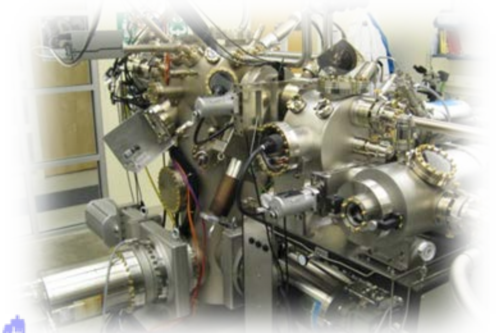
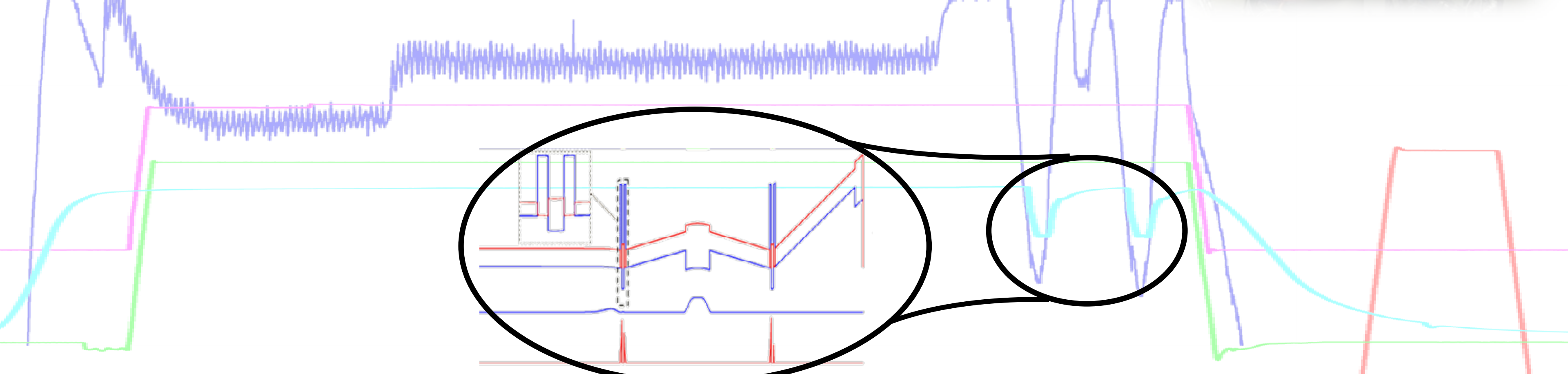
Equipment, Techniques, and Growth of Ultra-High Purity AlGaAs-GaAs Heterostructures by Molecular Beam Epitaxy

Purdue Materials Engineering Dissertation Defense



Geoffrey C Gardner,
May 15, 2017

Advisor: Professor Michael Manfra



Outline

- Brief Motivation
- GaAs – AlGaAs material system
- Ultra-High Mobility GaAs MBE
- Lessons learned during a growth campaign
- 2 experiments into 2DEG mobility
  - Intentional alloy disorder
  - Different Ga source material
- Conclusions
- Acknowledgments and Thank You

Applications for GaAs 2DEGs

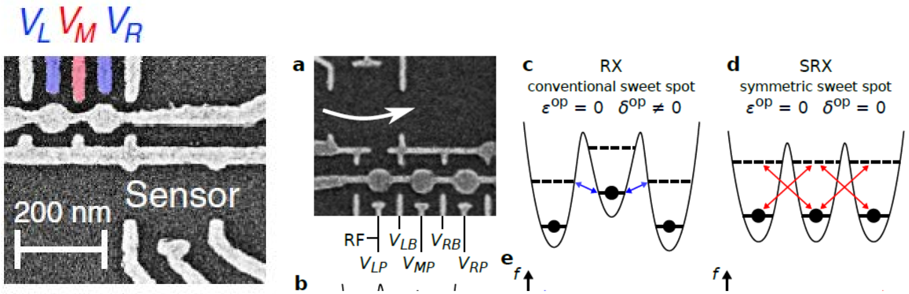
- **Spin Qubits for Quantum Computing**

  Quantum dots demonstrated as qubits including refinement in operations and noise suppression

  Charlie Marcus, University of Copenhagen

  Ferdinand Kuemmeth, Niels Bohr Institute

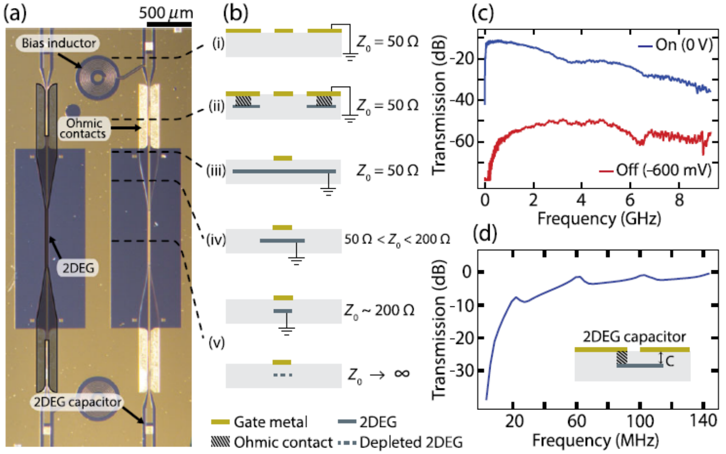
  Saeed Fallahi, Purdue University



- **Cryogenic Control Architecture for Large-Scale Quantum Computing**

  A microarchitecture for control and readout of quits using HEMTs and capacitive switching elements.

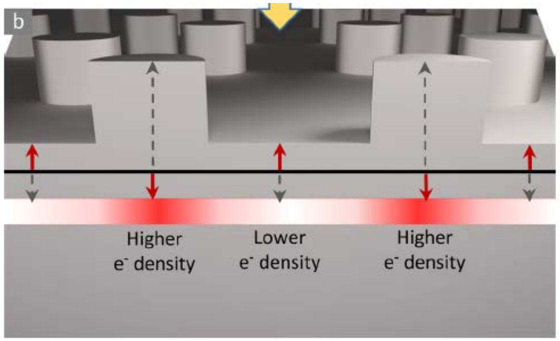
  David Riley, University of Sydney

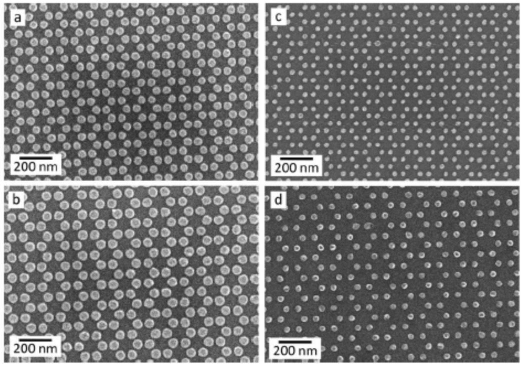


- **Artificial graphene**

  Dry etching process to create of a honeycomb lattice in UHP GaAs to study graphene properties with controllable topology, massless Dirac Fermions

  Pinczuk and Wind, Columbia University





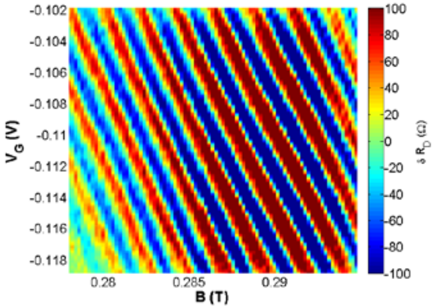
Applications for UHP GaAs

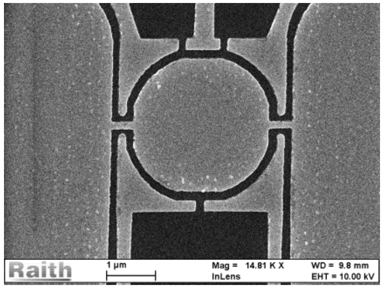
- **Interferometers for study of collective electron phases**

  Used to study coherent wave phenomena in the mesoscopic systems. Specifically measuring interference of quasiparticles with fractional charges

  M. Heiblum, Weizmann Institute

  James Nakamuram, Purdue University





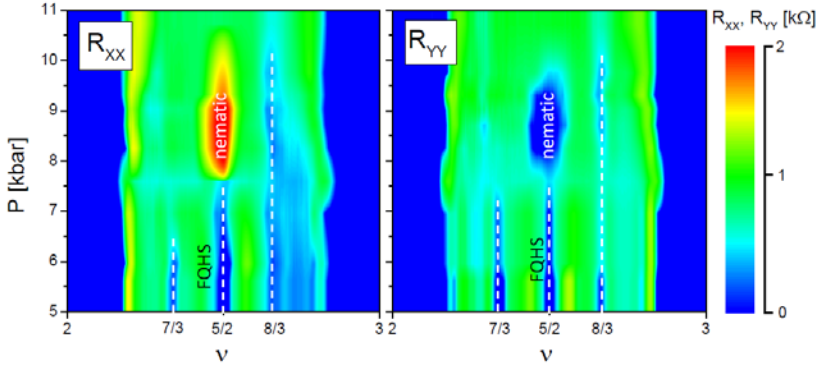
- **Novel quantum Hall phases and transition including stripes, nematics**

  Studies using in-plan magnetic field, pressure or other symmetry breaking mechanisms elucidate field coupling and reorientation processes for changes in topological order

  Michael Zudov, Univeristy of Minnesota

  Gabor Csathy, Purdue University

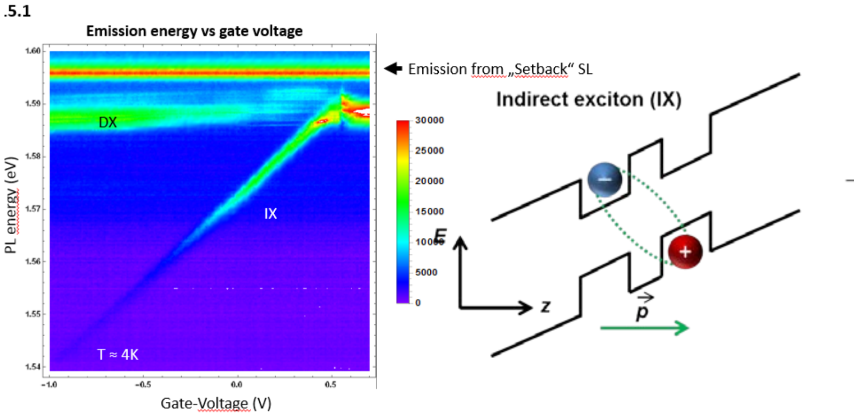
  Qi Quan, Purdue University



- **Optical emission studies**

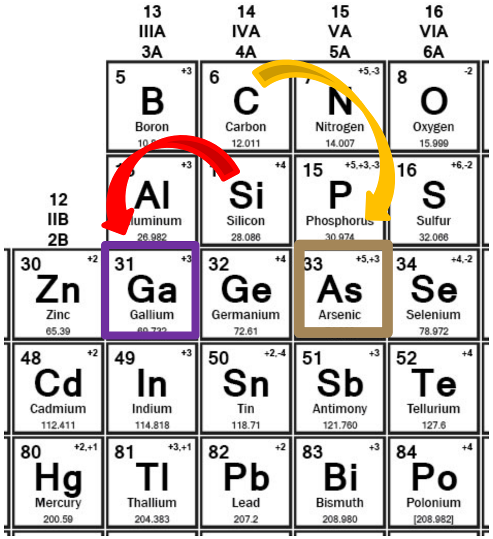
  Spin wave measurements by resonant inelastic light scattering and photoluminescence of indirect excitons that follow the quantum confined stark effect which link optical emission with collective phases of electrons

  Ursula Wurstbaur, Univeristy of Muchen

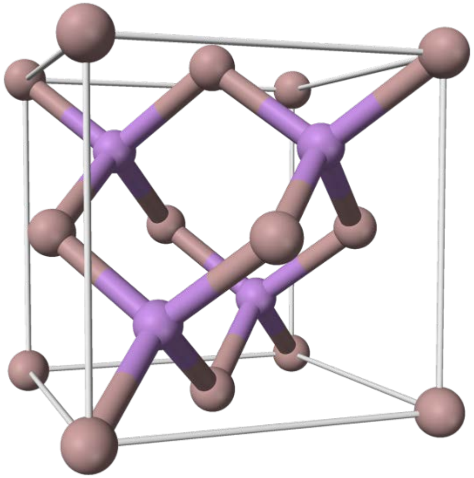


Single Crystal Gallium Arsenide

- Zincblende
- Lattice constant = 0.565 nm
- Gallium and arsenic are similar sized.
- Similar mass fraction
- Tetrahedral coordination geometry
- Ability to dope n or p-type with C or S (both group IV)
- High quality, commercially available substrates
  - LEC, VGF, cut polished, (100), “Epi-ready”
  - Semi-Insulating Ωcm >10^7, or highly doped



http://sciencenotes.org/printable-periodic-table-element-charges/

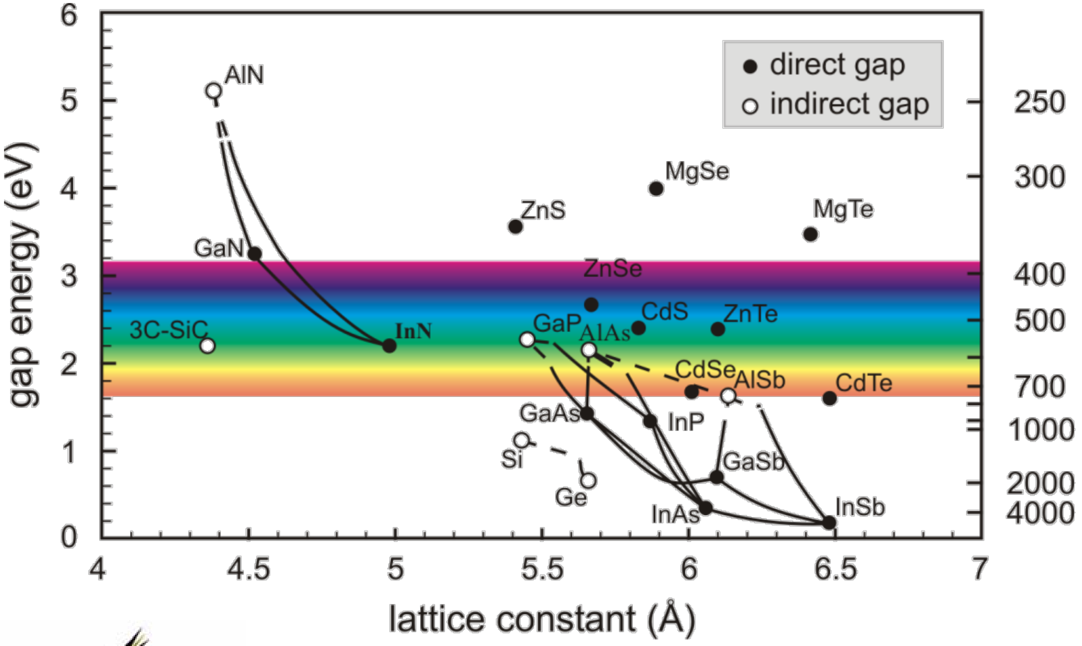


https://en.wikipedia.org/wiki/Gallium_arsenide#/media/File:Gallium-arsenide-unit-cell-3D-balls.png by Benjah-bmm27

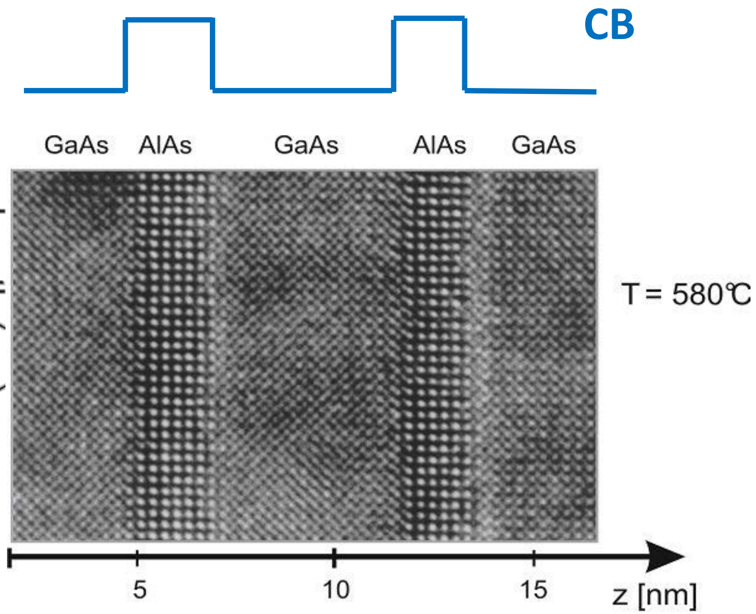
Single Crystal Aluminum Gallium Arsenide

	GaAs	$Al_xGa_{1-x}As$	AlAs
Crystal Structure	Zincblende	Zincblende	Zincblende
Lattice Constant	0.565 nm	0.56533 + 0.00078x nm	0.566 nm
Band Gap	1.42 eV	1.424 + 1.247x	2.16 eV

- Lattice match with differing band gap is a *gift of nature*
- Allows us to fabricate different functional structures all lattice matched



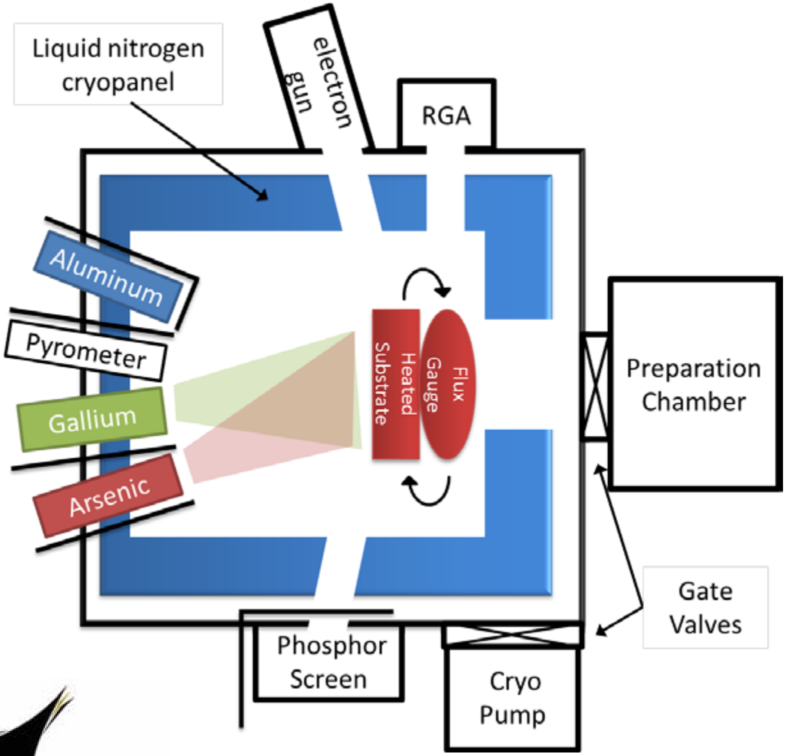
H. Ibach and H. Lueth. *Solid-State Physics*. Springer Verlag, 2003.

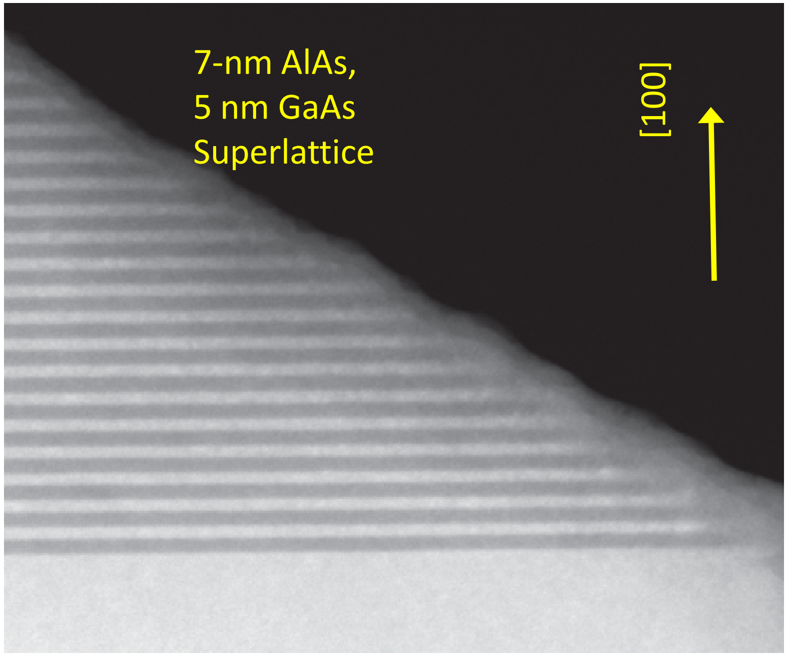


Simone Montanari PhD thesis (2005)
University of Aachen (RWTH, Germany)

Molecular Beam Epitaxy Overview

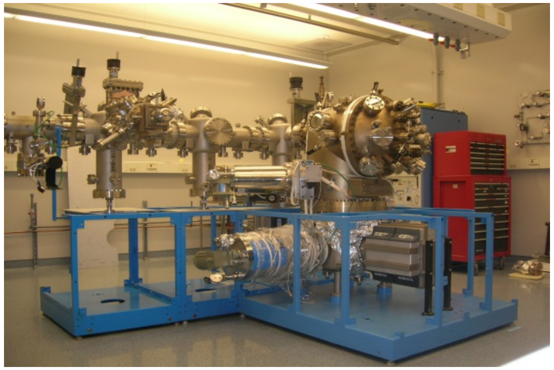
- Ultra High Vacuum (UHV), base pressure < 1×10^{-11} Torr
- Physical vapor deposition technique, pioneered by H. Kroemer, A. Cho
- Source materials are thermally evaporated or thermally sublimated
- Source power is supplied to DC resistive filaments, typically 50 to 750 W
- Temperatures are regulated with PID controllers, typically to 0.1°C
- Growth rates are calibrated by Reflection high-energy electron diffraction (RHEED), typically 1 ML/s
- Layer thicknesses can be accurately controlled to sub nm, typically 2-500 nm
- Layer content controlled by mechanical shutter

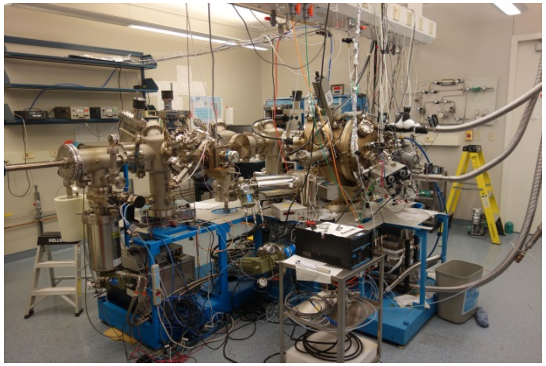




Molecular Beam Epitaxy of Ultra-High-Quality AlGaAs/ GaAs Heterostructures: Enabling Physics in Low-Dimensional Electronic Systems
M. J. Manfra Annu. Rev. Condens.Matter Phys. 5:347–73 (2014)

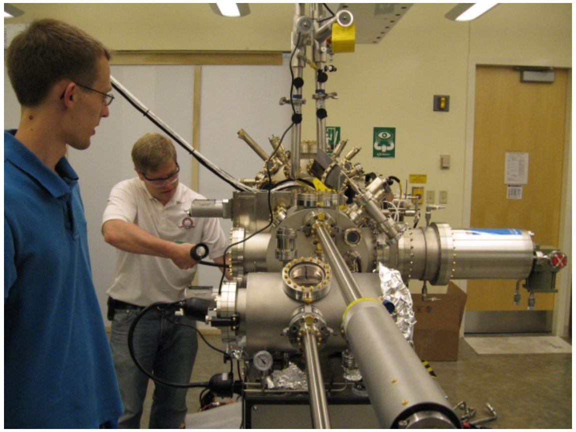
Assembling an MBE

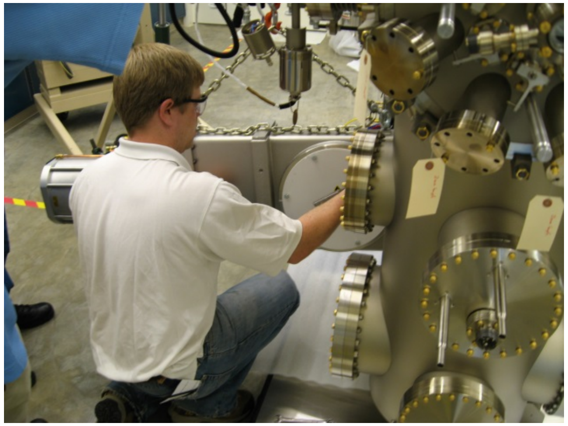


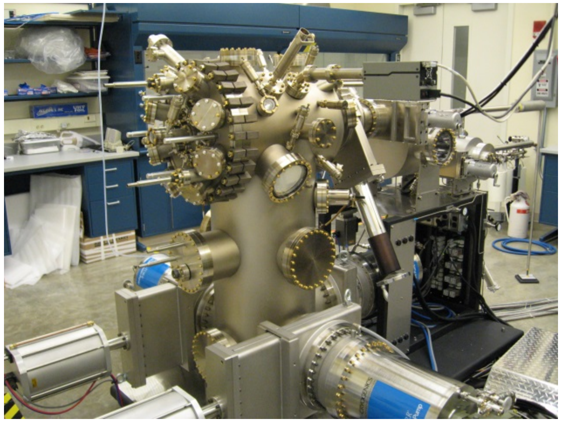


Riber 3200 for GaN

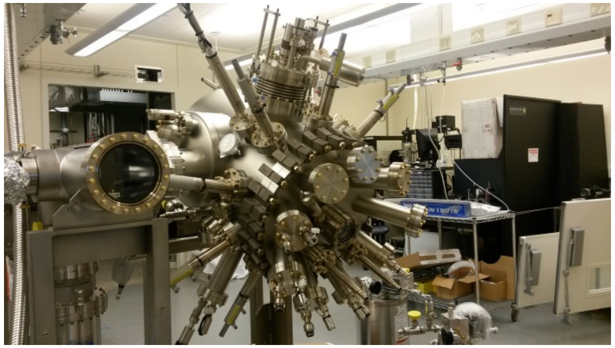
Moved from Bell Labs to Birck

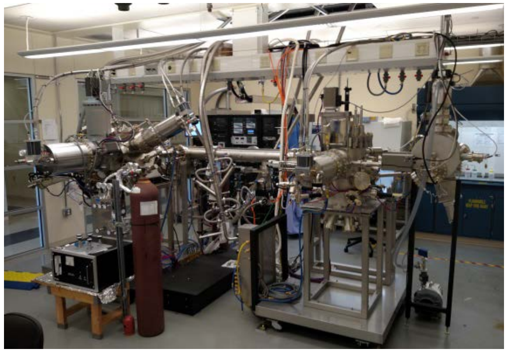




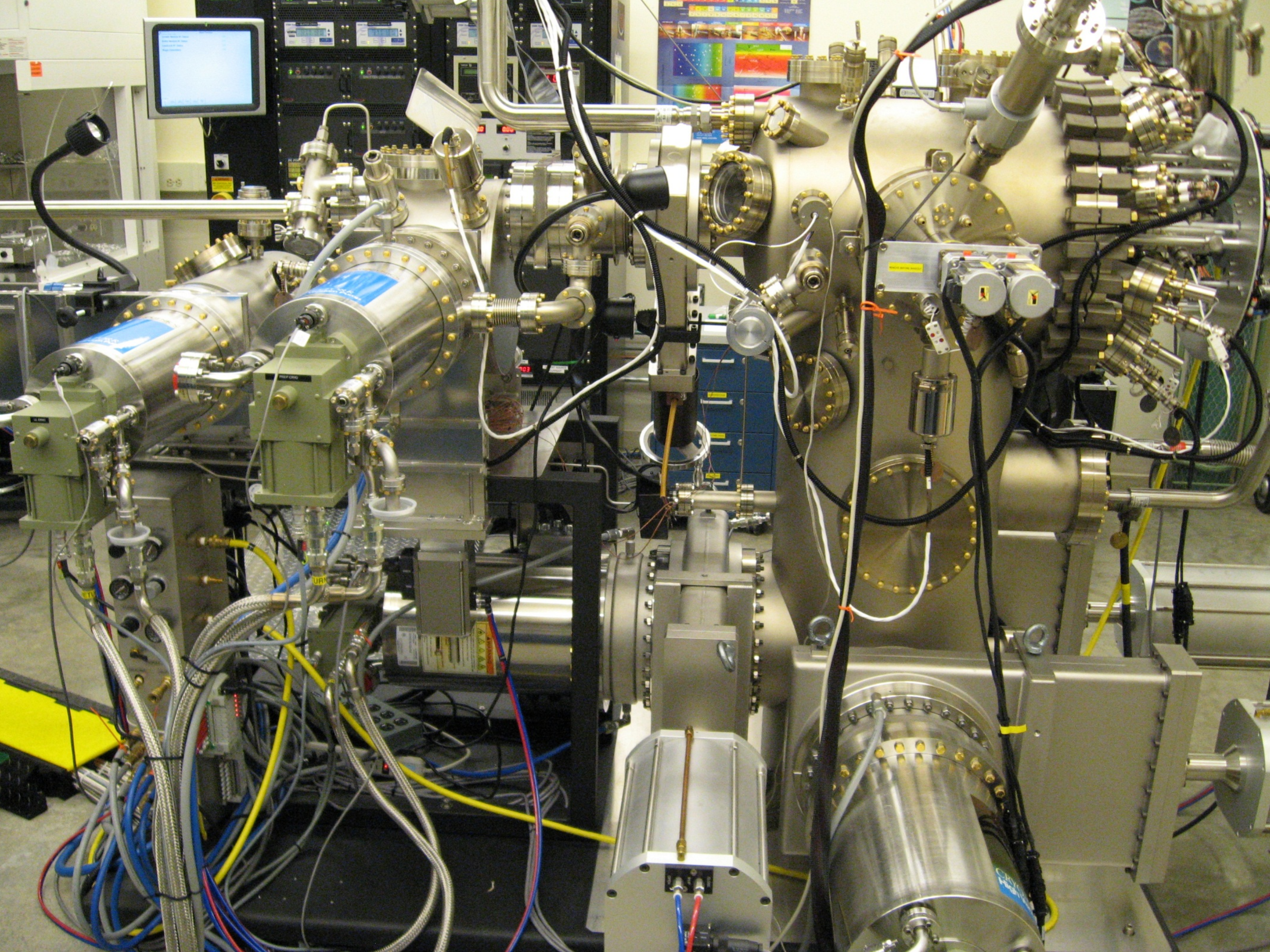


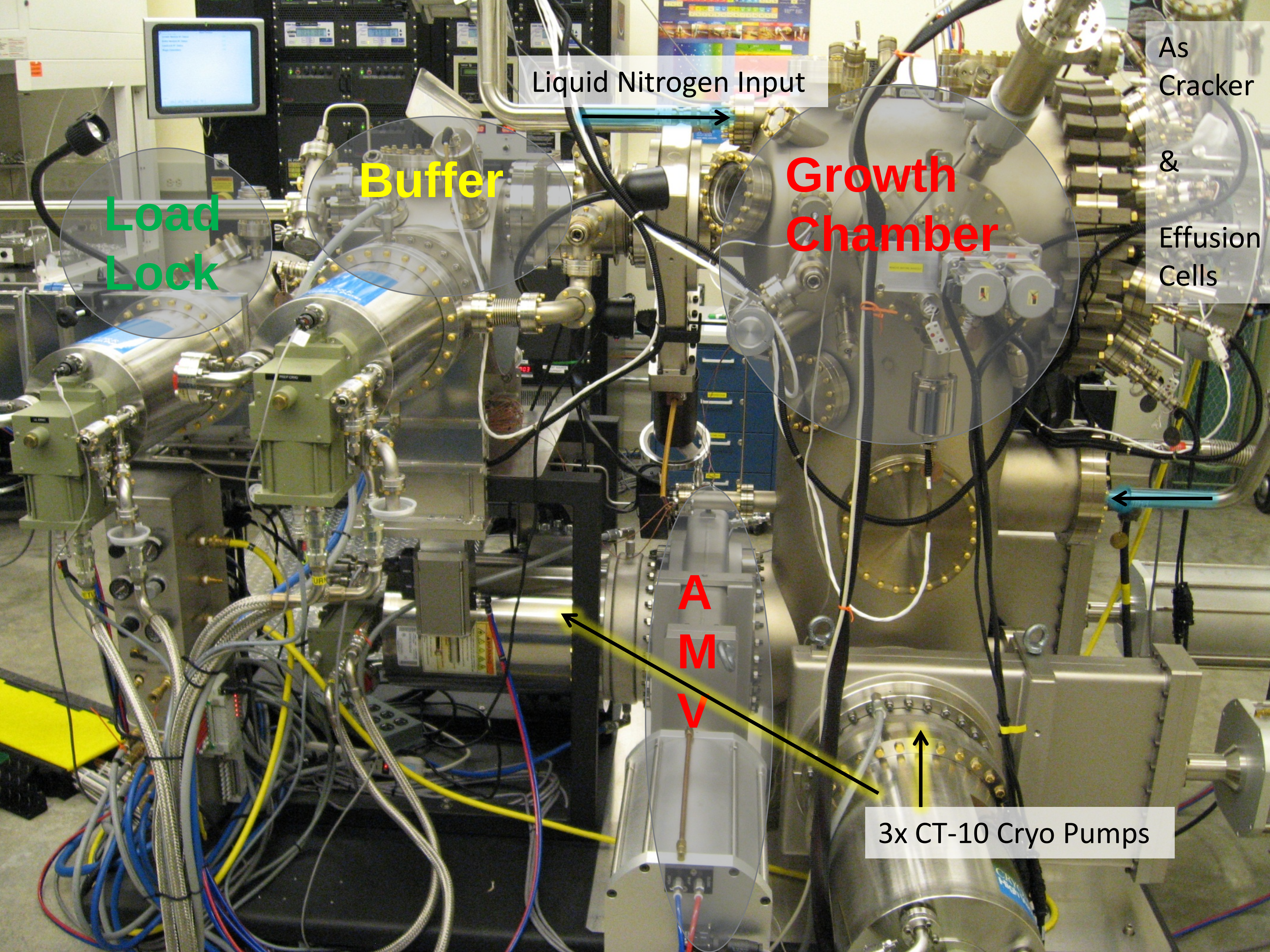
High Mobility GaAs MBE





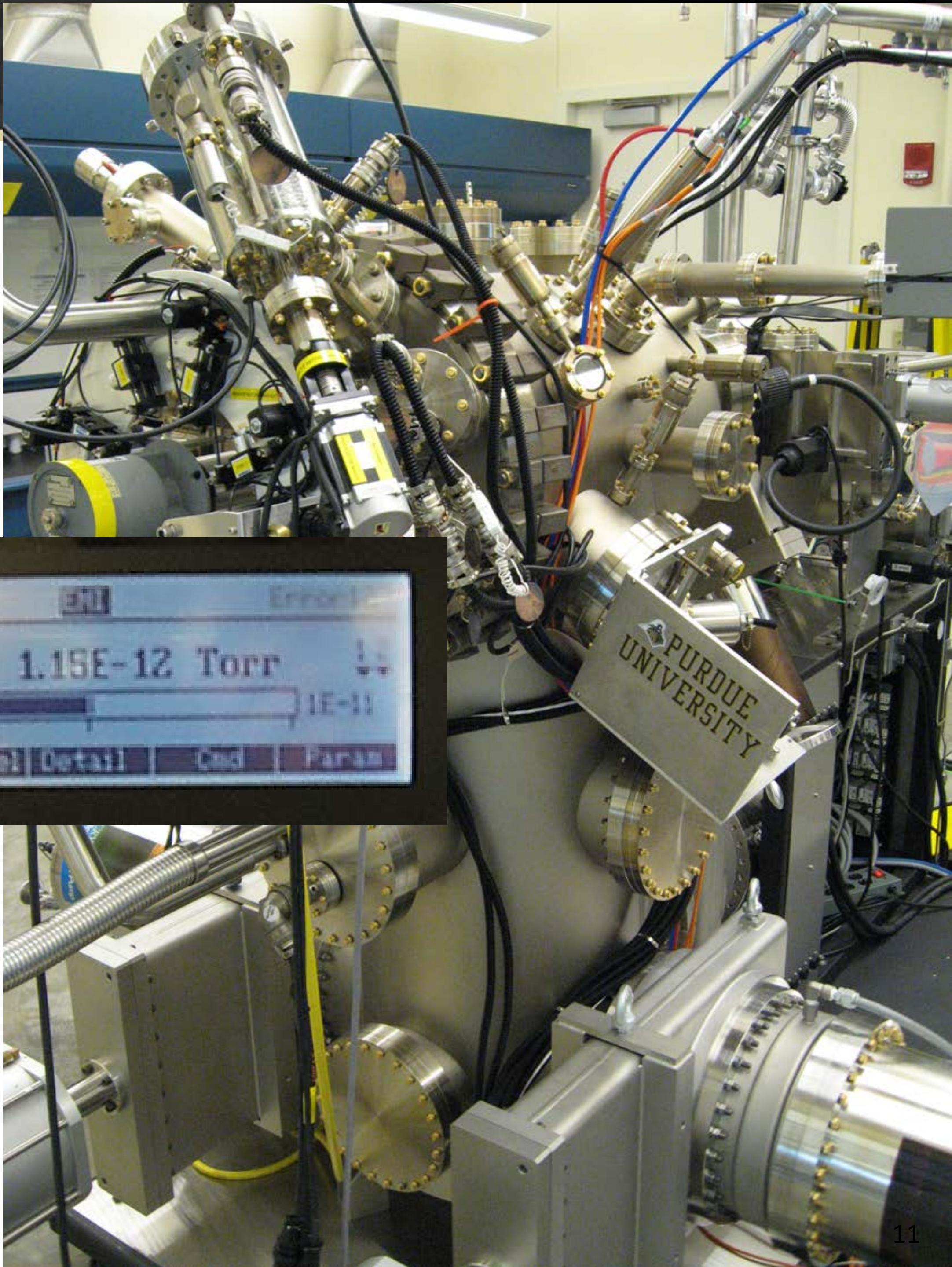
Veeco Gen 930 +620 for Station Q

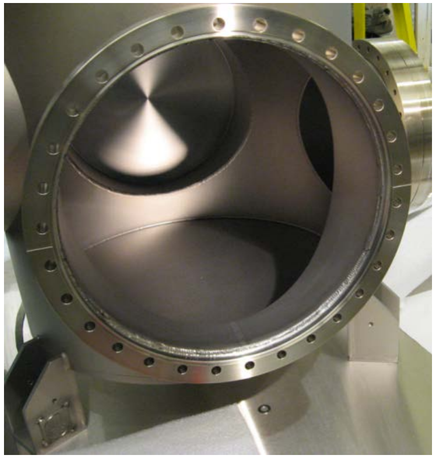



Liquid Nitrogen Input
As
Cracker
&
Effusion
Cells
Load
Lock
Buffer
Growth
Chamber
A
M
V
3x CT-10 Cryo Pumps

System Highlights

- 5(only) materials
  - Custom, high efficiency effusion cells for In, Al, Ga
  - 2x Ga and 2x Al
  - Filament source for Si, C
  - Arsenic Cracking Source
- Optical Pyrometer
- Pneumatic shutter actuators
- Stepper Motor controllers
  - Valves
  - Substrate rotation and indexing
- Rheed Gun, Screen, custom DAQ
- Titanium Sublimation Pump
- LN2 to Shrouds
- UHP Ar plumbing
- Residual Gas Analysis, (RGA)





Importance of Vacuum Quality

- Pressure is the number of particles in the system

$$n = \frac{P\,V}{RT}$$

- Number of particles hitting the substrate per given time ($4x10^8$ /cc s)

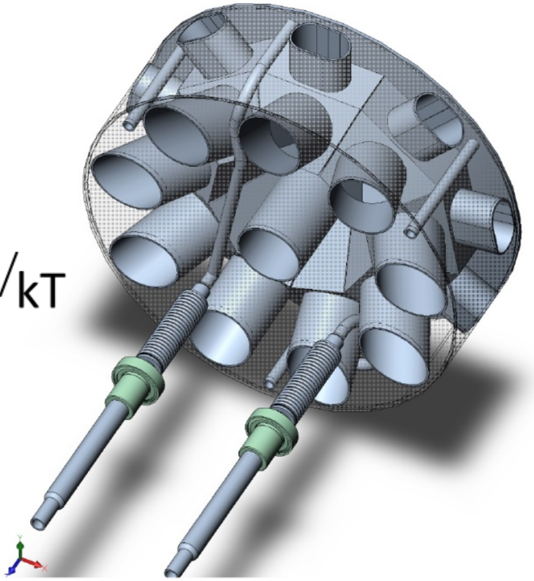
$$\frac{dn_r}{dt} = \frac{p_r}{\sqrt{2\pi m_r k_B T}}$$

- Free mean path in the chamber (100’s m)
  - Molecules in chamber do not interact

$$\lambda = \frac{1}{\sqrt{2}\,\pi\, d^2 n}$$

- Only truly dry pumps used
  - Cryopumps
  - TSP
  - Cryo Panels

$$r_d(T) = f(T)\, e^{-E/\mathrm{kT}}$$

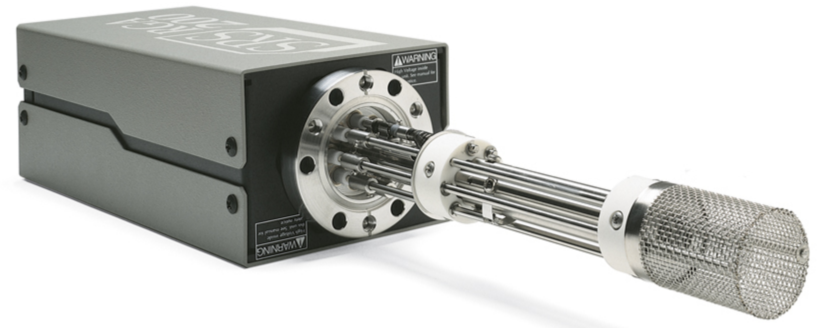


Liquid Nitrogen Delivery

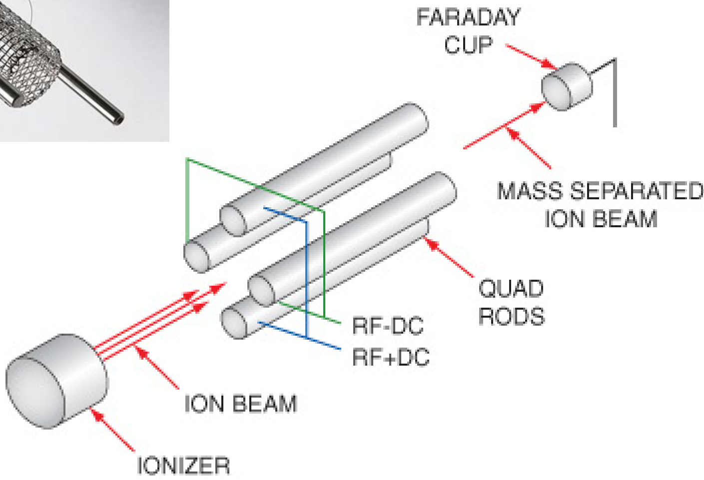
Evaluation of the vacuum

Residual Gas Analysis (RGA)

1. Ionization
   - Remove or knock out an electron from the element(s) to be sorted.
   - Dual ThO_2/Ir filaments used for thermionic electron emission
   - Typical current is 10^{-4}A
   - Process subject to ionization efficiency or sensitivity
2. Deflection
   - Concept, consider a magnetic sector
   - 2 pairs of parallel, equidistant rods (quadrupole)
   - biased at opposite fixed DC potentials and swept RF (this is the sorting field)
   - Deflection related to m/e
3. Detection
   - Faraday Cup (simple counter)
   - High gain, continuous dynode electron multiplier

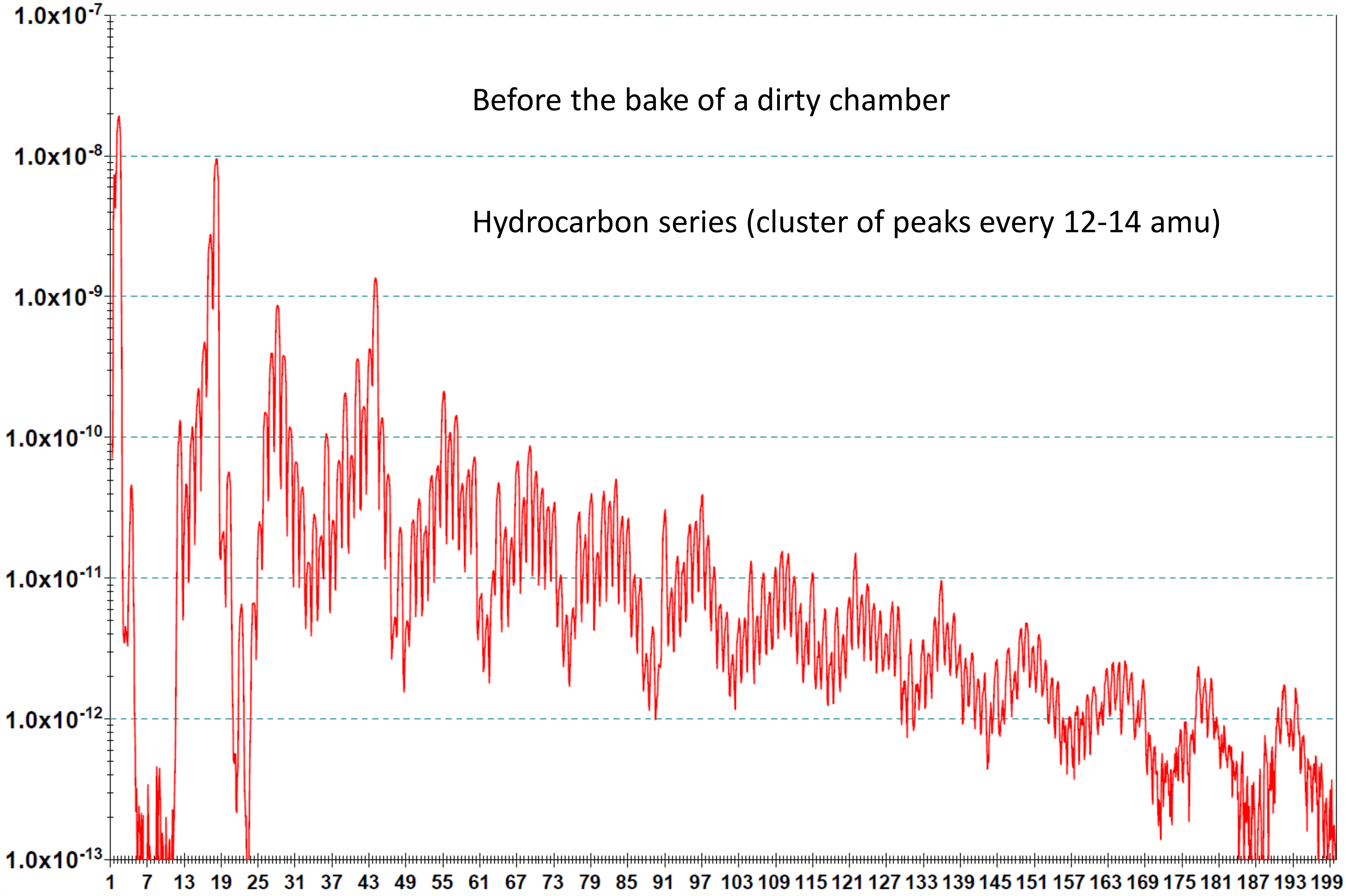


http://www.thinksrs.com/products/RGA.htm



http://www.lesker.com/newweb/technical_info/vacuumtech/rga_01_howrgaworks.cfm?

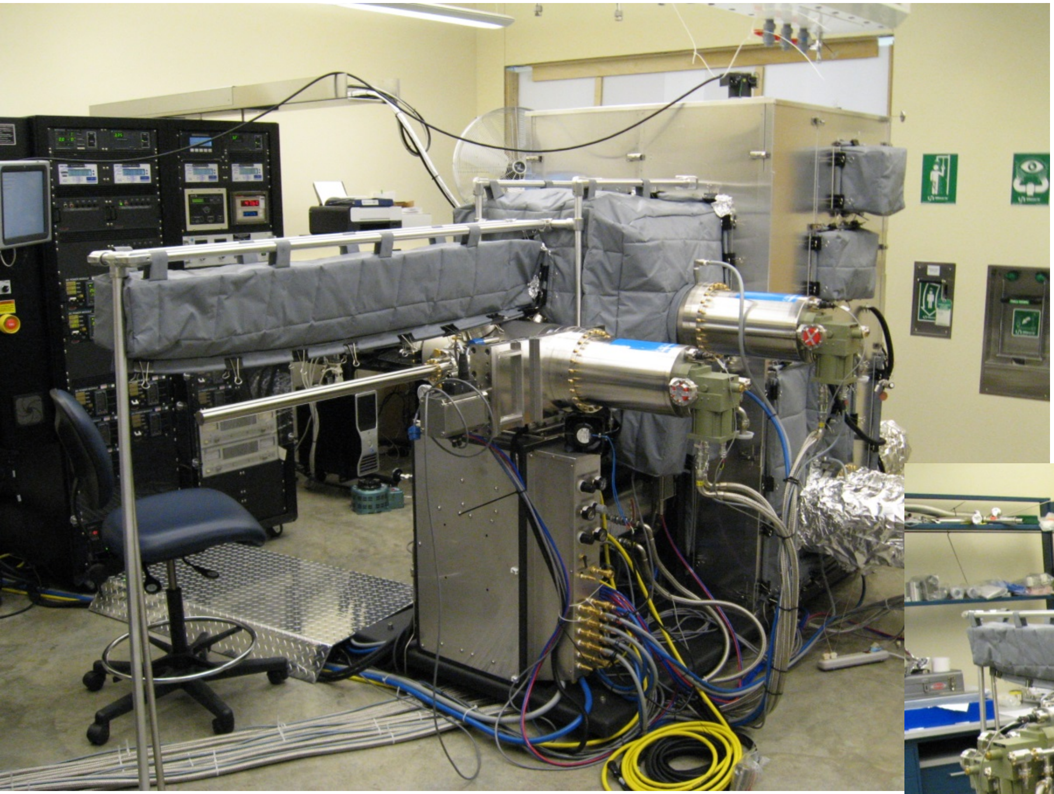
RGA Spectra

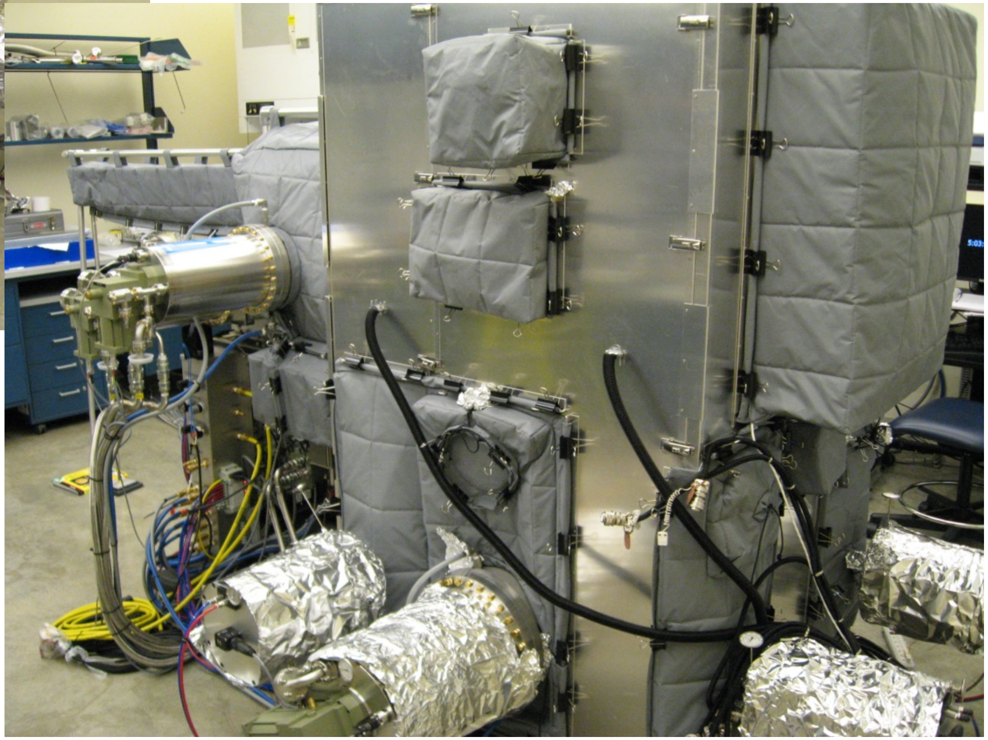


Before the bake of a dirty chamber

Hydrocarbon series (cluster of peaks every 12-14 amu)

Preparing a chamber for UHP



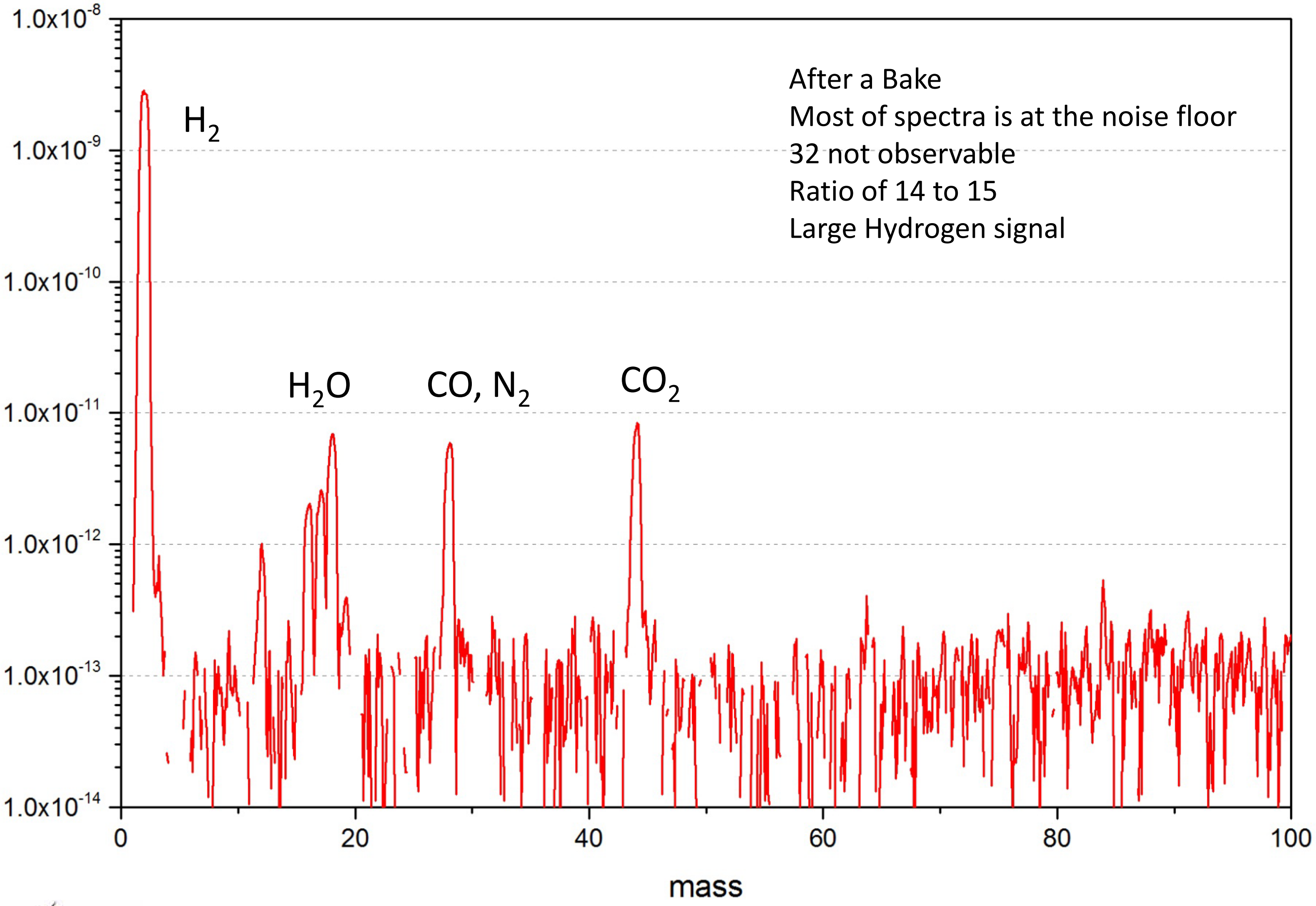


Build an oven around the chamber

Outgassing rates of baked SS drops by 2-4 orders of magnitude after extended (days) bake at 200C, demonstrated by Pfieffer

ALL Equipment must be high-temperature compatible.

RGA Spectra

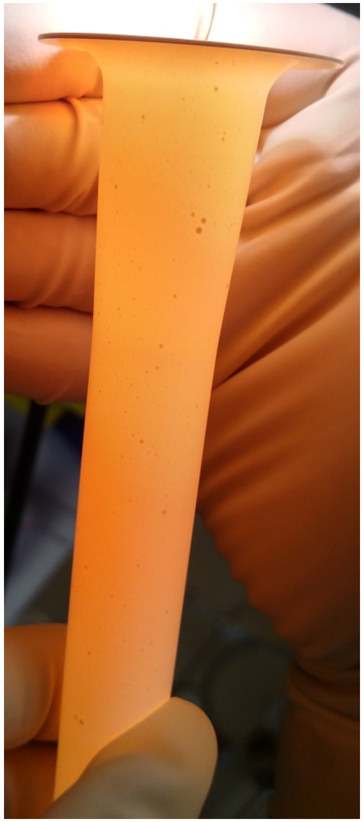


After a Bake
Most of spectra is at the noise floor
32 not observable
Ratio of 14 to 15
Large Hydrogen signal

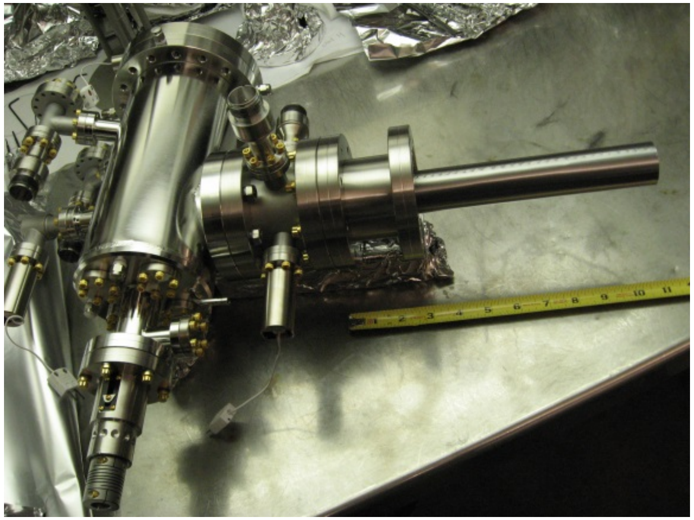
III-V Source Cells

- Effusion Cells
  - Al, Ga, In

- PBN Crucible



- Valved Cracking Source
  - As_4 to As_2



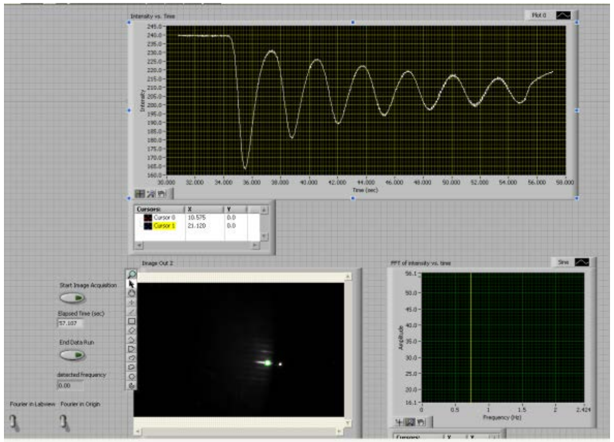
Cells use a type C thermocouple

W-5%Re vs. W-26%Re

Custom doping sources

Rheed Measurements

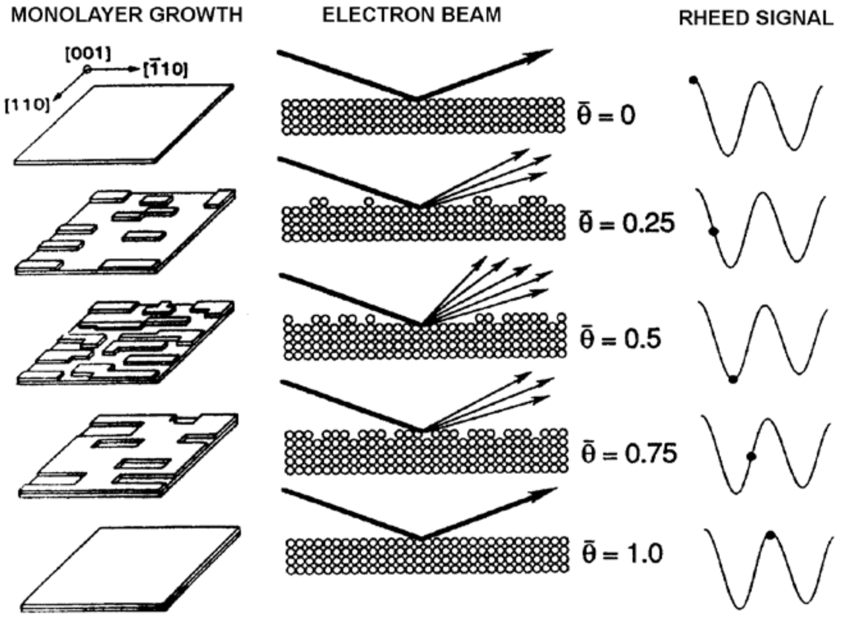
- Reflection high-energy electron diffraction
- We watch intensity oscillations across a specific crystallographic plane.
  - Intensity maxima corresponds to complete monolayer (ML)
  - Intensity minima corresponds to many islands
- We use custom labview to capture data from a firewire camera
- Watch GaAs growth rate (typically ~1ML/s)
- Watch AlAs growth rate (typically ~.33 ML/s for X=24%)



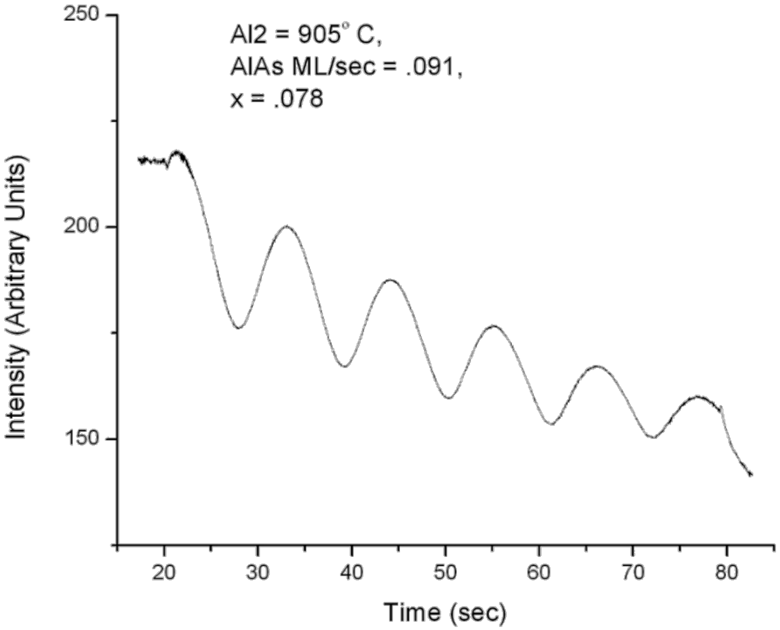
Cursors:	X	Y
Cursor 0	10.575	0.0
Cursor 1	21.120	0.0

Elapsed Time (sec): 57.107

detected Frequency: 0.00

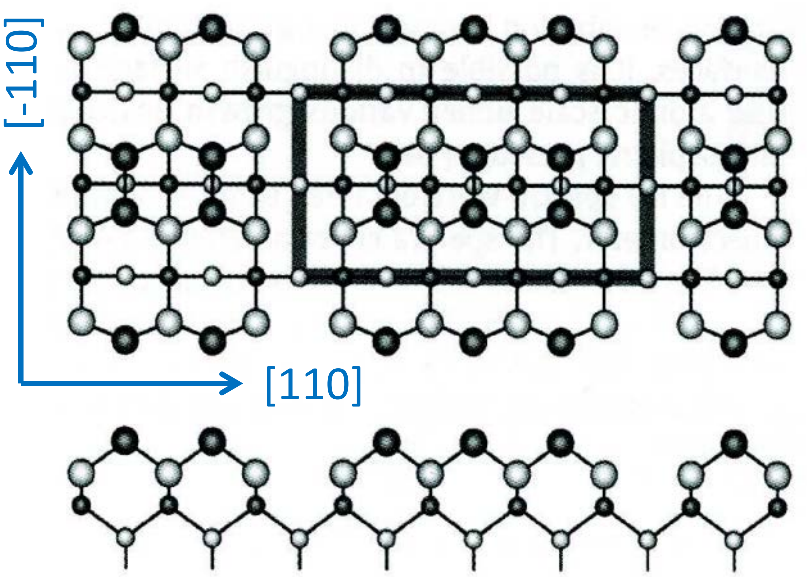


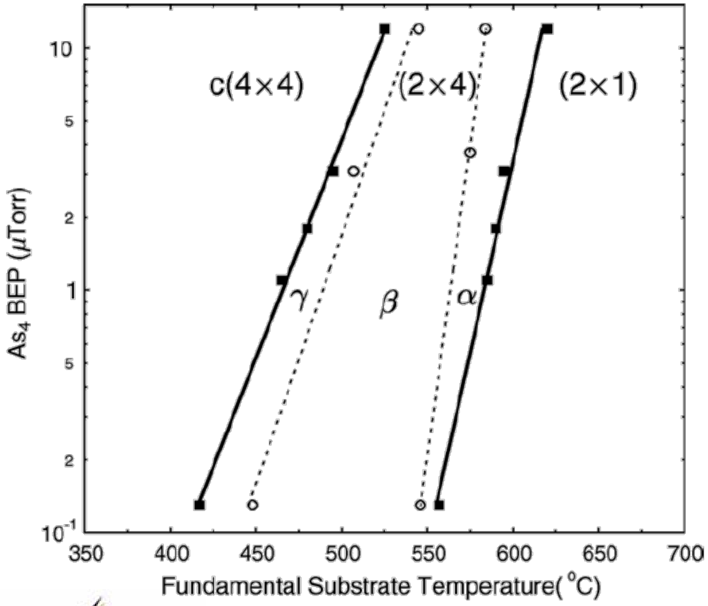
M. Ohring, The Material Science of Thin Films, Academic Press, 1992



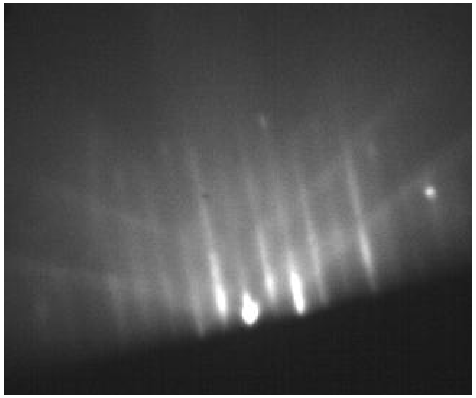
Rheed to Observe Surface Phase

- We maintain an “As-terminated”
- Surface has incomplete bonds
- As-As dimer bonds will begin to form to minimize the free surface energy
- GaAs(001) - (2x4) principle surface for MBE growth

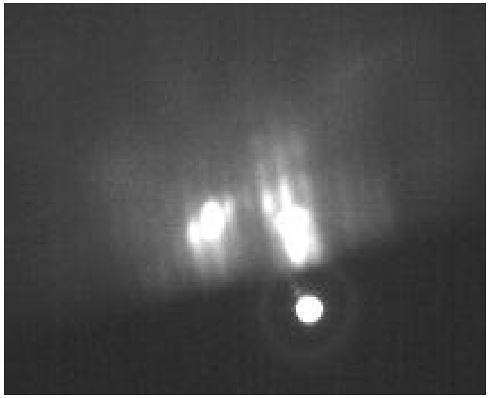




V.P. LaBella, D.W. Bullock, C. Emery, Z. Ding, P.M. Thibado, Appl. Phys. Lett. 79 (2001) 3065.

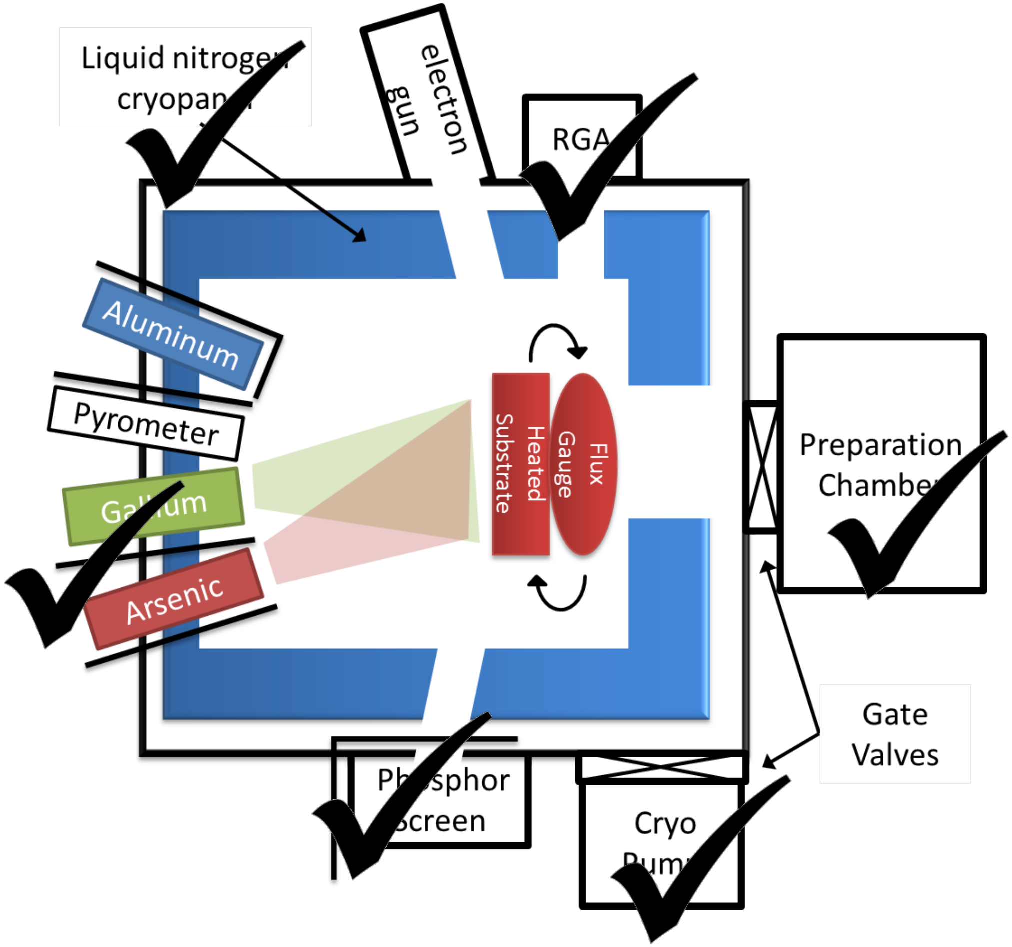


2x [110]



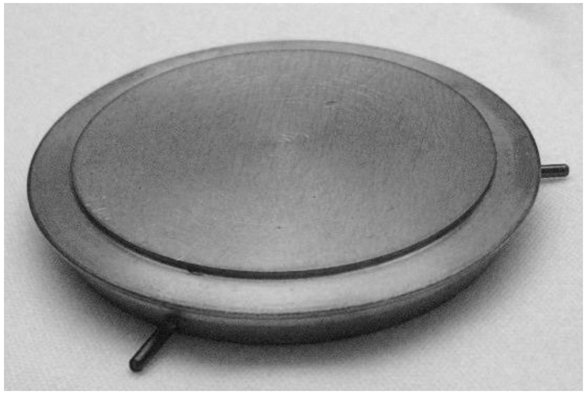
4x [-110]

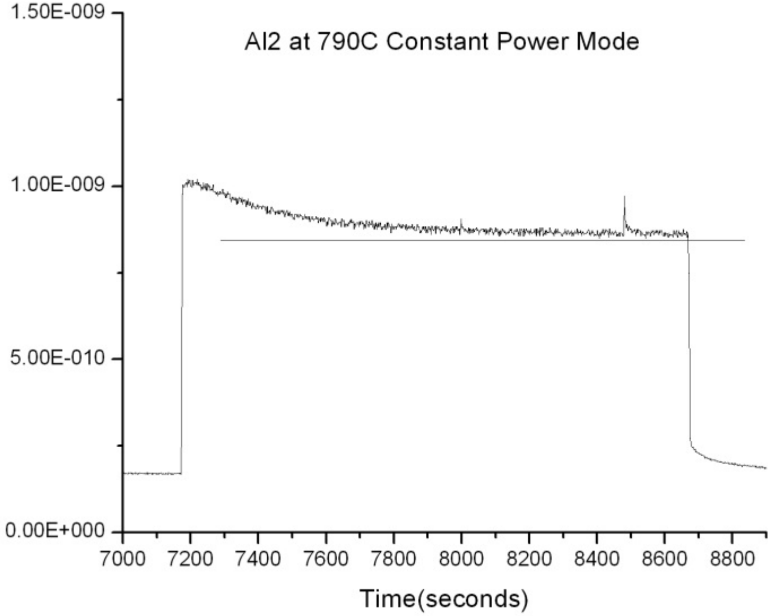
Quick Review



Growth of a Sample

- Solid Ta Block
  - Mechanical carrier
  - Isotherm
- Wafers bonded with liquid Ga
- Before growth, substrates are outgassed
  - 4 hr @ 100°C
  - 4.5 hr @ 350°C
- Determine structure & create recipe
- Warm up source cells
  - Ga 600˚ C → 850˚C
  - Al 775˚ C → 1000˚ C
  - 30 min to stabilize
- Flux measurements
- Open As valve 10^{-6} Torr, beam equivalent glux
- Warm Rheed Sample to ~600˚ C
  - 30 C / min = ~15 min
- Tune growth temperatures by Rheed oscillations
- Cool Rheed sample
- Load and warm growth sample to ~600˚ C
- Desorb native oxide ~600˚ C
- Growth Temp of ~635˚ C
- Tune power output
- Begin recipe
  - Supper Lattice, Smoothing Layers, QW





The 2 Dimensional Electron Gas

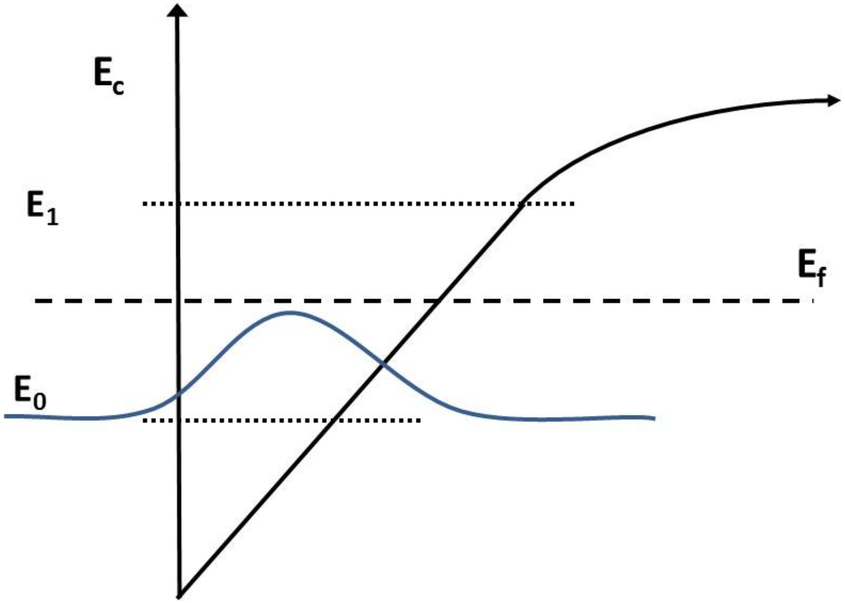
- Realized in a single interface heterojunction, or square well.
- Due to conduction band bending, electrons become trapped in single two dimensional plane, XY with no Z freedom
- Confinement leads to quantized energy states
  - Classic undergrad quantum mechanics
- Electrons trapped in single ground state, truly 2D

$$n_{2d}(E) = \frac{m}{\pi h^2}(E_F)$$

- Mobility

$$\mu = \frac{e\tau}{m^*} \qquad \sigma = ne\mu$$

where τ is the transport lifetime

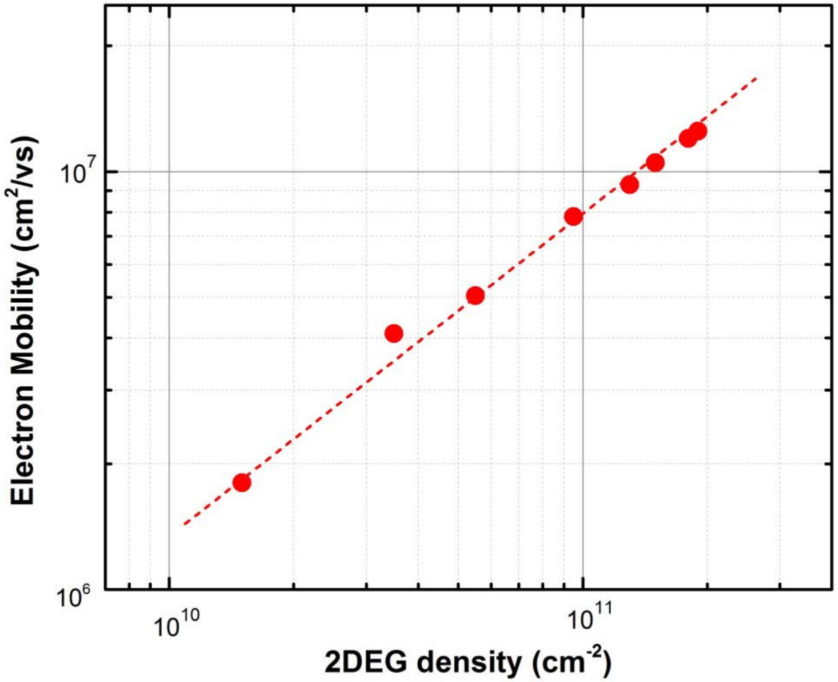


- 2DEGs can exist in MOSFET type devices
- 2DEGs can also exist in oxides
- Two-dimensional hole gas (2DHG)

Types of disorder (scattering events)

1. Unintentional background charged impurities
    - This is the primary source of scattering!
    - Background vacuum, hot materials*
        - UHV necessary but not sufficient
    - GaAs substrate
    - Source material*
2. Remote ionized donors
    - Current structures screen and limit this affect
3. Interface roughness and other lattice defects
    - Very small, epitaxial nature of material system
4. Alloy disorder
    - In the barriers
    - Random potential, small tail in the AlGaAs

$$\mu = \frac{e\tau}{m^*}$$



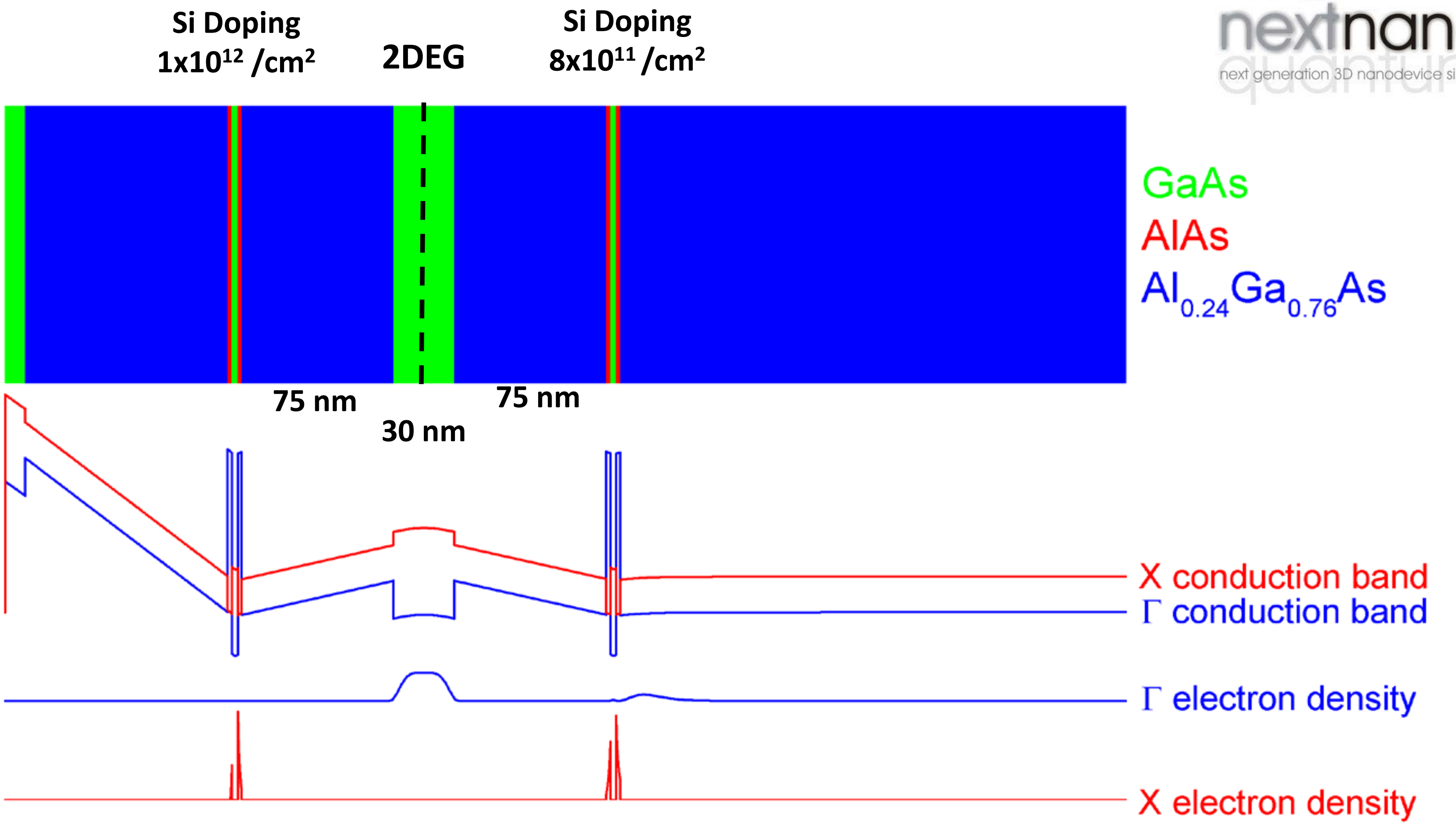
Theory is supported by experimental data

$$\mu \sim n_e^{\alpha} \begin{cases} \alpha \approx 1.5 \text{ Silicon Donors} \\ \alpha \approx 0.7 \text{ Uniform background impurities} \end{cases}$$

The mobility density dependence at low temperature showing α~0.7

Umansky V, de-Picciotto R, Heiblum M. 1997. Appl. Phys. Lett. 71:683–85

Doping well heterostructure



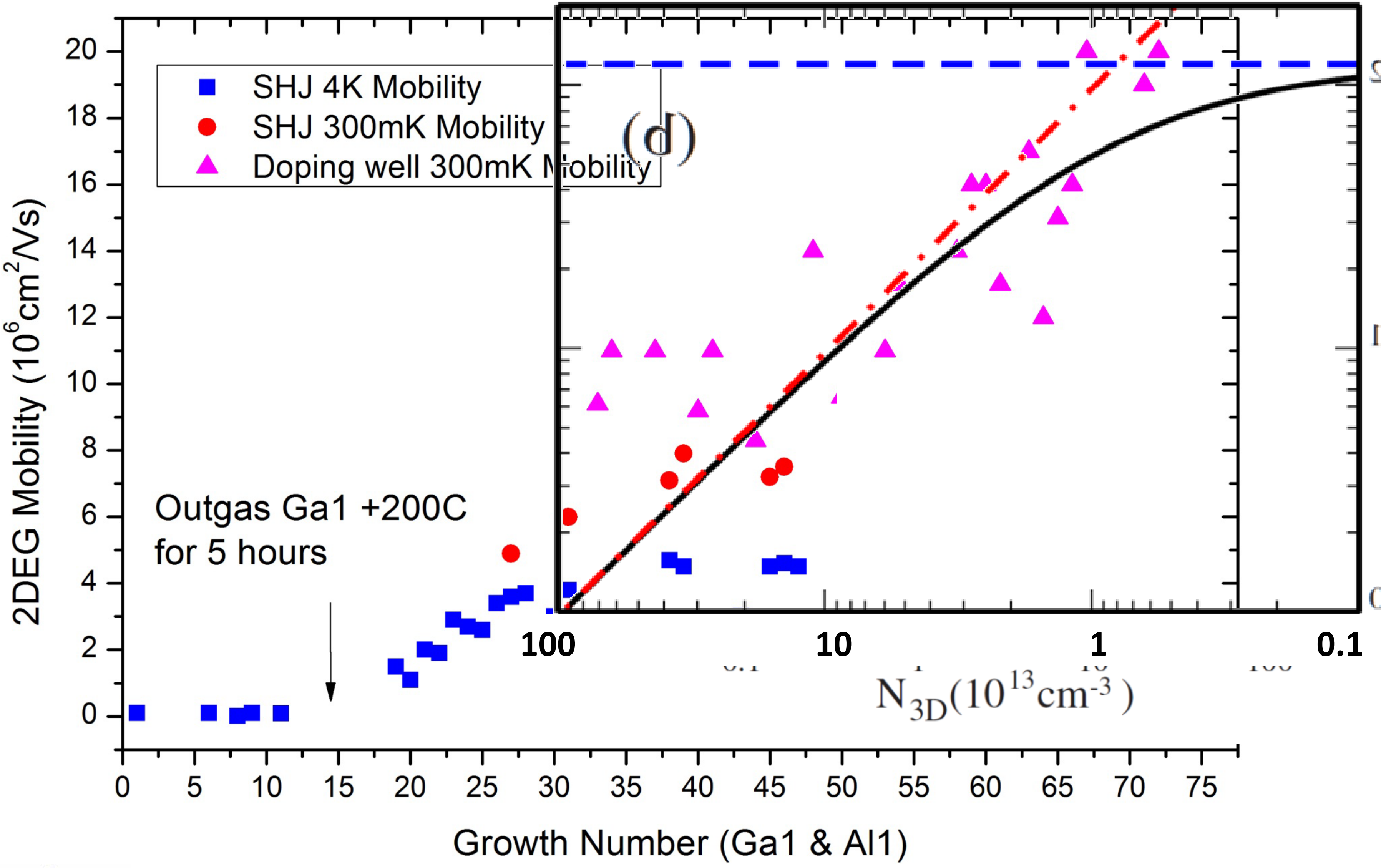
- Nextnano3 solves Schrodinger and Poisson equations
- Used for;
  - Band Structure, Charge densities, General structure trends, new structures, Checked empirically !!!

Quick Review

- We have an MBE that can grow epitaxially perfect AlGaAs-GaAs heterostructures with very high purity
- Heterostructures can produce 2DEGs which limit the effect of donor impurities
- We can use 2DEG mobility to evaluate the background impurities

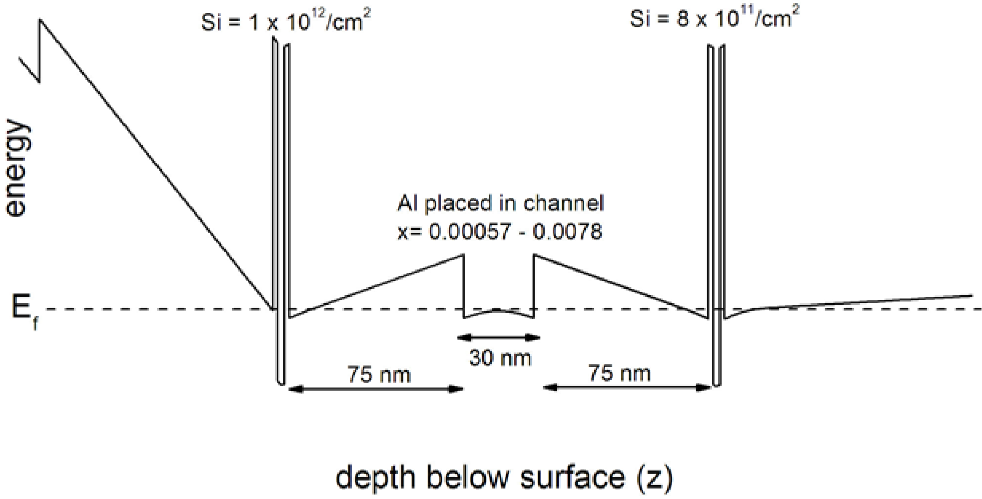
$$\mu = \frac{e\tau}{m^*}$$

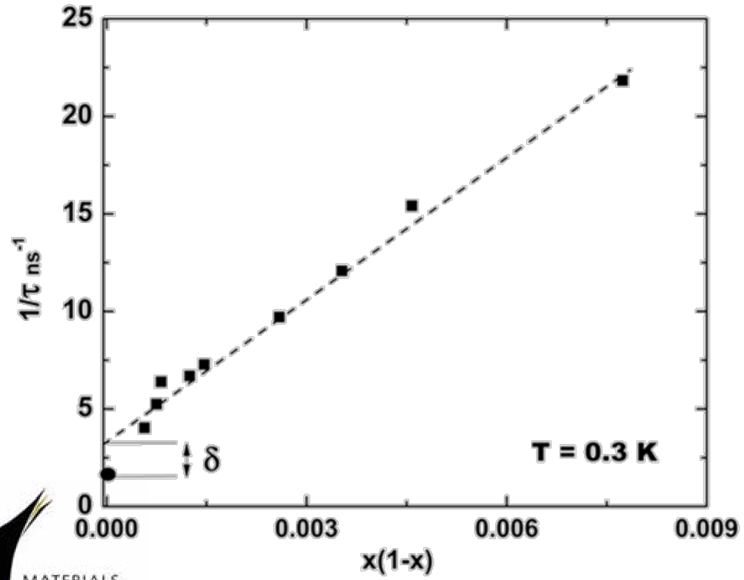
Results of our first campaign

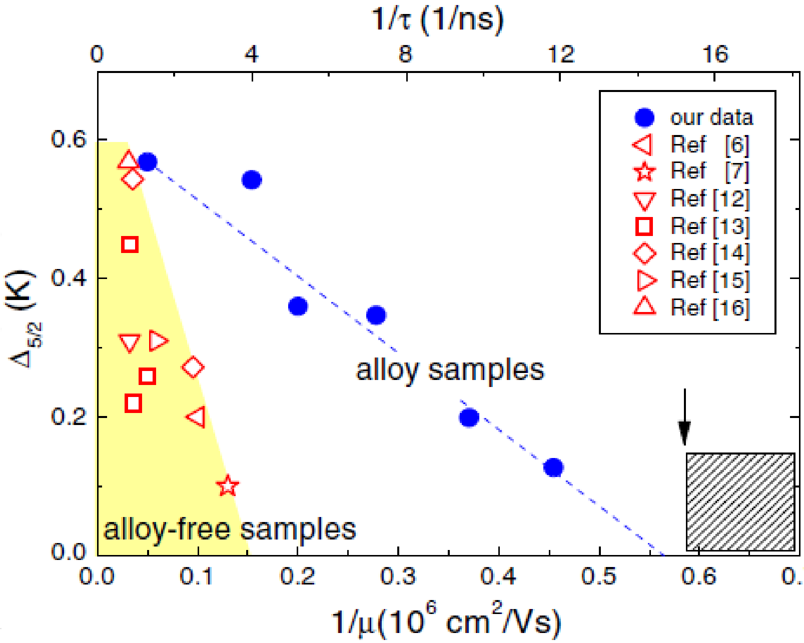


Intentional Alloy Disorder

- Standardized Structure
- Varied the amount of alloy (Al) disorder placed intentionally into the well.
- 10 samples
  - X= 0.00057 to 0.0078
- Studying **VERY LOW** quantities of material to perturb the fragile mobility
- Learned that mobility is not a good measure of excitation gap at 5/2.
- In fact, 5/2 state appeared at significantly reduced mobility's when compared to samples where alloy disorder is not the limiting scattering mechanism

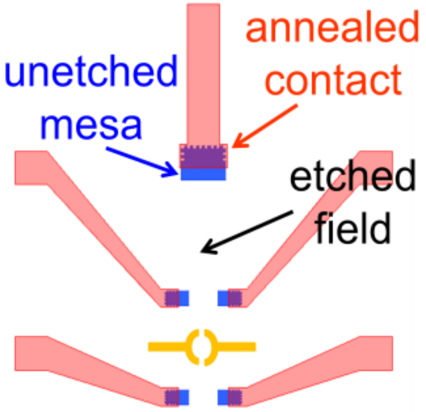


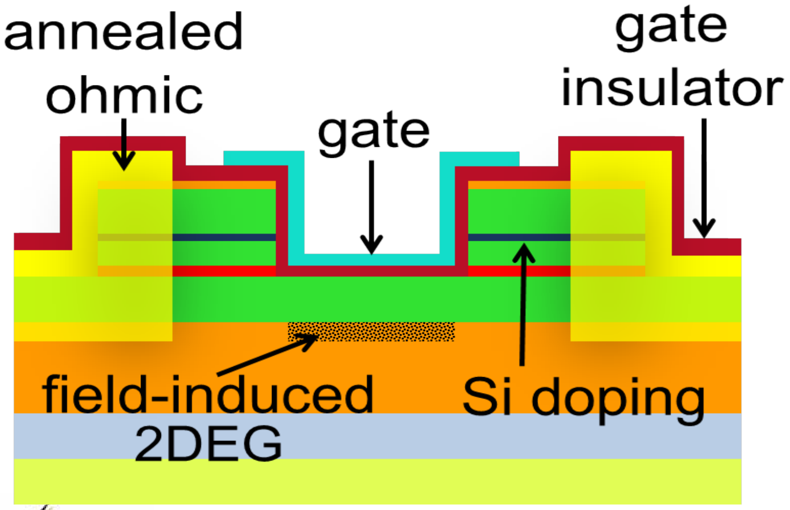


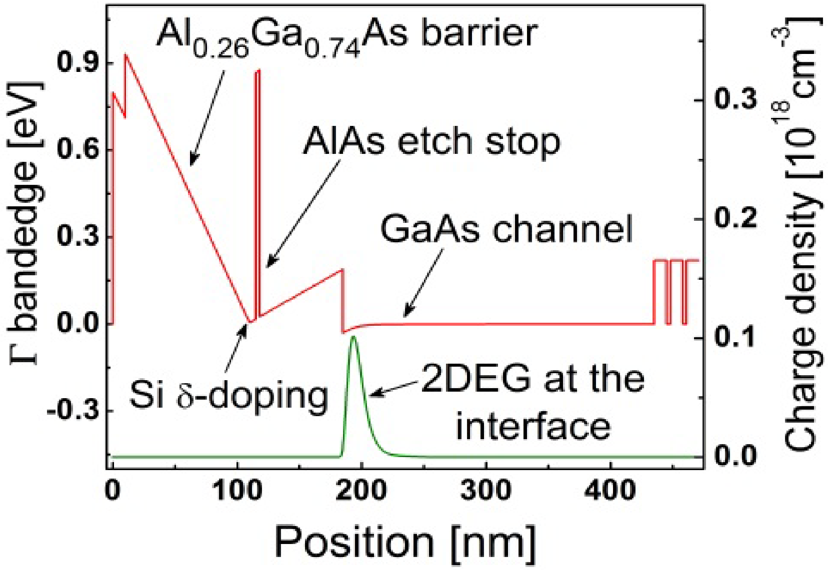


Novel FET device

- Time-dependent charge fluctuations in the ionized dopants inherent to the modulation-doping have a detrimental effect on the nanostructure behavior.
  - Dopants are trap sites for electrons being injected or tunneling from the gates.
- HIGFET, is a workhorse, but fabrication becomes difficult as 2DEG get shallower
- Absence of dopants makes fabrication of reliable ohmic contacts with high yield and low contact resistance challenging

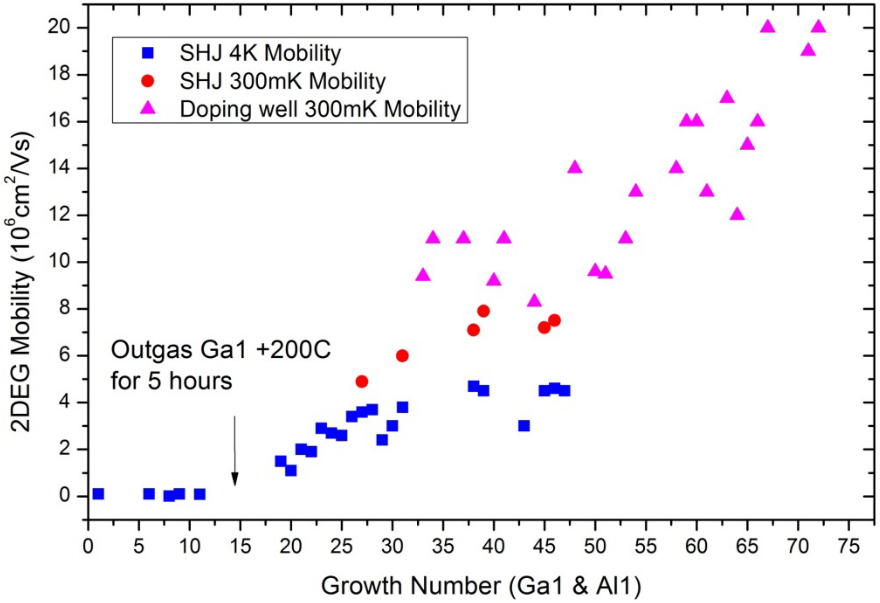






Return to mobility evolution plot

- This confirms for us that 2DEG mobility is limited by background impurities.

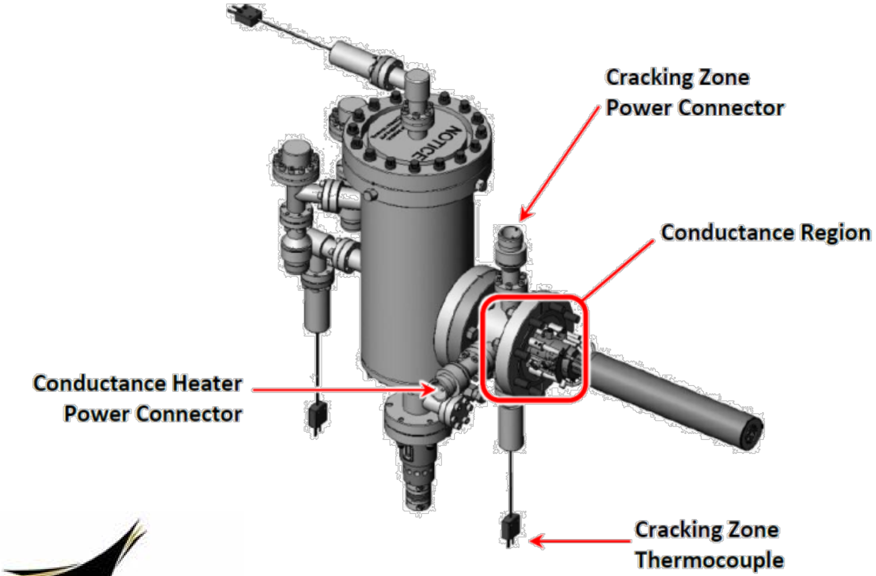


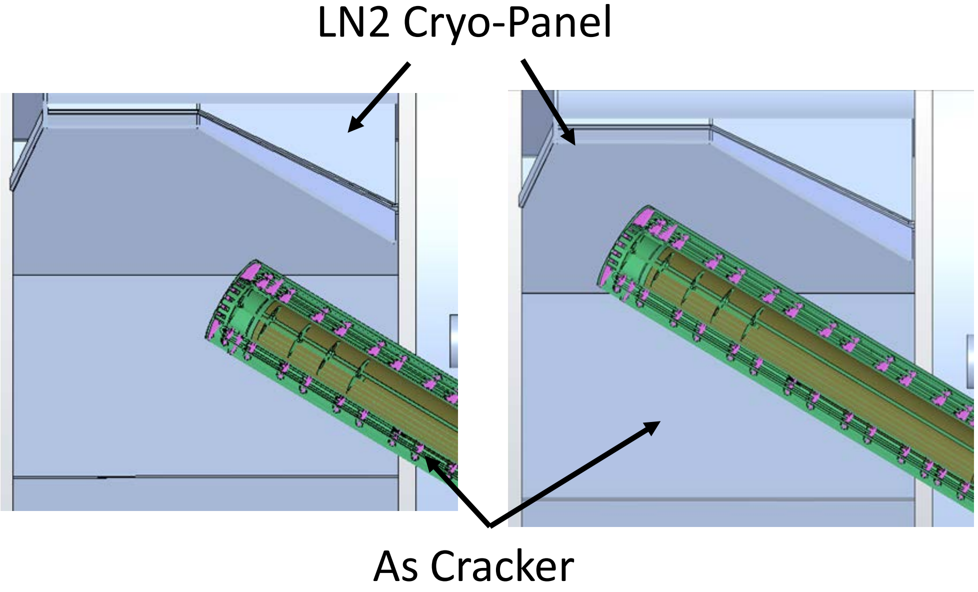
- But where do they come from?
  - Background vacuum, hot materials*
  - GaAs substrate
  - Source material*
- Clues
  - We can improve it over time
- How do we move forward to reduce impurities

Modifications to MBE

Substrate Heater

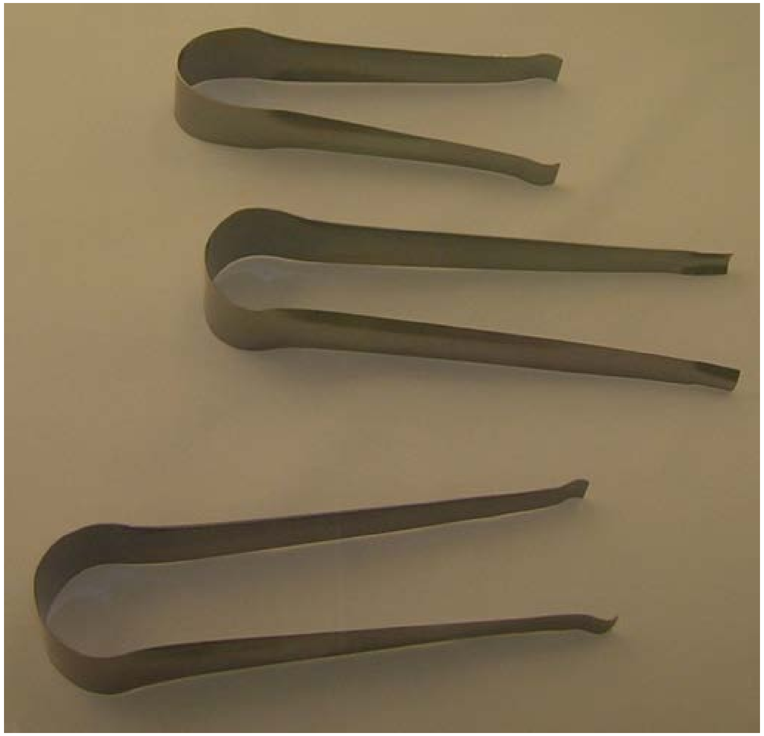
Arsenic Source



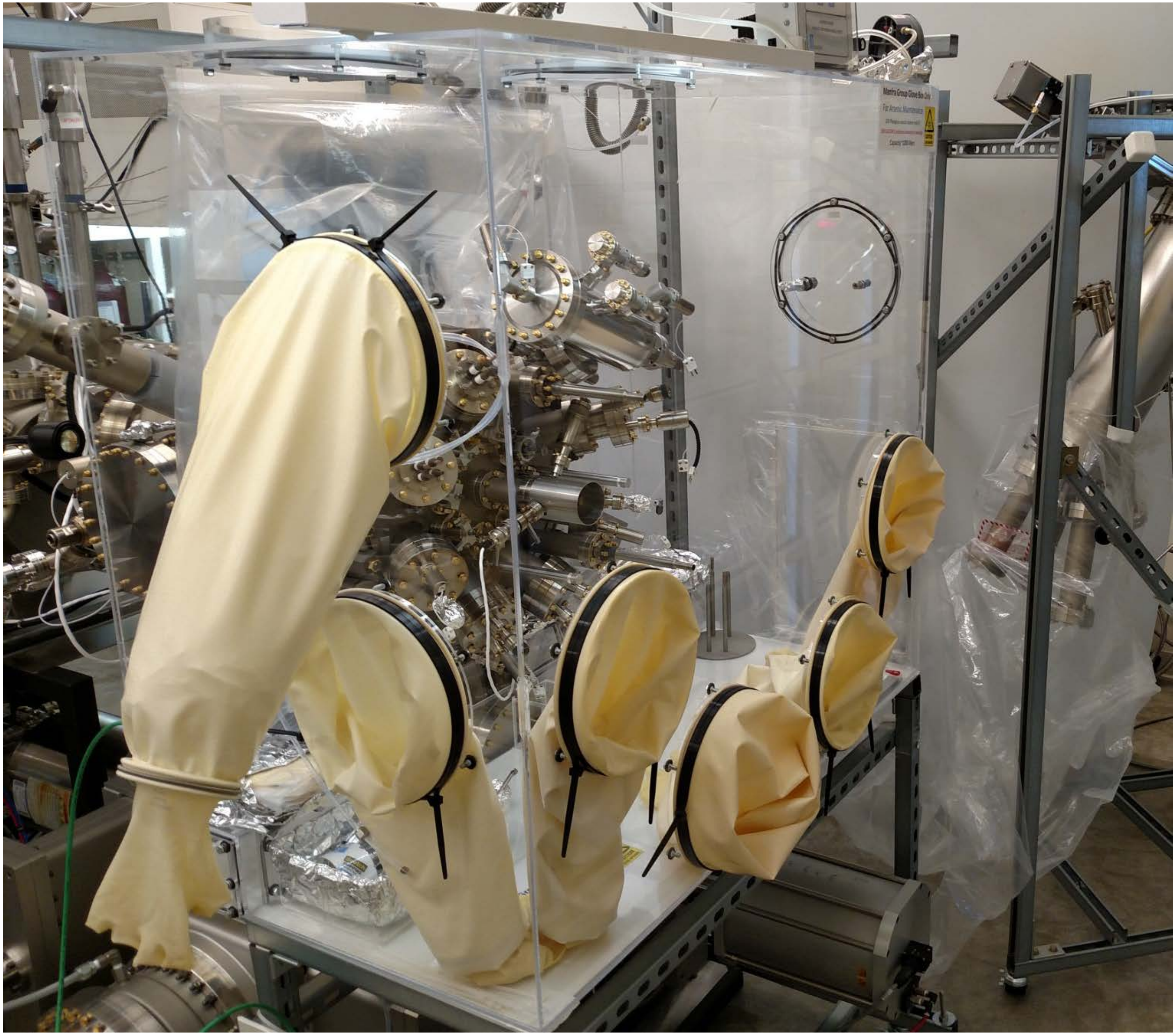


Source material and handling

- UHP Gallium Supplied by Molycorp THE RARE EARTHS COMPANY → neo
- Gallium with custom Ta wrappers between Ga and HDPE package
- Custom Ta forceps for loading ingot into crucible

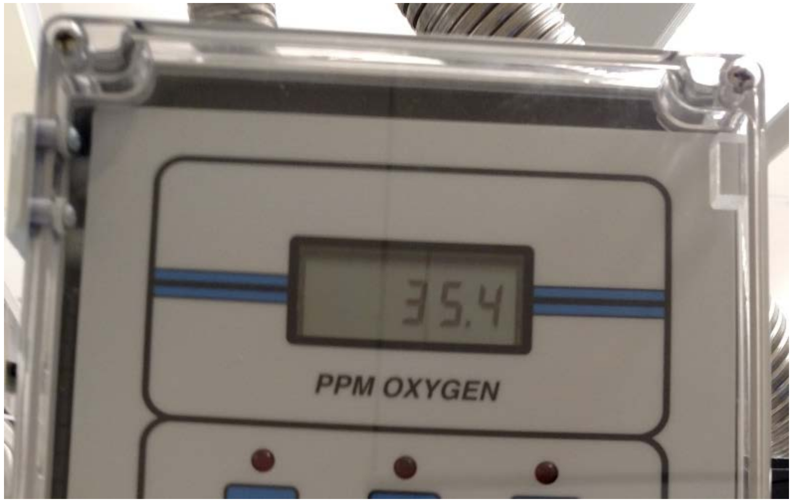


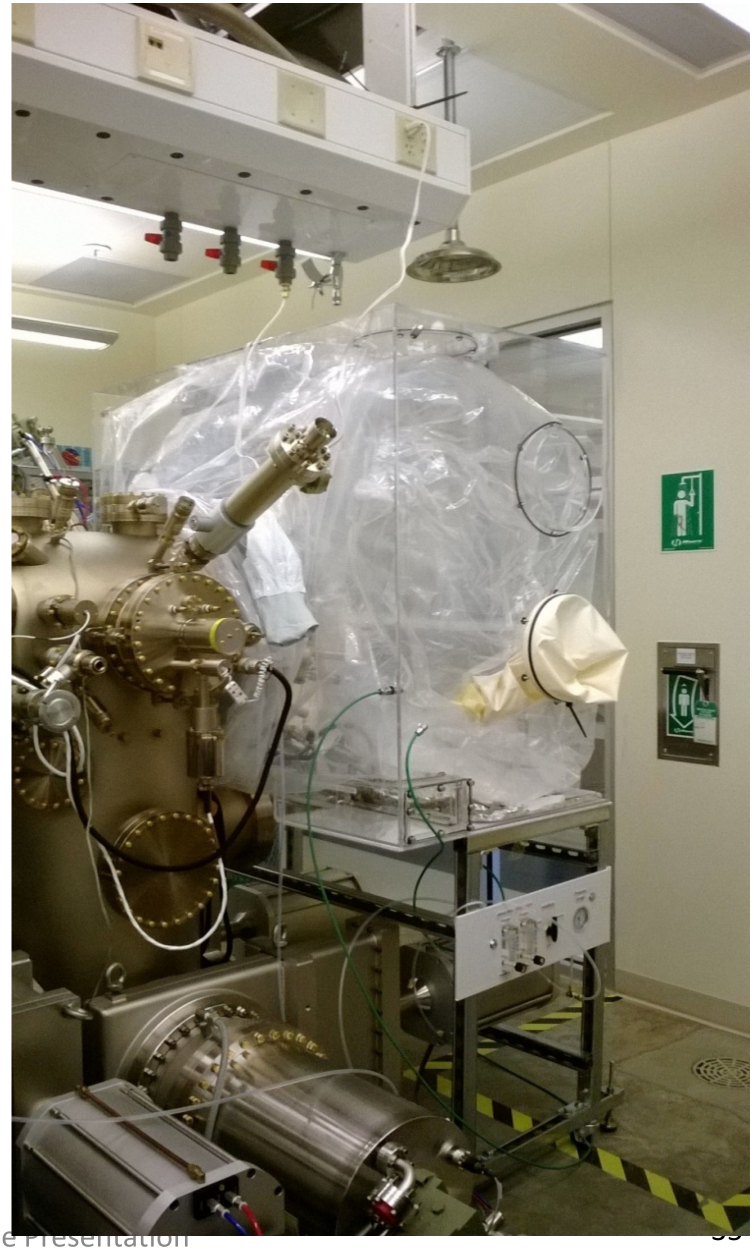
Glovebox and mobile UHV chamber



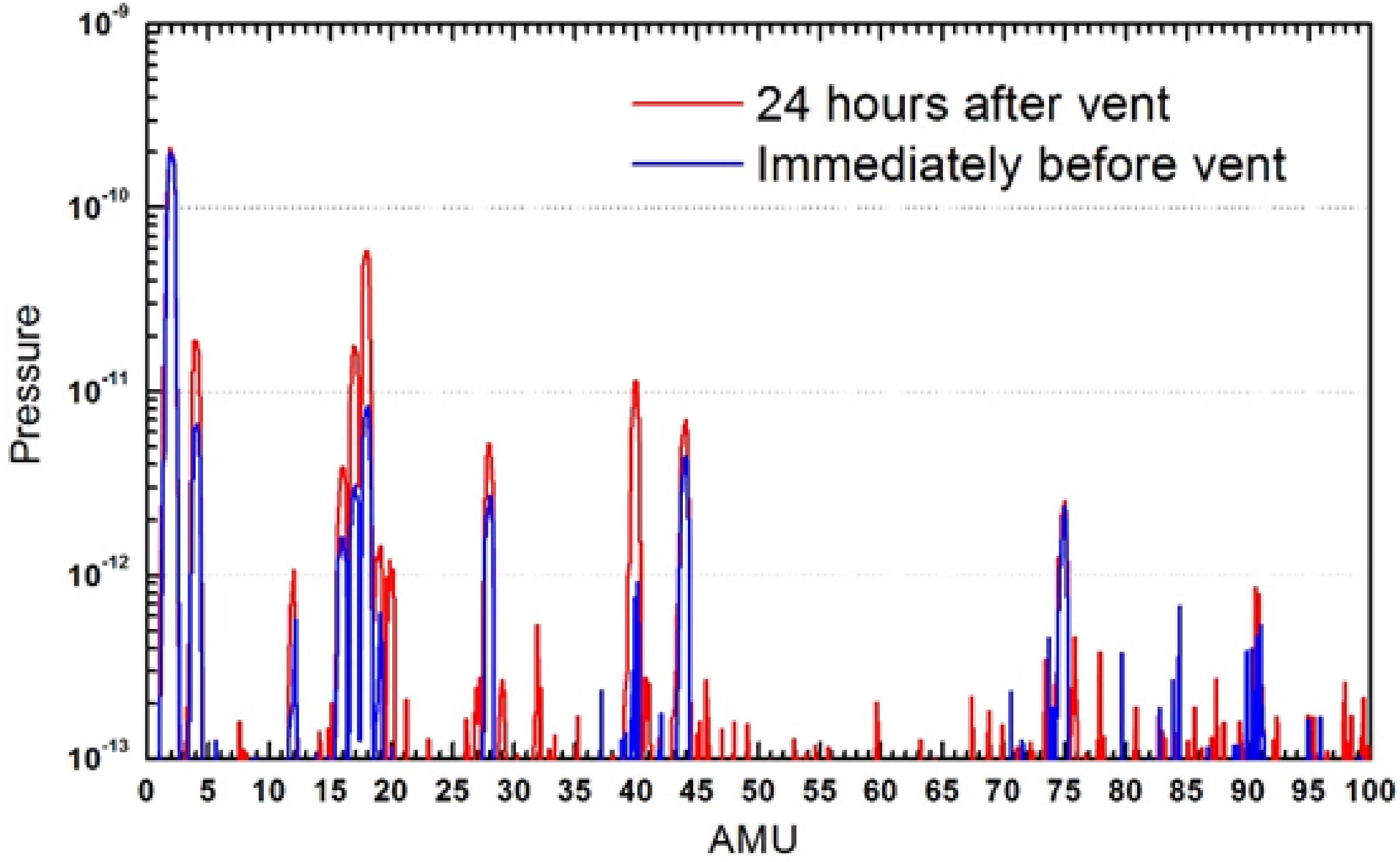
Glove Box Operations

- Active Purge of the chamber with argon
  - We use a diaphragm to displace “dirty air” to achieve a clean environment
    - Original Air remaining= $(1\text{-}X)^N$ where
    - X is volume displaced by the diaphragm
    - N is number of times purge is completed
    - Ex) X=1/2, N=10, When complete only = 0.1% remains
- System kept positive, > 0.2” H_20
- Work takes place <50 ppm O_2





Glove box results



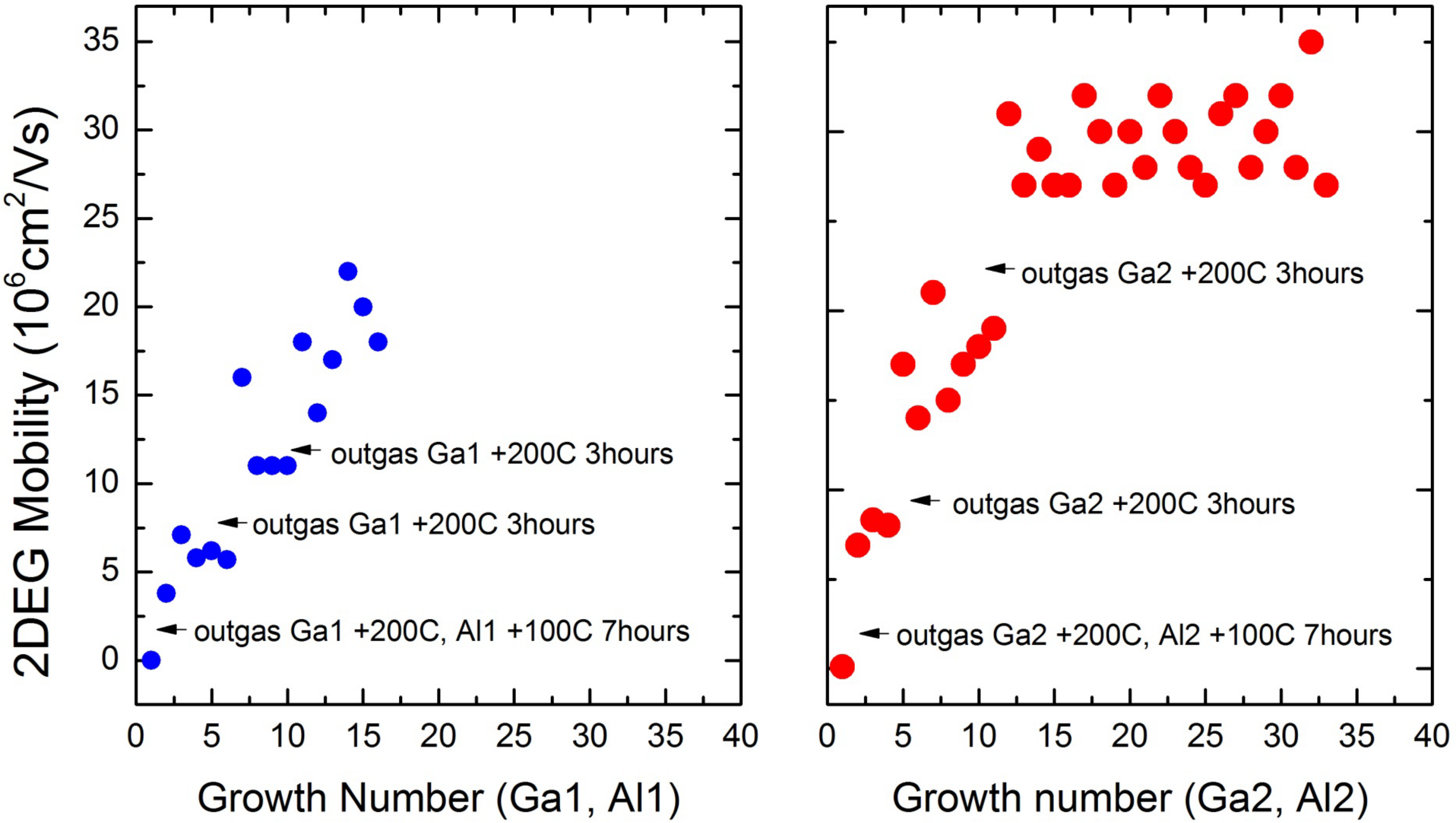
Absolute Pressure recovers within 24

An experiment!

- We worked to minimize impurities from background vacuum and hot materials.

- A test
  - Load two different Ga’s, (each will have different level of impurities)
  - Plan to intentionally outgas Ga!

Gallium Comparisons

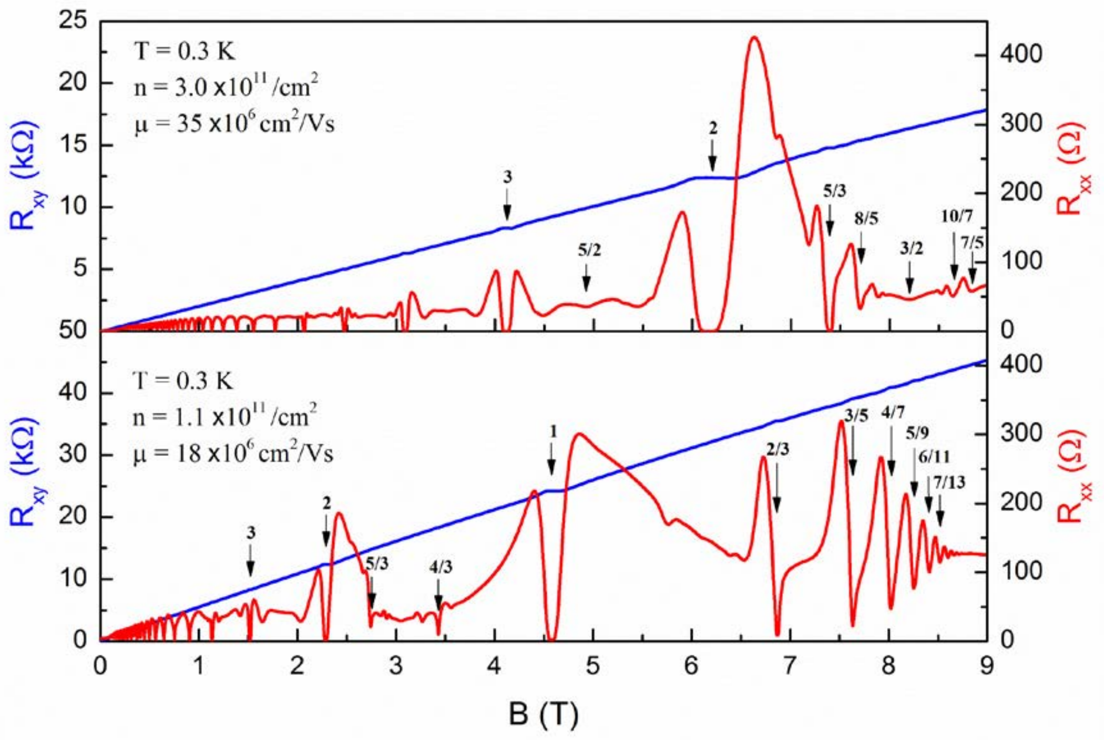


What conclusions can be drawn?

- We use 2DEG mobility to evaluate background impurities.

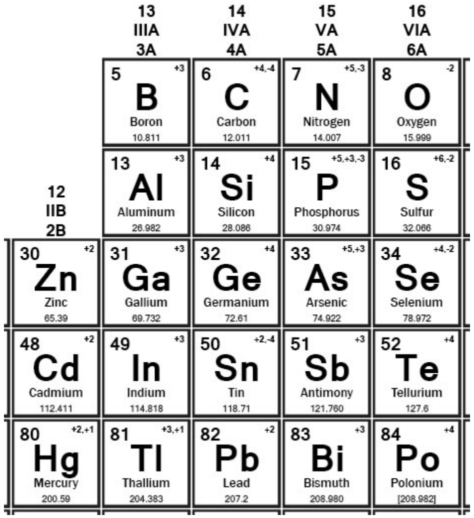
- Unintentional background charged impurities were held constant
  - ~~Background vacuum, hot materials*~~
  - ~~GaAs substrate~~
  - Source material*

- 2DEG mobility demonstrates the atomic purity of the lattice hosting the 2DEG

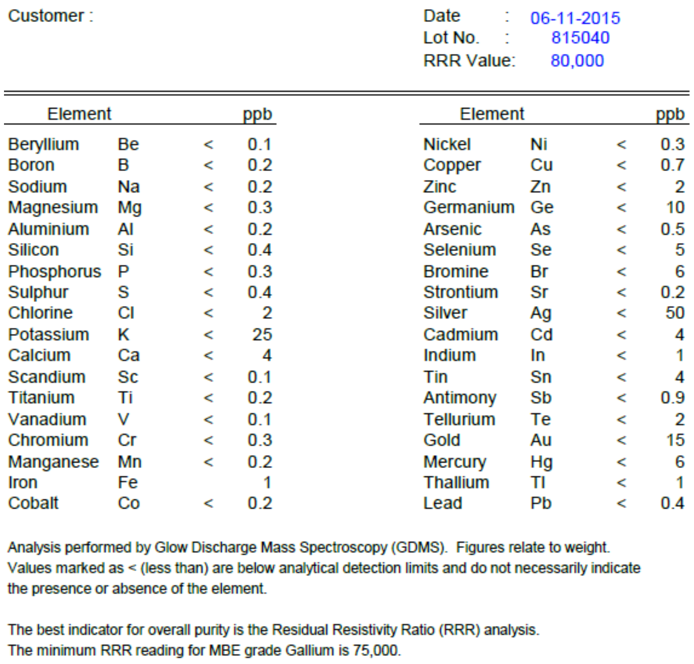


Discussion on Possible Ga contaminates

- Crystallographic incorporation
  - Substitutional,
    - Specific site or amphoteric
  - Interstitial
- Specific elements
  - Gallium Oxides,
    - these have been observed coming from a new Ga source as it was initially heated to growth temperature
  - Germanium,
    - We have measured high values in some of our material
    - Is amphoteric in GaAs, but has lower vapor pressure
  - Oxygen, (deep acceptor)
    - oxygen may create several distinct traps states within the GaAs bandgap, not explicitly shallow p-type
  - Zinc (acceptor)
    - Observed to come from wipes
  - Carbon, p-type dopant, ubiquitous,
- Analysis results (and techniques)
  - GDMS, Sub-ppb
  - ICP-MS, Sub-ppt, using organic solvent extraction process
  - Both techniques are subject to interference, and contamination



12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A
	5 +3 B Boron 10.811	6 +4,-4 C Carbon 12.011	7 +5,-3 N Nitrogen 14.007	8 -2 O Oxygen 15.999
	13 +3 Al Aluminum 26.982	14 +4 Si Silicon 28.086	15 +5,+3,-3 P Phosphorus 30.974	16 +6,-2 S Sulfur 32.066
30 +2 Zn Zinc 65.39	31 +3 Ga Gallium 69.732	32 +4 Ge Germanium 72.61	33 +5,+3 As Arsenic 74.922	34 +4,-2 Se Selenium 78.972
48 +2 Cd Cadmium 112.411	49 +3 In Indium 114.818	50 +2,-4 Sn Tin 118.71	51 +3 Sb Antimony 121.760	52 +4 Te Tellurium 127.6
80 +2,+1 Hg Mercury 200.59	81 +3,+1 Tl Thallium 204.383	82 +2 Pb Lead 207.2	83 +3 Bi Bismuth 208.980	84 +4 Po Polonium [208.982]



Customer :

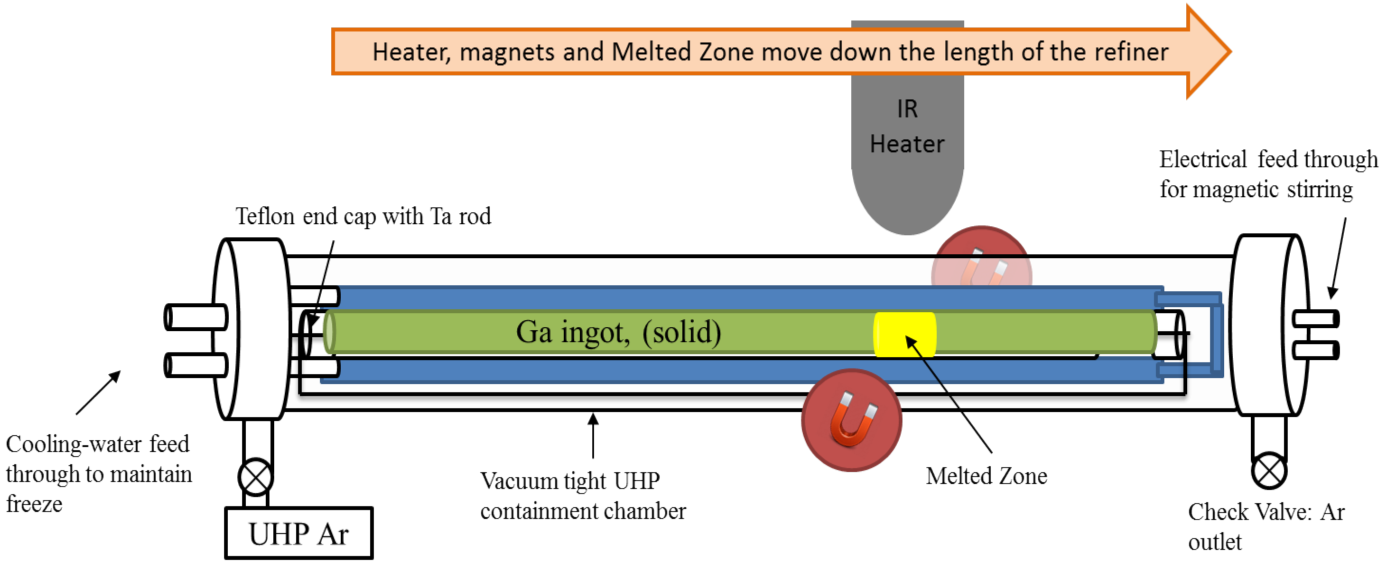
Date : 06-11-2015
Lot No. : 815040
RRR Value: 80,000

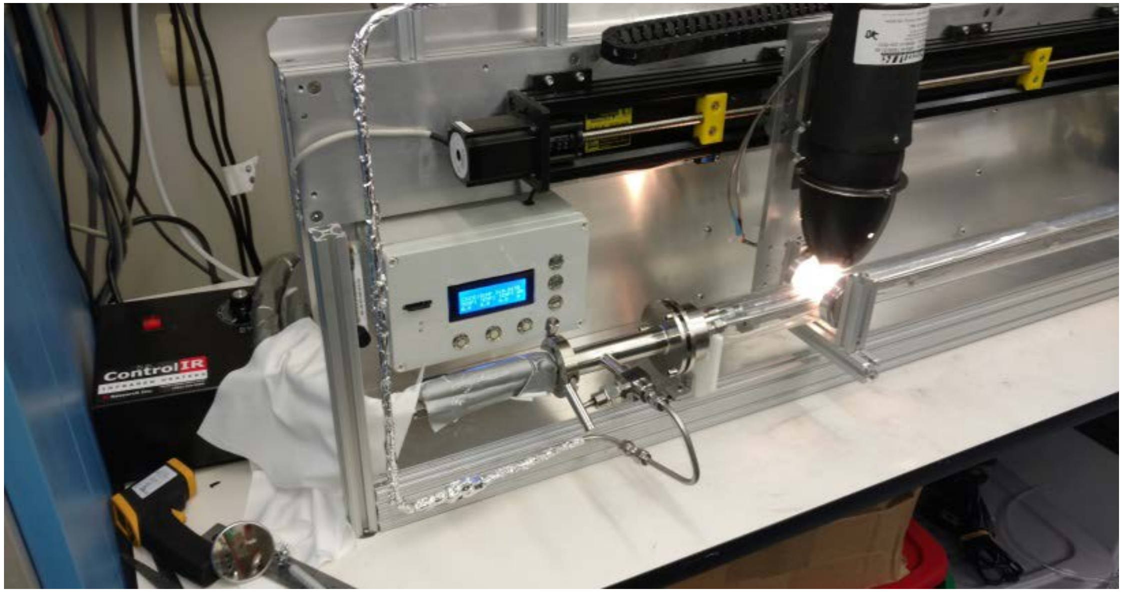
Element			ppb	Element			ppb
Beryllium	Be	<	0.1	Nickel	Ni	<	0.3
Boron	B	<	0.2	Copper	Cu	<	0.7
Sodium	Na	<	0.2	Zinc	Zn	<	2
Magnesium	Mg	<	0.3	Germanium	Ge	<	10
Aluminium	Al	<	0.2	Arsenic	As	<	0.5
Silicon	Si	<	0.4	Selenium	Se	<	5
Phosphorus	P	<	0.3	Bromine	Br	<	6
Sulphur	S	<	0.4	Strontium	Sr	<	0.2
Chlorine	Cl	<	2	Silver	Ag	<	50
Potassium	K	<	25	Cadmium	Cd	<	4
Calcium	Ca	<	4	Indium	In	<	1
Scandium	Sc	<	0.1	Tin	Sn	<	4
Titanium	Ti	<	0.2	Antimony	Sb	<	0.9
Vanadium	V	<	0.1	Tellurium	Te	<	2
Chromium	Cr	<	0.3	Gold	Au	<	15
Manganese	Mn	<	0.2	Mercury	Hg	<	6
Iron	Fe		1	Thallium	Tl	<	1
Cobalt	Co	<	0.2	Lead	Pb	<	0.4

Analysis performed by Glow Discharge Mass Spectroscopy (GDMS). Figures relate to weight. Values marked as < (less than) are below analytical detection limits and do not necessarily indicate the presence or absence of the element.

The best indicator for overall purity is the Residual Resistivity Ratio (RRR) analysis. The minimum RRR reading for MBE grade Gallium is 75,000.

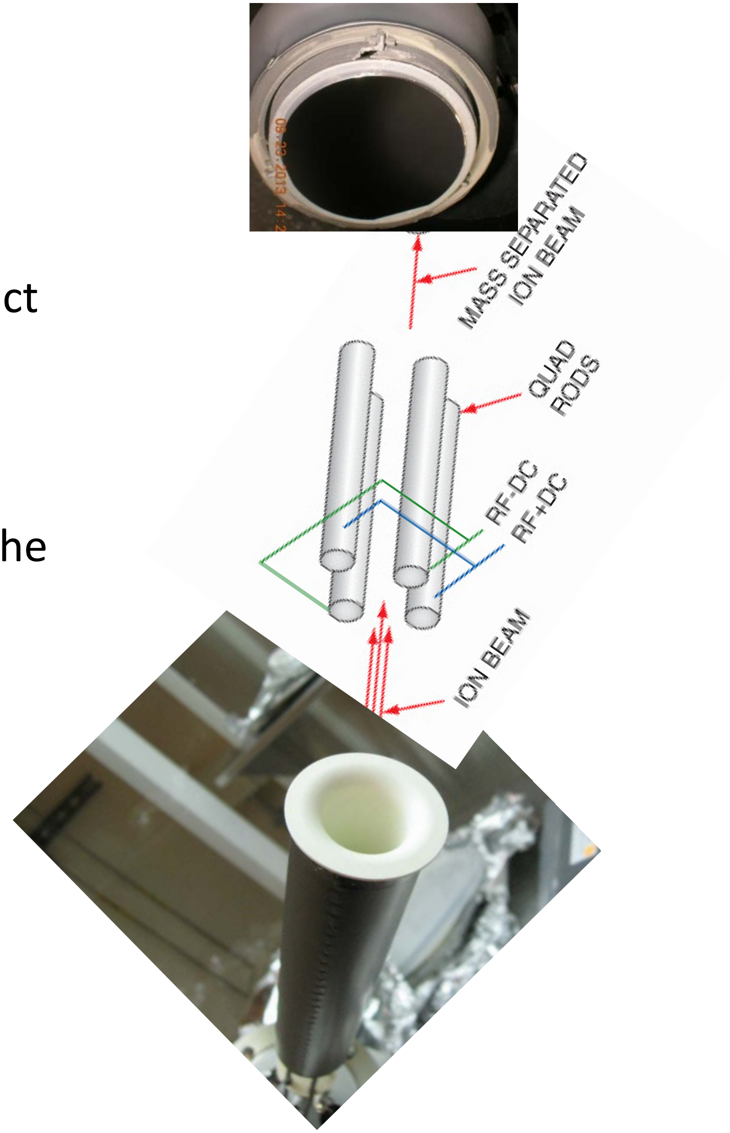
A path to cleaner Gallium





Proposal for new source cell

- The G-Cell
  - Combine proven RGA technology with traditional effusion cells.
  - Allow the quadrupole mass filter to sit at a single m/*e* ratio
  - Twin potentials create RF & DC fields which deflect the ions
  - Will help isotopic purity
- Concerns
  - Adequately designing the quadrupole to exist in the high Ga flux environment.
  - Adequately designing the ionization hardware to exist in the high flux environment.
  - Some of the impurities of concern have similar masses
  - Ionization efficiency of high flux



Conclusion

- Many research areas utilize and benefit from gains UHP or UHQ AlGaAs/GaAs heterostructures

- MBE is <u>the</u> technique to grow high quality heterostructures

- Modifications to MBE hardware and Ga handling procedures can reduce introduction of impurities.

- Samples with controlled amounts of alloy disorder were generated which elucidated the mobility vrs. $\Delta_{5/2}$ gap dichotomy

- A novel FET type structure was designed and fabricated quantum devices

- Ga purity currently limits 2DEG mobility

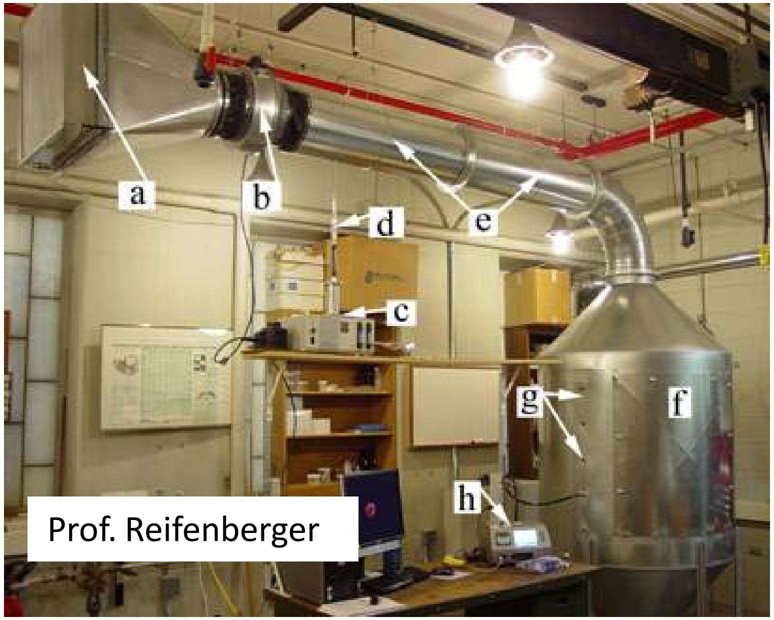
- MBE source Ga can be purified in-situ

- Acknowledgements

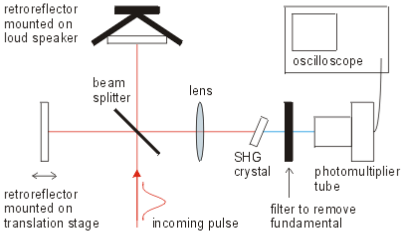
Acknowledgments

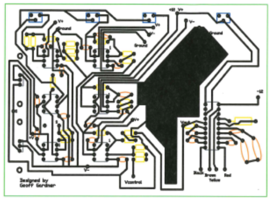
Manfra Group Colleagues

Dr. Hasan Sharifi and Birck Eng-Staff

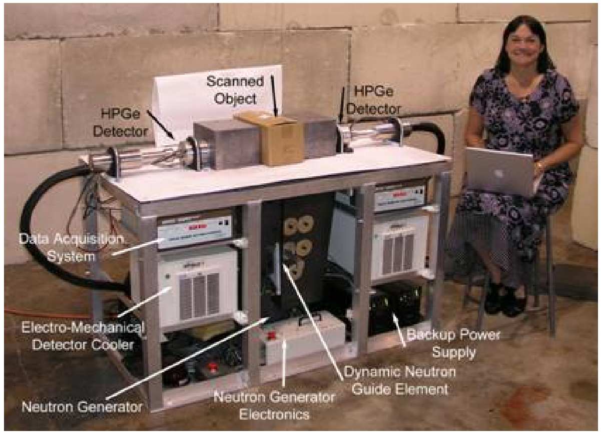


Prof. Reifenberger

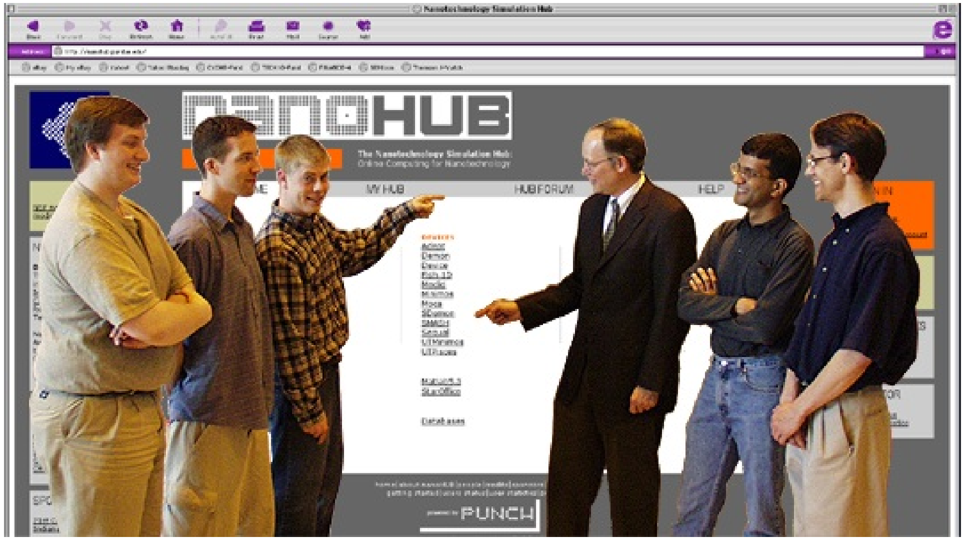




Prof. Savikhin



Prof. Koltick



Professors Johnson, Trumble, Bahr, Kvam, Handwerker

Prof. Lundstrom