



Lecture #1 – Greatest Hits of MBE

Darrell G. Schlom

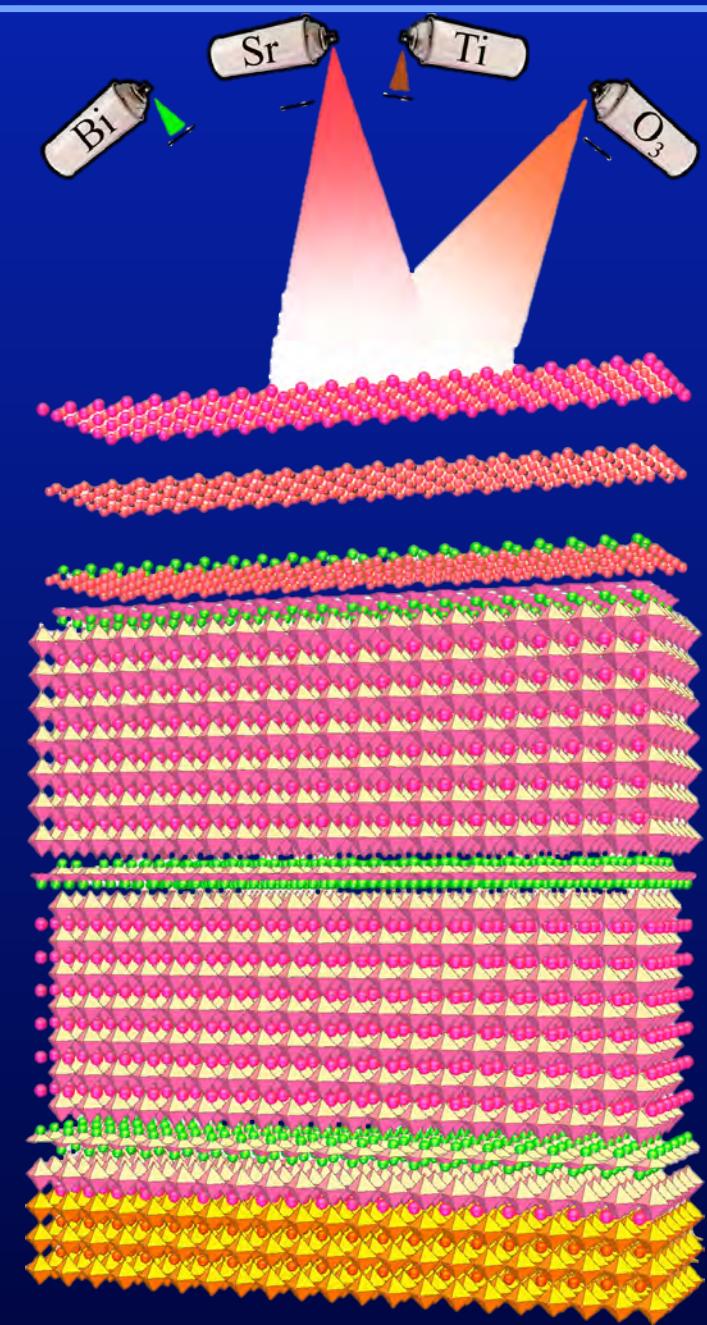
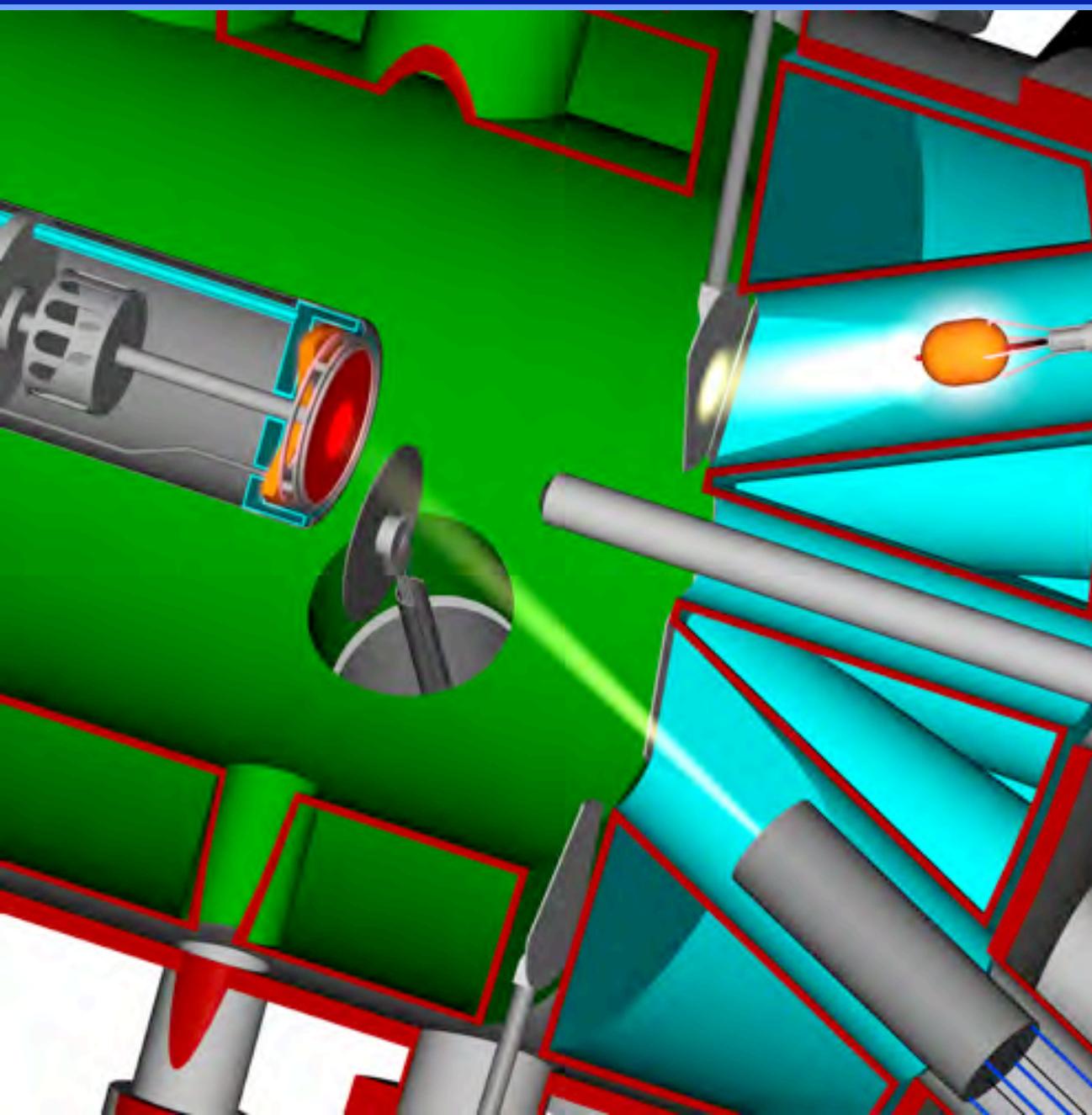
*Department of Materials Science and Engineering
Cornell University*

Kavli Institute at Cornell for Nanoscale Science

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—*Case studies Sr₂RuO₄ and ZnO*
- How can I gain access to an oxide MBE if I don't have one?
Use PARADIM's oxide MBE (+ ARPES + ...)

MBE \approx Atomic Spray Painting



When GaAs is Heated ...

J. Phys. Chem. Solids Pergamon Press 1967. Vol. 28, pp. 2257-2267. Printed in Great Britain.

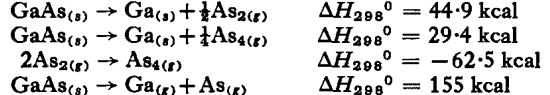
VAPOR PRESSURES AND PHASE EQUILIBRIA IN THE Ga-As SYSTEM

J. R. ARTHUR

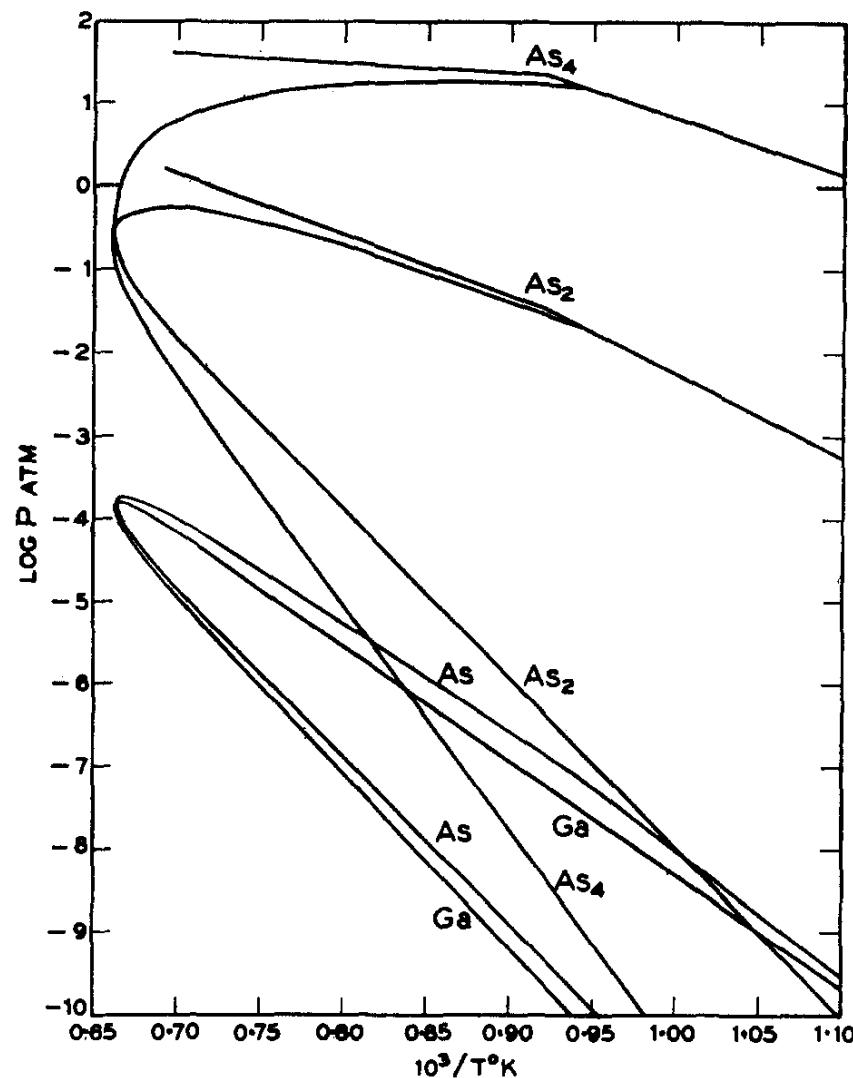
Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey

(Received 9 March 1967; in revised form 18 May 1967)

Abstract—Mass spectrometric and weight loss measurements of the species effusing from a Knudsen cell containing GaAs were used to obtain vapor pressures over the temperature range 900–1200°K. The As_2/As_4 ratio was observed in these measurements to be substantially larger than previously reported^(2,3) when precautions were taken to prevent the buildup of arsenic vapor in the mass spectrometer ionization chamber. A third law treatment of the data gave enthalpies for the reactions:



These results were used to correct Thurmond's calculations of vapor pressures and activity coefficients along the GaAs liquidus.⁽¹⁾



J.R. Arthur

"Vapor Pressures and Phase Equilibria in the Ga-As System"

J. Phys. Chem. Solids 28 (1967) 2257-2267.

FIG. 5. Equilibrium vapor pressures of As, As₂, As₄ and Ga along the binary liquidus as a function of T^{-1} . Pressures of As₂ and As₄ over pure solid and liquid As are also shown.

Consider Evaporation of PbO

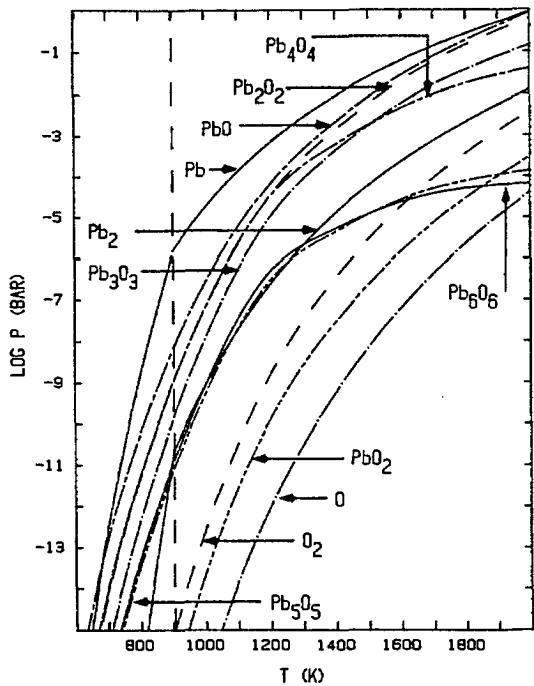


FIG. 53. PbO vaporization in 10^{-15} bar O_2 below 905 K and vaporization of Pb-PbO mixture above 905 K.

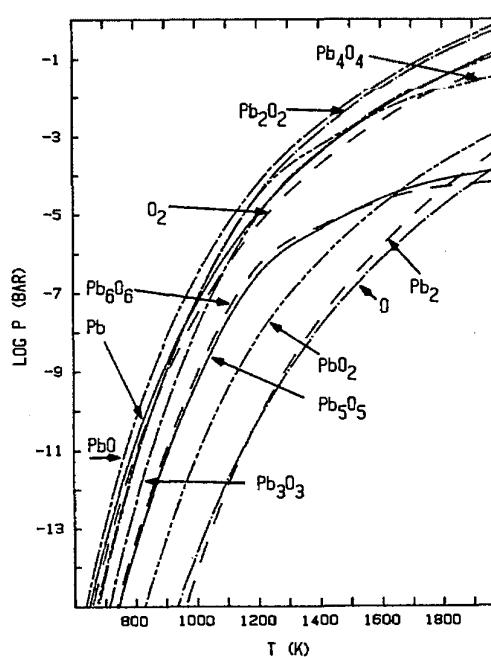


FIG. 54. PbO congruent vaporization.

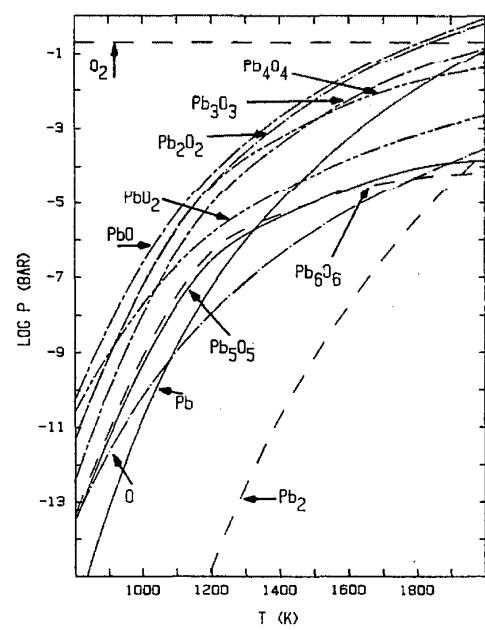


FIG. 55. PbO vaporization in 0.2 bar O_2 .

R.H. Lamoreaux, D.L. Hildenbrand, and L. Brewer,
"High-Temperature Vaporization Behavior of Oxides II.
Oxides of Be, Mg, Ca, Sr, Ba, B, Al, Ga, In, Tl, Si, Ge,
Sn, Pb, Zn, Cd, and Hg"
J. Phys. Chem. Ref. Data **16** (1987) 419-443.

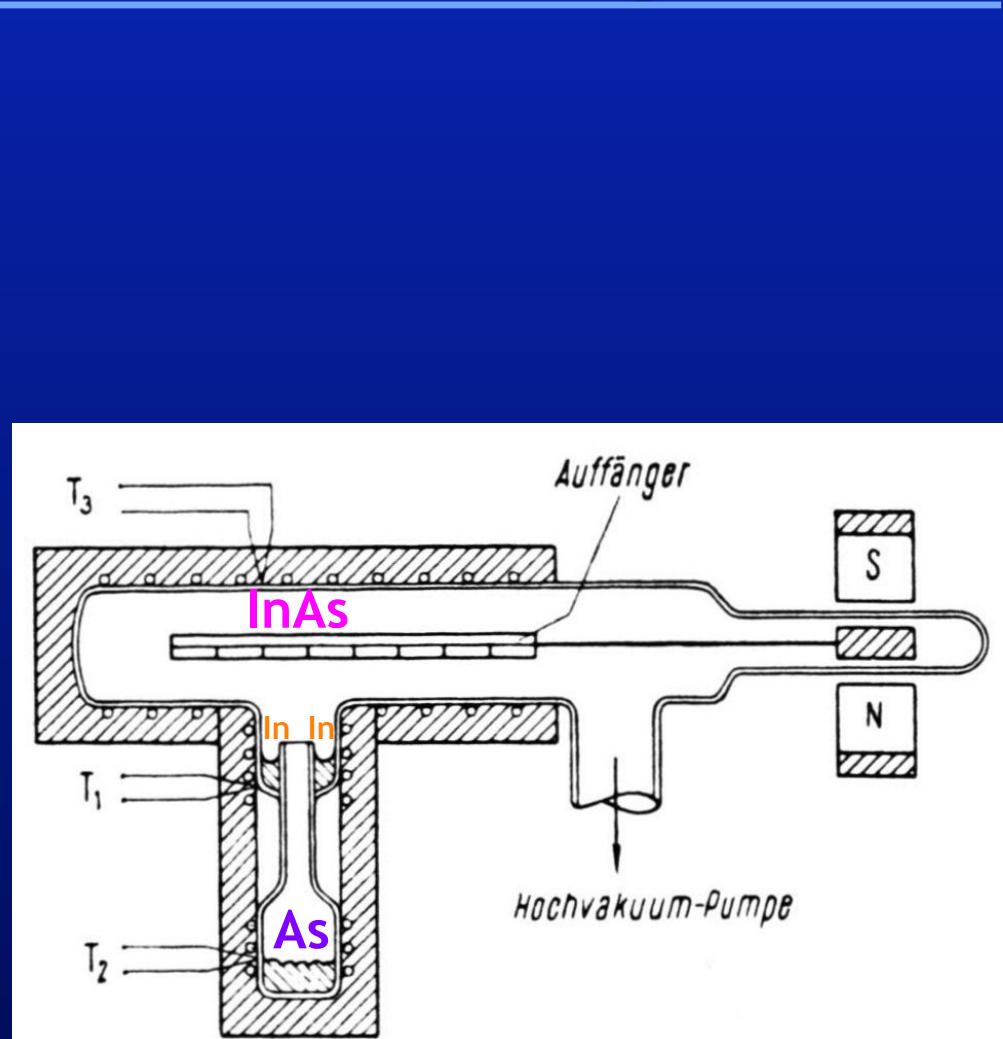
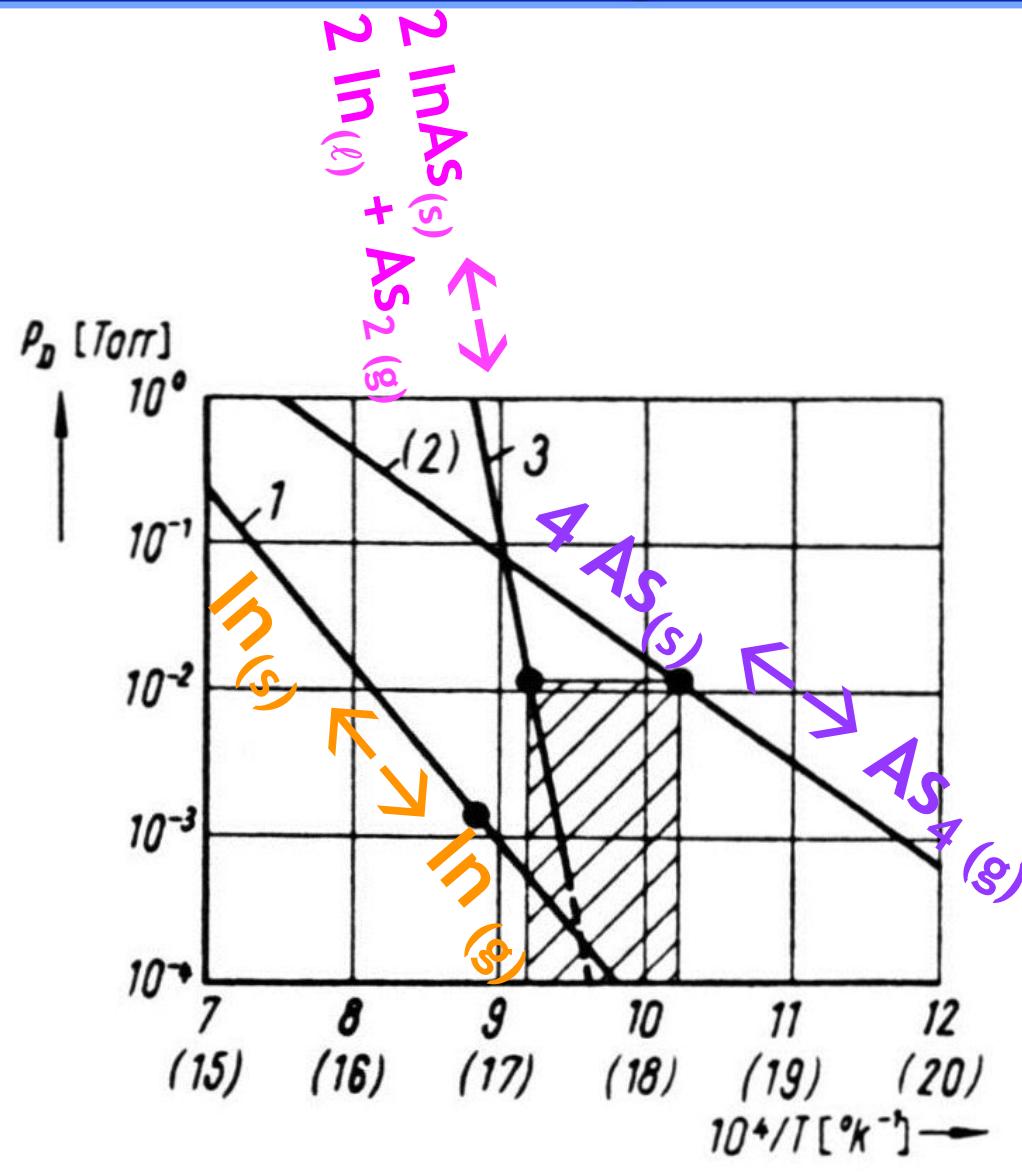
Key Enablers of MBE

- “3-Temperaturaufdampfverfahren” for Growth of III-V Semiconductor Films by Vacuum Evaporation

K.G. Günther, “Aufdampfschichten aus halbleitenden III-V Verbindungen,” *Zeitschrift für Naturforschung A* **13** (1958) 1081–1089.

H. Freller and K.G. Günther, “Three-temperature method as an origin of molecular beam epitaxy,” *Thin Solid Films* **88** (1982) 291–307.

3-Temperature Technique



Key Enablers of MBE

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H. Freller and K.G. Günther, “Three-temperature method as an origin of molecular beam epitaxy,” *Thin Solid Films* **88** (1982) 291–307.

- Reliable UHV Sealing Technology

W.R. Wheeler and M. Carlson, “Ultra-High Vacuum Flanges,” *Transactions of the Eighth National Vacuum Symposium*, edited by L.E. Preuss (Pergamon, New York, 1962), pp. 1309-1318.

M.A. Carlson and W.R. Wheeler, “Metal Vacuum Joint,” U.S. Patent #3,208,758 (Sept. 28, 1965).

UHV Seals—Varian Conflat®

Sept. 28, 1965

M. A. CARLSON ET AL

3,208,758

METAL VACUUM JOINT

Filed Oct. 11, 1961

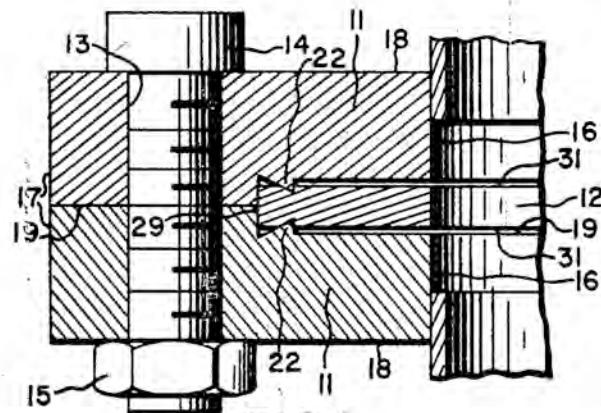


FIG.1

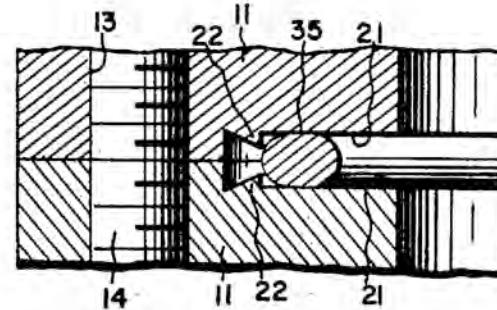


FIG.3

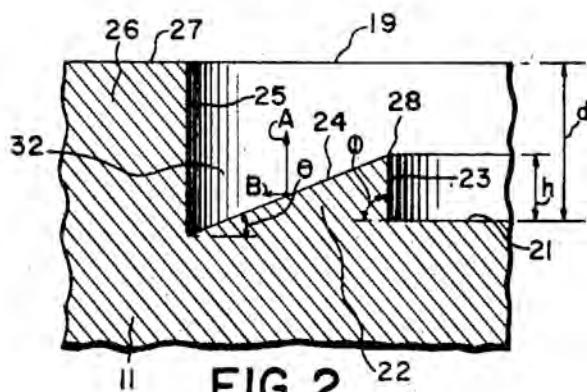


FIG.2

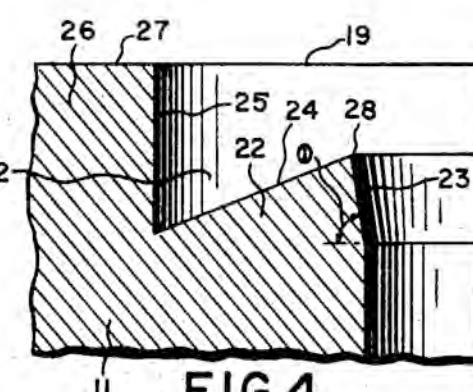


FIG.4

M.A. Carlson and W.R. Wheeler
“Metal Vacuum Joint,” U.S. Patent #3,208,758 (Sept. 28, 1965)

Epitaxial GaAs by 3-Temperature Technique

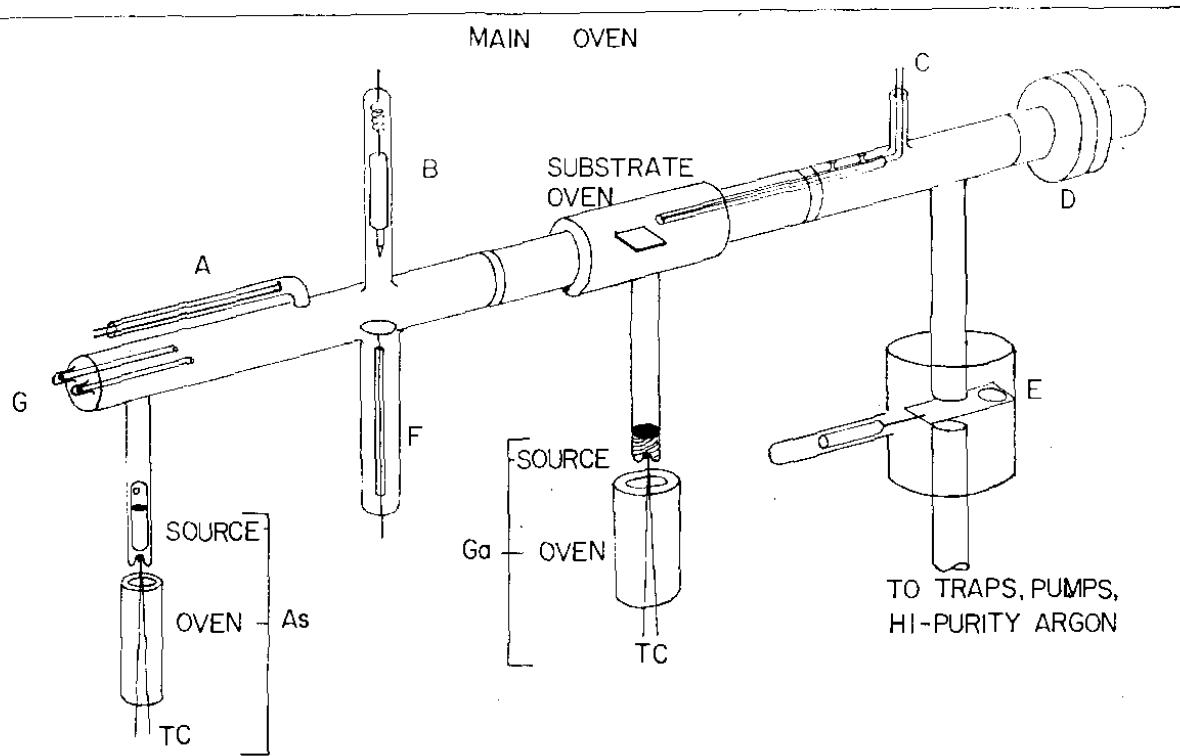
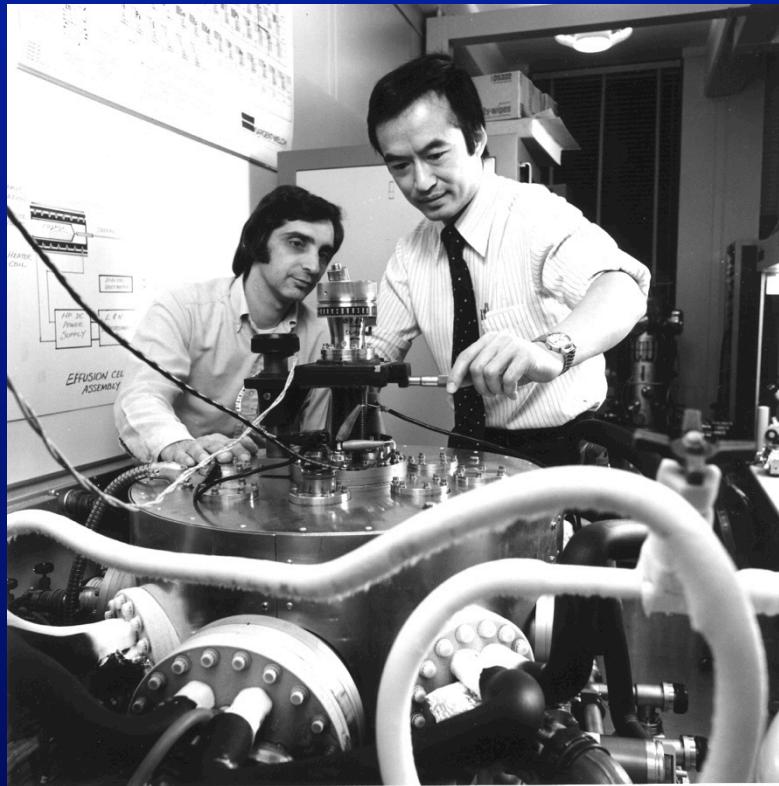


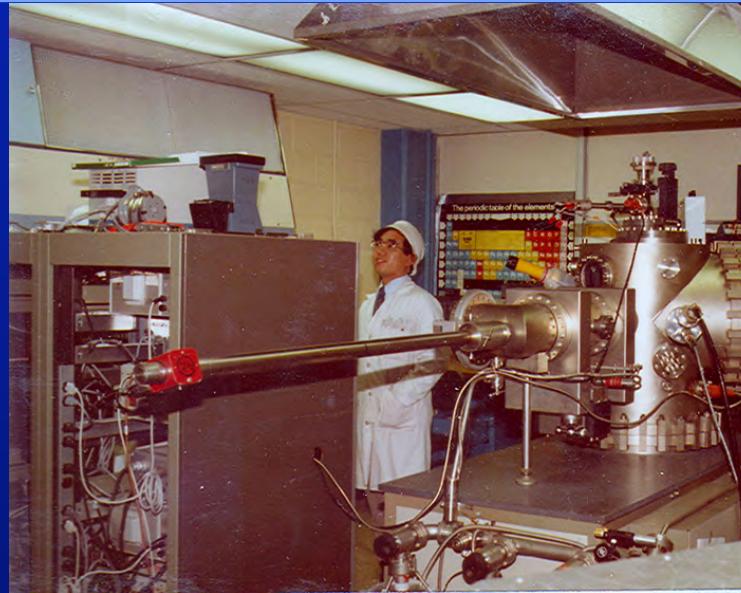
FIG. 1. GaAs film evaporation system: (A) Pirani gauge; (B) electrical contact to diode structure; (C) thermocouple; (D) metal flanges and viton gaskets as an entrance port for loading system; (E) particulate valve; (F) circular Ta plate; positive electrode in diode structure; (G) quartz rods which extend the length of the envelope and which guide the substrate carrier.

Evolution of MBE



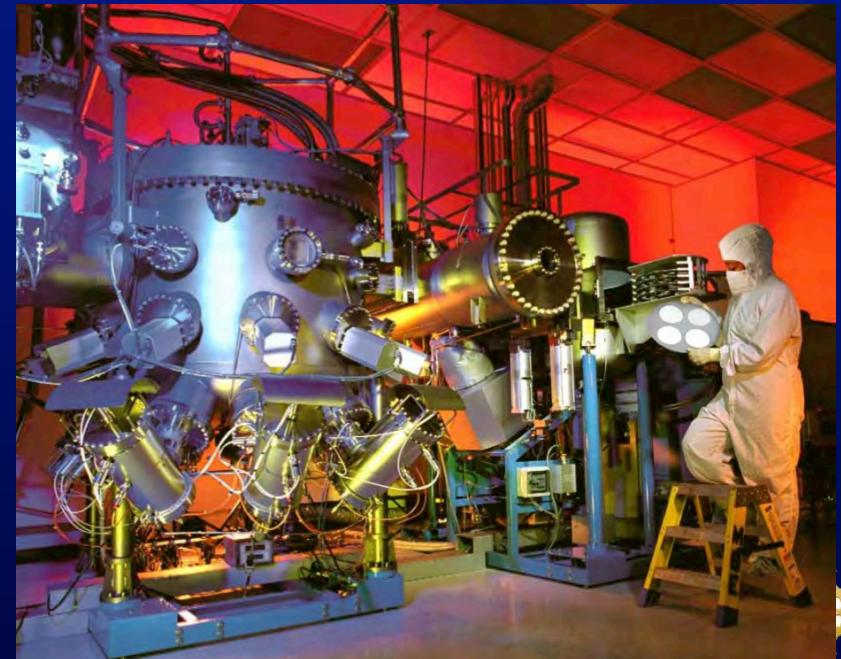
1st MBE
Al Cho at Bell Labs, 1972

PARADIM



1st
University
MBE
Cornell,
1978

Production
MBE
Today
(courtesy of TRW)



MBE production tool performance data



HIGH YIELD

UNIFORMITIES / Wafer

Thickness $< \pm 0.5\%$

Composition $< \pm 0.5\%$

Doping $< \pm 1\%$

Source material: supply consistency

Stable process and monitoring: $< 2\%$

REPRODUCIBILITY

HIGH THROUGHPUT

VERY HIGH UPTIME

$> 94\%$, run 6 to 9 months, 7 days/wk, 24/24

RUN CAPABILITY

13x2'' or 5x3'', 4x6'' or 9x4'', (4x8'') 7x6''

RUN SWITCHING

less than 2 minutes (platen exchange)

Reflection High-Energy Electron Diffraction (RHEED) Oscillations

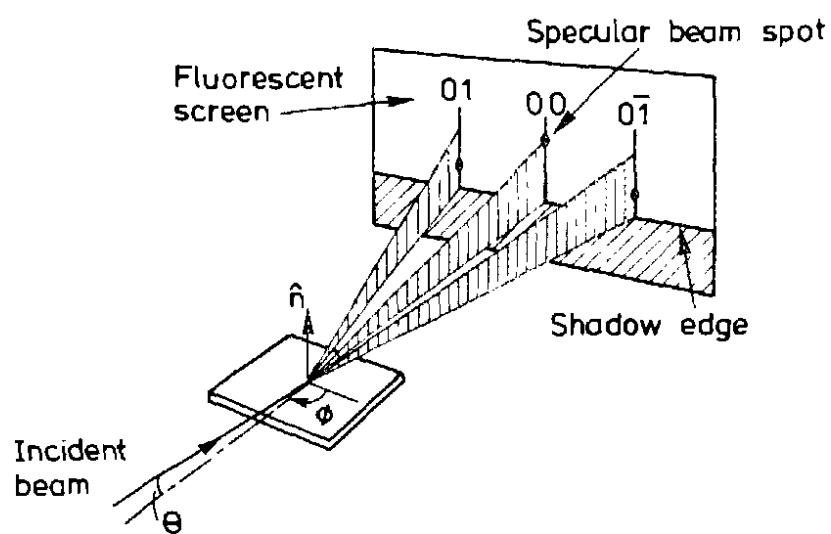
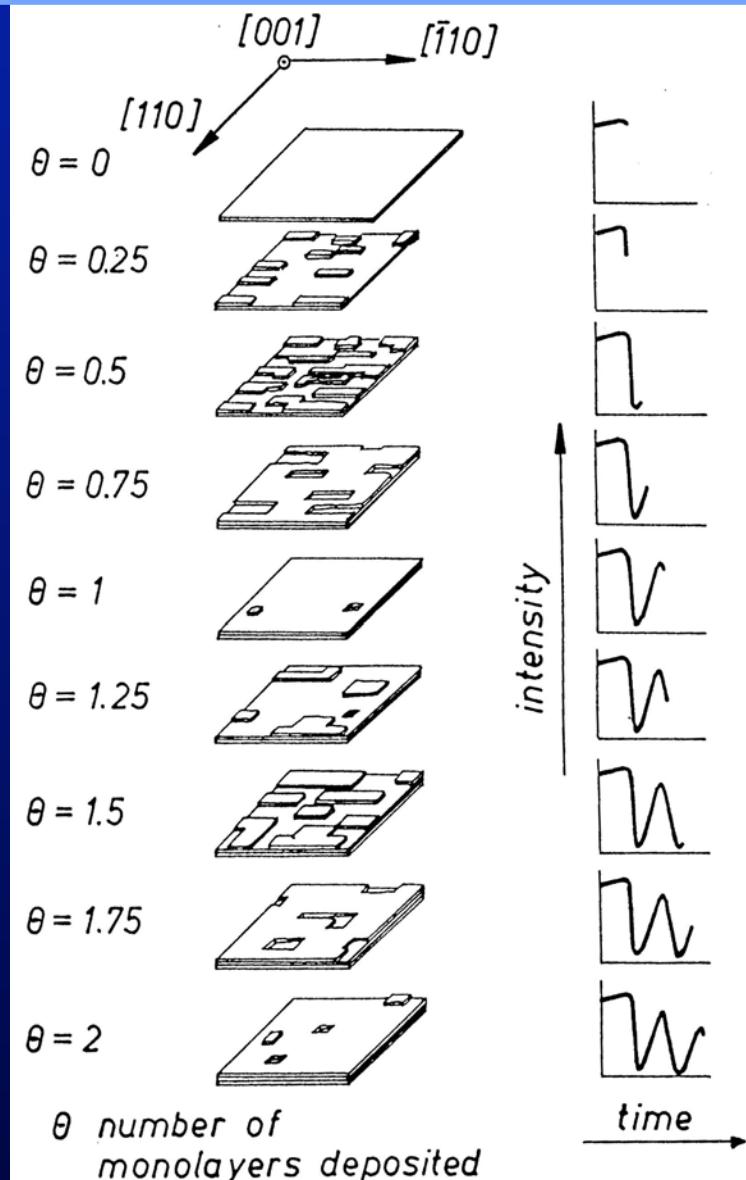


FIG. 1. Schematic diagram of RHEED geometry showing the incident beam at an angle θ to the surface plane; azimuthal angle φ . The elongated spots indicate the intersection of the Ewald sphere with the 01 , 00 , and $0\bar{1}$ rods.

B. Bölger and P. K. Larsen
Review of Scientific Instruments **57** (1986) 1363-1367.

B.A. Joyce, P.J. Dobson, J.H. Neave,
K. Woodbridge, J. Zhang,
P.K. Larsen, and B Bölger,
Surface Science **168** (1986) 423-438.



What is MBE?

- (a) Molecular-Beam Epitaxy
- (b) Mega-Buck Evaporator
- (c) Many Boring Evenings
- (d) Mainly Broken Equipment
- (e) All of the above

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- Detailed Examples of Oxide MBE
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- How can I gain access to an oxide MBE if I don't have one?
Use PARADIM's oxide MBE (+ ARPES + ...)

MBE for Science / Technology

- 1998 Nobel Prize in Physics—Fractional Quantum Hall Effect
 - Horst Ludwig Störmer
 - Daniel Chee Tsui
 - Robert B. Laughlin
- 2000 Nobel Prize in Physics—Semiconductor Optoelectronics
 - Zhores Ivanovich Alferov
 - Herbert Kroemer

Modulation Doping



R. Dingle, H.L. Störmer, A.C. Gossard, and W. Wiegmann, *Applied Physics Letters* **33** (1978) 665-667.

Figure 2 Four pioneers of modulation doping gather around an early MBE machine at Bell Labs in 1978: (left-right) Willy Wiegmann, Art Gossard, Horst Störmer and Ray Dingle. Störmer and his Bell Labs colleague Daniel Tsui shared the Nobel prize for discovering the fractional quantum Hall effect in devices made by Gossard and co-workers with MBE.

Modulation Doping

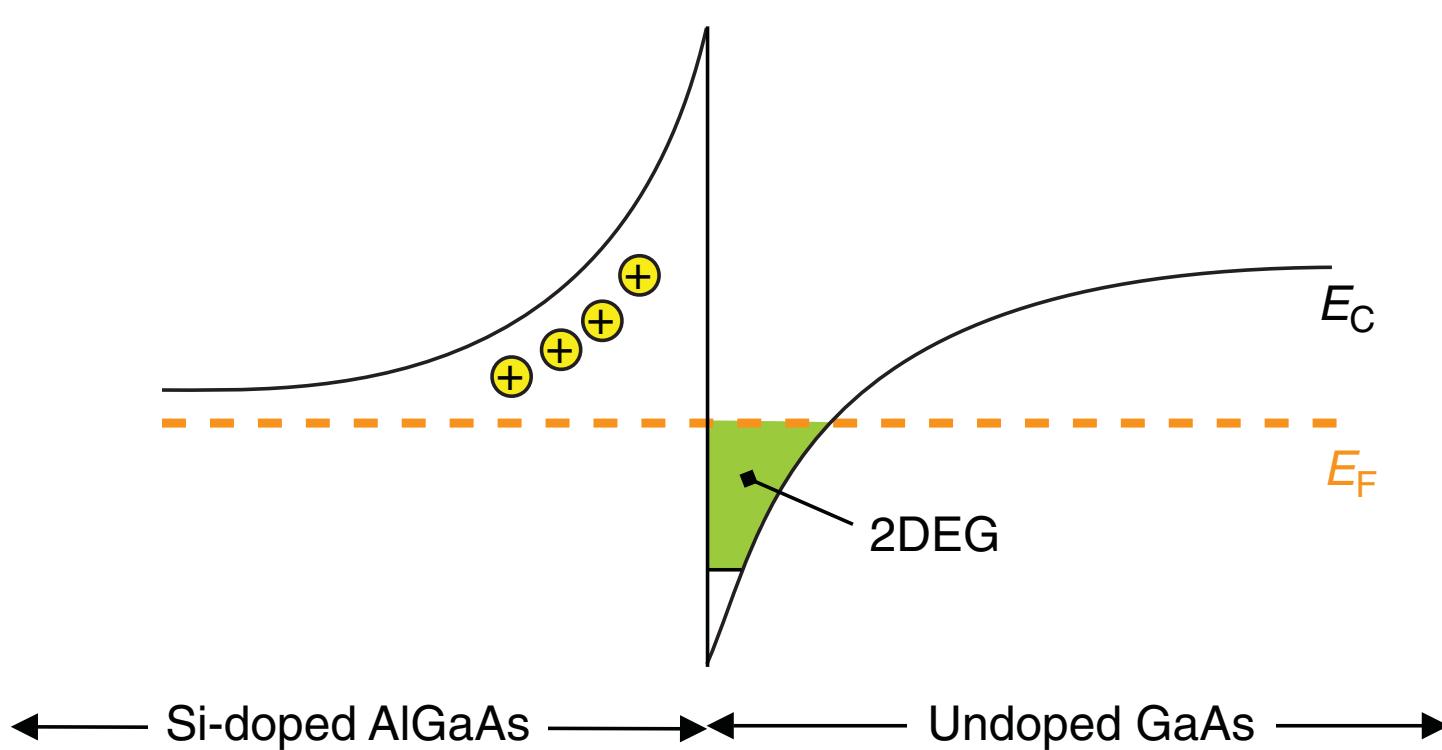
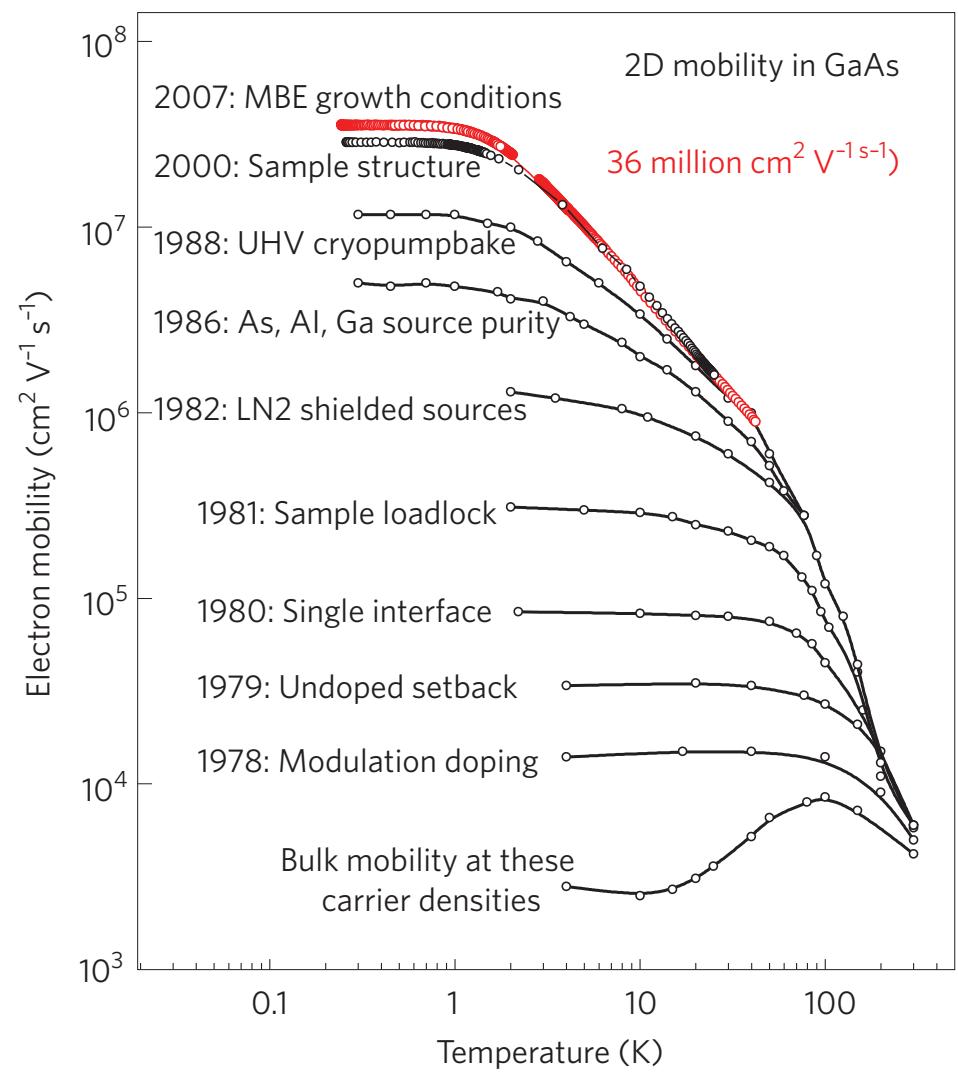
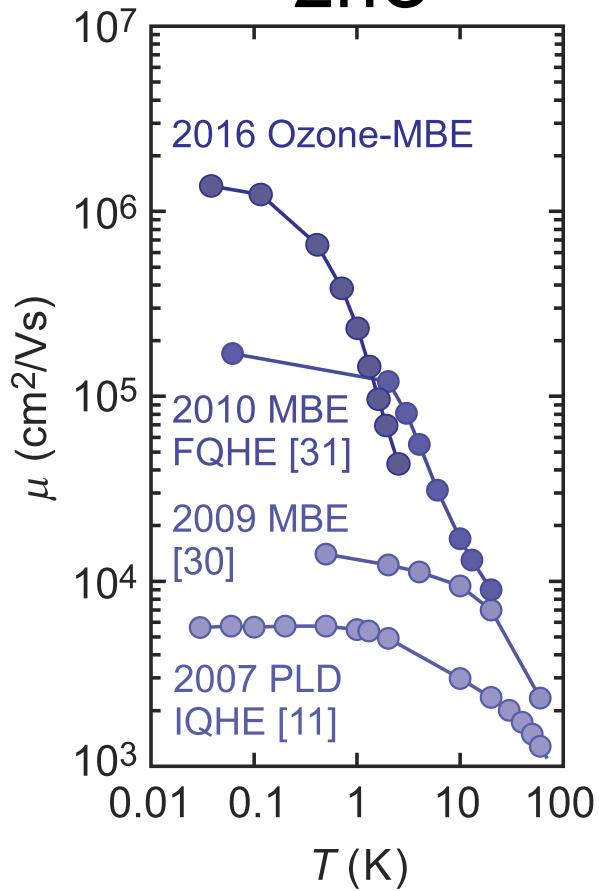


Figure 1. Band diagram showing the formation of a two-dimensional electron gas (2DEG) at a Si-doped AlGaAs–GaAs heterojunction. *Note:* E_F is the value of the Fermi energy, and E_C gives the energy of the conduction band edge.

Mobility Achieved with MBE

$$m_{e,\text{ZnO}}^* > 4 m_{e,\text{GaAs}}^*$$

ZnO



J. Falson, Y. Kozuka, M. Uchida, J.H. Smet, T.-H. Arima,
A. Tsukazaki, and M. Kawasaki, *Scientific Reports* **6**
(2016) 26598.

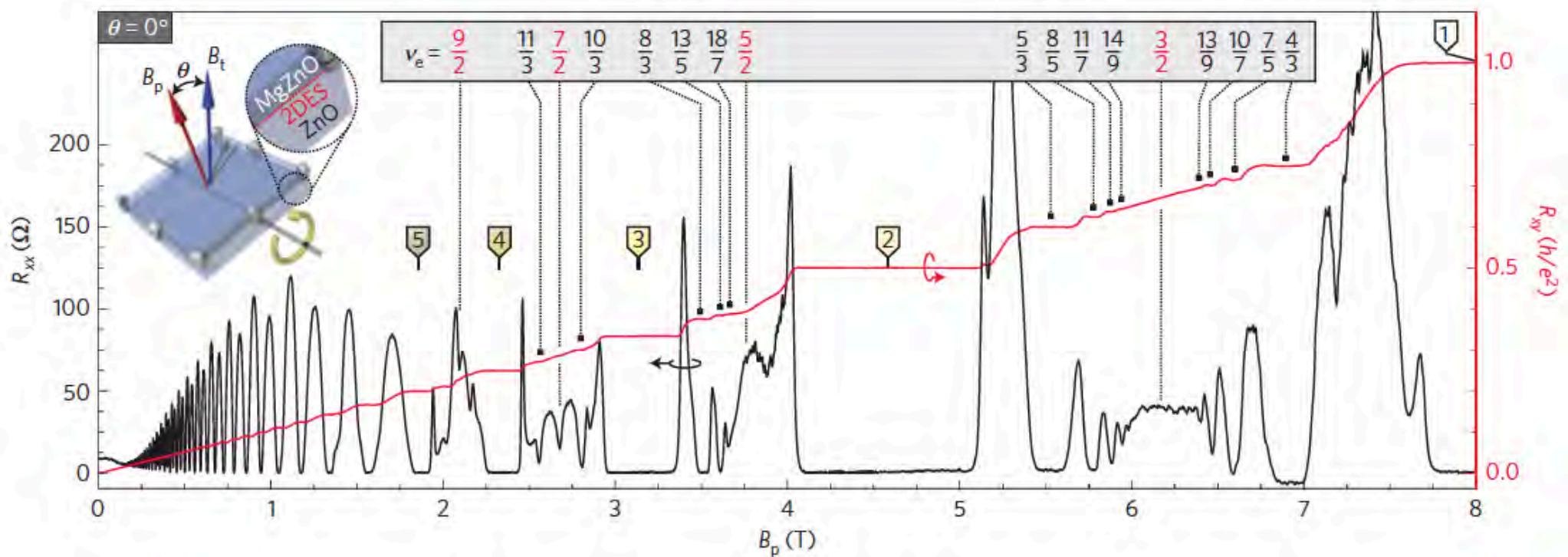
PARADIM

L. Pfeiffer and K.W. West, *Physics E* **20** (2003) 57-64.

D.G. Schlom and L.N. Pfeiffer,
Nature Materials **9** (2010) 881-883.



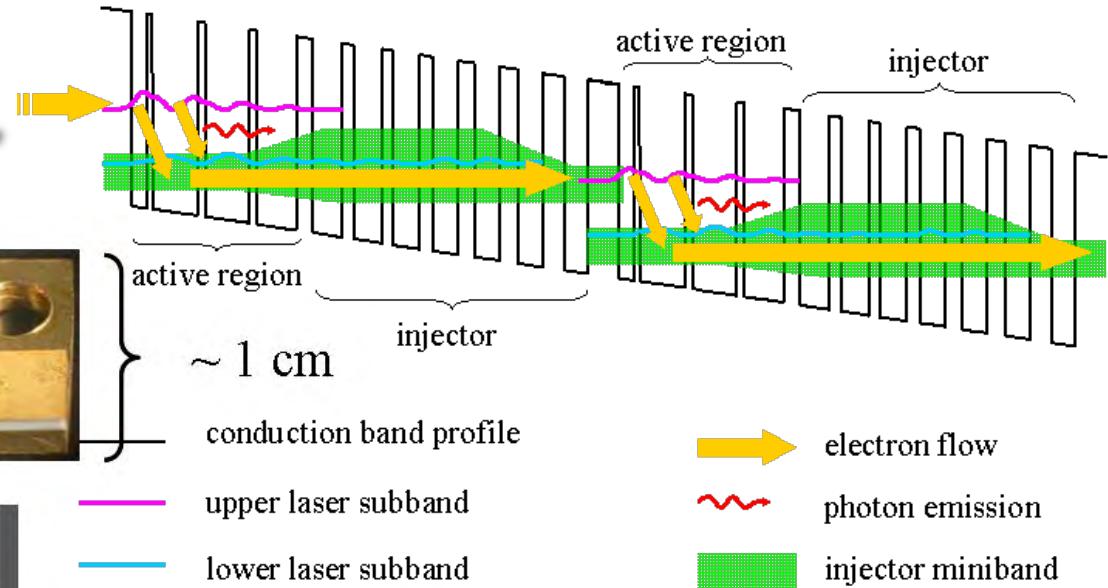
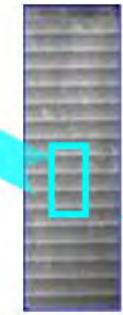
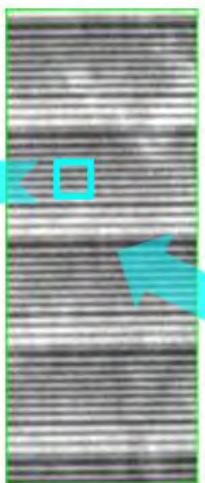
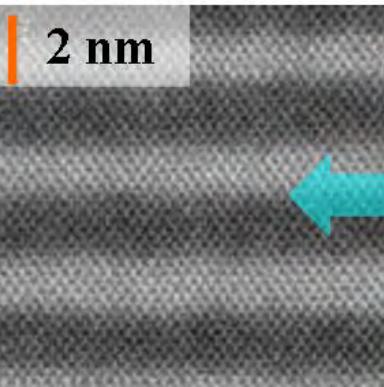
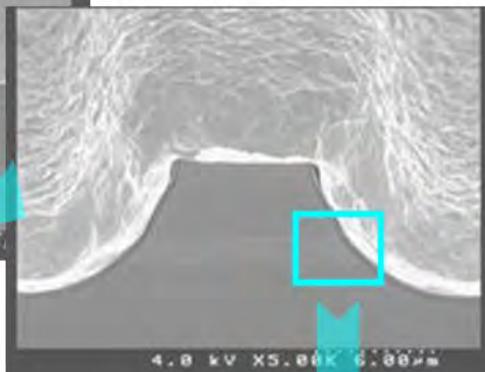
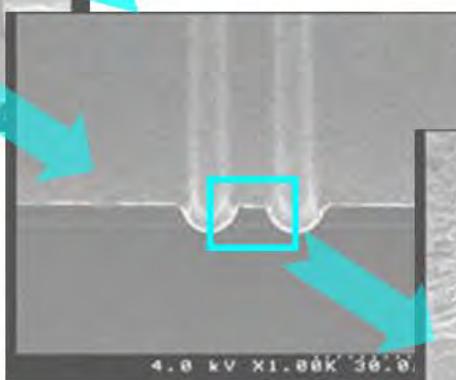
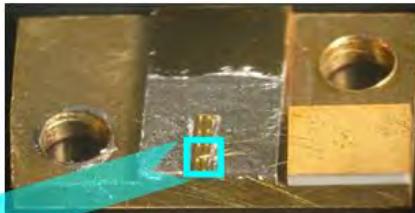
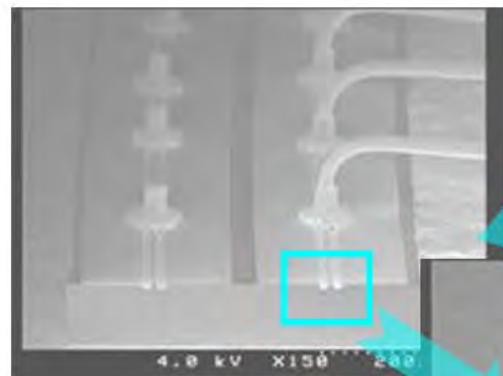
Mobility Achieved with MBE



J. Falson, D. Maryenko, B. Friess, D. Zhang, Y. Kozuka, A. Tsukazaki, J. H. Smet, and M. Kawasaki,
“Even-denominator Fractional Quantum Hall Physics in ZnO”

Nature Physics **11** (2015) 347–351.

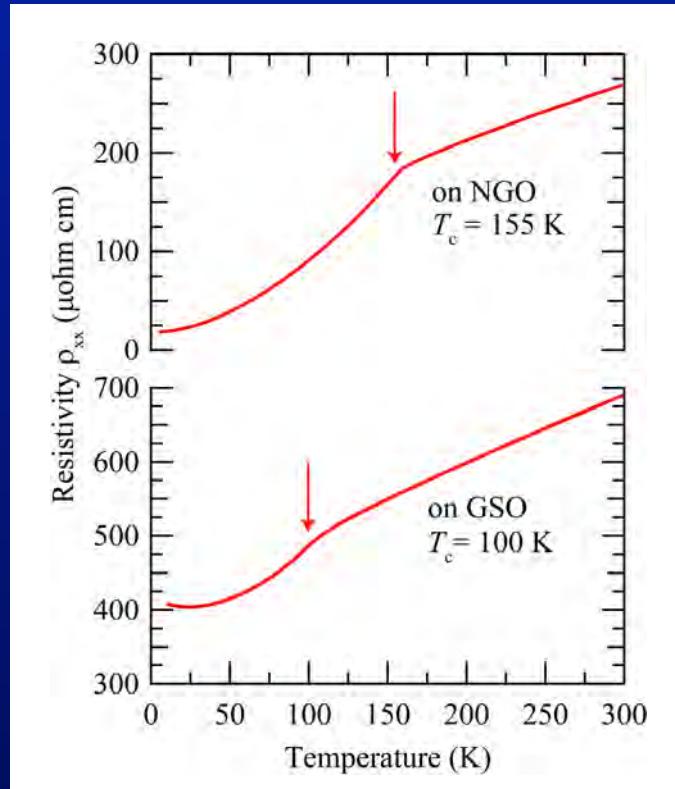
Quantum Cascade Laser



Transport of SrRuO₃ Films

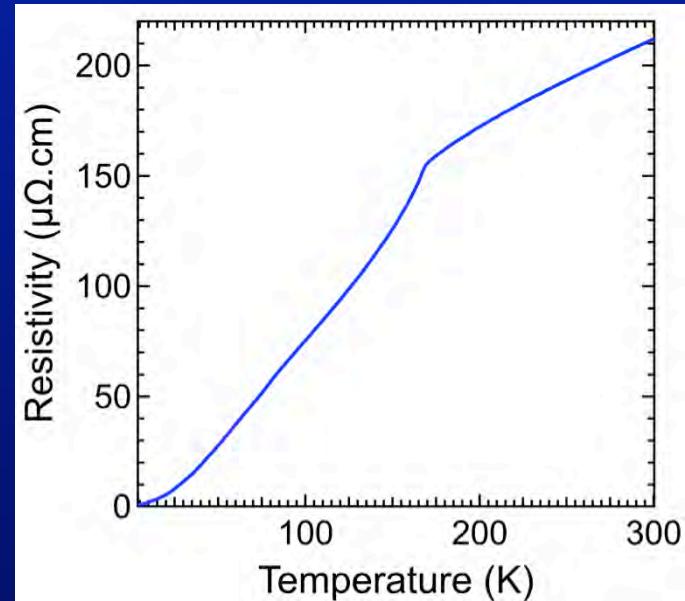
Best PLD Film

$$\rho_{300\text{ K}} / \rho_{10\text{ K}} = 14.1$$



Best MBE Film

$$\rho_{300\text{ K}} / \rho_{10\text{ K}} = 115$$



~20 nm SrRuO₃ / (110) NdGaO₃

D. Kan, R. Aso, H. Kurata, and Y. Shimakawa,
J. Appl. Phys. **113** (2013) 173912.

48 nm SrRuO₃ / (110) DyScO₃

H.P. Nair, presented at Spring MRS Meeting (2019).

See also H.P. Nair, Y. Liu, J.P. Ruf, N.J. Schreiber, S-L. Shang, D.J. Baek, B.H. Goodge, L.F. Kourkoutis, Z.K. Liu, K.M. Shen, and D.G. Schlom
APL Materials **6** (2018) 046101.

Comparison of Oxide Properties

Material	Best MBE Figure of Merit	Best non-MBE Figure of Merit	References
ZnO	$\mu_e = 230,000 \text{ cm}^2/(\text{V}\cdot\text{s})$ at 1 K	$\mu_e = 5,500 \text{ cm}^2/(\text{V}\cdot\text{s})$ at 1 K	1,2
SrTiO ₃	$\mu_e = 53,200 \text{ cm}^2/(\text{V}\cdot\text{s})$ at 2 K	$\mu_e = 6,600 \text{ cm}^2/(\text{V}\cdot\text{s})$ at 2 K	3,4
SrRuO ₃	$R_{300 \text{ K}} / R_{10 \text{ K}} = 115$	$R_{300 \text{ K}} / R_{10 \text{ K}} = 14$	5,6
Sr ₂ RuO ₄	superconducting $T_{c,\text{midpoint}} = 1.8 \text{ K}$	superconducting $T_{c,\text{midpoint}} = 0.8 \text{ K}$	7,8
SrVO ₃	$R_{300 \text{ K}} / R_{5 \text{ K}} = 222$	$R_{300 \text{ K}} / R_{5 \text{ K}} = 2$	9,10
EuO	Metal-insulator transition $\Delta R/R=10^{11}$	Metal-insulator transition $\Delta R/R=5\times10^4$	11,12

¹J. Falson *et al.*, *Scientific Reports* **6** (2016) 26598.

²A. Tsukazaki, A. Ohtomo, T. Kita, Y. Ohno, H. Ohno, and M. Kawasaki, *Science* **315** (2007) 1388–1391.

³T. A. Cain, A.P. Kajdos, and S. Stemmer, *Applied Physics Letters* **102** (2013) 182101.

⁴Y. Kozuka, Y. Hikita, C. Bell, and H.Y. Hwang, *Applied Physics Letters* **97** (2010) 012107.

⁵H. Nair, presented at the Spring MRS Meeting (2019).

⁶D. Kan, R. Aso, H. Kurata, and Y. Shimakawa, *Journal of Applied Physics* **113** (2013) 173912.

⁷H.P. Nair, *et al.*, *APL Materials* **6** (2018) 101108.

⁸Y. Krockenberger *et al.*, *Appl. Phys. Lett.* **97** (2010) 082502.

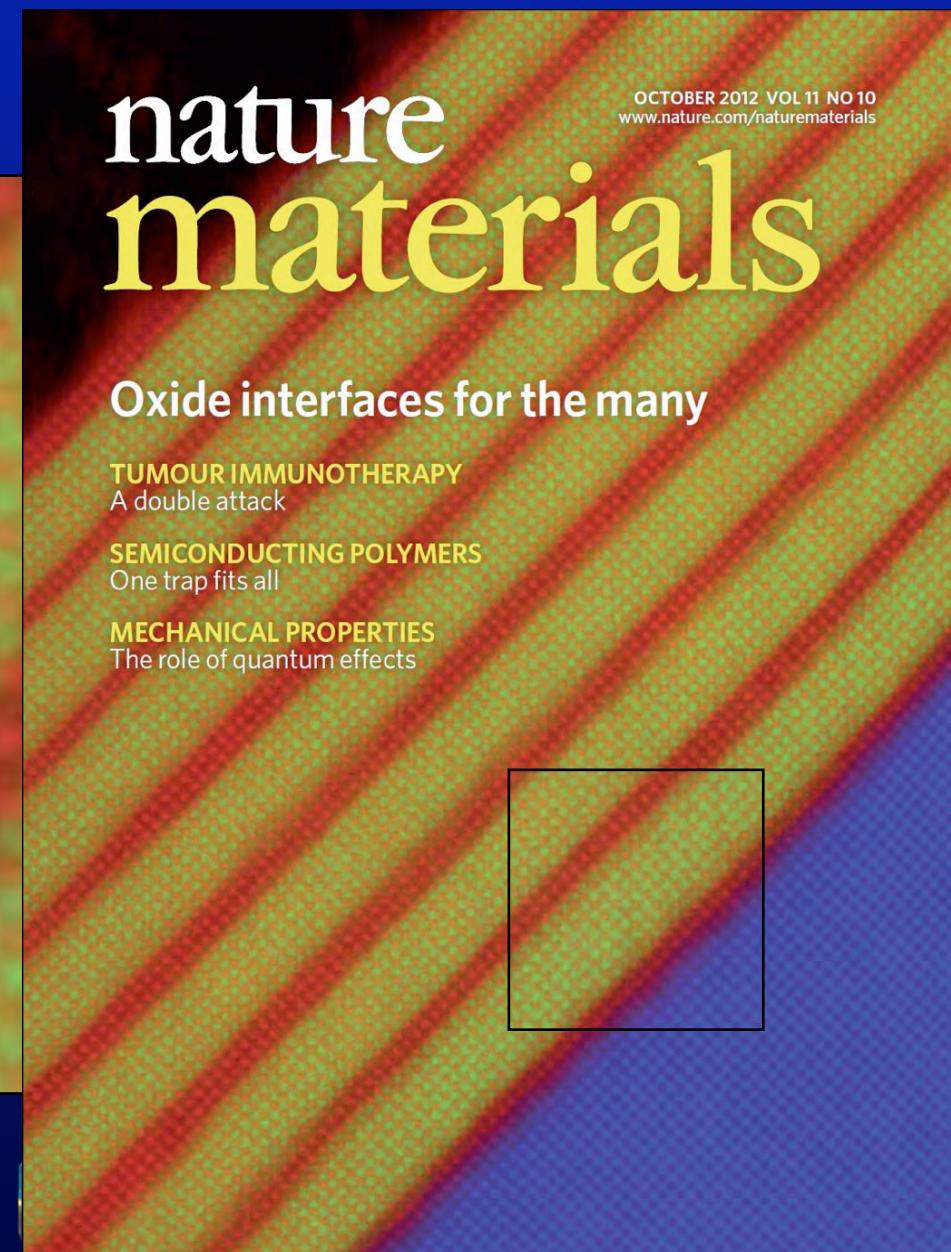
⁹J.A. Moyer, C. Eaton, and R. Engel-Herbert, *Advanced Materials* **25** (2013) 3578–3582.

¹⁰W.C. Sheets, B. Mercey, and W. Prellier, *Applied Physics Letters* **91** (2007) 192102.

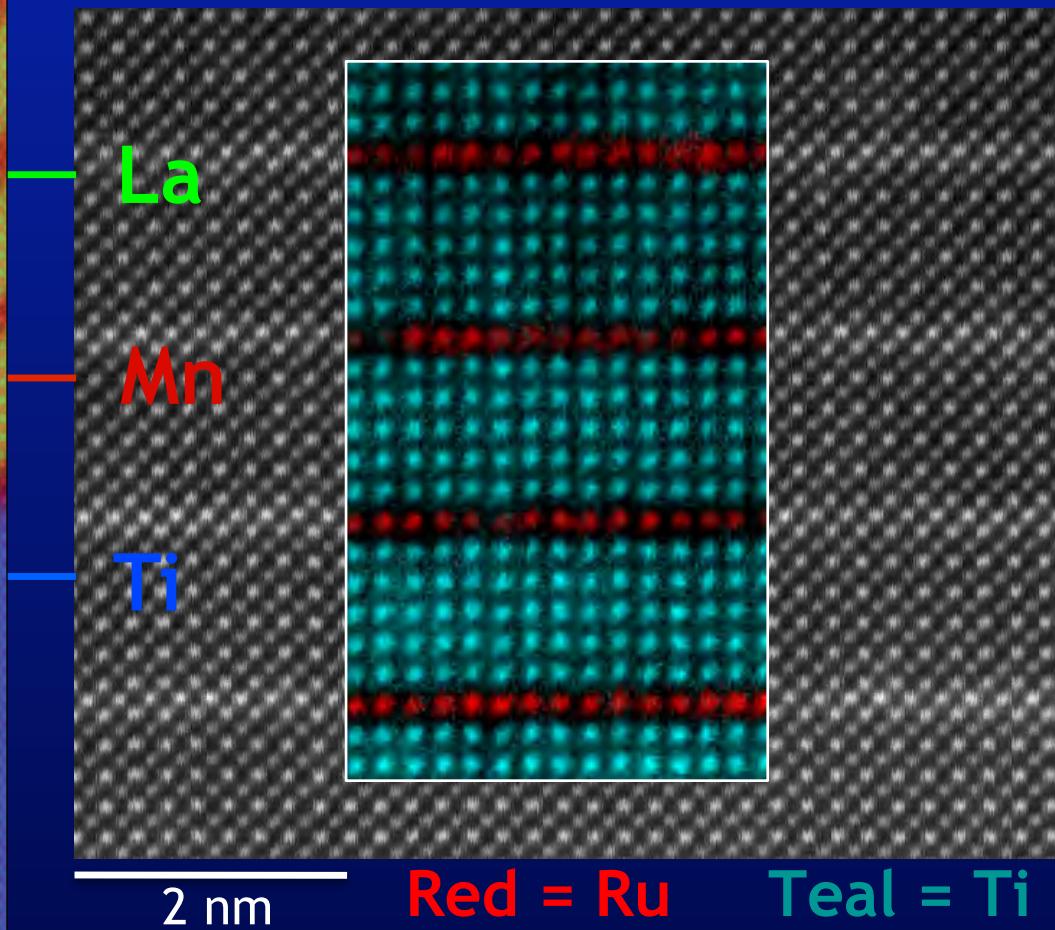
¹¹D.V. Averyanov *et al.*, *Nanotechnology* **29** (2018) 195706.

¹²T. Yamasaki *et al.*, *Applied Physics Letters* **98** (2011) 082116.

Ability to Customize Oxides



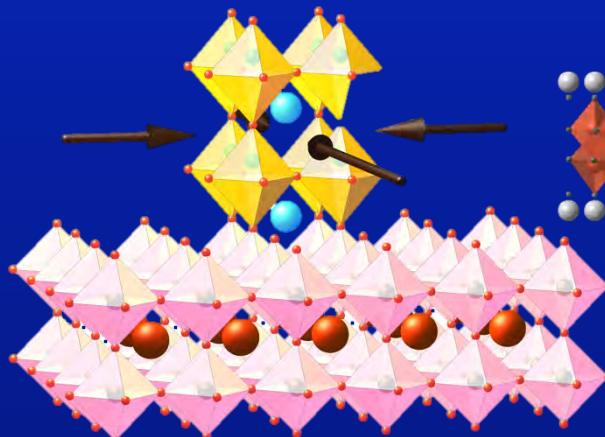
$(\text{SrRuO}_3)_1 / (\text{SrTiO}_3)_5$
Superlattice



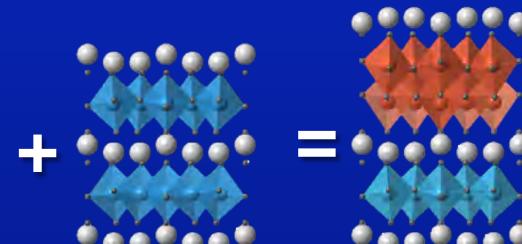
E.J. Monkman, C. Adamo, J.A. Mundy, D.E. Shai, J.W. Harter, D. Shen, B. Burganov, D.A. Muller, D.G. Schlom, and K.M. Shen, *Nature Materials* **11** (2012) 855-859.



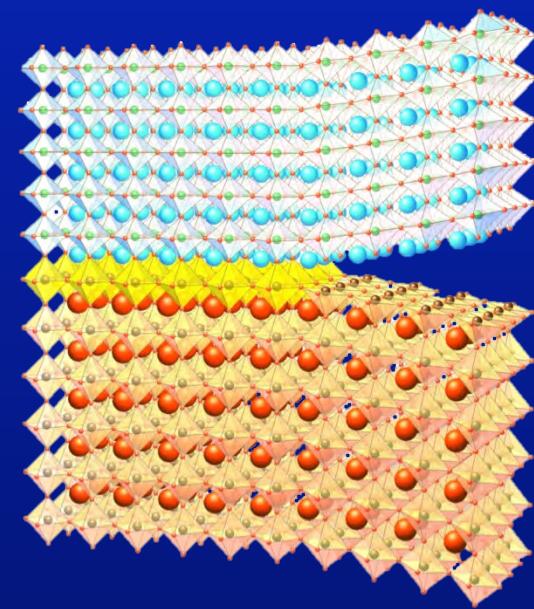
Epitaxial Routes to Engineer Properties



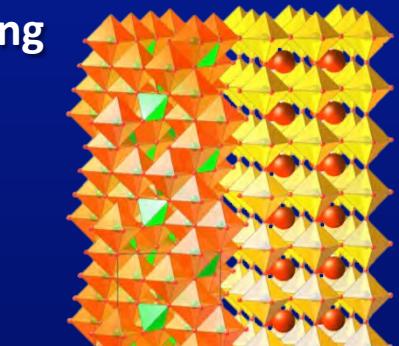
Strain Engineering



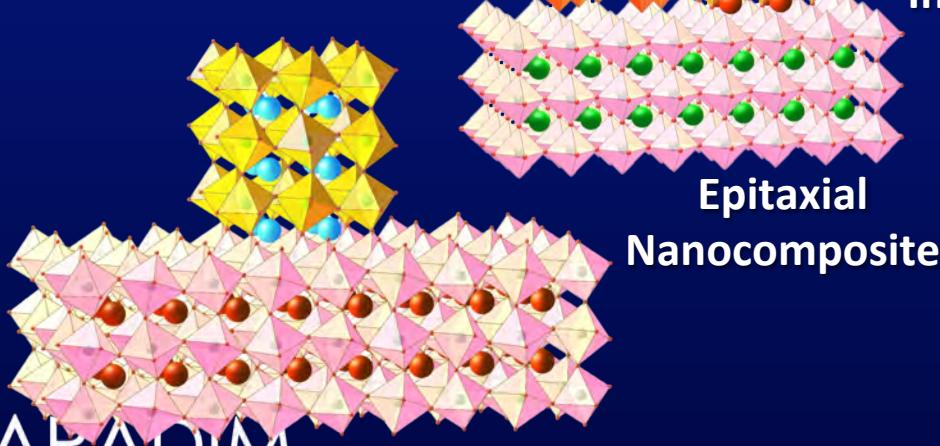
Breaking Symmetries



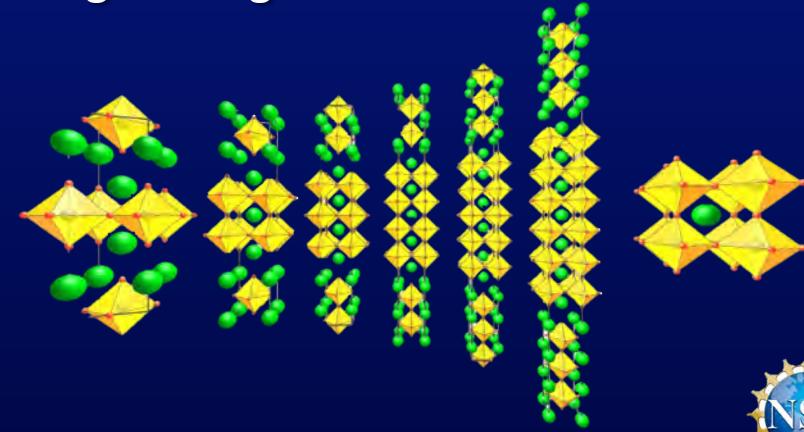
Polarization Doping
and Proximity Effects



Interface Engineering

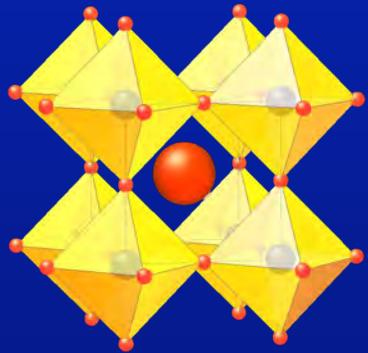


Epitaxial
Nanocomposite



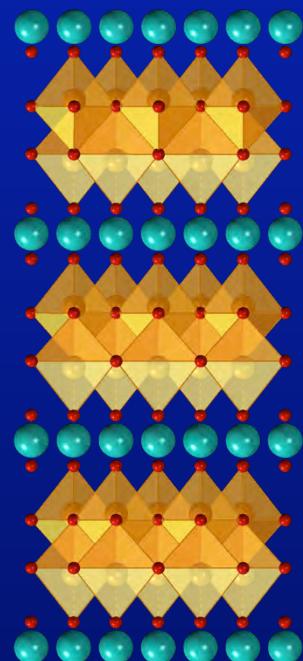
Dimensional Confinement

Examples of Oxides we Grow



BaSnO₃

today's record
transparent transistors

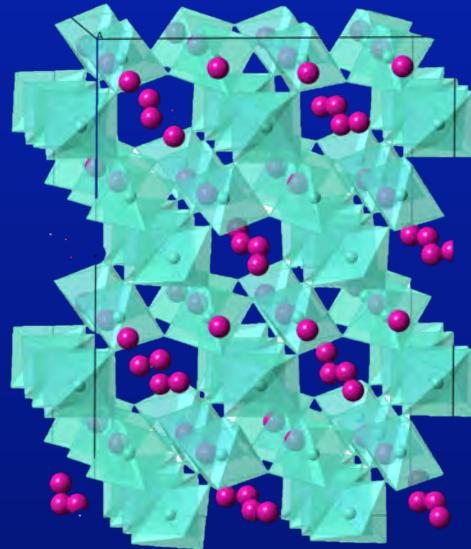


LuFe₂O₄

today's record
room-temperature
multiferroic
(superlattices)

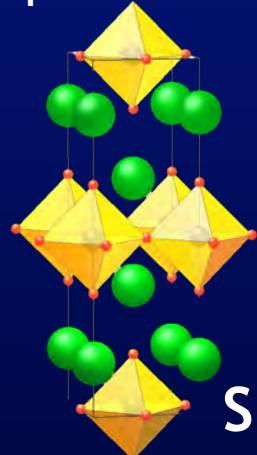
LuFeO₃

PARADIM



$\alpha\text{-Bi}_2\text{Sn}_2\text{O}_7$
(352 atoms/unit cell)

leading
candidate
odd-parity
topological
superconductor

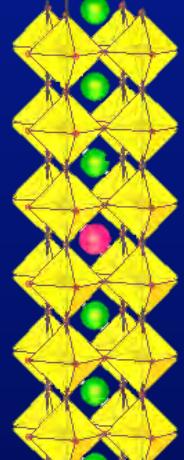
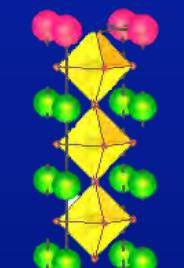


Sr₂RuO₄

today's record
tunable microwave dielectric

Sr₇Ti₆O₁₉

BaSr₆Ti₆O₁₉



MBE Summary

Advantages

- Extreme Flexibility
- Independent Growth Parameters
- Compatible with wide range of *in situ* Diagnostics
- Clean
- Gentle
- Precise Layering Control at the Atomic Level

Disadvantages

- Extreme Flexibility (uncontrolled flexibility = chaos!)
- High Cost
- Long Set-up Time
- MBE (the other meanings...)

Your friend wants to deposit a $\text{YBa}_2\text{Cu}_3\text{O}_7$ film with the highest critical current density; what technique do you recommend?

- (a) MBE
- (b) Pulsed-laser deposition (PLD)
- (c) Sputtering
- (d) Metal-Organic Chemical Vapor Deposition (MOCVD)
- (e) Chemical-Solution Deposition (Sol-Gel)

