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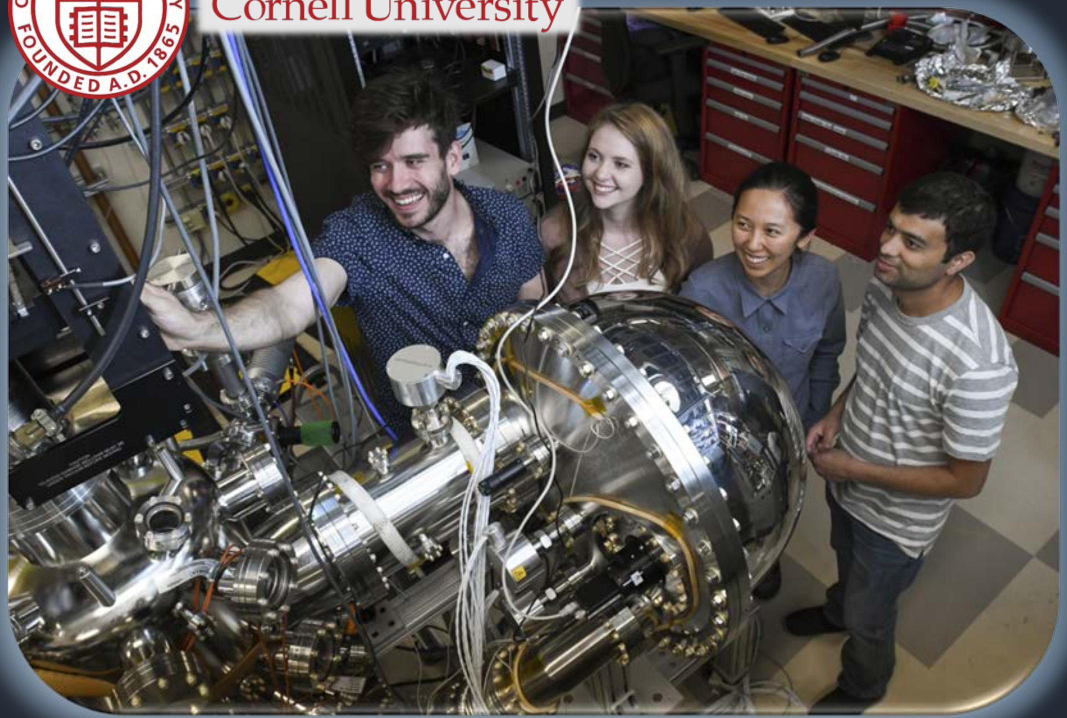
Summer School 2022

Cornell University



MBE + ARPES:

Customizing Quantum Materials with Atomic Layer Precision and Measuring their Electronic Structure

June 13-17, 2022

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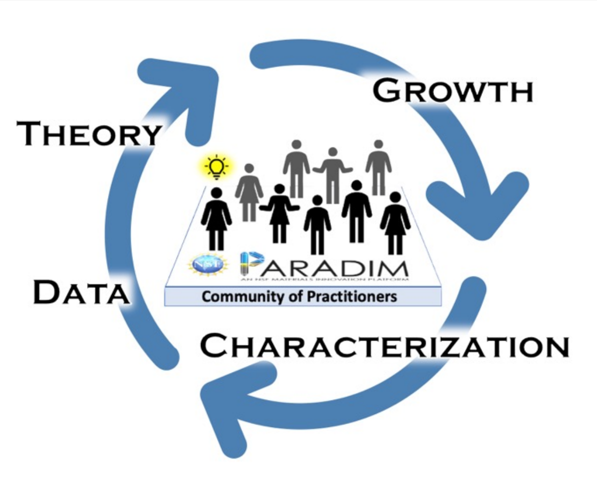

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LECTURE #1—
GREATEST HITS OF MBE

Darrell G. Schlom

Department of Materials Science and Engineering
Cornell University

Kavli Institute at Cornell for Nanoscale Science

Leibniz-Institut für Kristallzüchtung

Outline of MBE Lectures

AN NSF MATERIALS INNOVATION PLATFORM

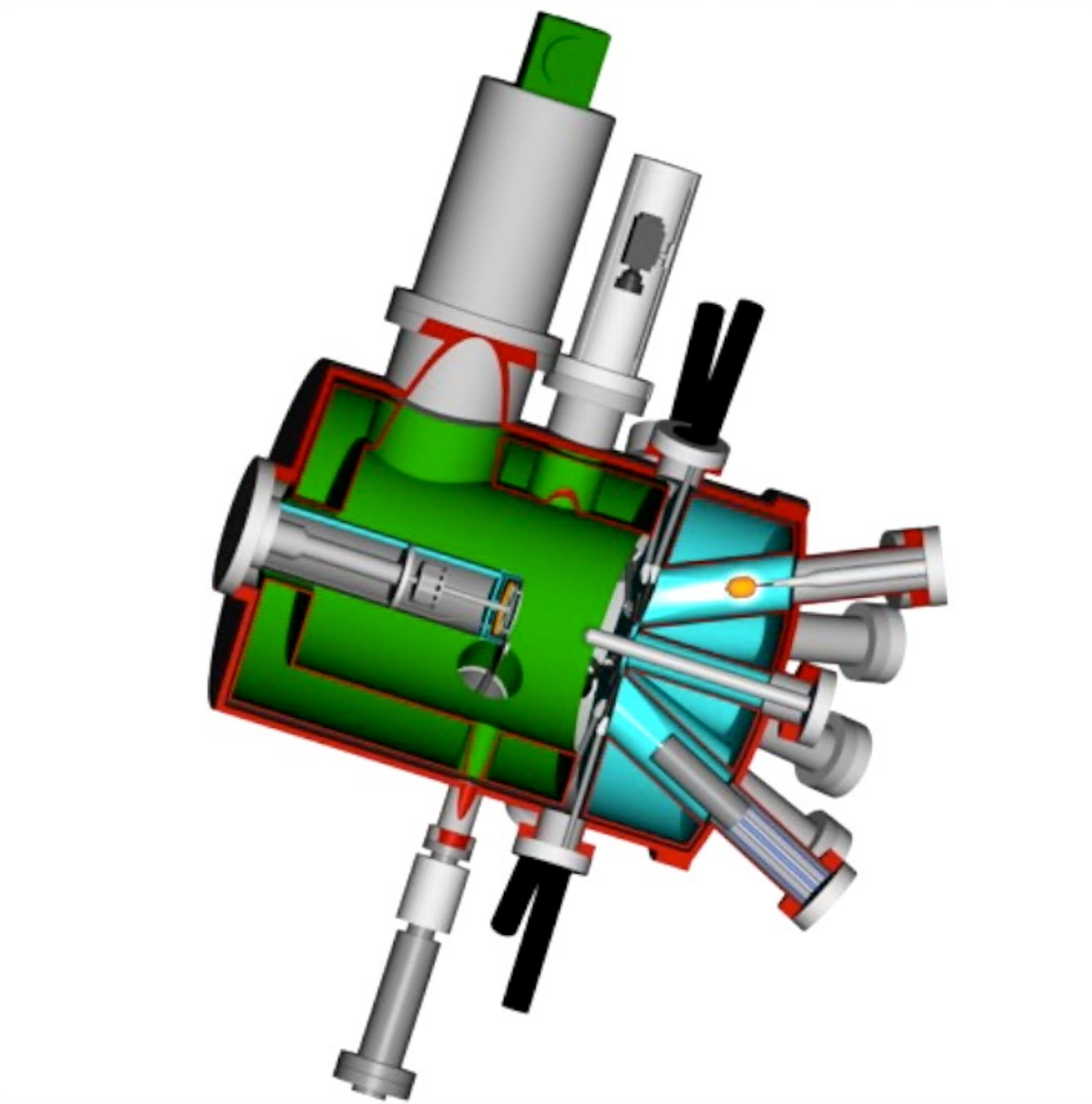
- What is MBE and what is it good for?
  Lecture #1 — Greatest hits of MBE

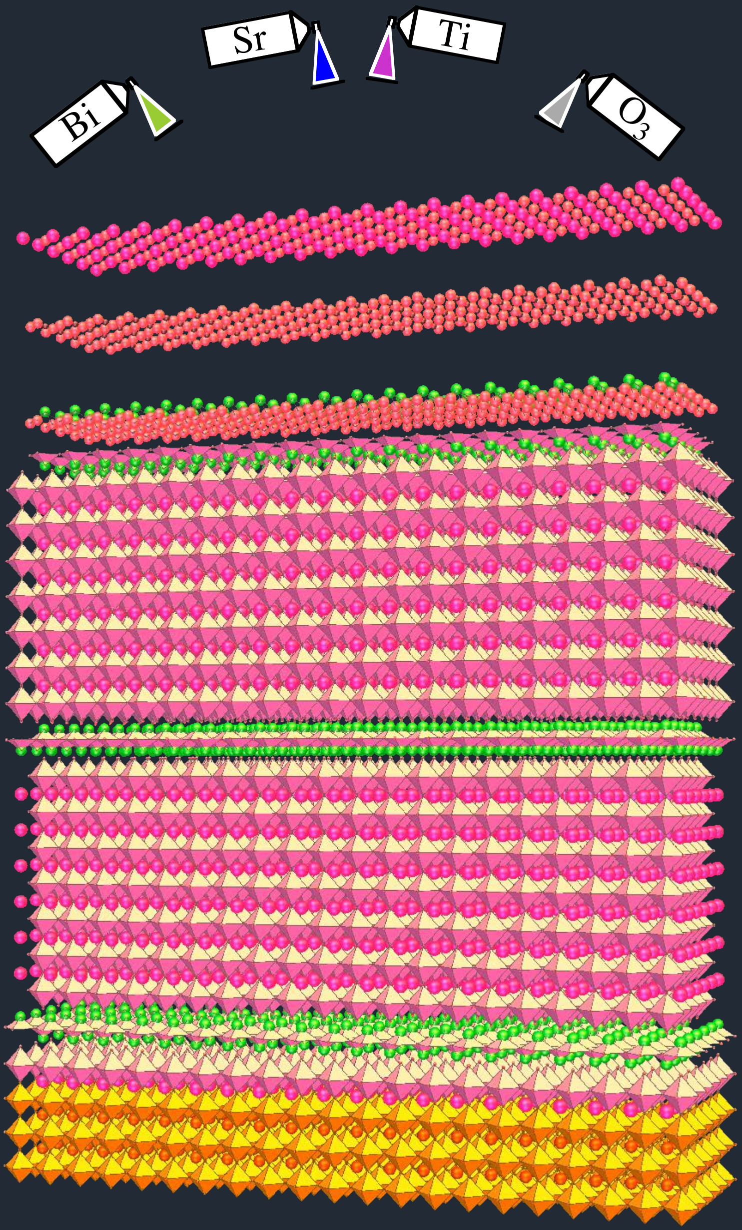
- How to grow your favorite oxide by MBE?
  Lectures #2-4 — Nuts and bolts of oxide MBE

- 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 + ...)

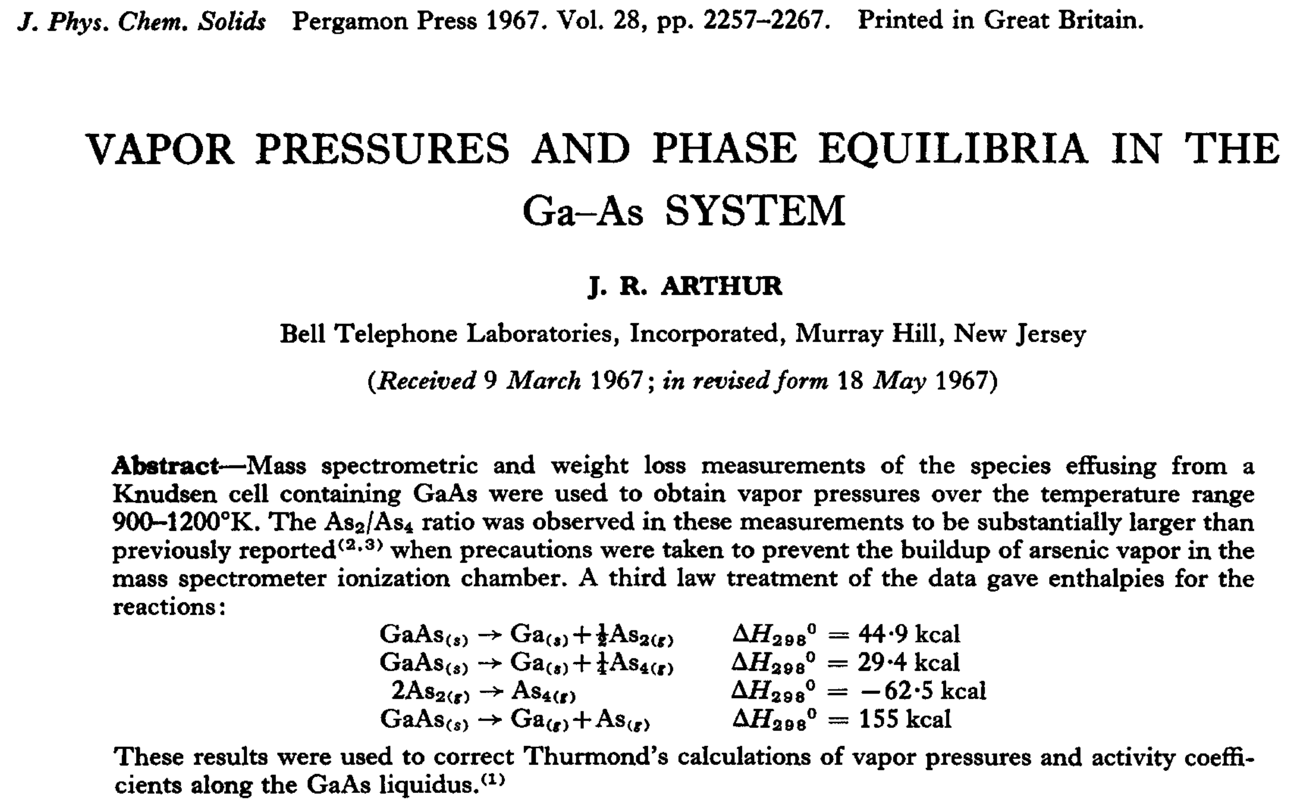
MBE ≈ Atomic Spray Painting





Video by **Andreas Schmehl**

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:

$$\begin{aligned} &GaAs_{(s)} \rightarrow Ga_{(s)} + \tfrac{1}{2}As_{2(g)} && \Delta H_{298}{}^0 = 44\cdot9 \text{ kcal} \\ &GaAs_{(s)} \rightarrow Ga_{(s)} + \tfrac{1}{4}As_{4(g)} && \Delta H_{298}{}^0 = 29\cdot4 \text{ kcal} \\ &2As_{2(g)} \rightarrow As_{4(g)} && \Delta H_{298}{}^0 = -62\cdot5 \text{ kcal} \\ &GaAs_{(s)} \rightarrow Ga_{(g)} + As_{(g)} && \Delta H_{298}{}^0 = 155 \text{ kcal} \end{aligned}$$

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

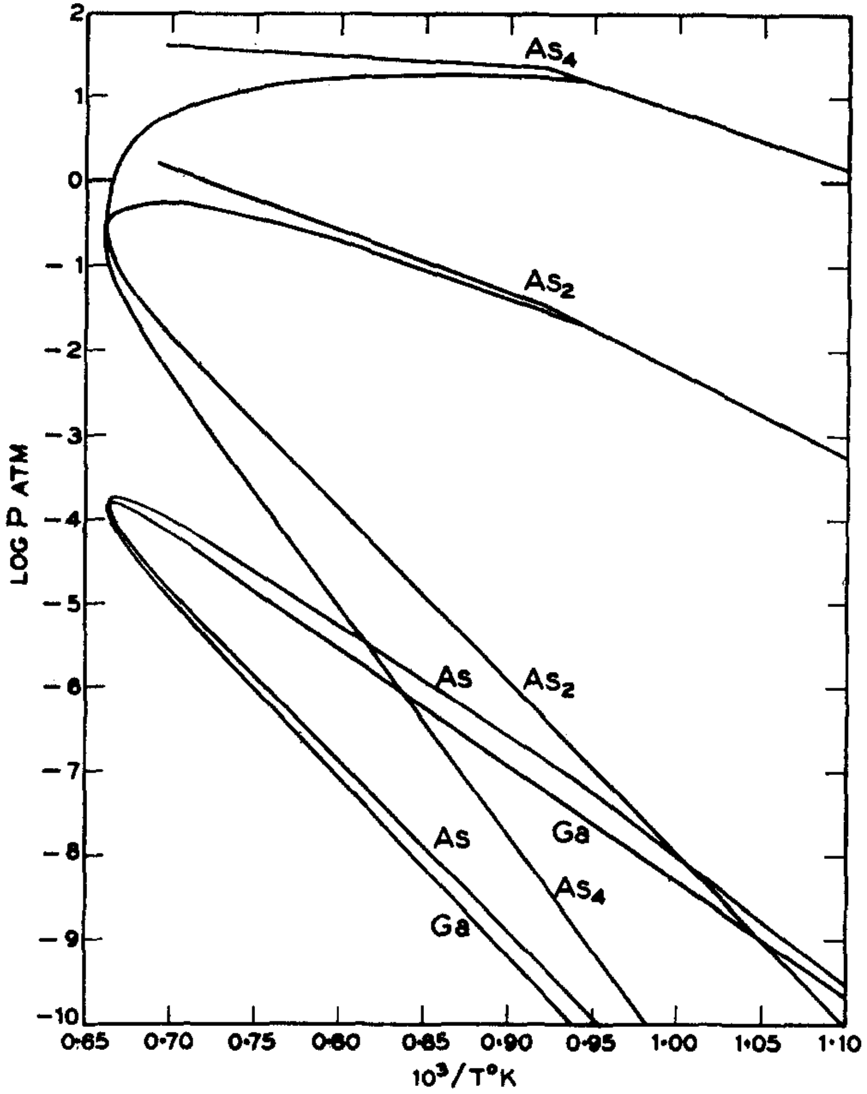


FIG. 5. Equilibrium vapor pressures of As, As_2, As_4 and Ga along the binary liquidus as a function of T^{-1}. Pressures of As_2 and As_4 over pure solid and liquid As are also shown.

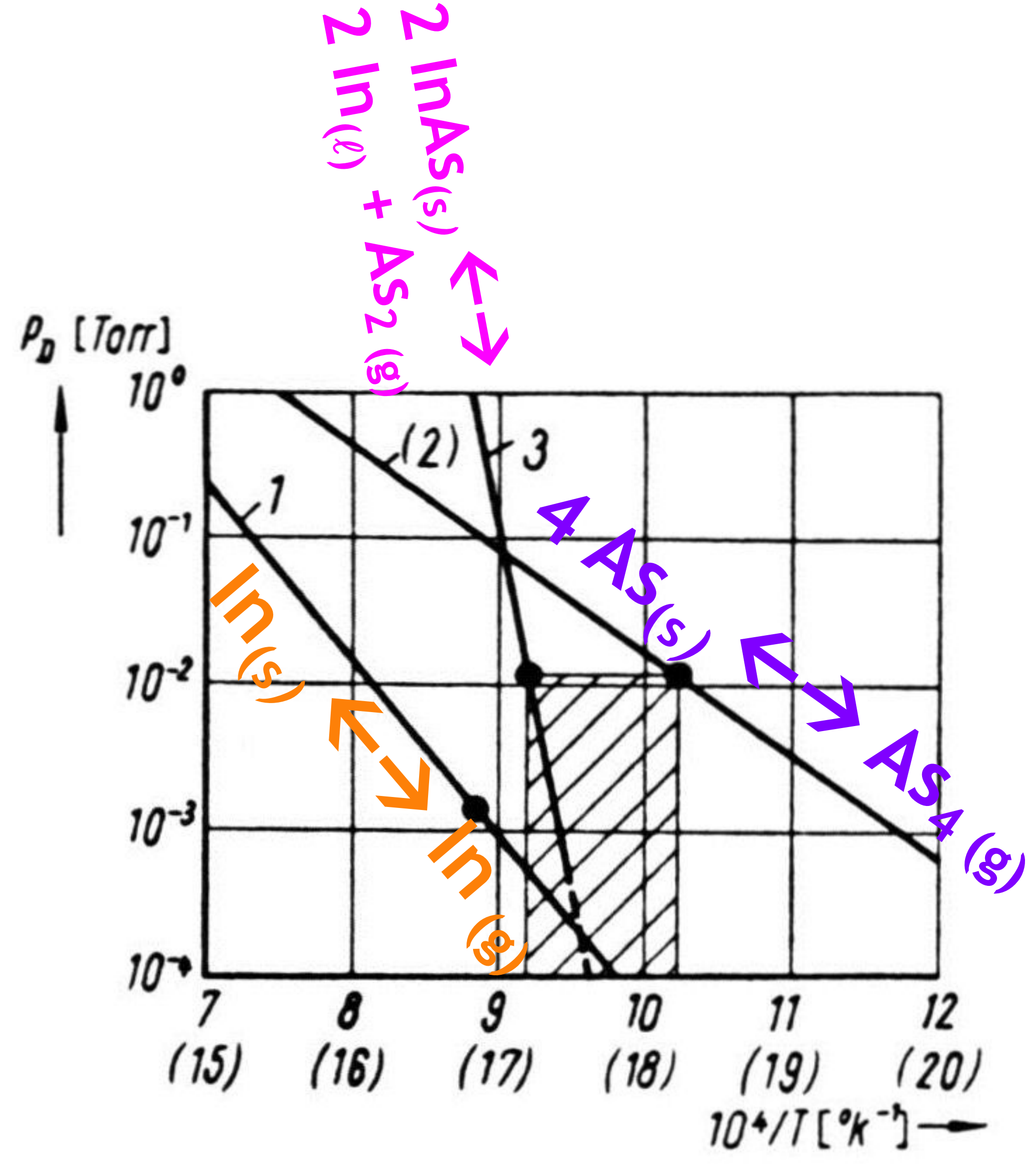
J.R. Arthur
"Vapor Pressures and Phase Equilibria in the Ga-As System"
J. Phys. Chem. Solids **28** (1967) 2257–2267.

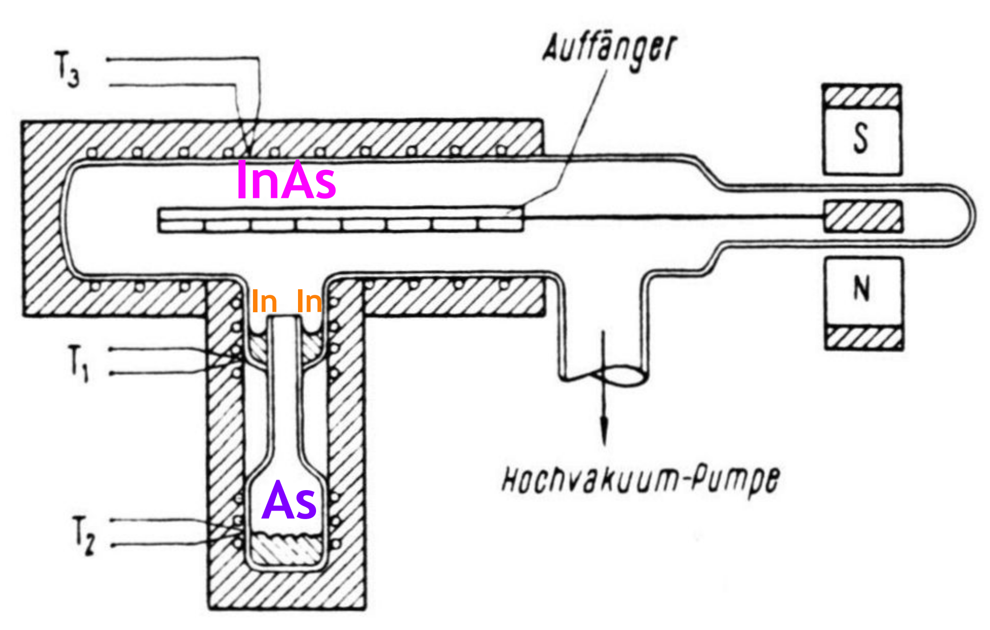
Key Enablers of MBE

- **“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





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

Key Enablers of MBE

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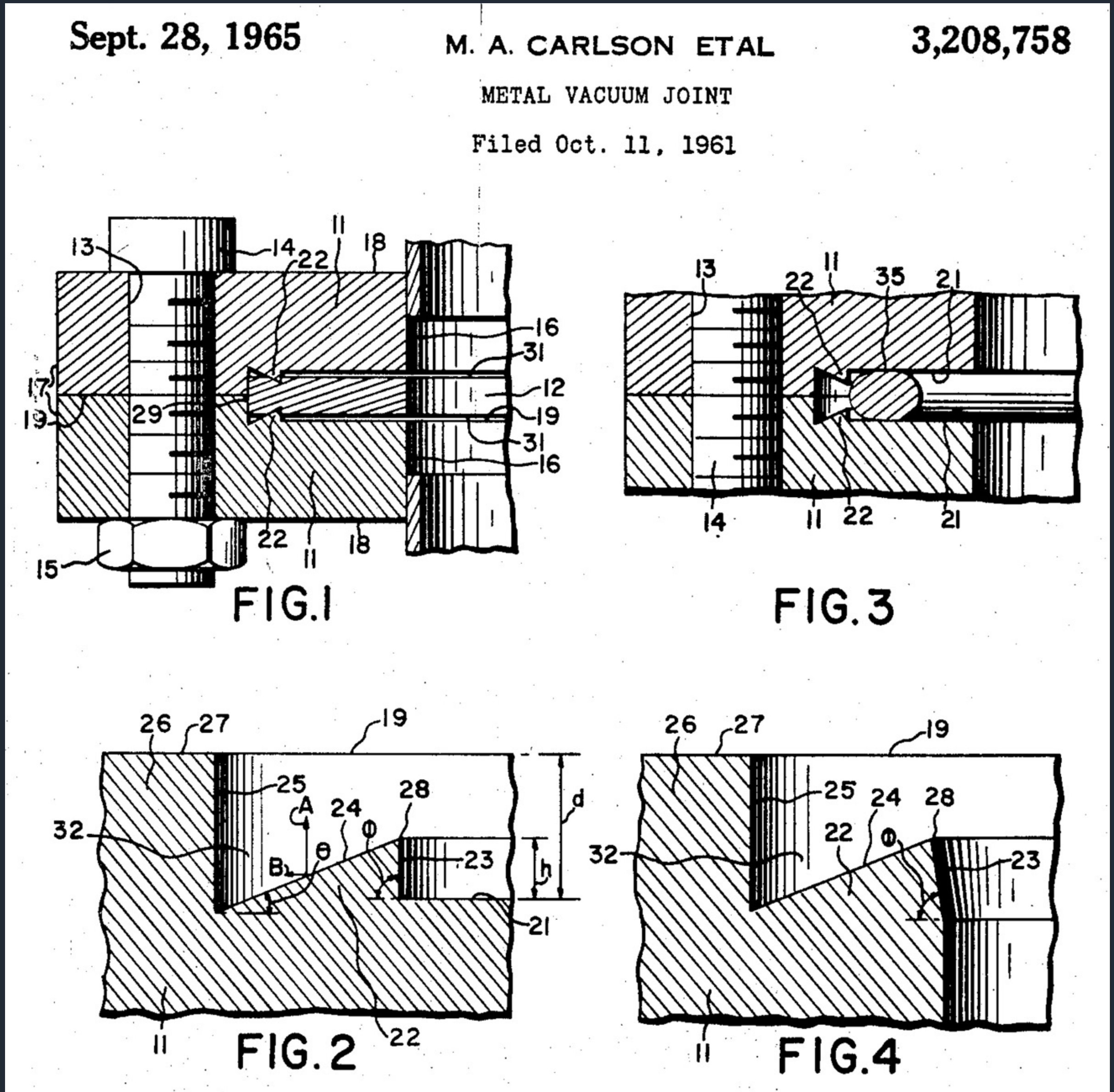
  H. Freller and K.G. Günther, “Three-temperature method as an origin of molecular beam epitaxy,” *Thin Solid Films* **88** (1982) 291–307.

- **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 ETAL 3,208,758

METAL VACUUM JOINT

Filed Oct. 11, 1961

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

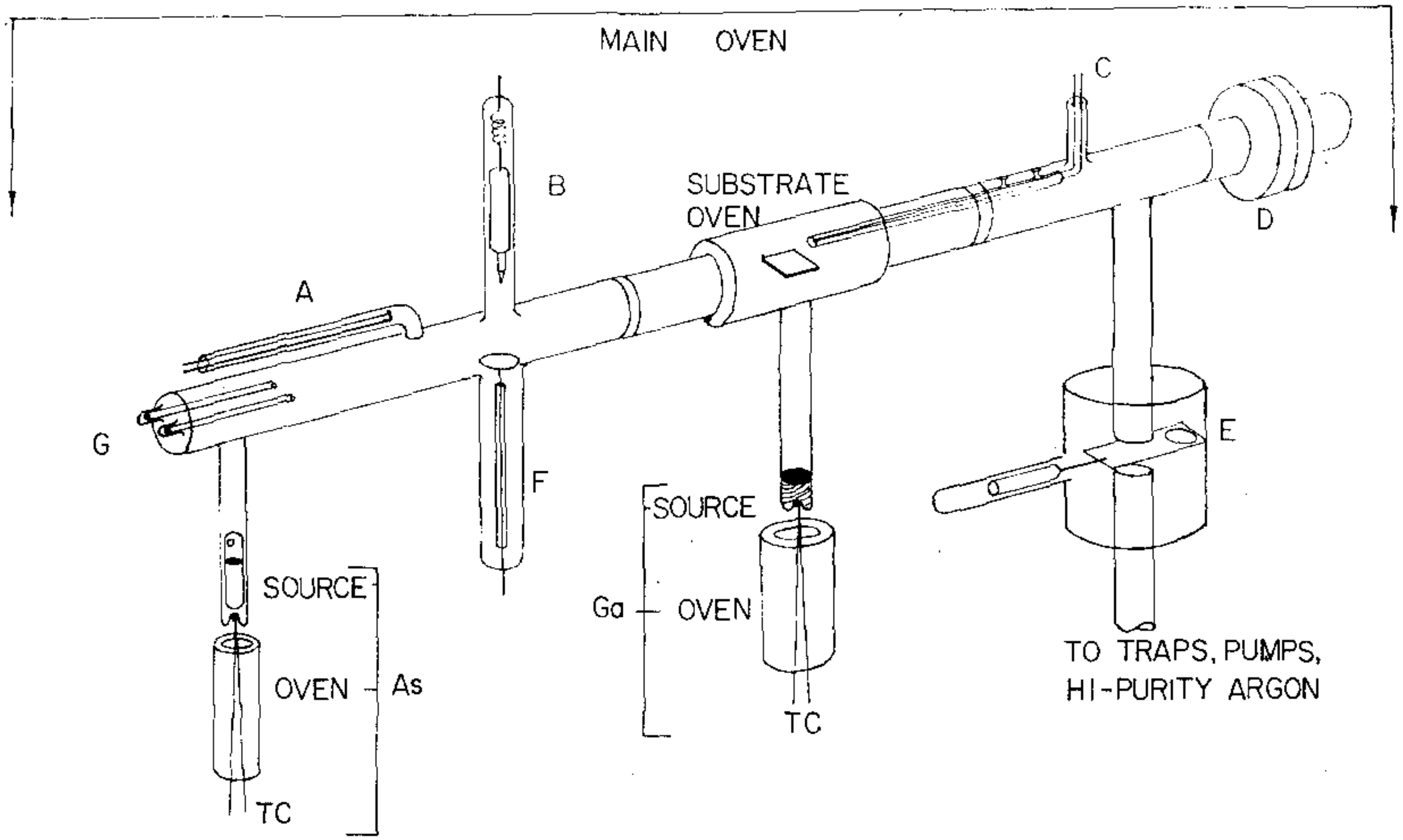
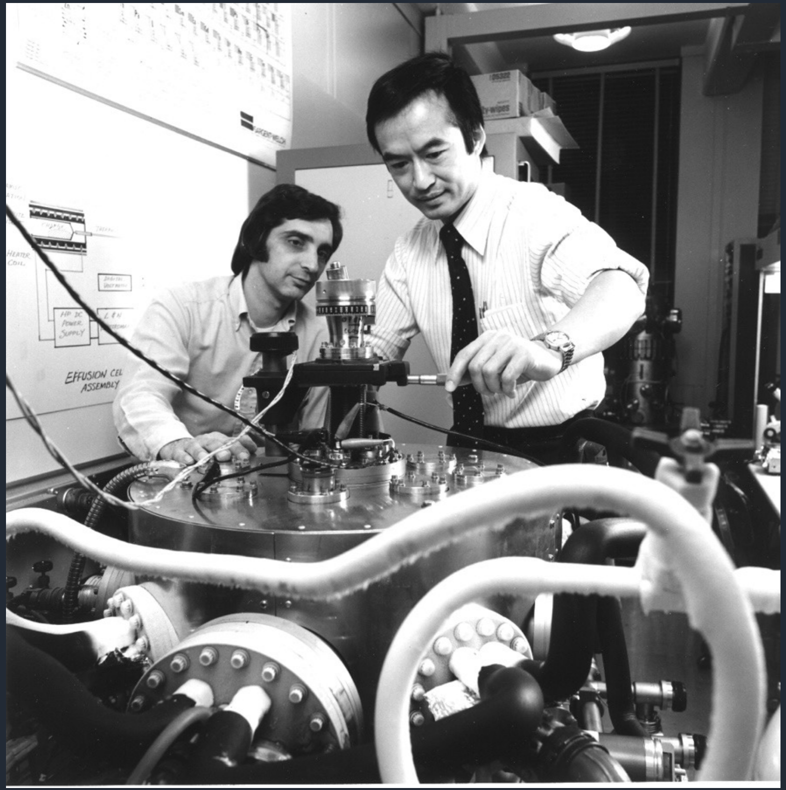


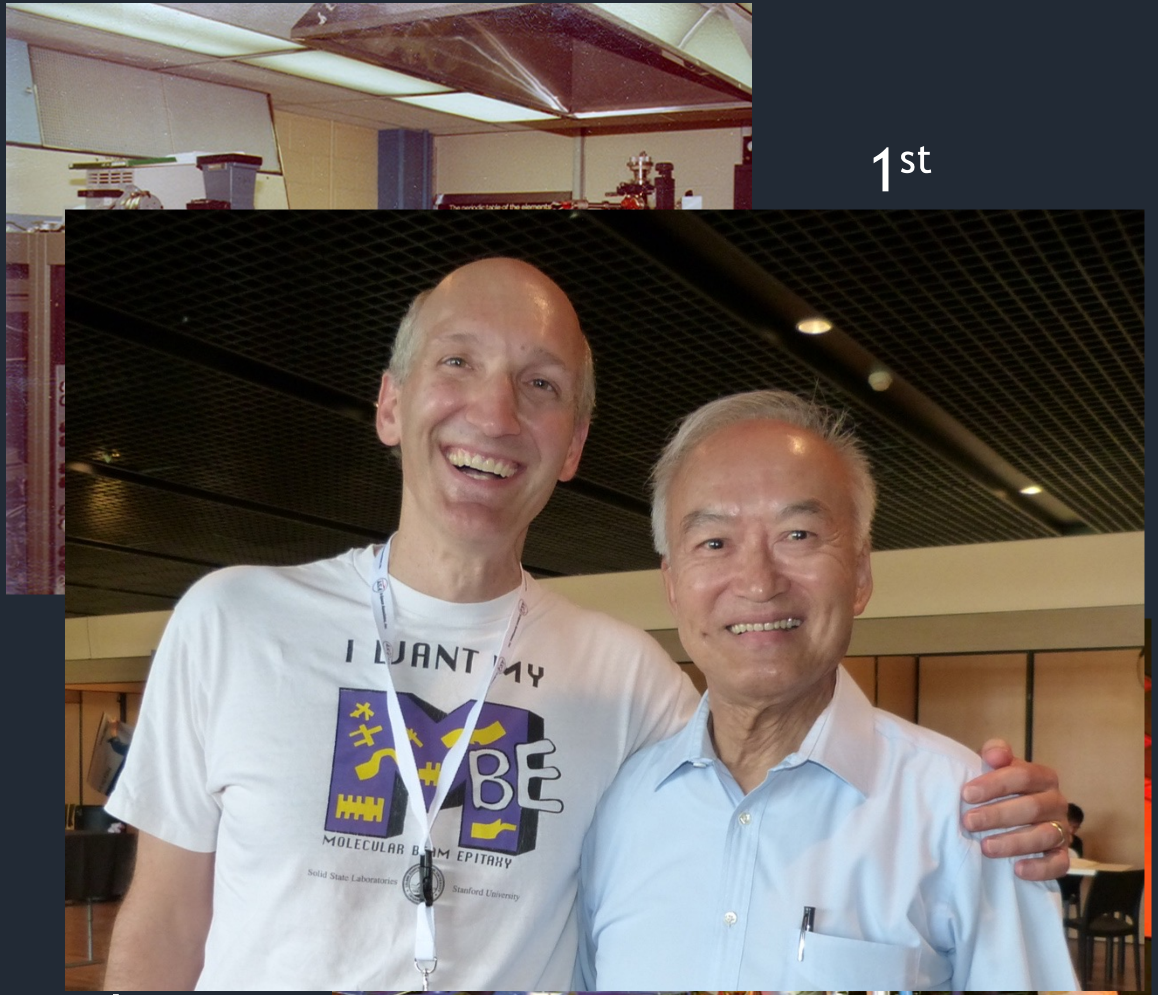
FIG. 1. GaAs film evaporation system: (A) Pirani gauge; (B) electrical contact to diode structure; (C) thermocouple; (D) metal flanges and viton gaskets as an entrance port for loading system; (E) particulate valve; (F) circular Ta plate; positive electrode in diode structure; (G) quartz rods which extend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

J.E. Davey and T. Pankey
“Epitaxial GaAs Films Deposited by Vacuum Evaporation”
Journal of Applied Physics **39** (1968) 1941–1948.

Evolution of MBE

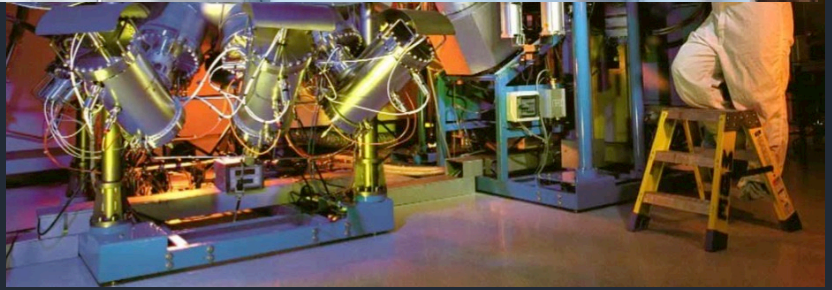


1st MBE
Al Cho at Bell Labs, 1972



1st

Production
MBE
Today
(courtesy of TRW)



RHEED and RHEED Oscillations

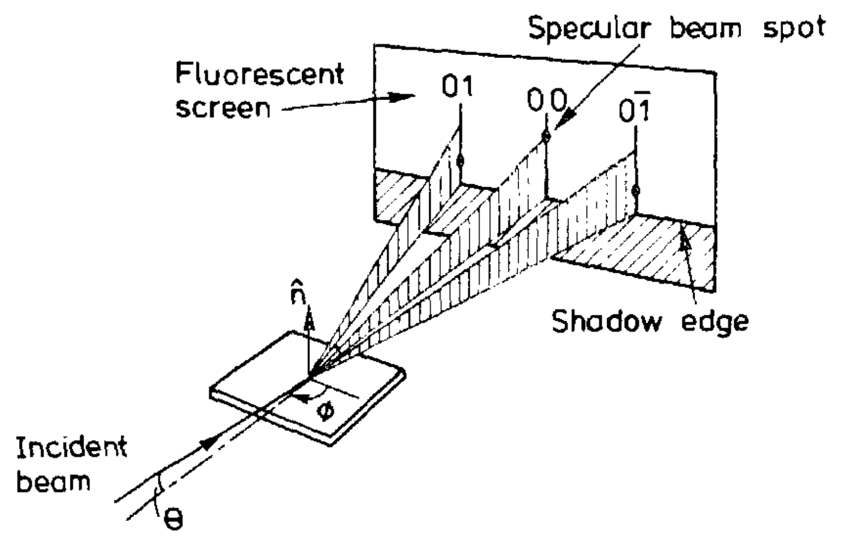
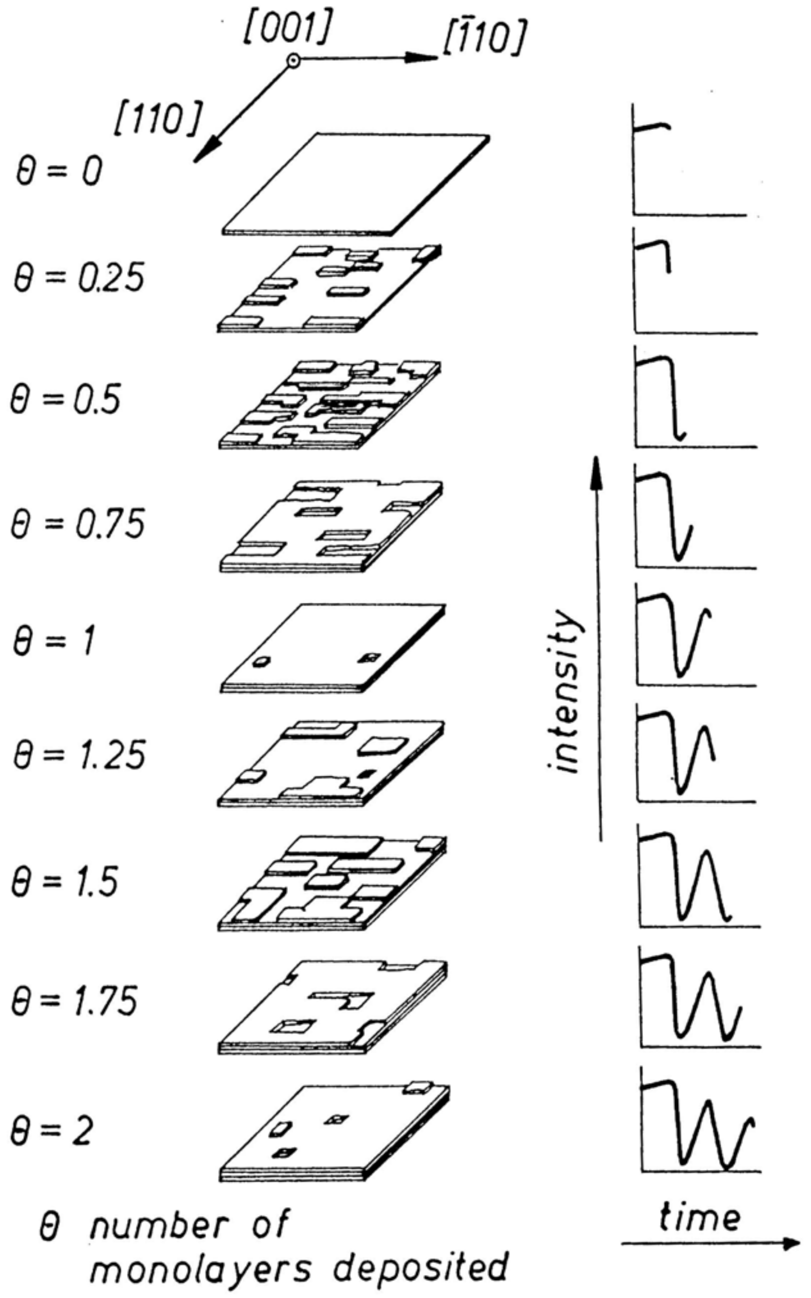


FIG. 1. Schematic diagram of RHEED geometry showing the incident beam at an angle θ to the surface plane; azimuthal angle φ. The elongated spots indicate the intersection of the Ewald sphere with the 01, 00, and 0$\bar{1}$ rods.

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.

Step Propagation vs. Birth and Spread

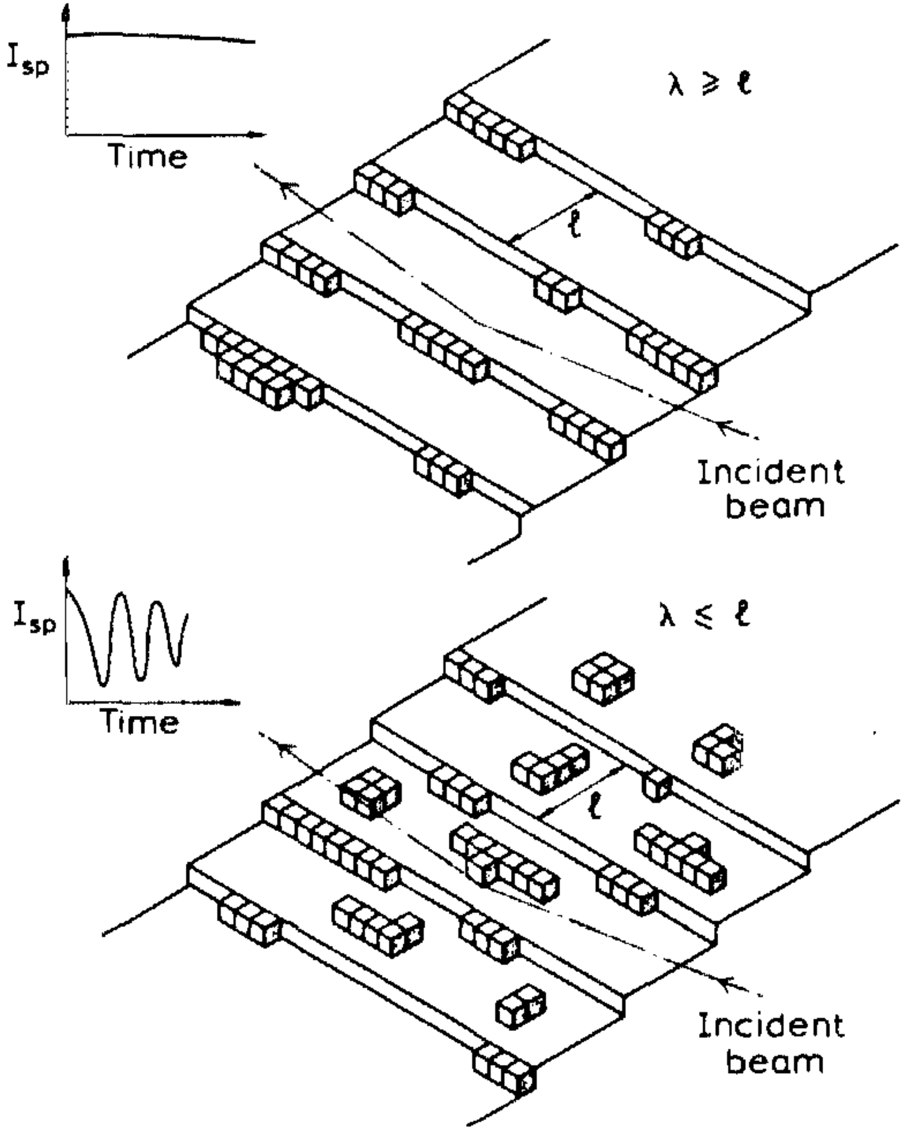
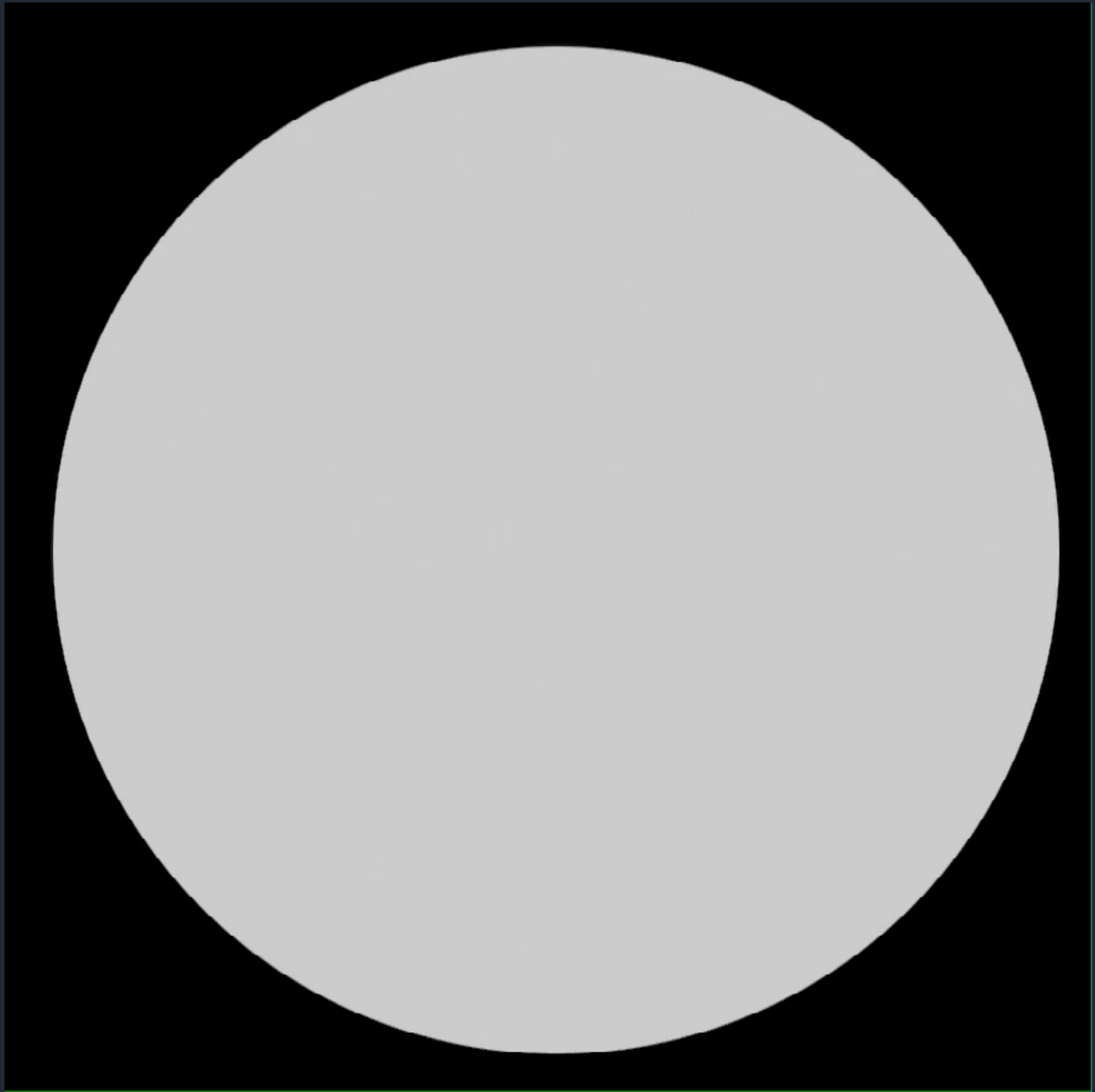


FIG. 1. Schematic illustration of the principle of the method, showing the change in RHEED information as the growth mode changes from "step flow" to 2-D nucleation. Steps lie along [100].

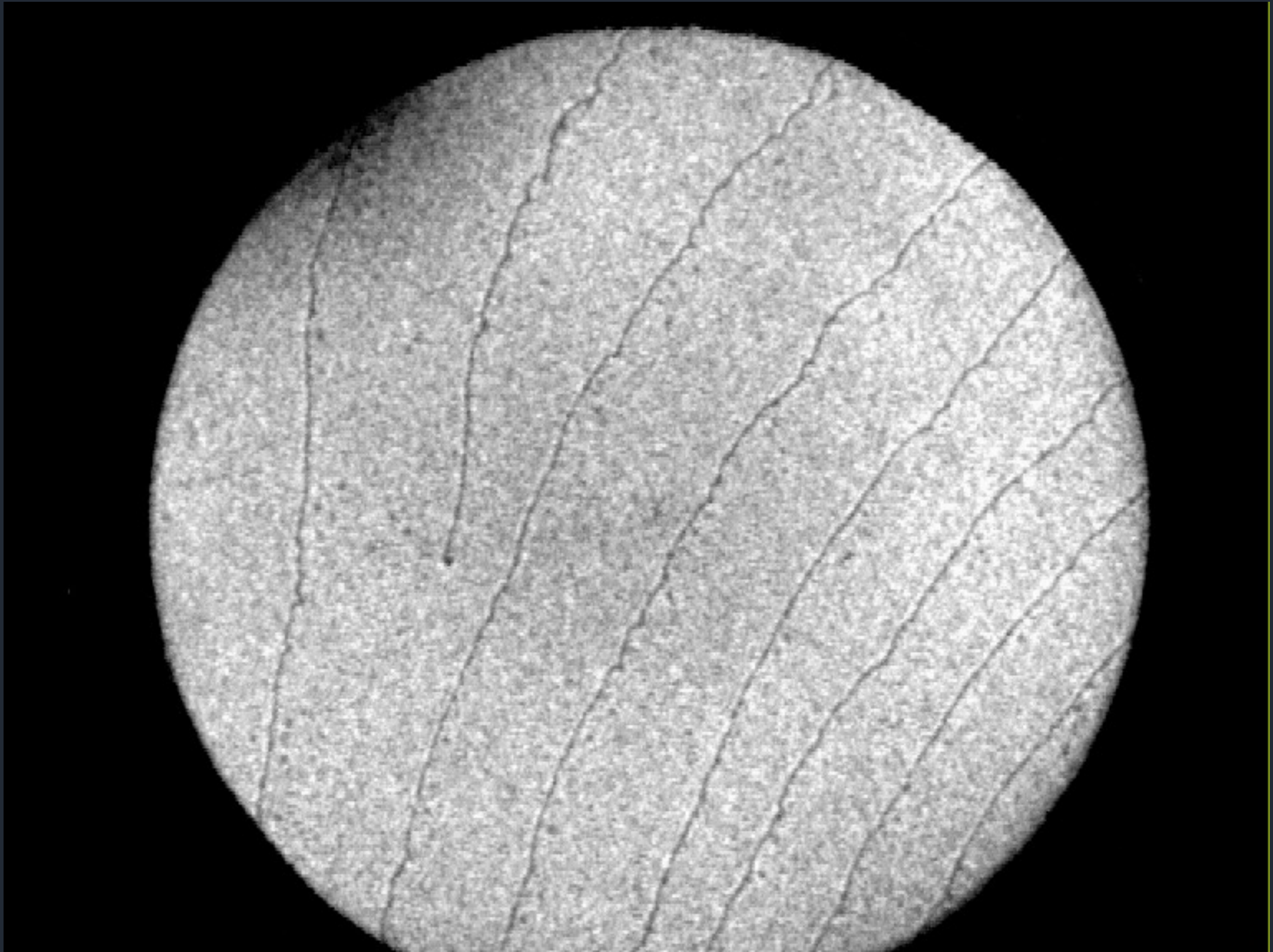
J.H. Neave, P.J. Dobson, B.A. Joyce, and J. Zhang,
"Reflection High-Energy Electron Diffraction Oscillations from Vicinal Surfaces—a New Approach to Surface Diffusion Measurements,"
Applied Physics Letters **47** (1985) 100–102.

LEEM of (111) Pt Homoepitaxy



Video courtesy of
Prof. Michael S. Altman
Hong Kong University of Science and Technology

LEEM of Sb-doped Si on (111) Si



Video courtesy of
Prof. Michael S. Altman
Hong Kong University of Science and Technology

W.F. Chung, K. Bromann, and M.S. Altman, *International Journal of Modern Physics B* **16** (2002) 4353–4362.

Growth Spirals in $YBa_2Cu_3O_7$

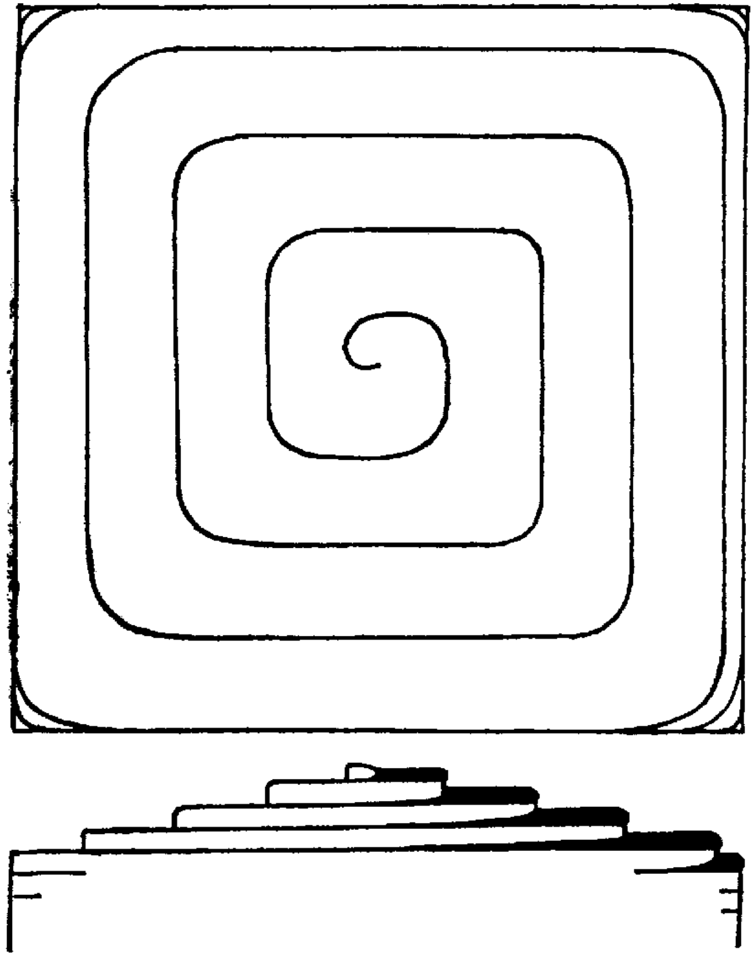
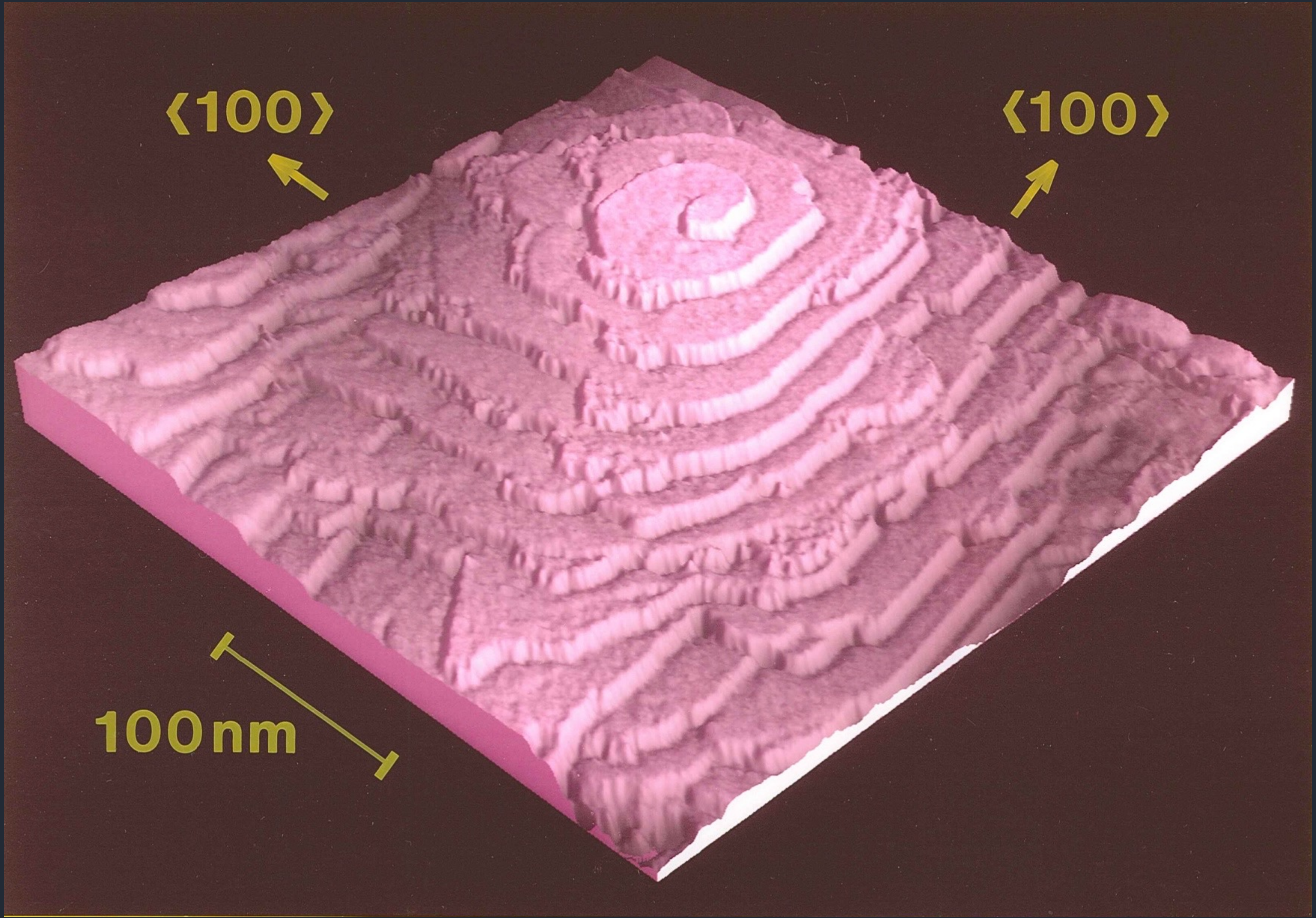


FIG. 5.—Spiral growth front attached to a single dislocation.

F.C. Frank, *Disc. Farad. Soc.* **5** (1949) 48-54, 66–79.



C. Gerber, D. Anselmetti, J.G. Bednorz, J. Mannhart, and D.G. Schlom, *Nature* **350** (1991) 279–280.

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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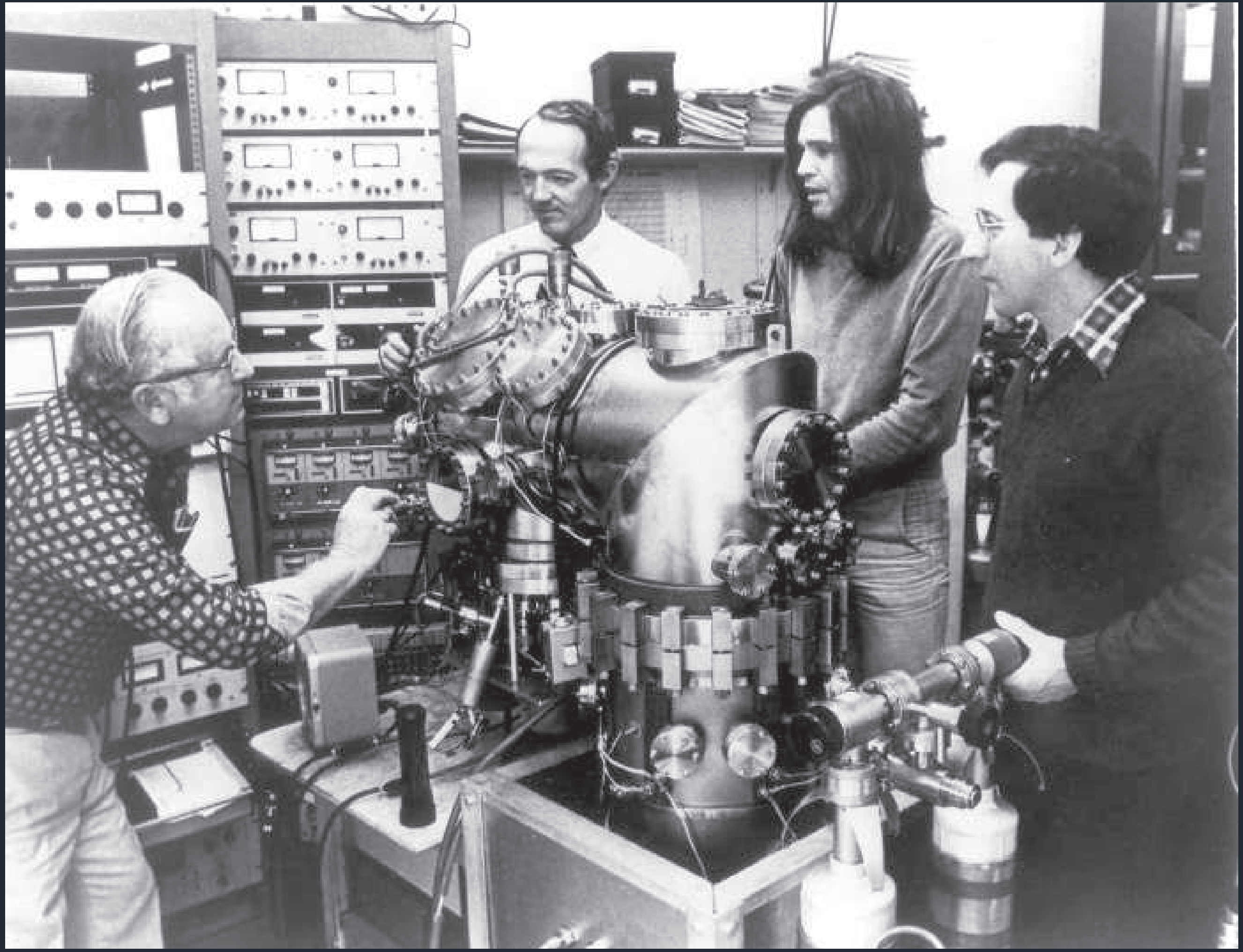
  Use PARADIM’s oxide MBE (+ ARPES + …)

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.

W.P. McCray, *Nature Nanotechnology* **2** (2007) 259-261.

Modulation Doping

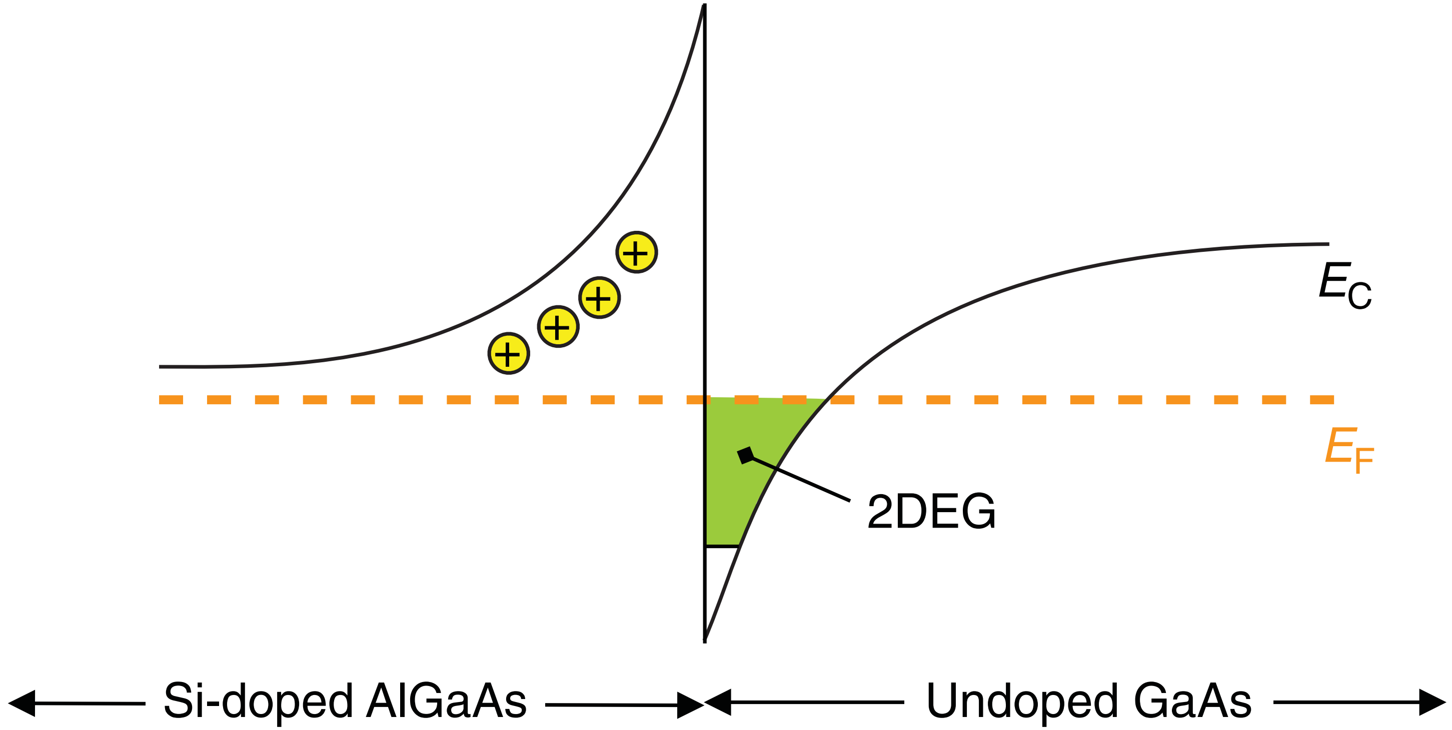
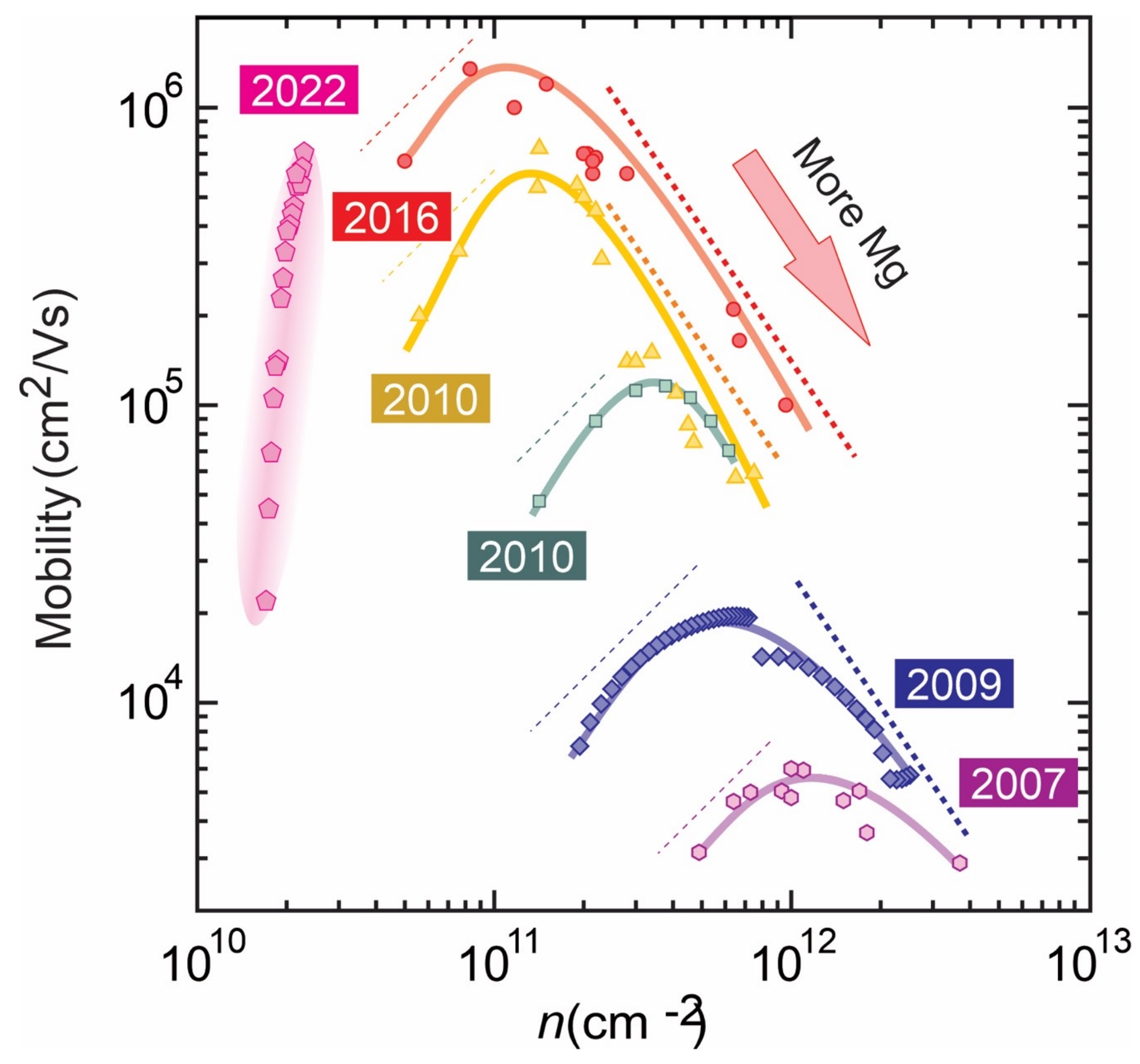
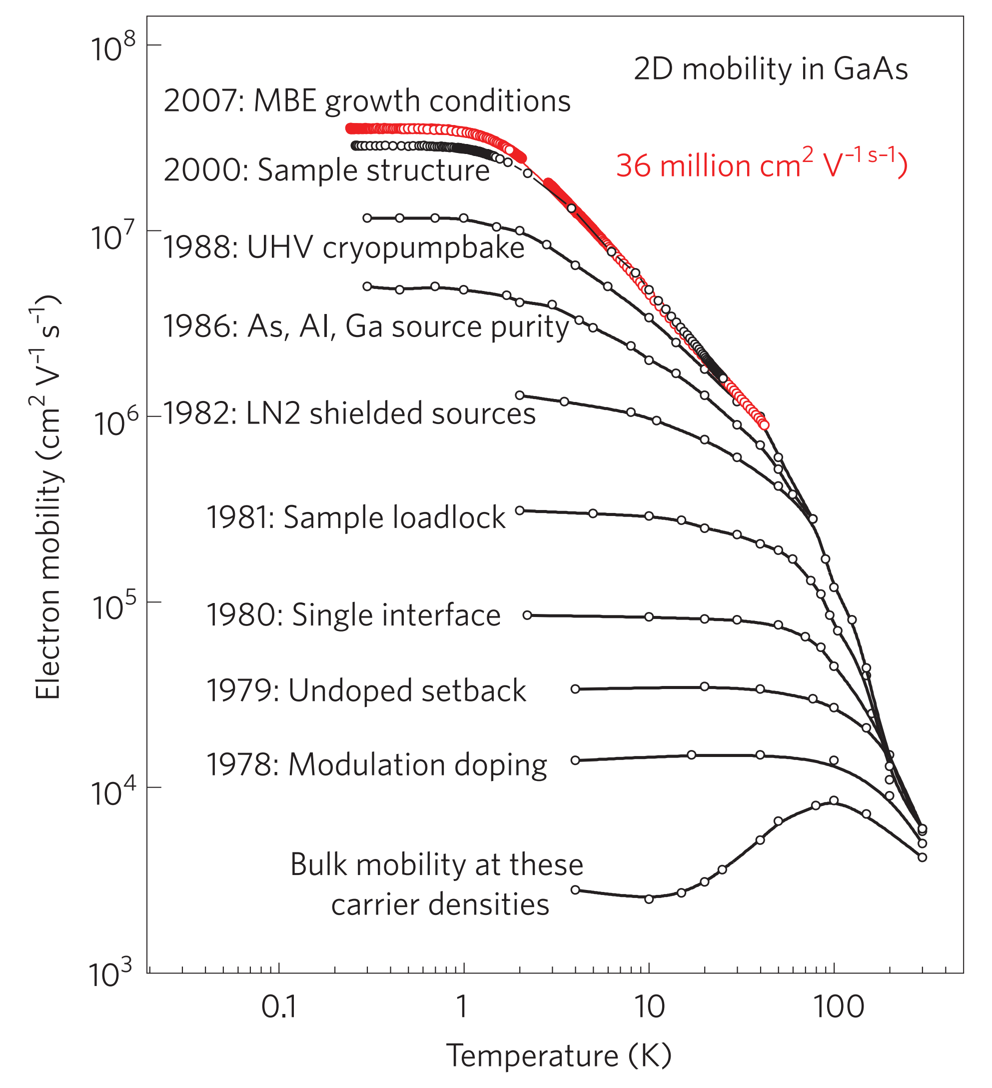


Figure 1. Band diagram showing the formation of a two-dimensional electron gas (2DEG) at a Si-doped AlGaAs–GaAs heterojunction. *Note:* E_F is the value of the Fermi energy, and E_C gives the energy of the conduction band edge.

J. Mannhart, D.H.A. Blank, H.Y. Hwang, A.J. Millis, and J.-M. Triscone
“Two-Dimensional Electron Gases at Oxide Interfaces”
MRS Bulletin **33** (2008) 1027–1034.

Mobility Achieved with MBE





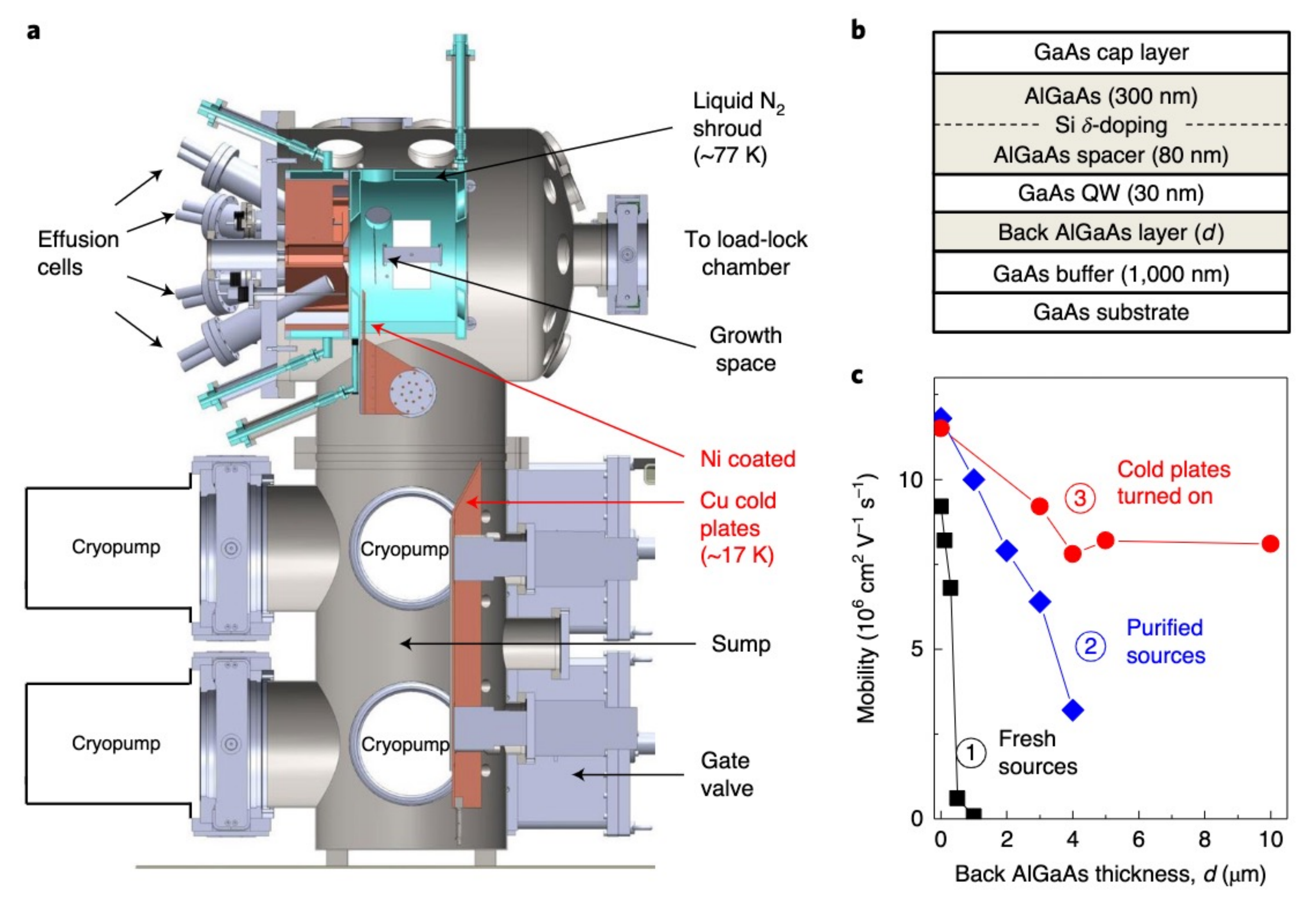
J. Falson, I. Sodemann, B. Skinner, D. Tabrea, Y. Kozuka, A. Tsukazaki, M. Kawasaki, K. von Klitzing, and J.H. Smet *Nature Materials* 21 (2022) 311-316.

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

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.

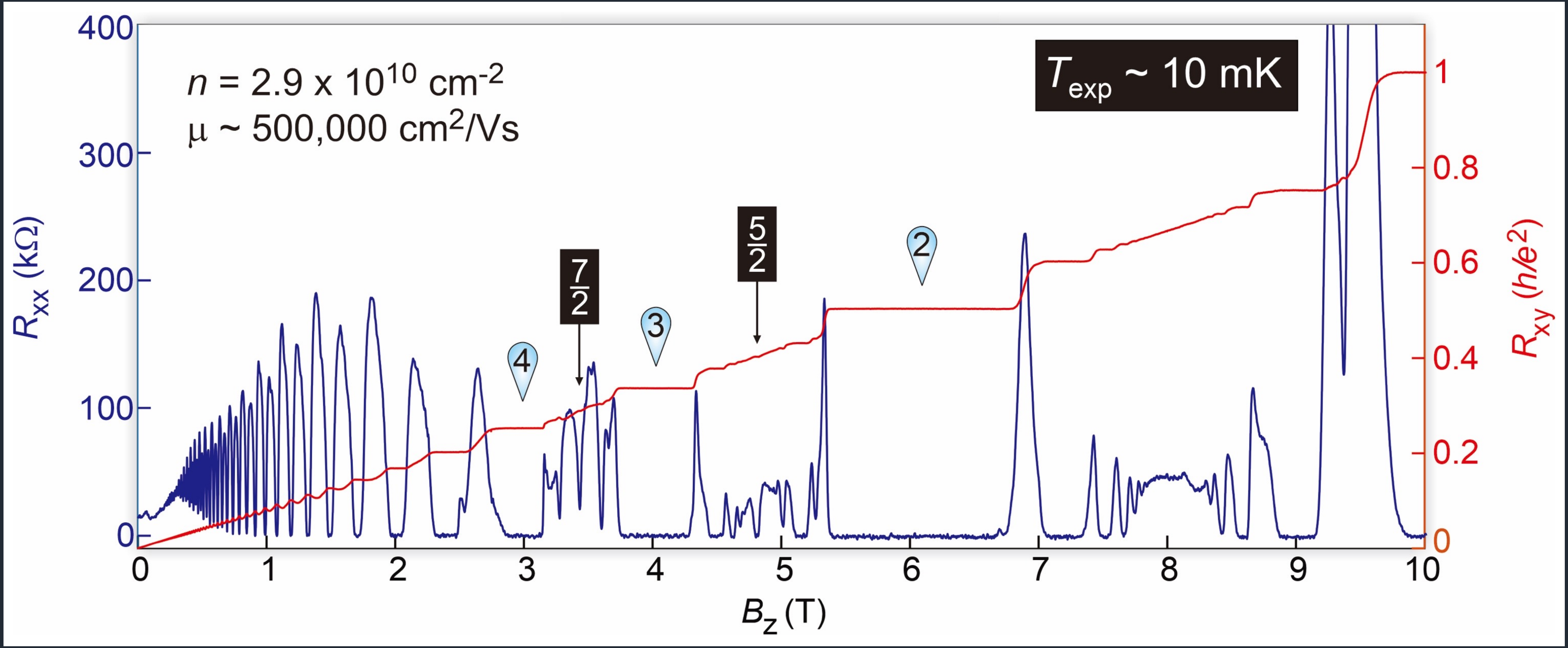
GaAs 2DEG with $\mu = 44\times10^6 \frac{\text{cm}^2}{\text{V}\cdot\text{s}}$ at 0.3 K



implies 1 impurity for every 10^{10} As/Ga atoms!
(0.1 ppb)

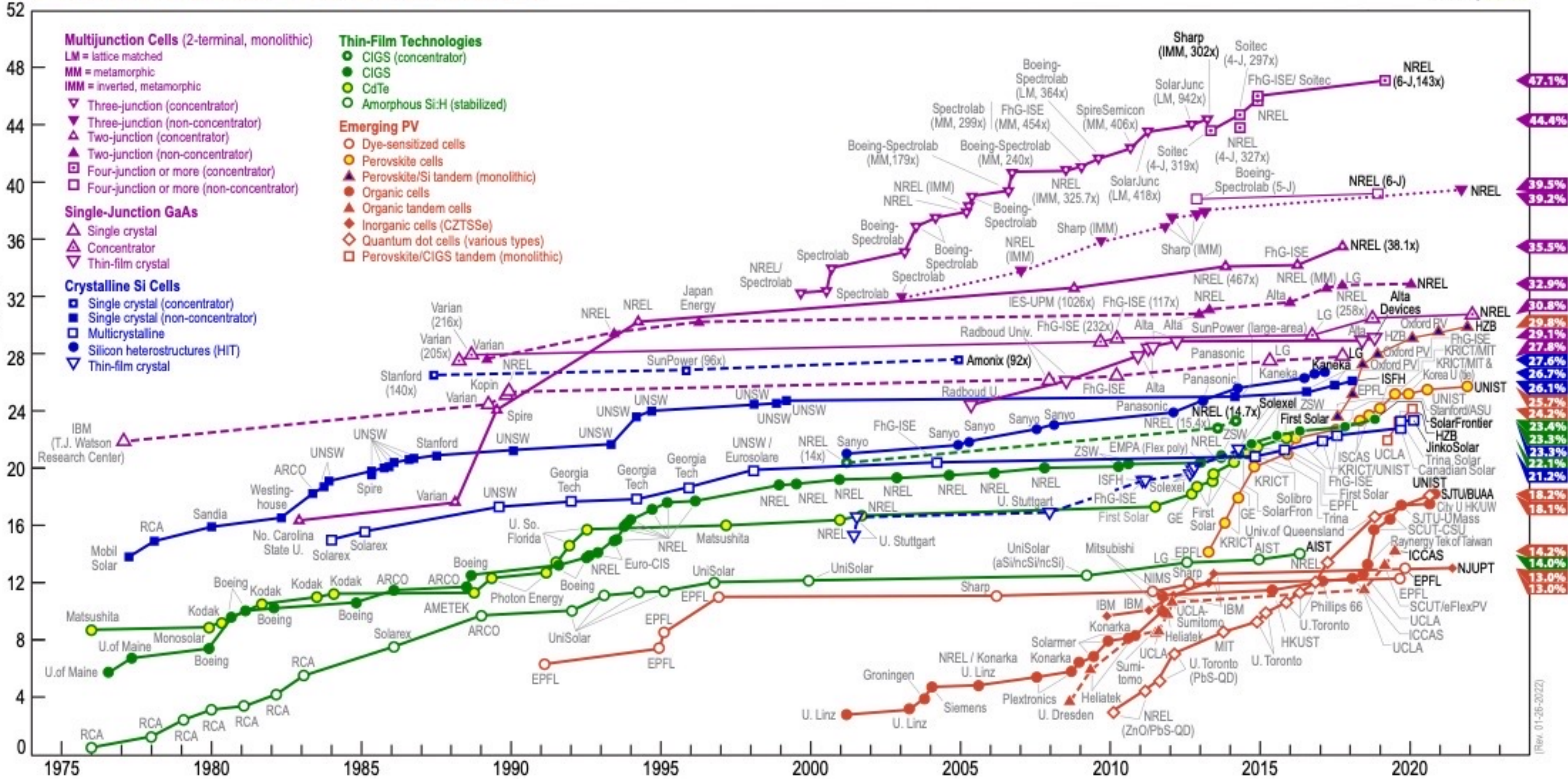
Y.J. Chung, K A.V. Rosales, K.W. Baldwin, P.T. Madathil, K.W. West, M. Shayegan, and L.N. Pfeiffer, "Ultra-High-Quality Two-Dimensional Electron Systems," *Nature Materials* **20** (2021) 632-637.

Mobility Achieved in ZnO with MBE

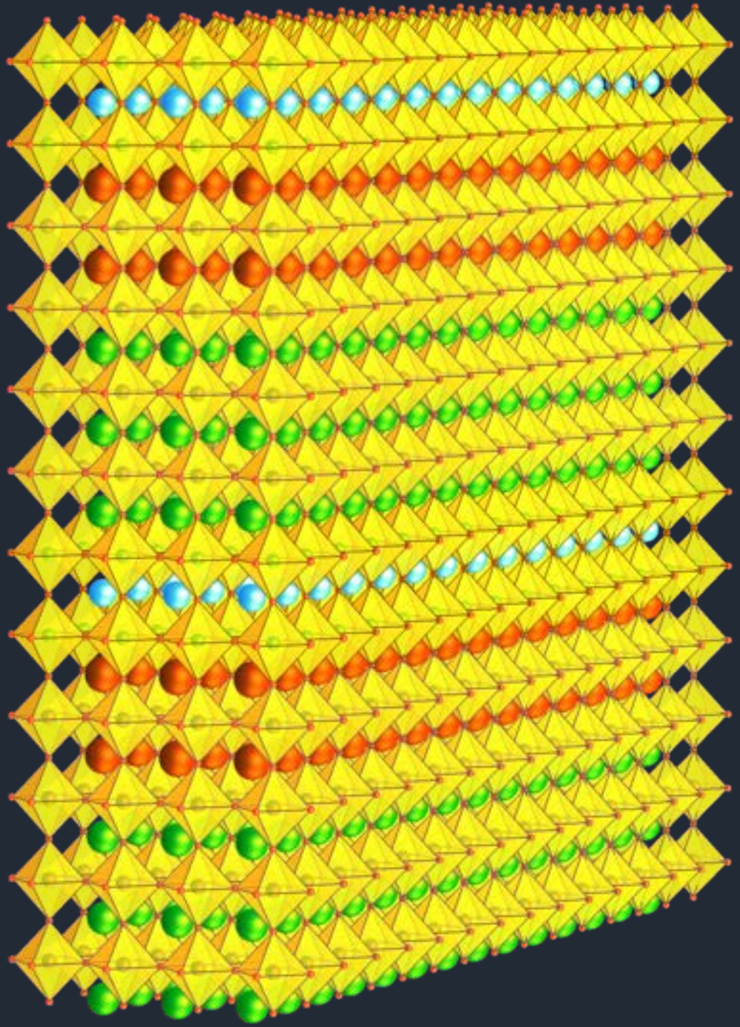


J. Falson, I. Sodemann, B. Skinner, D. Tabrea, Y. Kozuka, A. Tsukazaki, M. Kawasaki, K. von Klitzing, and J.H. Smet
Nature Materials **21** (2022) 311–316.

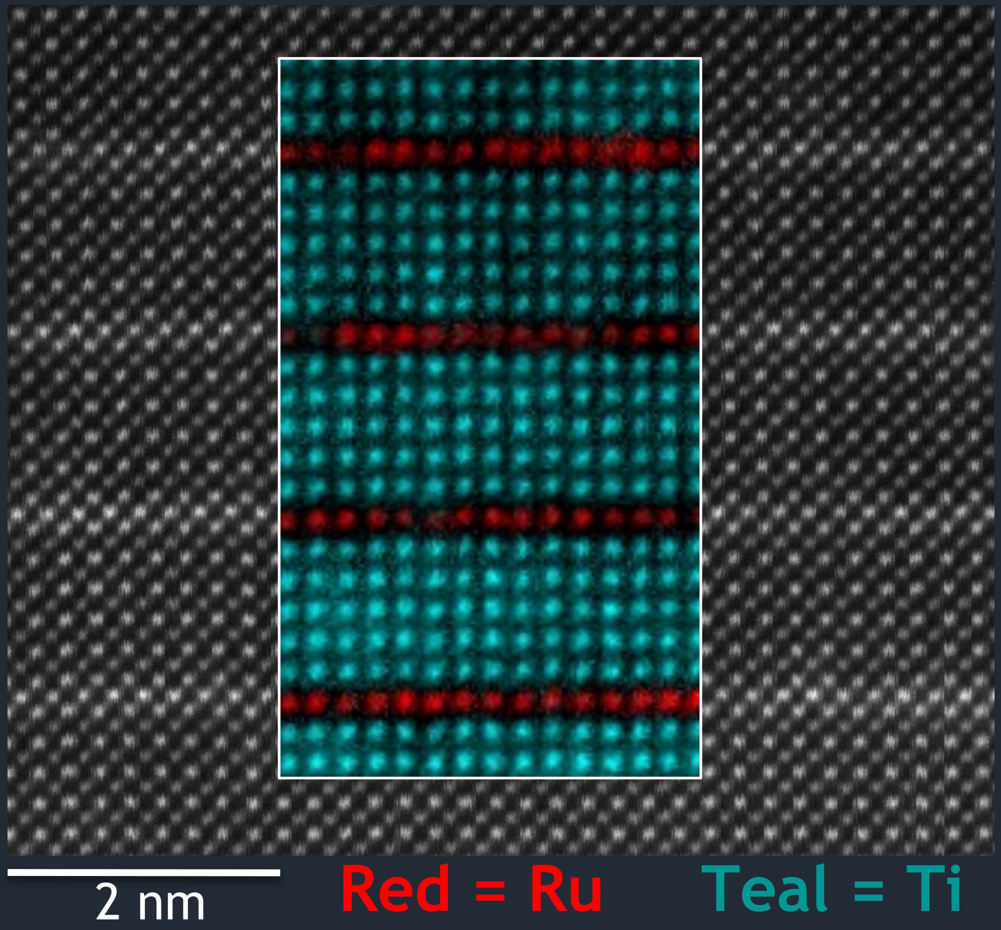
Best Research-Cell Efficiencies



MBE also Works for Oxides—Atomic Layer Control



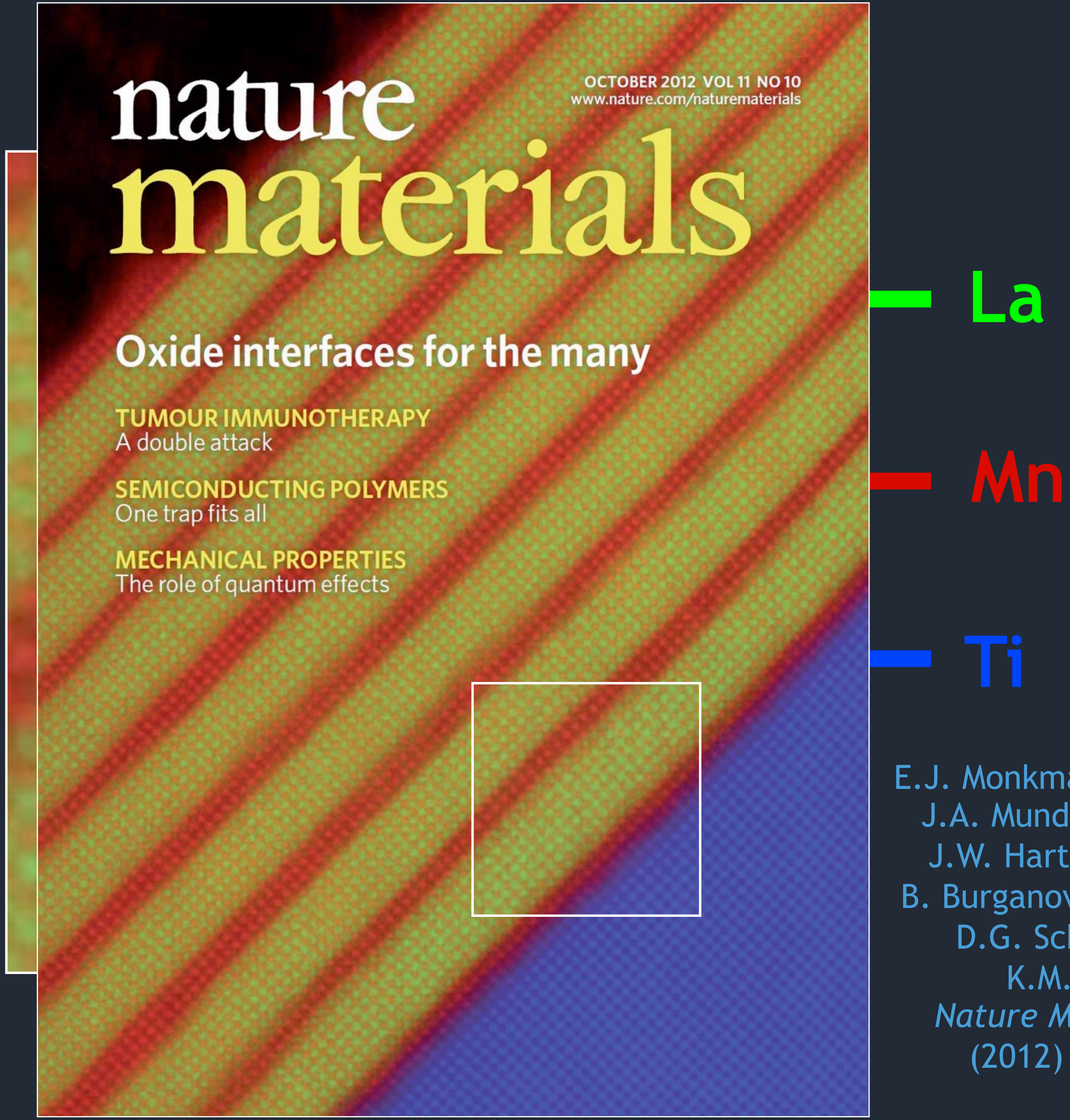
$(SrRuO_3)_1$ / $(SrTiO_3)_5$ Superlattice



Red = Ru Teal = Ti

H. Boschker, T. Harada, T. Asaba, R. Ashoori, A.V. Boris, H. Hilgenkamp, C.R. Hughes, M.E. Holtz, L. Li, D.A. Muller, H. Nair, P. Reith, X.R. Wang, D.G. Schlom, A. Soukiassian, J. Mannhart, *Physical Review X* **9** (2019) 011027.

MBE also Works for Oxides—Atomic Layer Control



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Oxide interfaces for the many

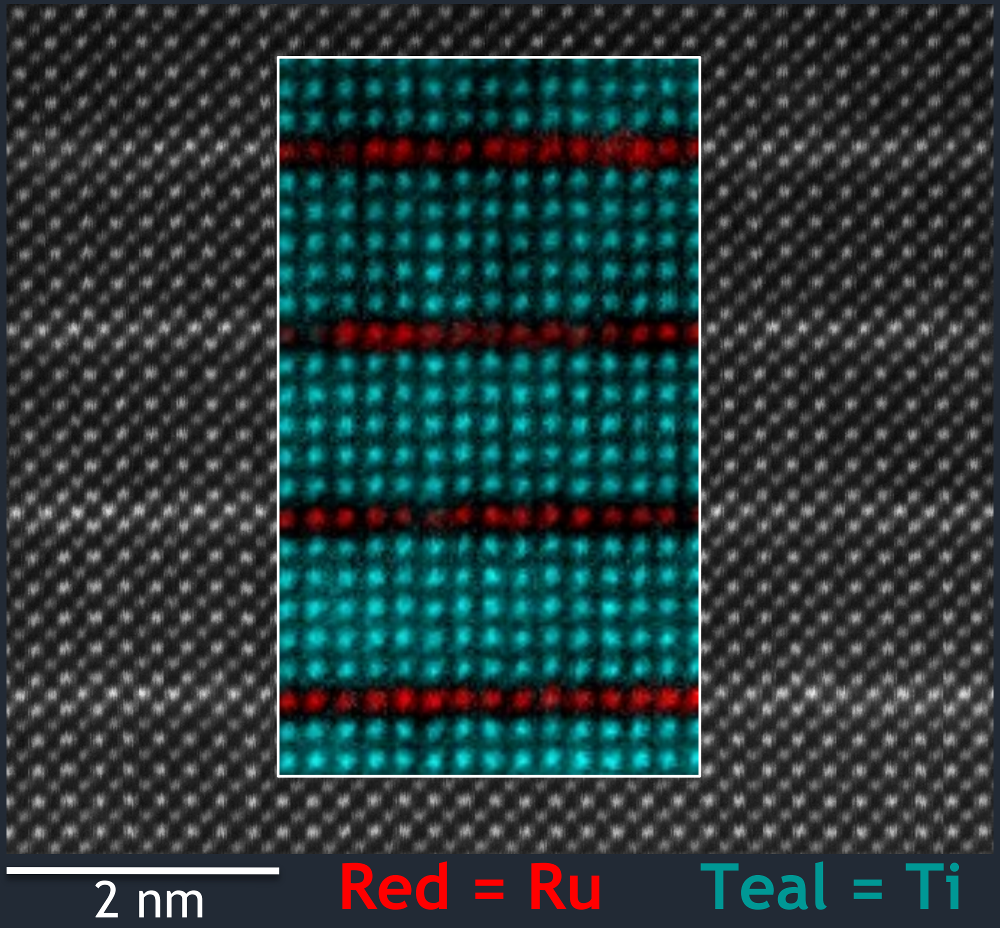
TUMOUR IMMUNOTHERAPY
A double attack

SEMICONDUCTING POLYMERS
One trap fits all

MECHANICAL PROPERTIES
The role of quantum effects

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.

$(SrRuO_3)_1$ / $(SrTiO_3)_5$ Superlattice



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H. Boschker, T. Harada, T. Asaba, R. Ashoori, A.V. Boris, H. Hilgenkamp, C.R. Hughes, M.E. Holtz, L. Li, D.A. Muller, H. Nair, P. Reith, X.R. Wang, D.G. Schlom, A. Soukiassian, J. Mannhart, *Physical Review X* **9** (2019) 011027.

MBE also Works for Oxides—Properties

Material	Best MBE Figure of Merit	Best non-MBE Figure of Merit	References
ZnO	μ_e = 230,000 cm^2/(V·s) at 1 K	μ_e = 5,500 cm^2/(V·s) at 1 K	1,2
$SrTiO_3$	μ_e = 53,200 cm^2/(V·s) at 2 K	μ_e = 6,600 cm^2/(V·s) at 2 K	3,4
$EuTiO_3$	μ_e = 3,200 cm^2/(V·s) at 2 K	μ_e = 30 cm^2/(V·s) at 2 K	5,6
$SrSnO_3$	μ_e = 70 cm^2/(V·s) at 300 K	μ_e = 40 cm^2/(V·s) at 300 K	7,8
$BaSnO_3$	μ_e = 183 cm^2/(V·s) at 300 K	μ_e = 140 cm^2/(V·s) at 300 K	9,10
$CaRuO_3$	$R_{300\ \mathrm{K}} / R_{4\ \mathrm{K}} = 75$	$R_{300\ \mathrm{K}} / R_{4\ \mathrm{K}} = 42$	11,12
$SrRuO_3$	$R_{300\ \mathrm{K}} / R_{10\ \mathrm{K}} = 115$	$R_{300\ \mathrm{K}} / R_{10\ \mathrm{K}} = 14$	13,14
Sr_2RuO_4	$T_{\mathrm{c,midpoint}}$ = 1.8 K	$T_{\mathrm{c,midpoint}}$ = 1.1 K	15,16
$SrVO_3$	$R_{300\ \mathrm{K}} / R_{5\ \mathrm{K}} = 222$	$R_{300\ \mathrm{K}} / R_{5\ \mathrm{K}} = 2$	17,18
EuO	Metal-insulator transition $\Delta R/R = 10^{11}$	Metal-insulator transition $\Delta R/R = 5\times10^4$	19,20

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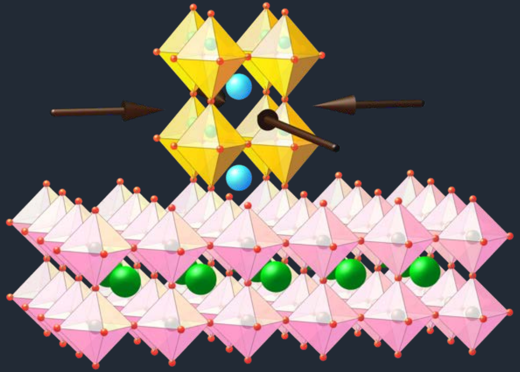
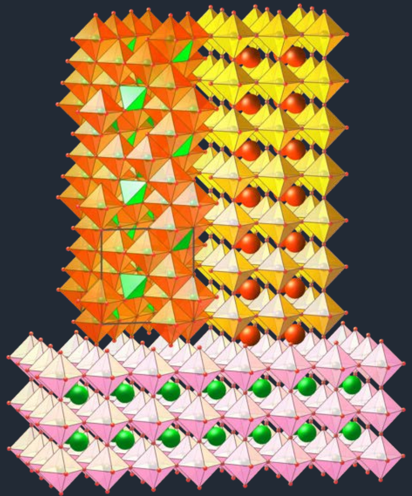
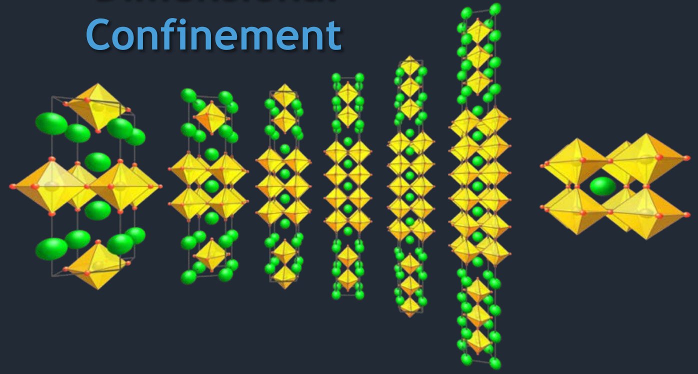
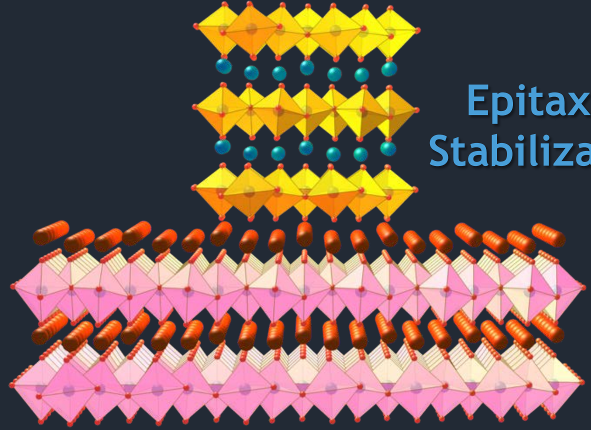
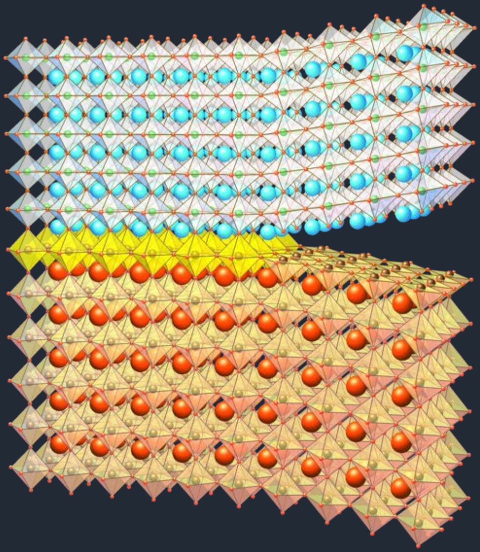
Epitaxial Routes to Engineer Properties

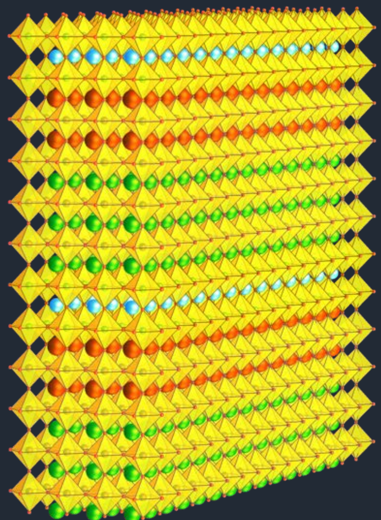

Strain Engineering

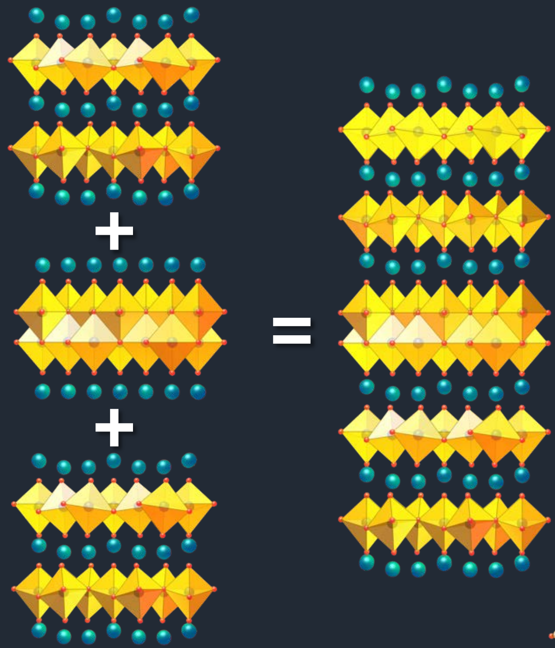

Epitaxial Nanocomposite


Dimensional Confinement

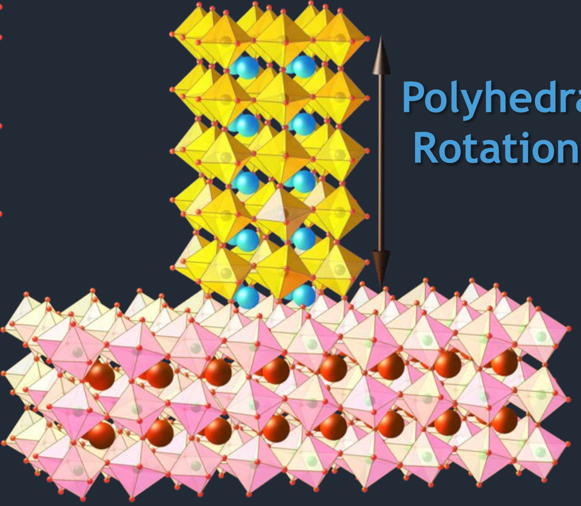

Epitaxial Stabilization

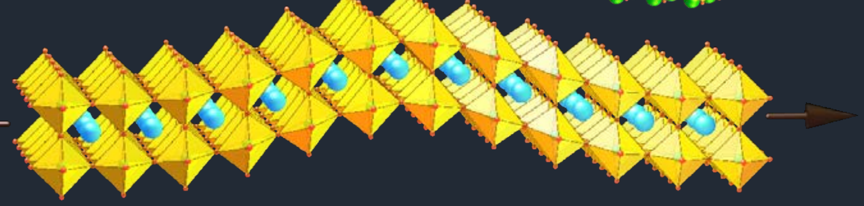

Polarization Doping and Proximity Effects


Interface Engineering



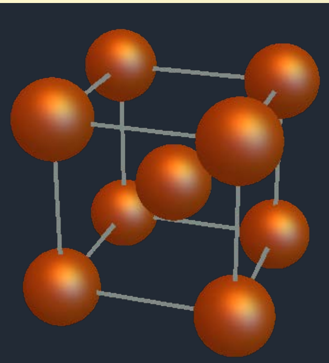
Breaking Symmetries


Polyhedral Rotations


Strained Membranes

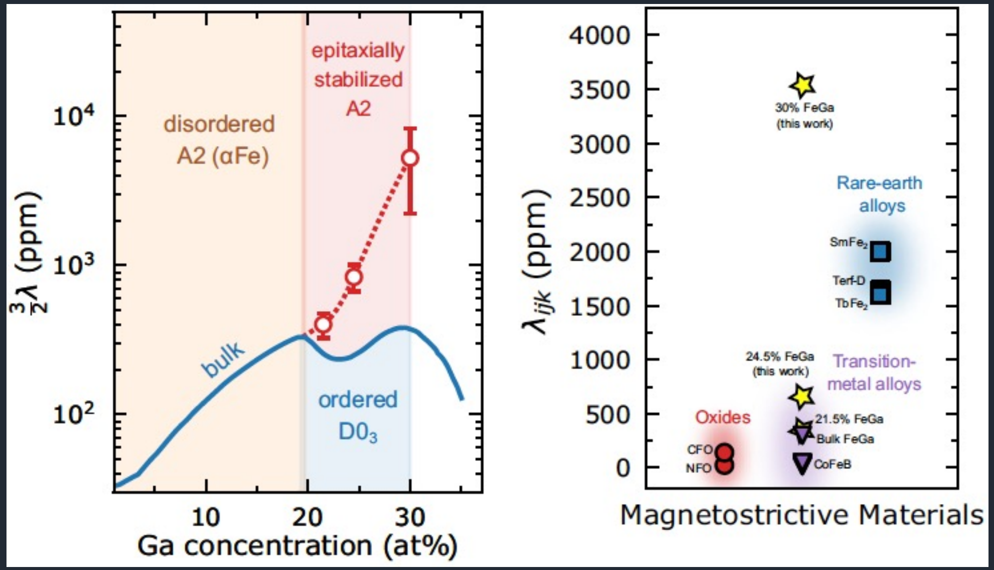
MBE Examples from PARADIM Users

AN NSF MATERIALS INNOVATION PLATFORM

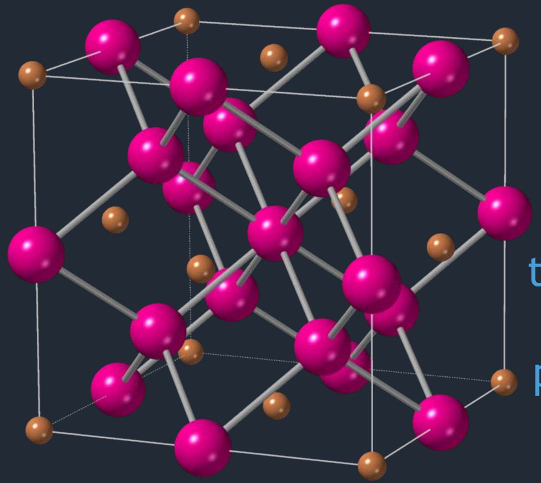


$Fe_{1-x}Ga_x$

today's record magnetostrictive material



P.B. Meisenheimer, … J.T. Heron, *Nature Communications* **12** (2021) 2757.

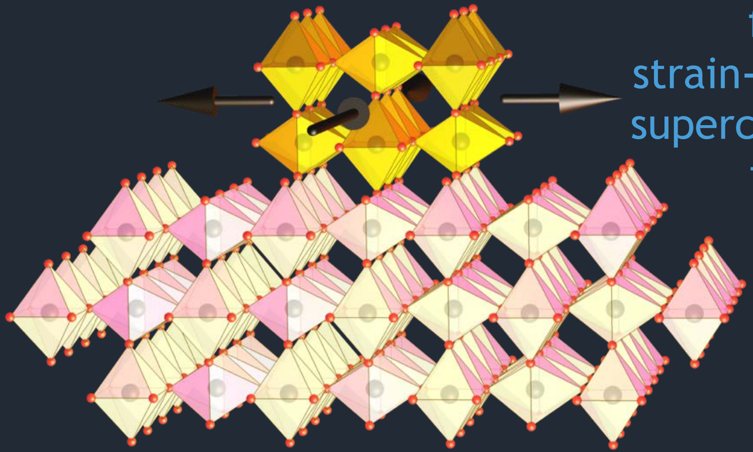


Cs_3Sb

today's record ultrathin photocathode

C.T. Parzyck, … J.M. Maxson
Physical Review Letters **128** (2022) 114801.

RuO_2

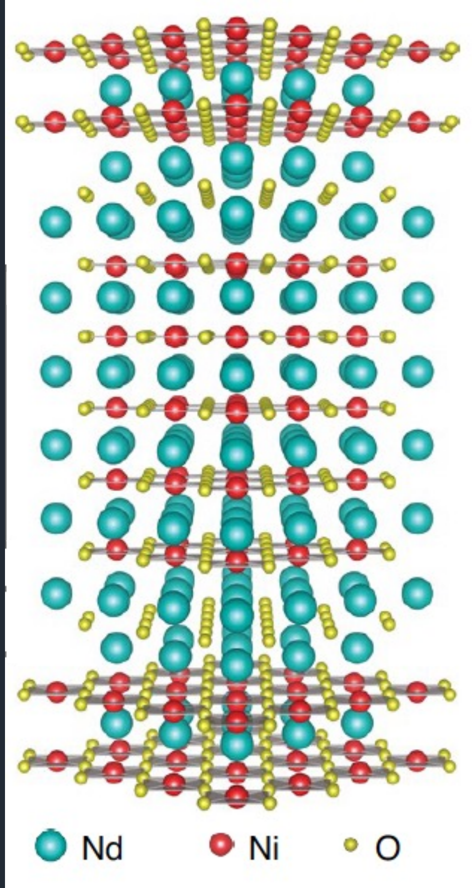


first strain-stabilized superconducting film

J.P. Ruf, … K.M. Shen, *Nature Communications* **12** (2021) 59.

new layered nickelate superconductor—predicted by theory and experimentally realized

$Nd_6Ni_6O_{12}$



G.A. Pan, … A.S. Botana, J.A. Mundy
Nature Materials **21** (2022) 160–164.

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
- Good for Adsorption-Controlled Growth

Disadvantages

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

Your friend wants to deposit a $YBa_2Cu_3O_7$ film with the highest critical current density;
what technique do you recommend?

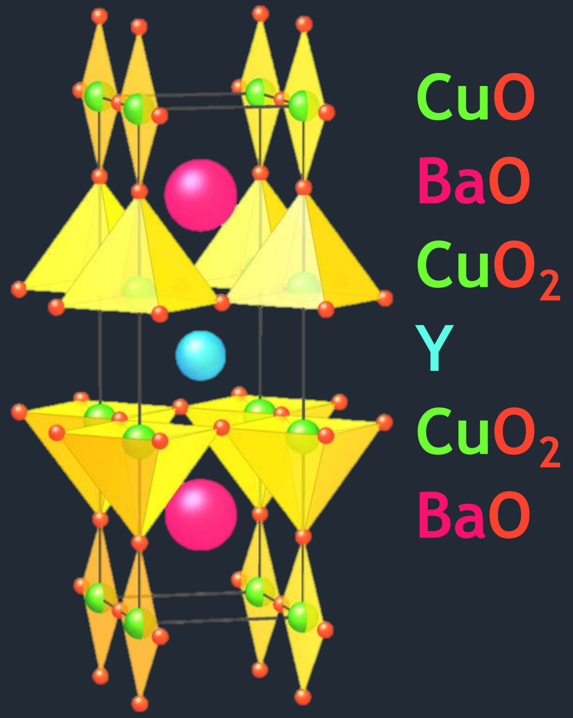
(a) MBE

(b) Pulsed-laser deposition (PLD)

(c) Sputtering

(d) Metal-Organic Chemical Vapor Deposition (MOCVD)

(e) Chemical-Solution Deposition (Sol-Gel)


$YBa_2Cu_3O_7$