Summer School 2022

MBE + ARPES: Customizing Quantum Materials with Atomic Layer Precision and Measuring their Electronic Structure

June 13-17, 2022

www.paradim.org
Summer School 2022

Recent Developments in and Future Quantum Applications of Superconductivity

July 31 – August 5, 2022

Apply now!

www.paradim.org

Baltimore, MD
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

- 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 \approx \text{Atomic Spray Painting}

Video by Andreas Schmehl
VAPOUR 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°F. 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:

\[
\begin{align*}
\text{GaAs} & \rightarrow \text{Ga} + \text{As}_2 \quad \Delta H _{298}^\circ = 44.9 \text{ kcal} \\
\text{GaAs} & \rightarrow \text{Ga} + \text{As}_4 \quad \Delta H _{298}^\circ = 29.4 \text{ kcal} \\
2\text{As}_2 & \rightarrow \text{As}_4 \quad \Delta H _{298}^\circ = -62.5 \text{ kcal} \\
\text{GaAs} & \rightarrow \text{Ga} + \text{As}_4 \quad \Delta H _{298}^\circ = 153 \text{ kcal}
\end{align*}
\]

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”

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


3-Temperature Technique

Key Enablers of MBE

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

Reliable UHV Sealing Technology
UHV Seals—Varian Conflat®

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

1st MBE
Al Cho at Bell Labs, 1972

Production MBE Today
(courtesy of TRW)
RHEED and RHEED Oscillations

Fig. 1. Schematic diagram of RHEED geometry showing the incident beam at an angle $\theta$ to the surface plane; azimuthal angle $\varphi$. The elongated spots indicate the intersection of the Ewald sphere with the 01, 00, and 01 rods.

B. Bölger and P. K. Larsen

B.A. Joyce, P.J. Dobson, J.H. Neave, K. Woodbridge, J. Zhang, P.K. Larsen, and B Bölger,
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].

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

Growth Spirals in YBa$_2$Cu$_3$O$_7$

C. Gerber, D. Anselmetti, J.G. Bednorz, J. Mannhart, and D.G. Schlom,  
What is MBE?

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


**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.

“Two-Dimensional Electron Gases at Oxide Interfaces”
Mobility Achieved with MBE

Atsushi Tsuchiya and colleagues led a tremendous work by a talented team, which resulted in about 2,000 papers being published. These papers have led to the recognition of the 1985 and 1998 Nobel Prizes in physics, respectively. In this issue, we discuss the subjects of the 1985 and 1998 Nobel Prizes.

In Figure 1, we compare the concentration of electrons as the 2DEGs. MBE, molecular-beam epitaxy; UHV, ultra-high vacuum; LN2, liquid nitrogen; 'undoped setback', an undoped layer.

A historical view of the upward mobility of electrons in ever-cleaner ZnO and GaAs heterostructures and the steps leading to this improvement.

Figure 2 shows the 2D mobility in GaAs and graphene. The curve labelled 'bulk' is for a GaAs single crystal doped with the same density as the 2DEGs.

The rate of improvements in crystalline perfection has skyrocketed in the past several decades. The use of molecular-beam epitaxy (MBE) has played a crucial role in achieving high-quality epitaxial films. The use of molecular-beam epitaxy (MBE) has allowed for the growth of ultra-low disorder 2DEG with mobility exceeding 35 million cm² V⁻¹ s⁻¹.

References:
GaAs 2DEG with $\mu = 44 \times 10^6 \frac{\text{cm}^2}{\text{V} \cdot \text{s}}$ at 0.3 K

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

Mobility Achieved in ZnO with MBE

\( n = 2.9 \times 10^{10} \text{ cm}^{-2} \)
\( \mu \sim 500,000 \text{ cm}^2/\text{Vs} \)

\( T_{\text{exp}} \sim 10 \text{ mK} \)


High-Efficiency Solar Cells

**Best Research-Cell Efficiencies**

**Multijunction Cells (Z-terminal, monolithic)**
- LM = lattice matched
- NM = metamorphic
- NM = inverted, metamorphic
- Three-junction (concentrator)
- Three-junction (non-concentrator)
- Two-junction (concentrator)
- Two-junction (non-concentrator)
- Four-junction or more (concentrator)
- Four-junction or more (non-concentrator)

**Single-Junction GaAs**
- Single crystal
- Concentrator
- Thin-film crystal

**Crystalline Si Cells**
- Single crystal (concentrator)
- Single crystal (non-concentrator)
- Multicrystalline
- Silicon heterostructures (HIT)
- Thin-film crystal

**Thin-Film Technologies**
- CIGS (concentrator)
- CIGS
- CdTe
- Amorphous Si:H (stabilized)

**Emerging PV**
- Dye-sensitized cells
- Perovskite cells
- Perovskite/S tandem (monolithic)
- Organic cells
- Organic tandem cells
- Inorganic cells (CdTe3Se)
- Quantum dot cells (various types)
- Perovskite/CIGS tandem (monolithic)
MBE also Works for Oxides—Atomic Layer Control

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

Superlattice

Red = Ru

Teal = Ti

MBE also Works for Oxides—Atomic Layer Control

(O_{3})_{1} / (SrTi_{3})_{5} Superlattice


### MBE also Works for Oxides—Properties

<table>
<thead>
<tr>
<th>Material</th>
<th>Best MBE Figure of Merit</th>
<th>Best non-MBE Figure of Merit</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>$\mu_e = 230,000 \text{ cm}^2/(\text{V} \cdot \text{s})$ at 1 K</td>
<td>$\mu_e = 5,500 \text{ cm}^2/(\text{V} \cdot \text{s})$ at 1 K</td>
<td>1,2</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>$\mu_e = 53,200 \text{ cm}^2/(\text{V} \cdot \text{s})$ at 2 K</td>
<td>$\mu_e = 6,600 \text{ cm}^2/(\text{V} \cdot \text{s})$ at 2 K</td>
<td>3,4</td>
</tr>
<tr>
<td>EuTiO$_3$</td>
<td>$\mu_e = 3,200 \text{ cm}^2/(\text{V} \cdot \text{s})$ at 2 K</td>
<td>$\mu_e = 30 \text{ cm}^2/(\text{V} \cdot \text{s})$ at 2 K</td>
<td>5,6</td>
</tr>
<tr>
<td>SrSnO$_3$</td>
<td>$\mu_e = 70 \text{ cm}^2/(\text{V} \cdot \text{s})$ at 300 K</td>
<td>$\mu_e = 40 \text{ cm}^2/(\text{V} \cdot \text{s})$ at 300 K</td>
<td>7,8</td>
</tr>
<tr>
<td>BaSnO$_3$</td>
<td>$\mu_e = 183 \text{ cm}^2/(\text{V} \cdot \text{s})$ at 300 K</td>
<td>$\mu_e = 140 \text{ cm}^2/(\text{V} \cdot \text{s})$ at 300 K</td>
<td>9,10</td>
</tr>
<tr>
<td>CaRuO$_3$</td>
<td>$R_{300 \text{ K}} / R_{4 \text{ K}} = 75$</td>
<td>$R_{300 \text{ K}} / R_{4 \text{ K}} = 42$</td>
<td>11,12</td>
</tr>
<tr>
<td>SrRuO$_3$</td>
<td>$R_{300 \text{ K}} / R_{10 \text{ K}} = 115$</td>
<td>$R_{300 \text{ K}} / R_{10 \text{ K}} = 14$</td>
<td>13,14</td>
</tr>
<tr>
<td>Sr$_2$RuO$_4$</td>
<td>$T_{c,\text{midpoint}} = 1.8 \text{ K}$</td>
<td>$T_{c,\text{midpoint}} = 1.1 \text{ K}$</td>
<td>15,16</td>
</tr>
<tr>
<td>SrVO$_3$</td>
<td>$R_{300 \text{ K}} / R_{5 \text{ K}} = 222$</td>
<td>$R_{300 \text{ K}} / R_{5 \text{ K}} = 2$</td>
<td>17,18</td>
</tr>
<tr>
<td>EuO</td>
<td>Metal-insulator transition</td>
<td>Metal-insulator transition</td>
<td>19,20</td>
</tr>
<tr>
<td></td>
<td>$\Delta R/R = 10^{11}$</td>
<td>$\Delta R/R = 5 \times 10^{4}$</td>
<td></td>
</tr>
</tbody>
</table>

---

15. H.P. Nair, APL Mater. 6 (2018) 101108.
MBE Examples from PARADIM Users

**Fe$_{1-x}$Ga$_x$**

- today’s record magnetostrictive material

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

**Cs$_3$Sb**

- today’s record ultrathin photocathode


**RuO$_2$**

- first strain-stabilized superconducting film


**Nd$_6$Ni$_6$O$_{12}$**

- new layered nickelate superconductor—predicted by theory and experimentally realized

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...)

Advantages

Disadvantages
Your friend wants to deposit a YBa$_2$Cu$_3$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)