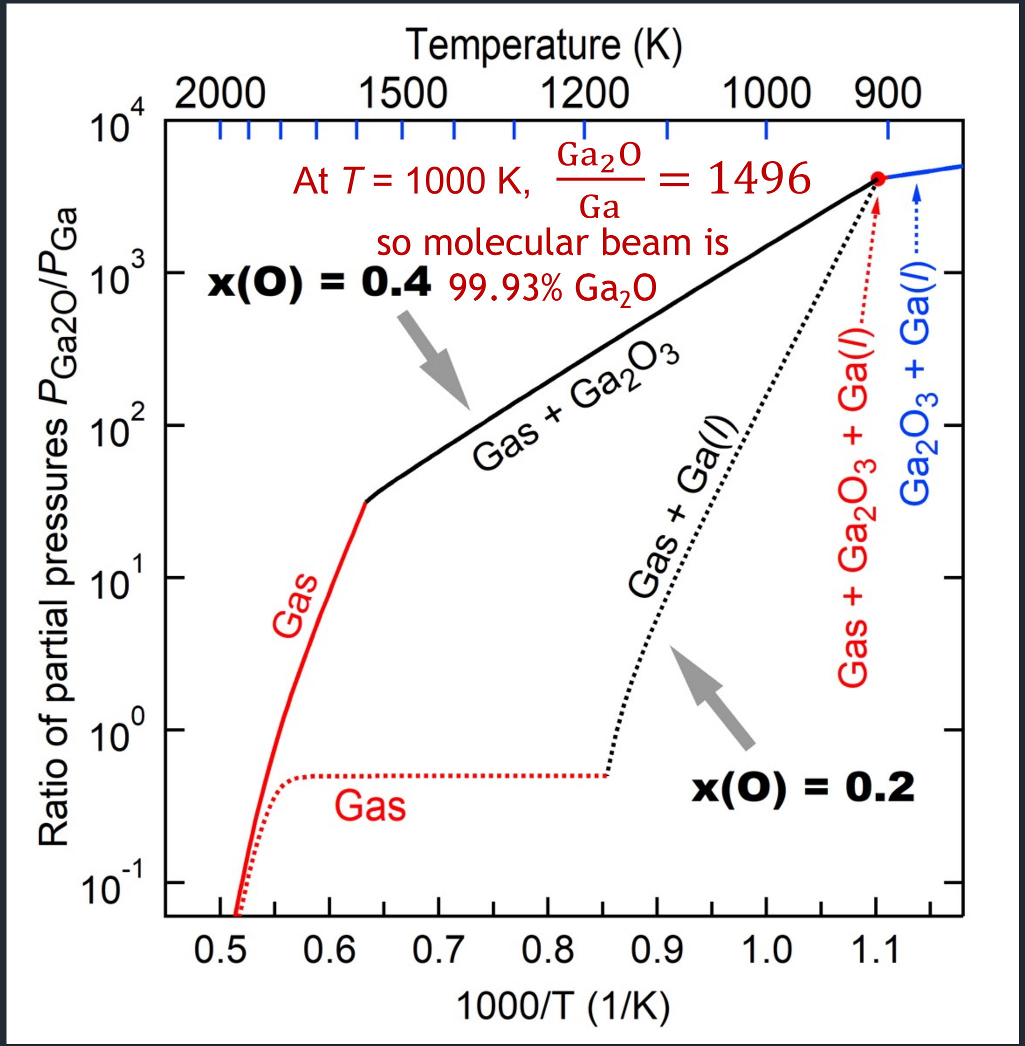

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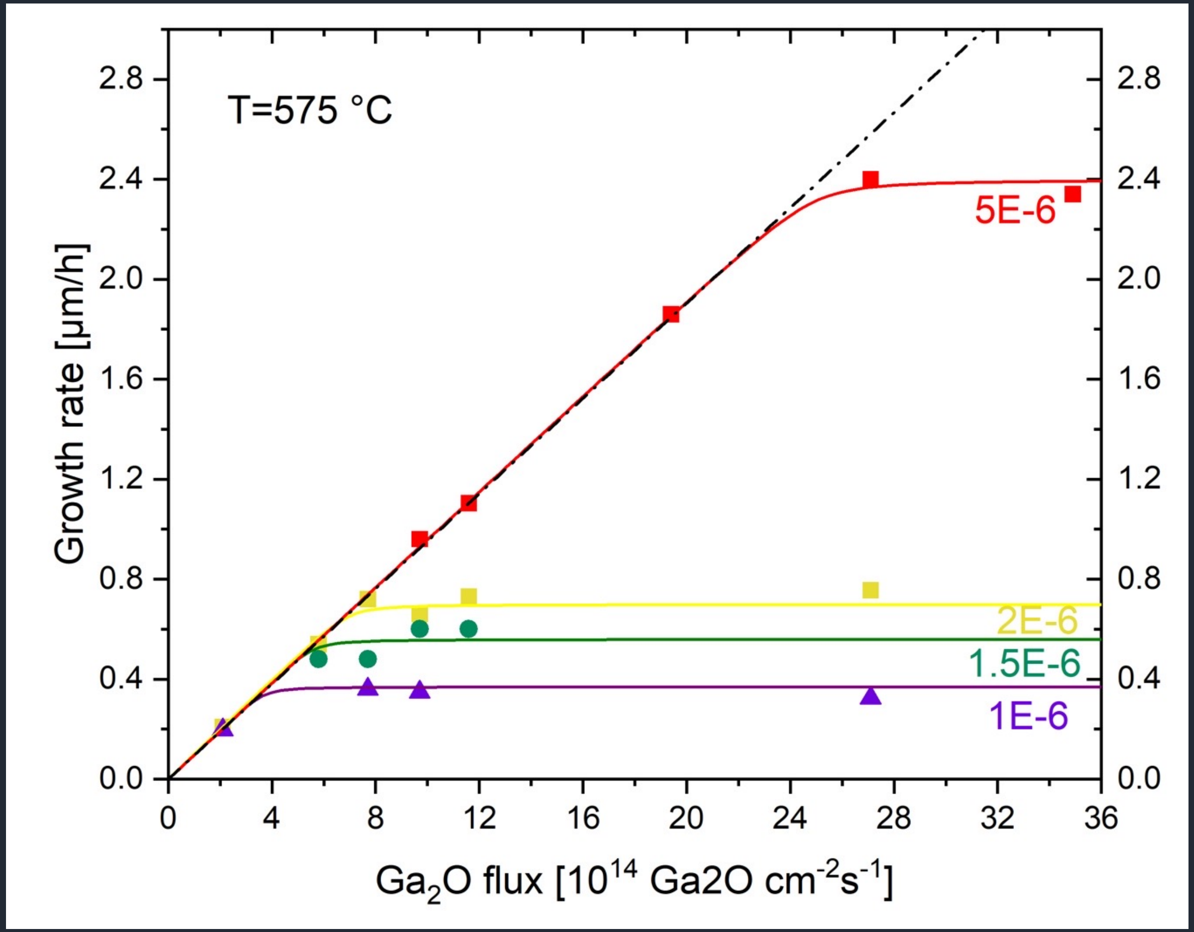
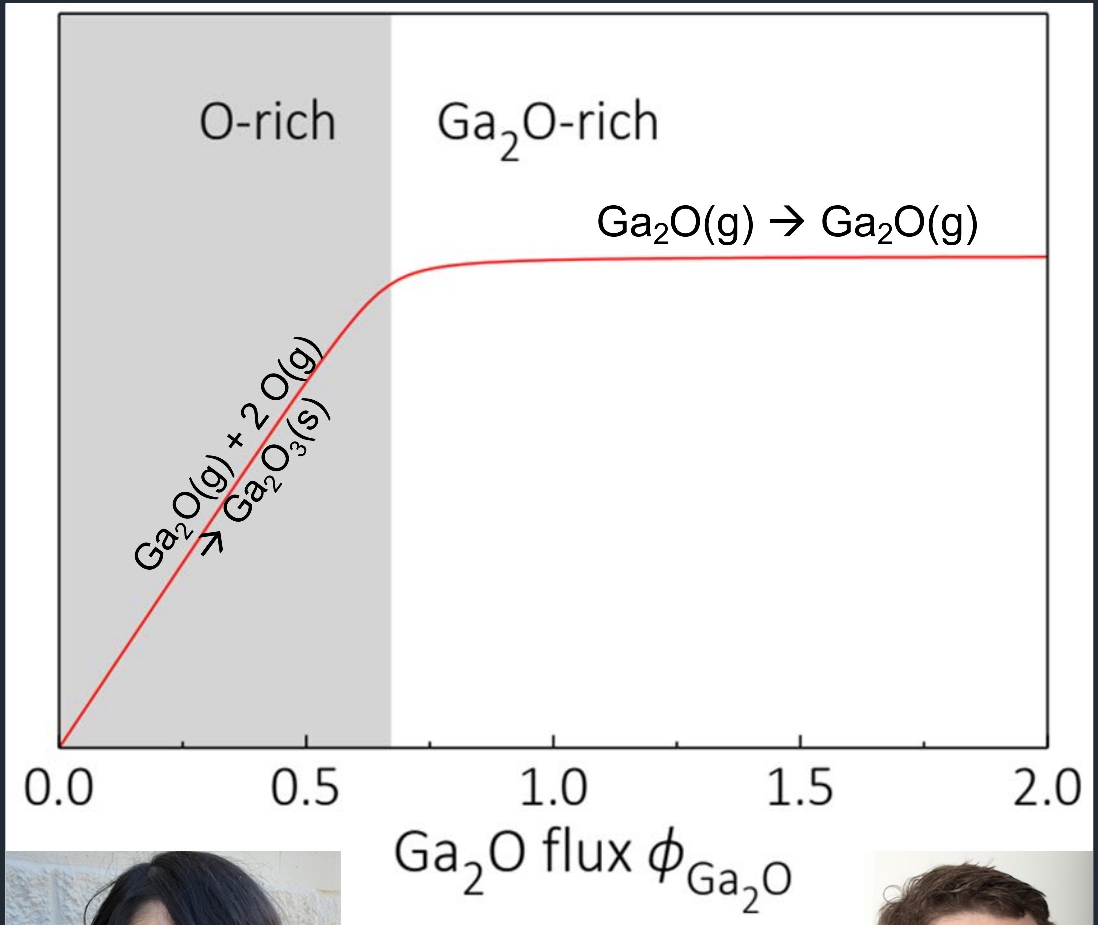
Ga_2O_3(s)-rich mixture provides *higher* Ga_2O/Ga Ratio in molecular beam

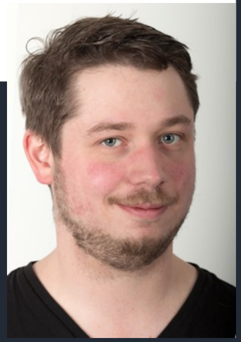
Use Ga(ℓ) + Ga_2O_3(s) Mixture





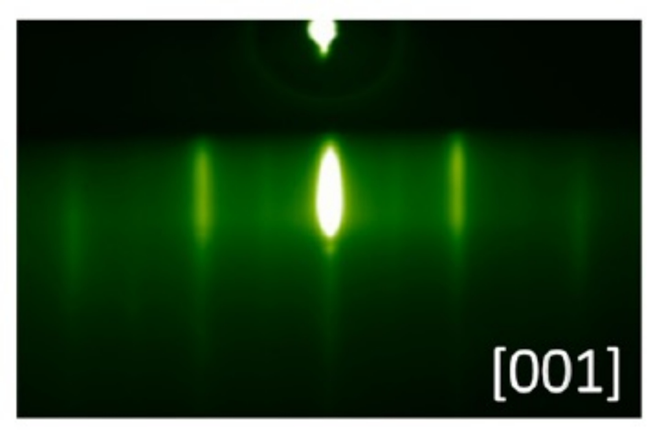
High growth rate (> 1 μm/hr) and epitaxial films at low T_{sub} (e.g., 450 ° C)

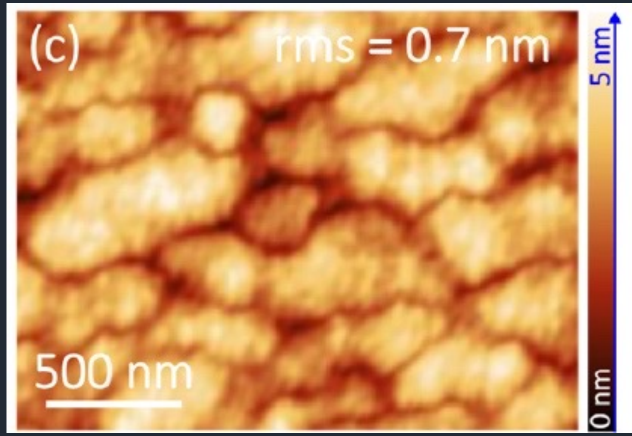
Kathy Azizie

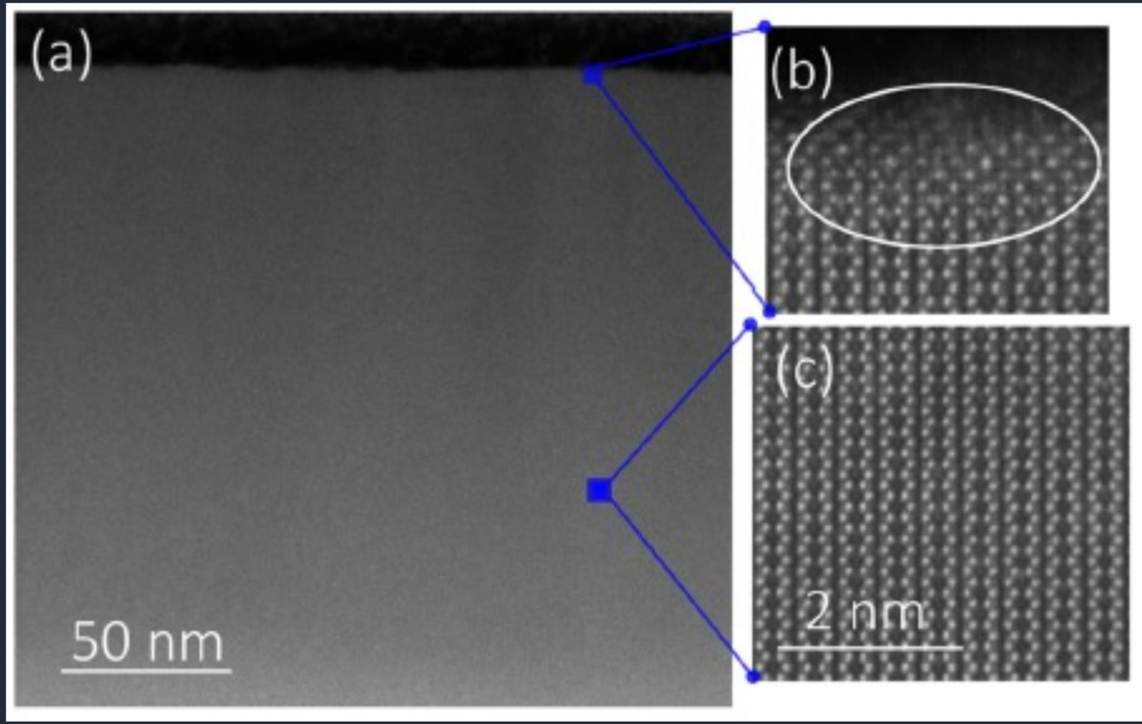


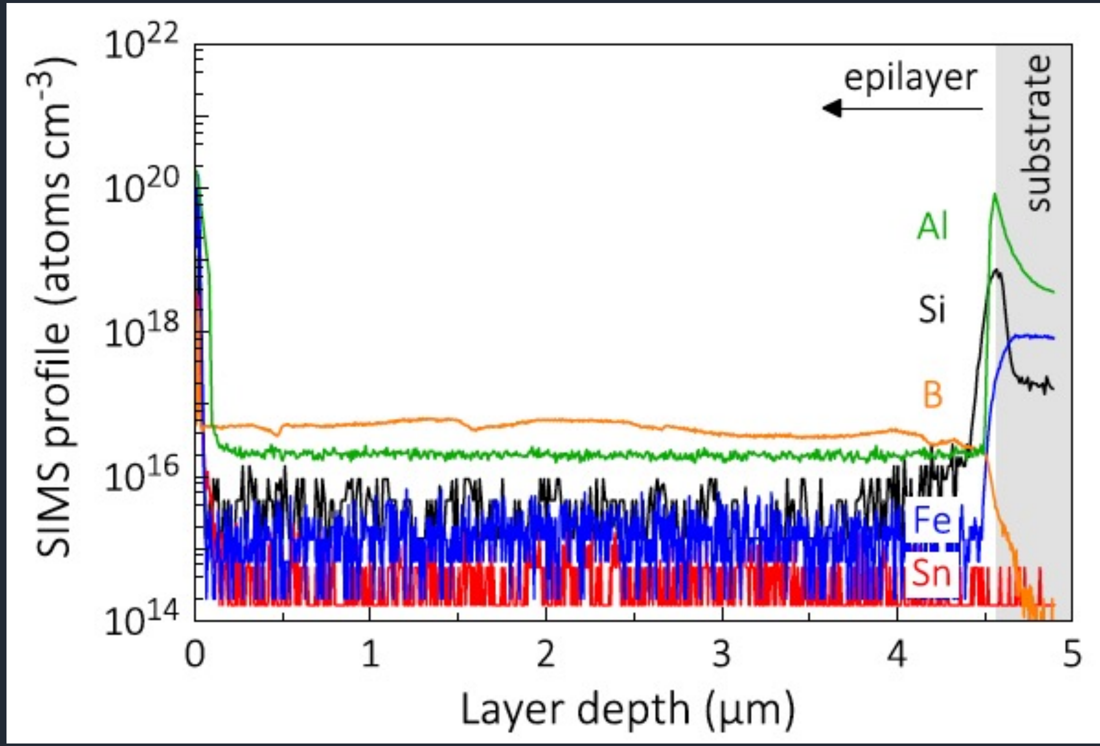
Felix Hensling

Suboxide MBE of β-Ga_2O_3 Grown at 1.2 μm/hr









4.5 μm thick film grown at

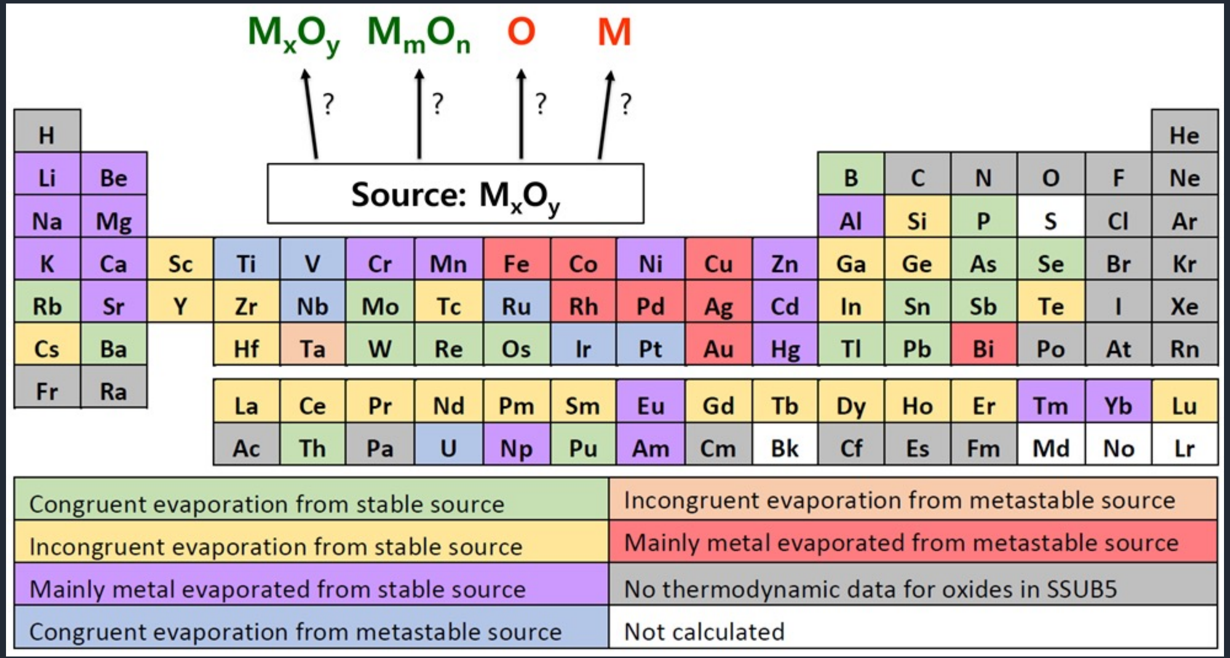
T_{sub} = 575 ° C

P_{O3} = 5×10^{-6} Torr

P. Vogt, F.V.E. Hensling, K. Azizie, C.S. Chang, D. Turner, J. Park, J.P. McCandless, H. Paik, B.J. Bocklund, G. Hoffman, O. Bierwagen, D. Jena, H.G. Xing, S. Mou, D.A. Muller, S-L. Shang, Z.K. Liu, and D.G. Schlom, "Adsorption-Controlled Growth of Ga_2O_3 by Suboxide Molecular-Beam Epitaxy," *APL Materials* **9** (2021) 031101.

Thermo of Suboxide MBE

NSF PARADIM
AN NSF MATERIALS INNOVATION PLATFORM



K.M. Adkison, S-L. Shang, B.J. Bocklund, D. Klimm, D.G. Schlom, and Z.K. Liu, "Suitability of Binary Oxides for Molecular-Beam Epitaxy Source Materials: A Comprehensive Thermodynamic Analysis," *APL Materials* **8** (2020) 081110.

Suboxides offer an alternate means to navigate kinetic pathways

- Comprehensive investigation of vapor pressures of all binary oxides (128 oxides + 27 mixtures)
- 16 evaporate nearly congruently (As_2O_3, B_2O_3, BaO, MoO_3, OsO_4, P_2O_5, PbO, PuO_2, Rb_2O, Re_2O_7, Sb_2O_3, SeO_2, SnO, ThO_2, Tl_2O, and WO_3)
- \+ 24 more that could be useful (CeO, Cs_2O, DyO, ErO, Ga_2O, GdO, GeO, HfO, HoO, In_2O, LaO, LuO, NdO, PmO, PrO, PuO, ScO, SiO, SmO, TbO, Te_2O_2, U_2O_6, VO_2, and YO_2)

Realizing a New Semiconductor for Power Electronic Applications

John T. Heron and Emmanouil Kioupakis, University of Michigan

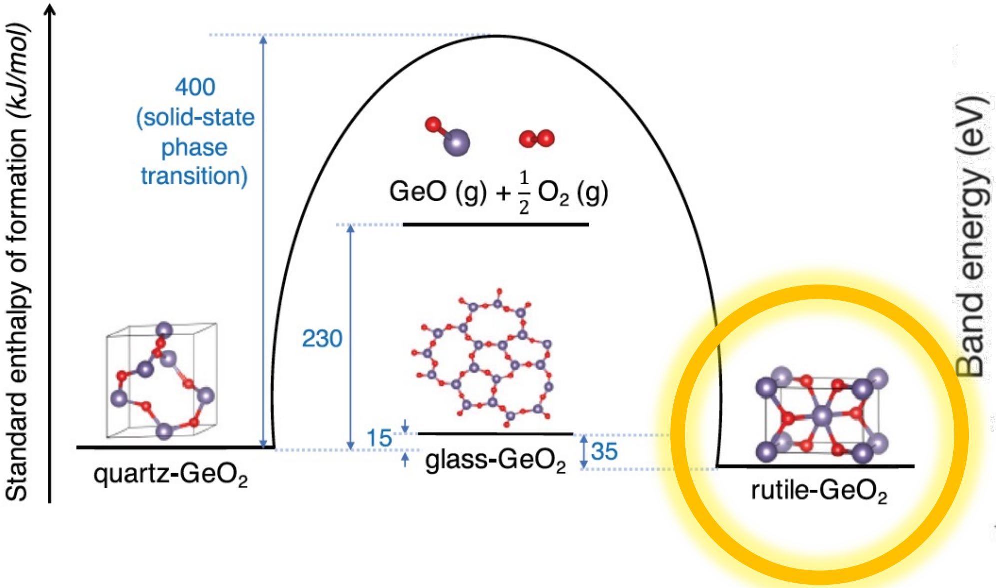
Materials discovery is more than calculating the properties that a material should have if the atoms were in desired positions. It is also key to get the atoms into those desired positions, to see what the properties really are, and thus realize the potential benefit of a new material. Making this happen takes a combination of ideas, capabilities, and execution—as the recent success by a team led by Assistant and Associate Professors from the University of Michigan illustrates.

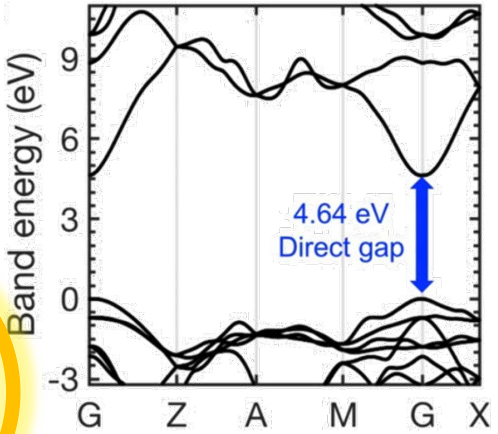
Theoretical work by the team established that rutile-GeO_2—with its ultra-high band gap (4.64 eV), high mobility, high heat conductivity, and desired dopability—could provide superior performance for power electronics. But can this material be made as a thin film? The common synthesis approach would rely on deposition of the constituting elements, but for GeO_2 growth is obstructed by a metastable glass phase and the volatile molecule GeO.

The team came to PARADIM and employed a recently established approach of "sub-oxide MBE"—using partially oxidized GeO instead of Ge—to realize the material in thin film form. Sieun Chae, the same graduate student who did the first-principles calculations, also grew the films. Her work has realized the first single crystal rutile GeO_2 thin films.

S. Chae *et al.* Appl. Phys. Lett. 117, 072105 (2020).

A promising material is identified by theory





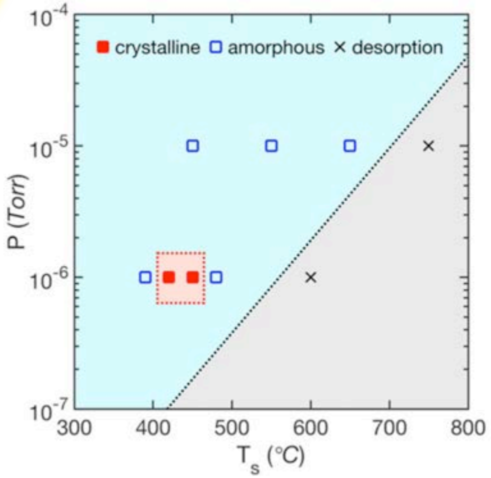
The promise:

high Band Gap ✔

high Mobility ✔

high Thermal Conductivity ✔

But can it be realized?



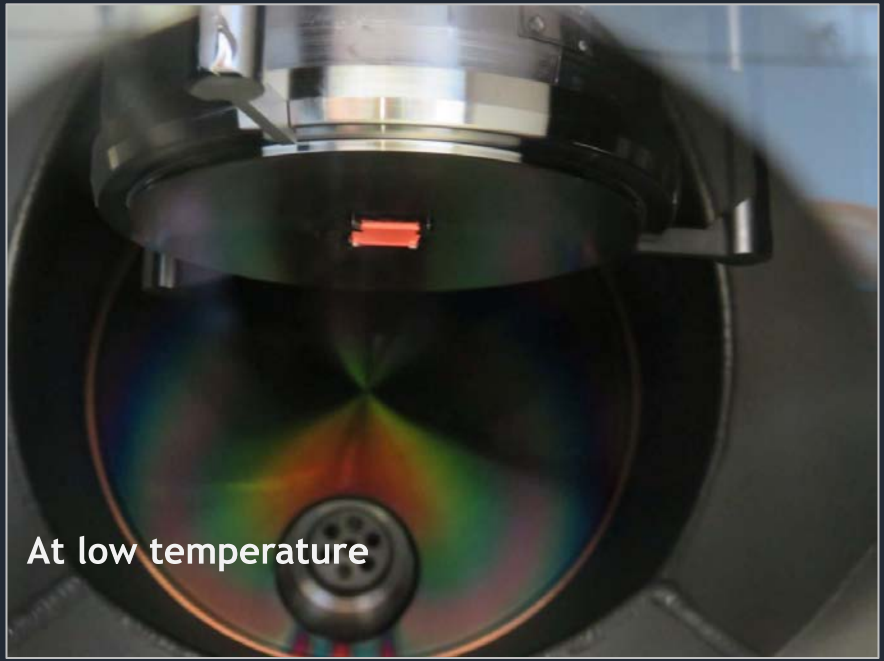
Adsorption-Controlled Growth of

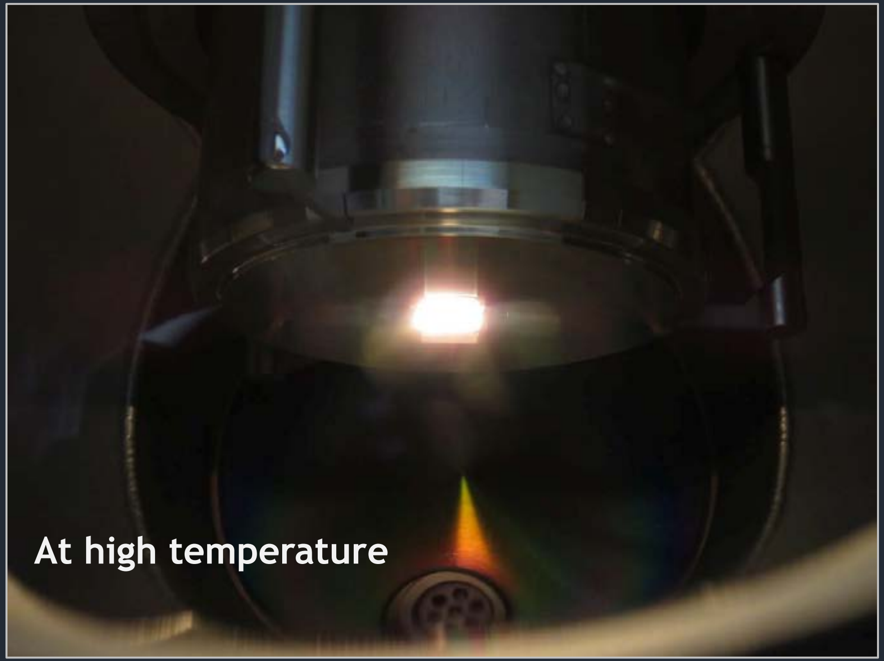
- **Stannates by Suboxide MBE**
  - $BaSnO_3$ – H. Paik *et al.*, *APL Materials* **5** (2017) 116107.
  - SnO – A.B. Mei *et al.*, *Phys. Rev. Mater.* **3** (2019) 105202.
  - Sr_3SnO – Y. Ma *et al. Adv. Mater.* **32** (2020) 2000809.
  - Ta_2SnO_6 – M. Barone *et al. J. Phys. Chem. C* **126** (2022) 3764–3775.
- **Gallates by Suboxide MBE**
  - Ga_2O_3 – P. Vogt *et al.*, *APL Mater.* **9** (2021) 031101.
- **Indates by Suboxide MBE**
  - In_2O_3 – P. Vogt *et al.*, *Phys. Rev. Appl.* **17** (2022) 034021 .

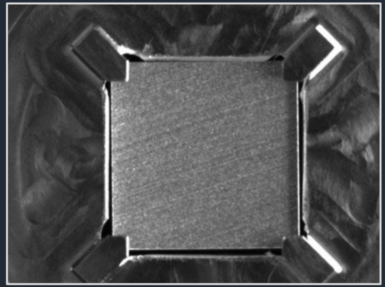
Laser Substrate Heater

CO_2 Laser Substrate Heater

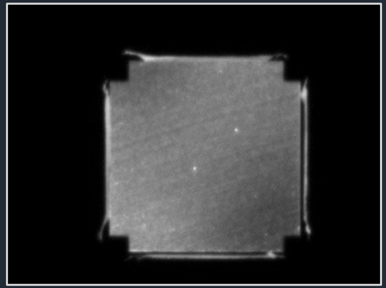
- From EpiRay https://epiray.de
- Currently being tested
- Expect On-Line in PARADIM by end of 2022



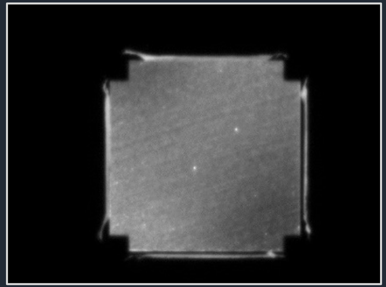




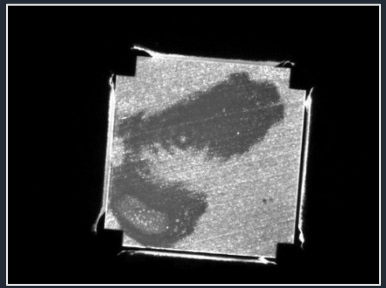
Laser off



Homogeneity at 1000 ° C



Homogeneity at 1800 ° C



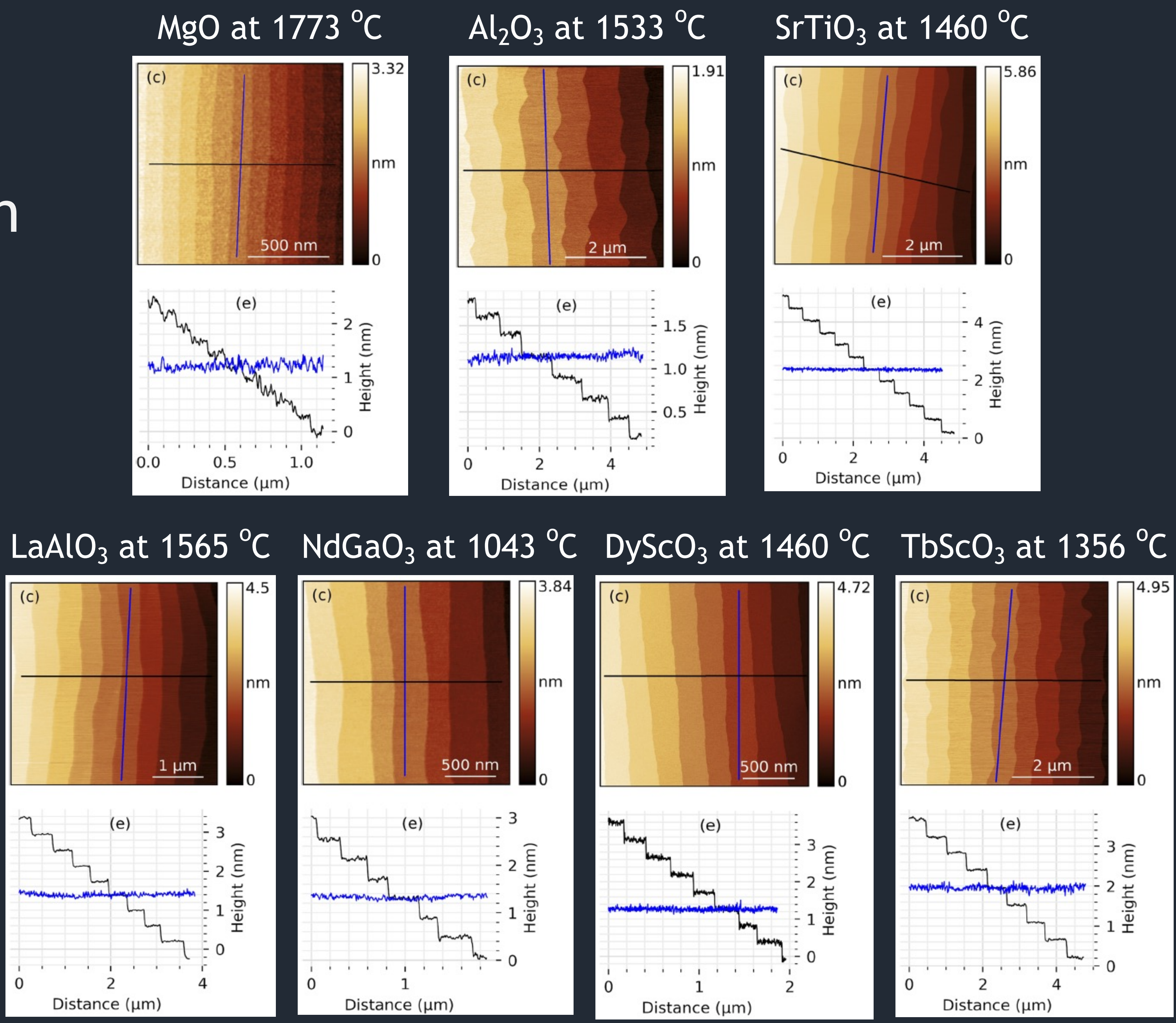
Laser power 95W
Melting starts
(2040 ° C)

All images courtesy Epiray

Laser Substrate Heater

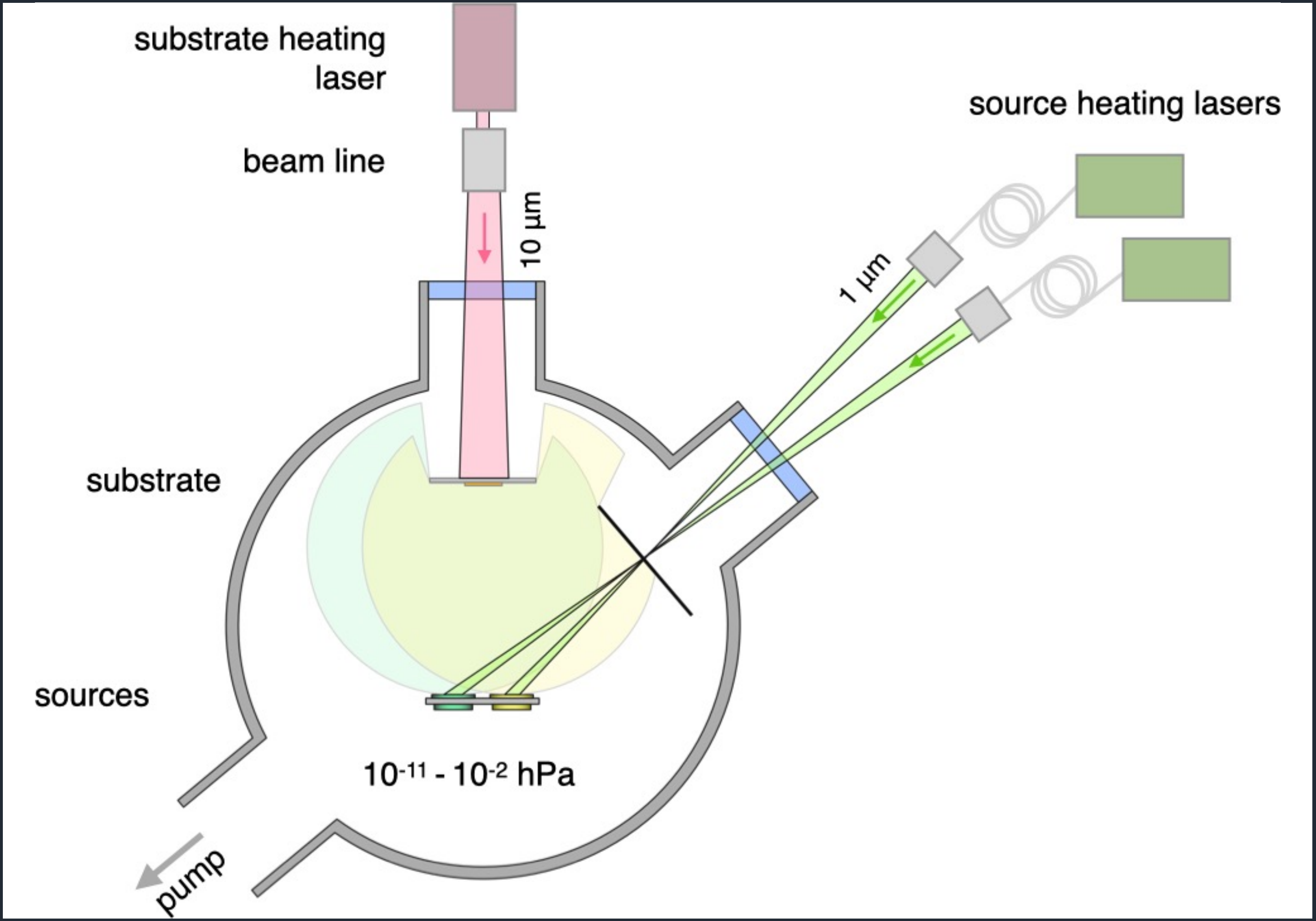
- Laser heater for MBE
  - T_{sub} up to 2000 °C
  - *In situ* substrate termination demonstrated for:
    MgO
    Al_2O_3
    $SrTiO_3$
    $LaAlO_3$
    $NdGaO_3$
    $DyScO_3$
    $TbScO_3$

Expect On-Line in PARADIM by end of 2022



W. Braun, M. Jäger, G. Laskin, P. Ngabonziza, W. Voesch, P. Wittlich, and J. Mannhart, "*In situ* Thermal Preparation of Oxide Surfaces," *APL Mater.* **8** (2020) 071112.

Future of Oxide MBE



W. Braun and J. Mannhart,
"Film Deposition by **Thermal Laser Evaporation**,"
AIP Advances **9** (2019) 085310.

Expanded Growth Conditions

Unlimited temperatures for substrate and sources

Robust

All heaters *outside* vacuum

Achieve Oxidation of the Film

O_3 up to 10^{-3} Torr

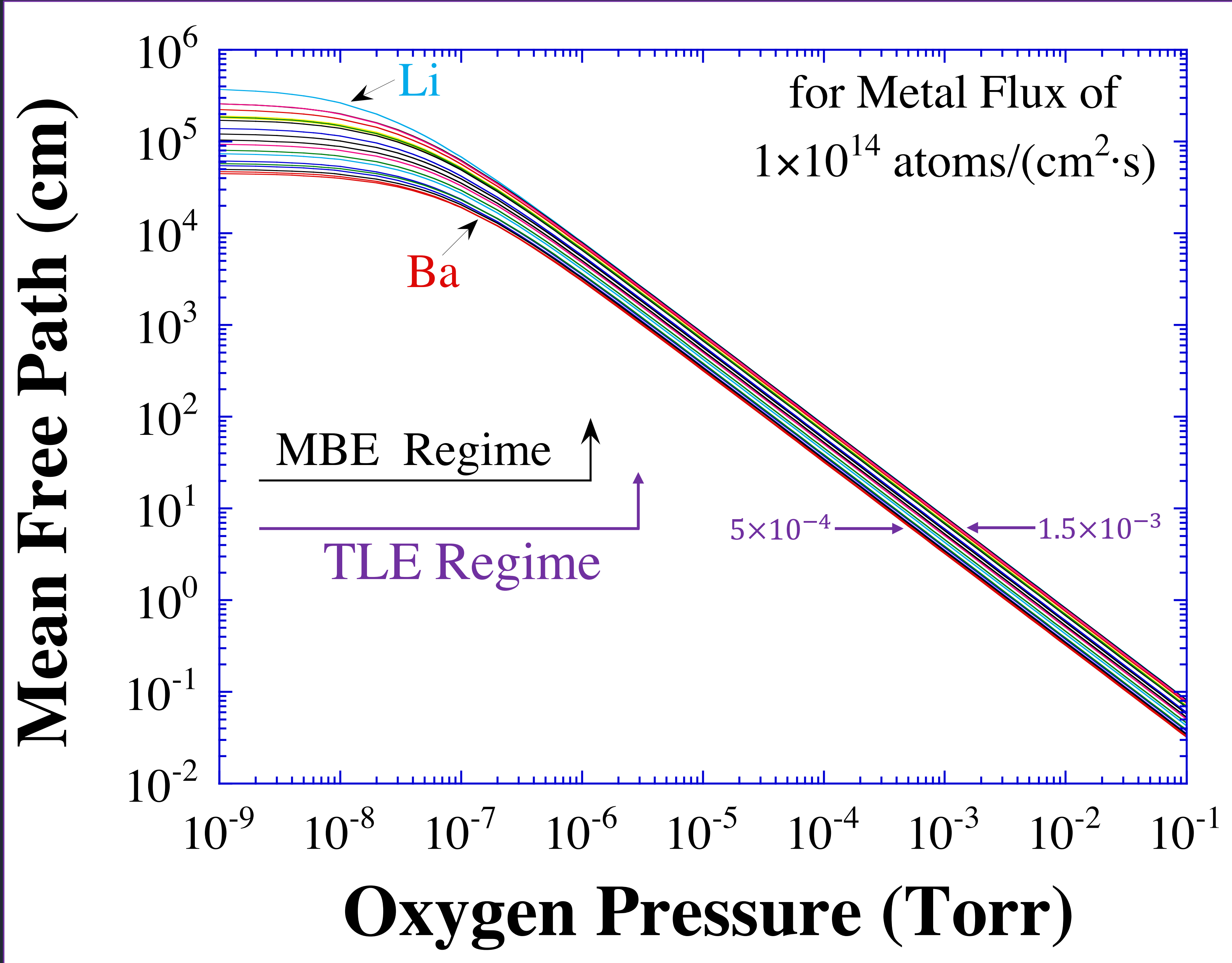
Prevent Problematic Oxidation of the Sources

Surface continuously evaporated

Substrate Termination

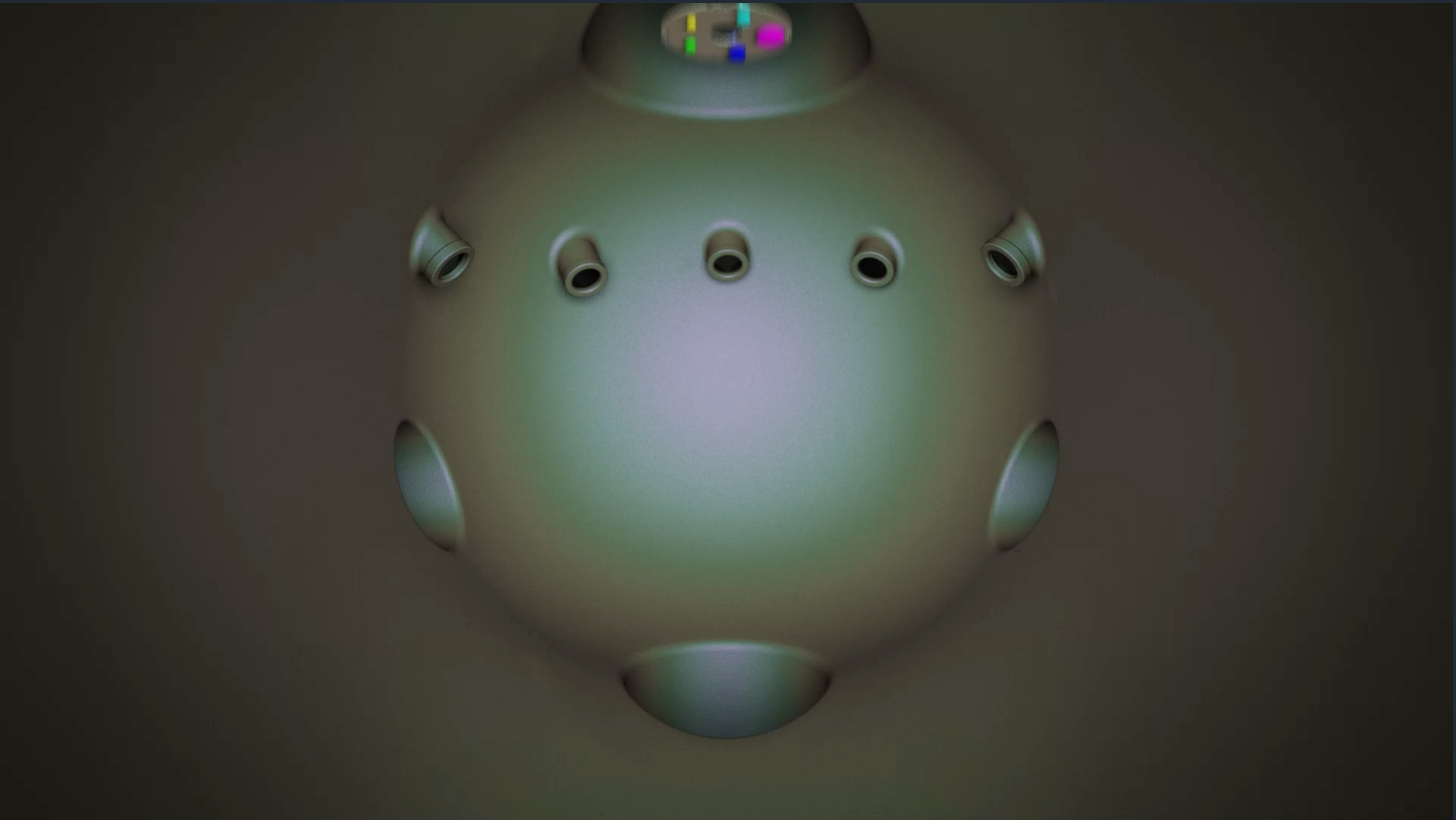
In situ thermal termination

Maximum O_2 Pressure for ~~MBE~~ TLE?



D.G. Schlom and J.S. Harris, Jr., in *Molecular Beam Epitaxy: Applications to Key Materials*, edited by R.F.C. Farrow (Noyes, Park Ridge, 1995), pp. 505-622.

TLE — since 2019



Video courtesy
of
Epiray GmbH

Got MBE?

Darrell G. Schlom

schlom@cornell.edu