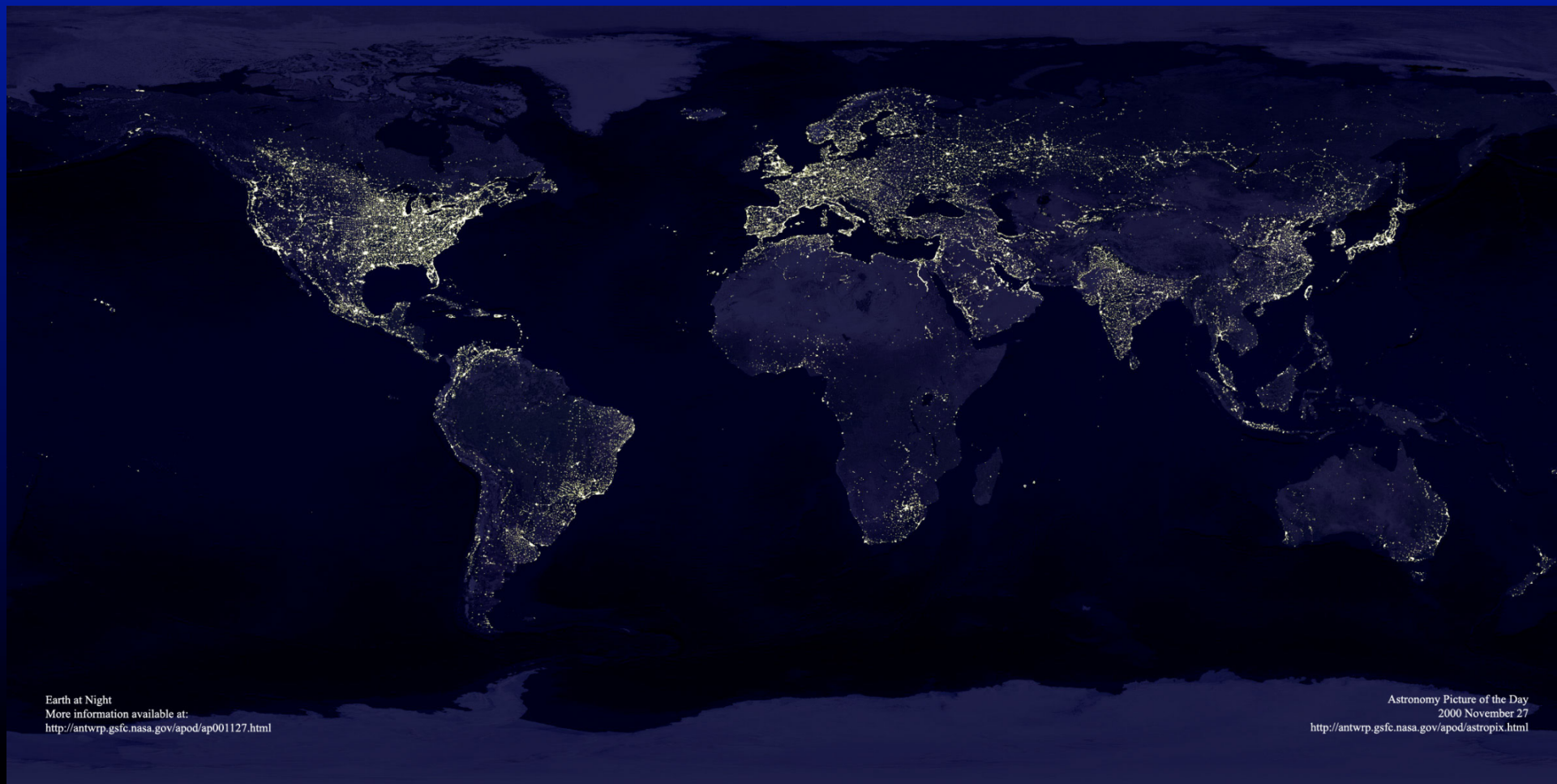
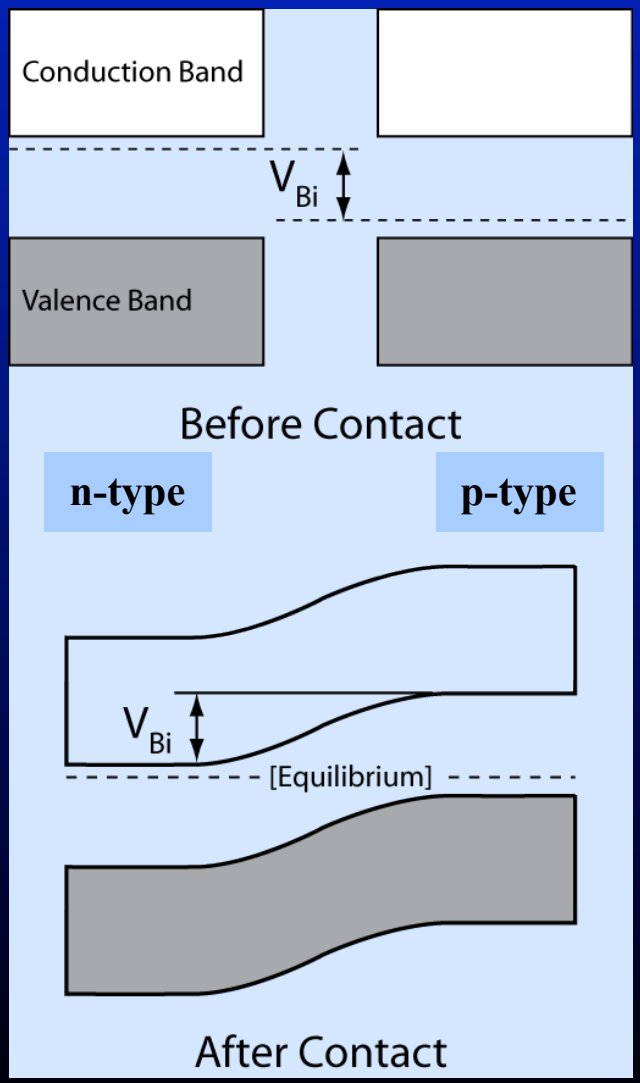
# Reaction Pathways in Processing Photons and Students

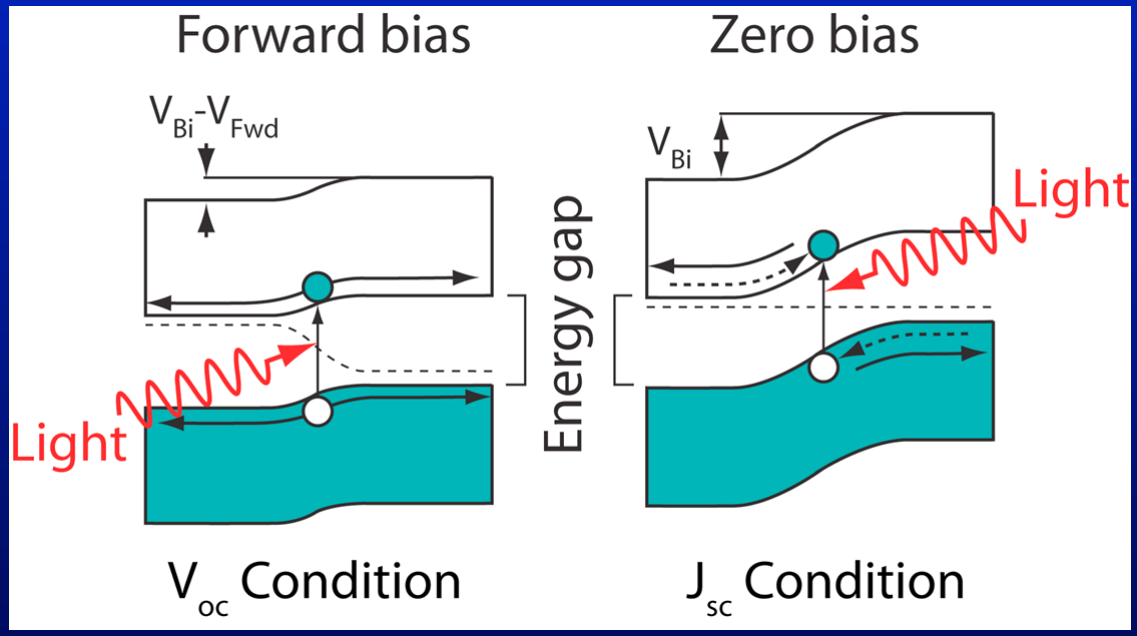
**Tim Anderson**

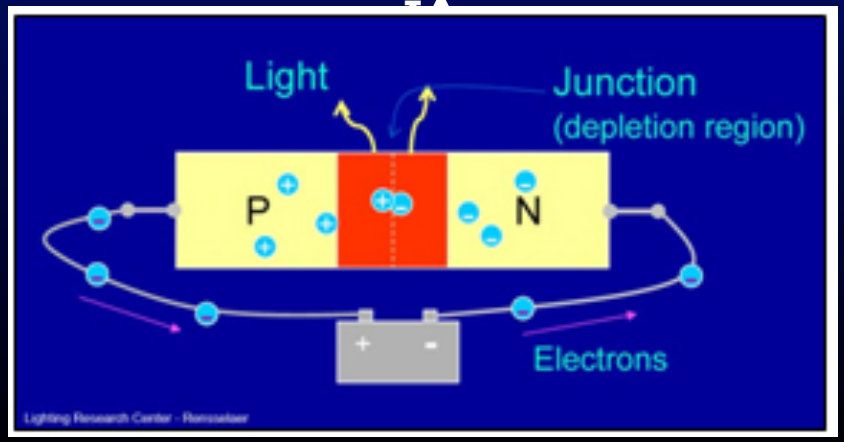
**University of Massachusetts**



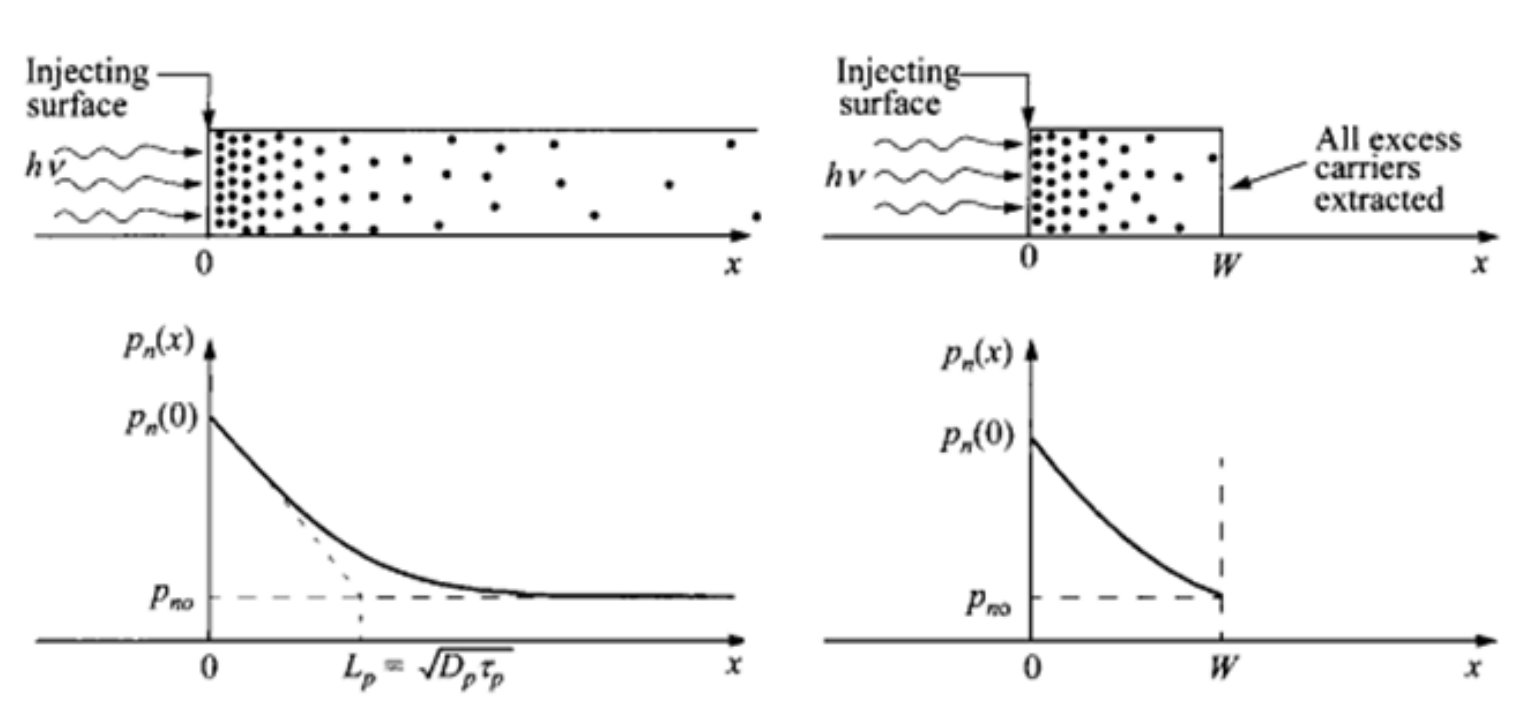
# The p-n Junction



# Steady State Carrier Injection from Side



# Reactions

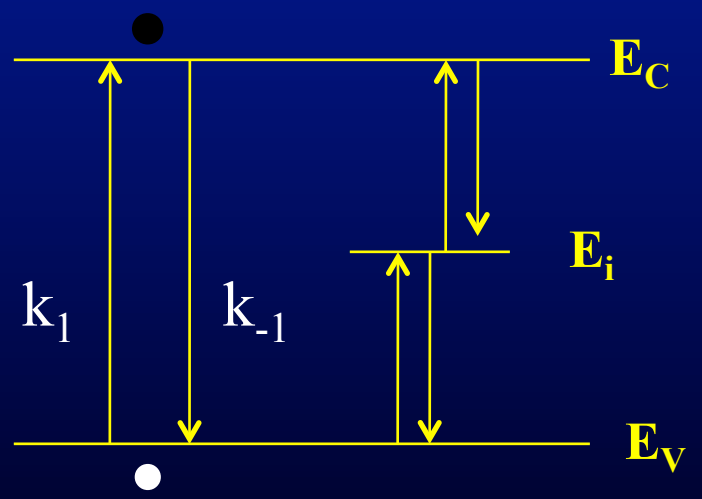
$O \leftrightarrow e^- + h^+$

$r_p = k_1 - k_{-1}np$

at equilibrium: $r_p = 0$

$k_1 = k_{-1}n_o p_o = k_{-1}n_i^2$

$r_p = k_{-1}(n_i^2 - np)$

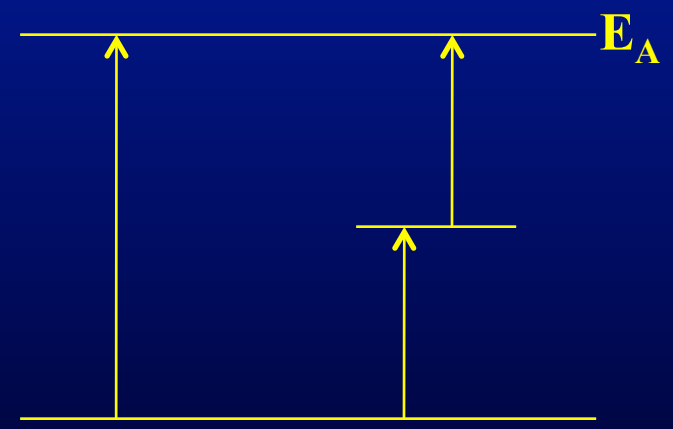



If $n_o \sim n$, then $r_p = -k_{-1}n_o(p - p_0)$

**or $r_p = (p - p_0)/\tau_p$, with $\tau_p = -1/-k_{-1}n_o$**

$$A \xrightarrow{E_A} B$$

$$A \xrightarrow[E_{A1}]{} C \xrightarrow[E_{A2}]{} B$$

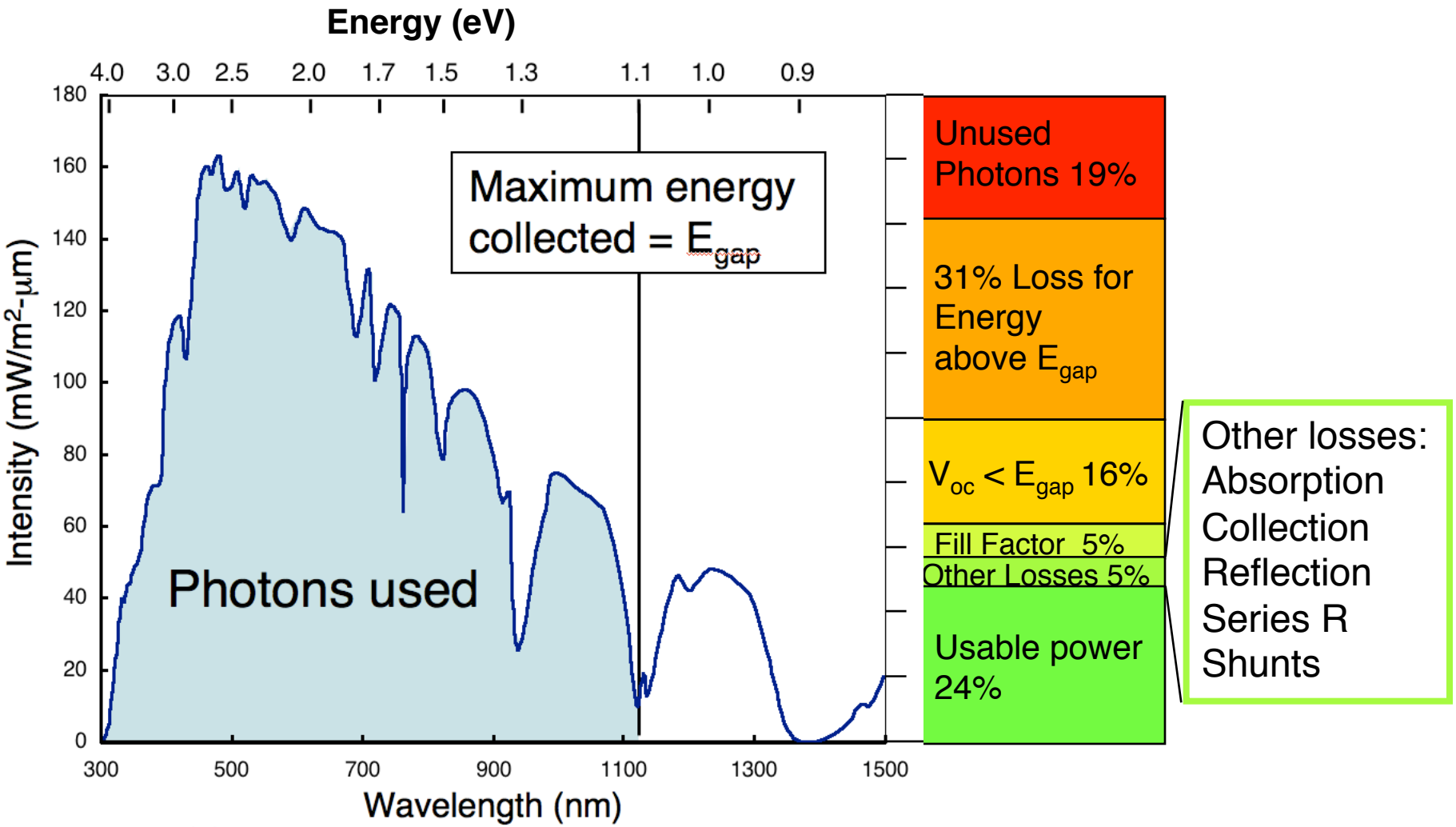



**Fastest Rate When**

**$E_{A1} = E_{A2} = 1/2E_A$**

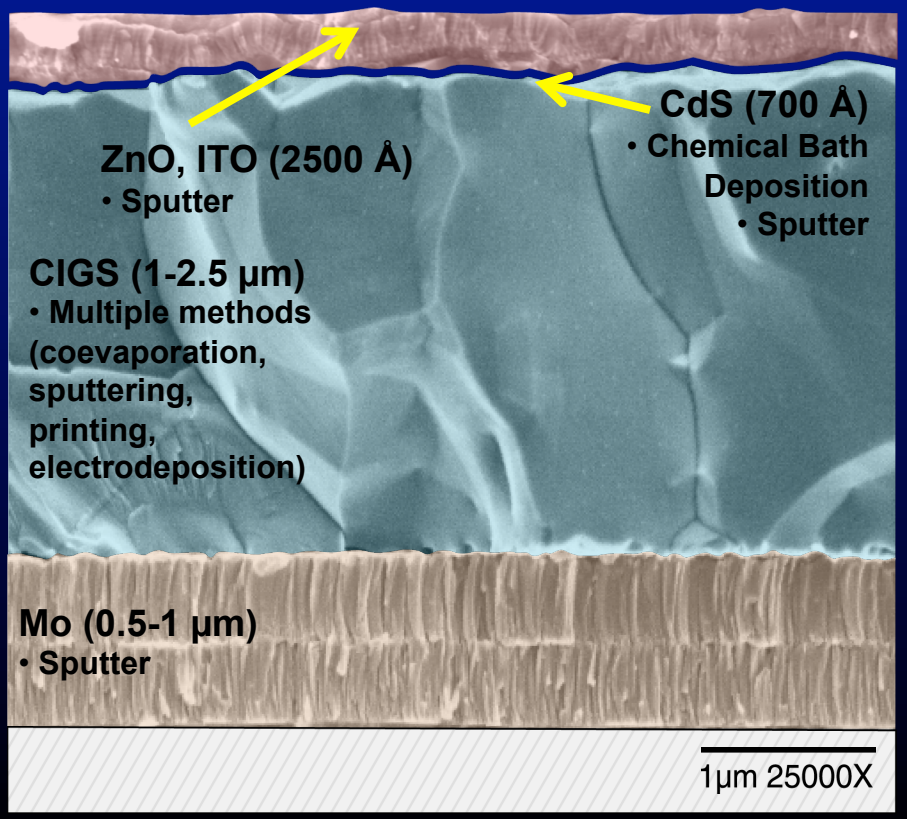
# Single Junction Cell

**Analysis for a 24%-efficient Si solar cell**

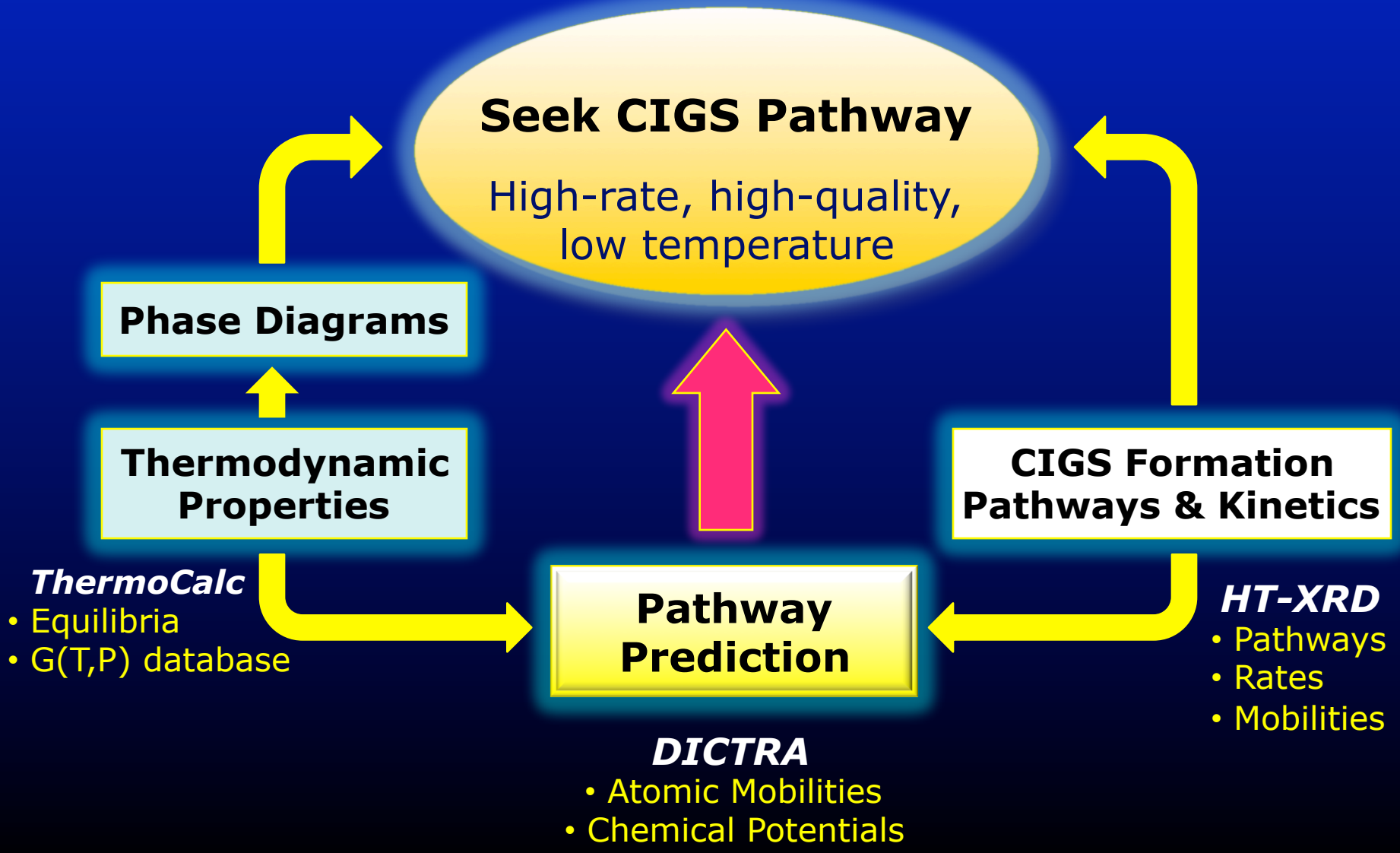


# $Cu(In_{1-x}Ga_x)Se_2$ Solar Cells

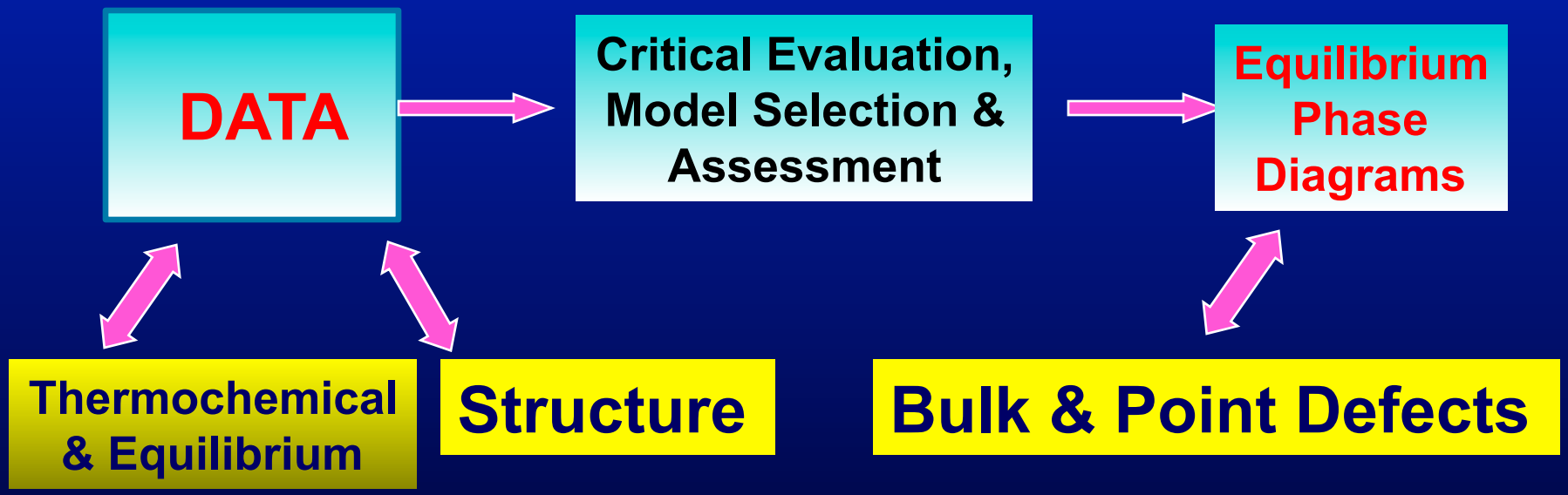
- ***Most Promising Thin Film Absorber Material***
  - High optical absorption coefficient: ~ 2 µm
  - Direct band gap (Eg ~ 1.2 eV)
  - High radiation resistance
  - High reliability
  - Lower cost/Watt installed
  - 20% conversion efficiency
  - Efficient in low-angle & light
  - Flexible substrates possible
  - Positive response under concentration



# Approach


Seek CIGS Pathway
High-rate, high-quality, low temperature
Phase Diagrams
Thermodynamic Properties
CIGS Formation Pathways & Kinetics
ThermoCalc
• Equilibria
• G(T,P) database
Pathway Prediction
HT-XRD
• Pathways
• Rates
• Mobilities
DICTRA
• Atomic Mobilities
• Chemical Potentials

# Approach to Developing Phase Diagrams




- Literature
- Measurements
  EMF, Equilibration
- First Principles
- Estimation

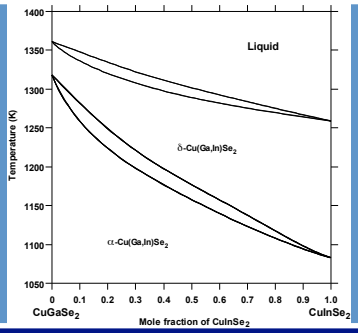
**Cu-Ga-In-Se System**

- 4 unary sub-systems
- 6 binary sub-systems
- 4 ternary sub-systems

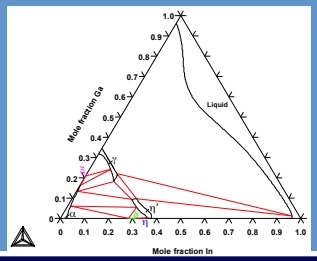
# Thermodynamics of CIGS

*66 solid phase, 20 liquid phase, and 18 gas species Gibbs models*

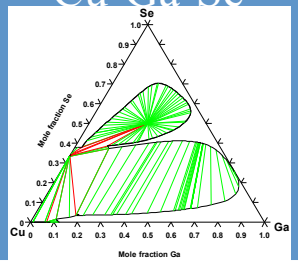
## Cu-Ga-In-Se



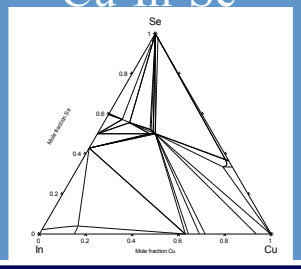

### Cu-Ga-In



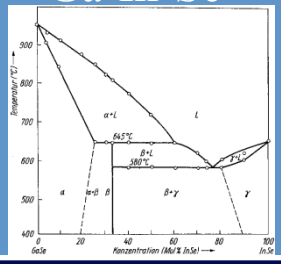

### Cu-Ga-Se



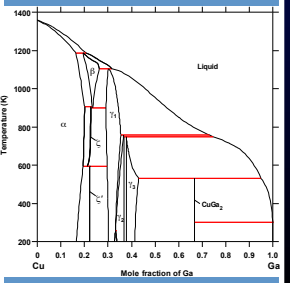

### Cu-In-Se



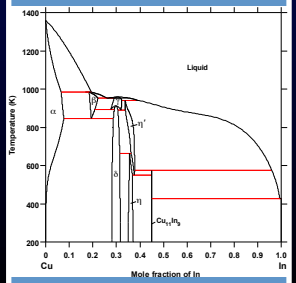

### Ga-In-Se



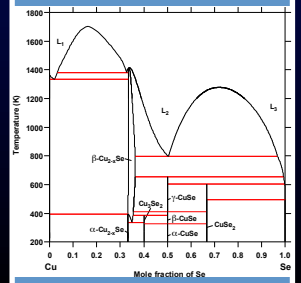

### Cu-Ga



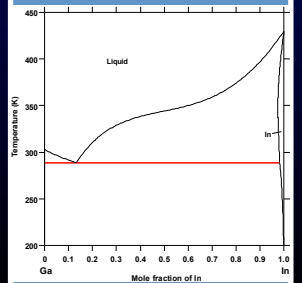

### Cu-In



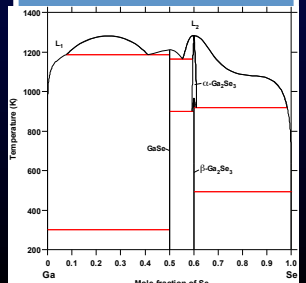

### Cu-Se



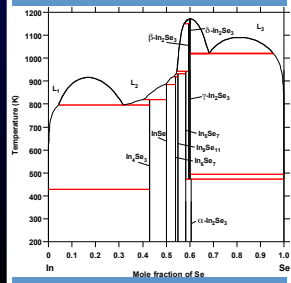

### Ga-In




### Ga-Se

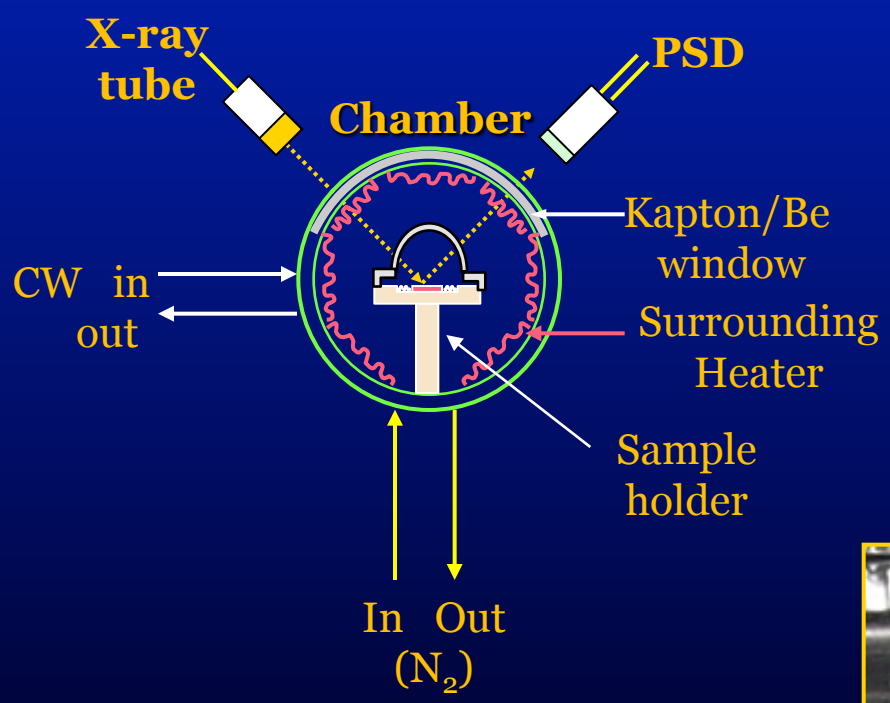


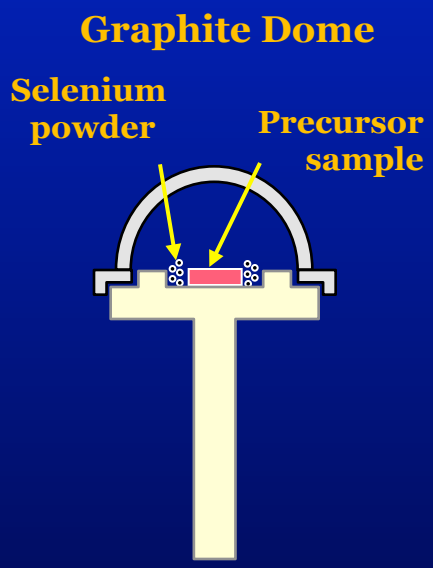

### In-Se

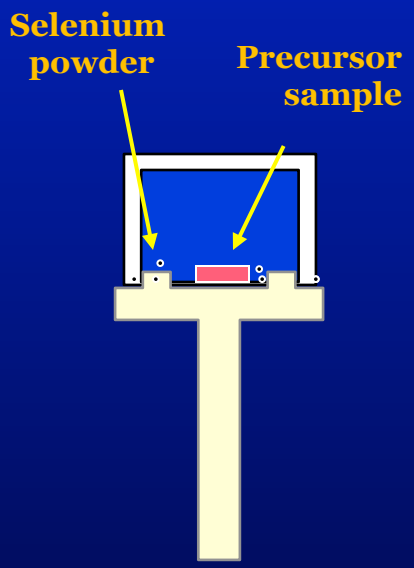


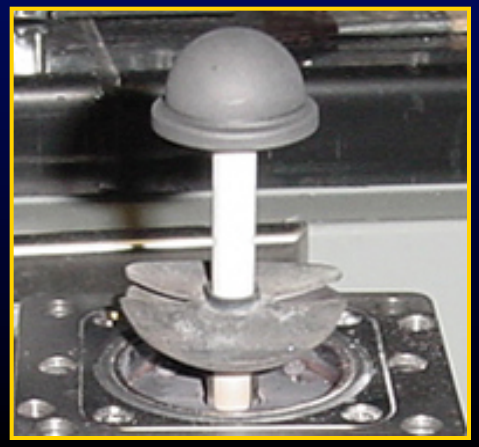
# HT-XRD System

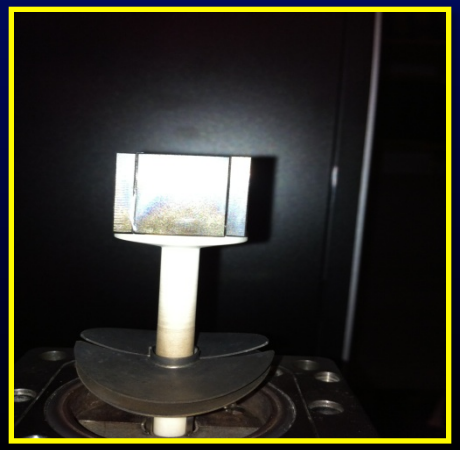
## Panalytical Philips X'pert System



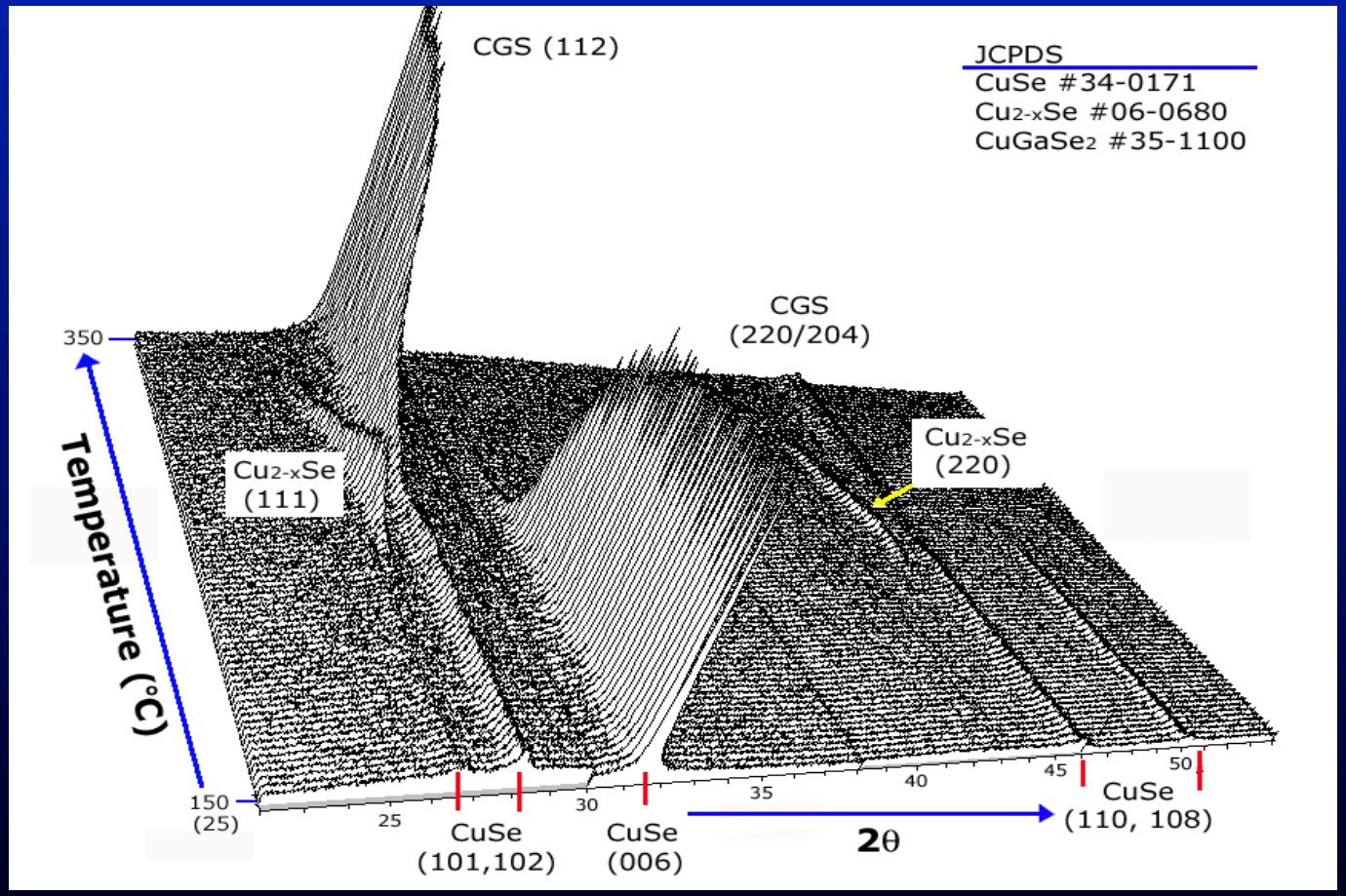



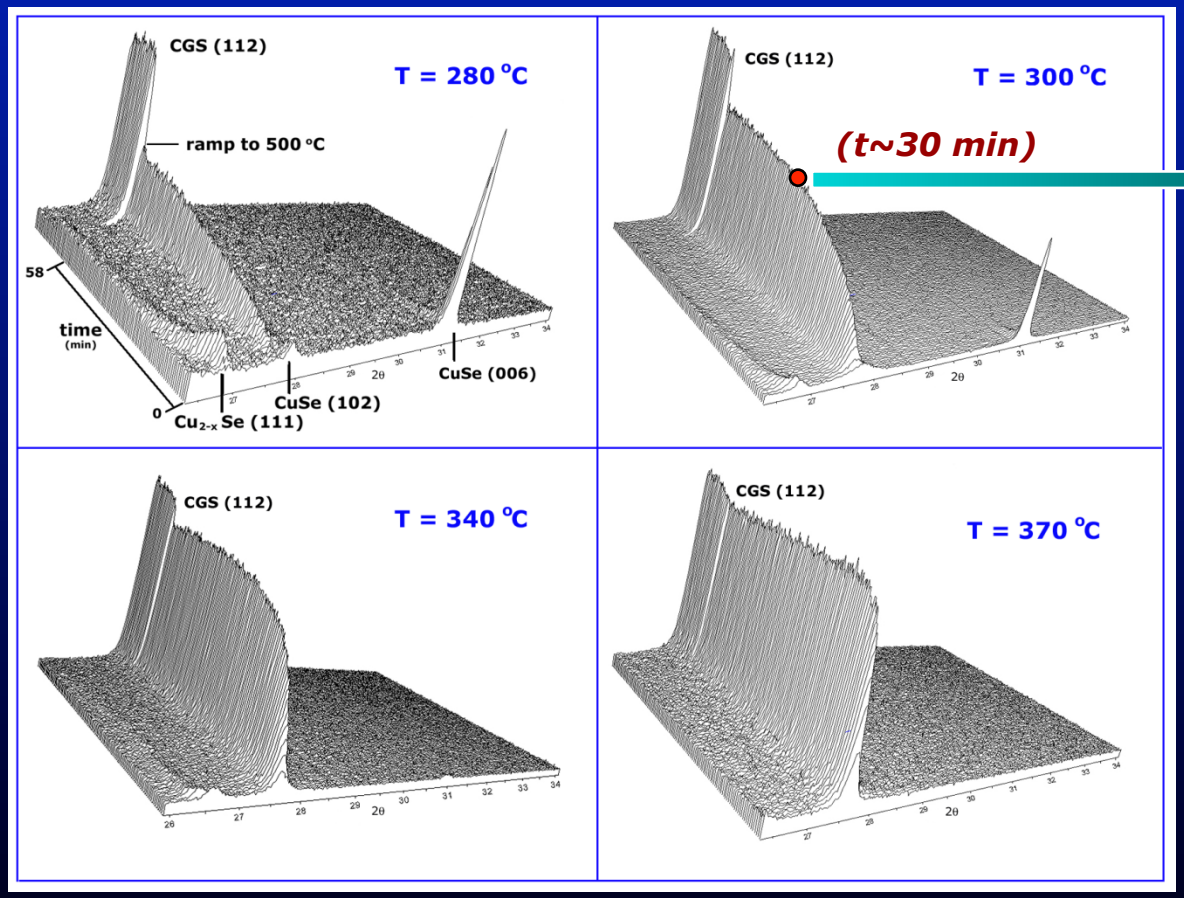





# Temperature Ramp Anneal



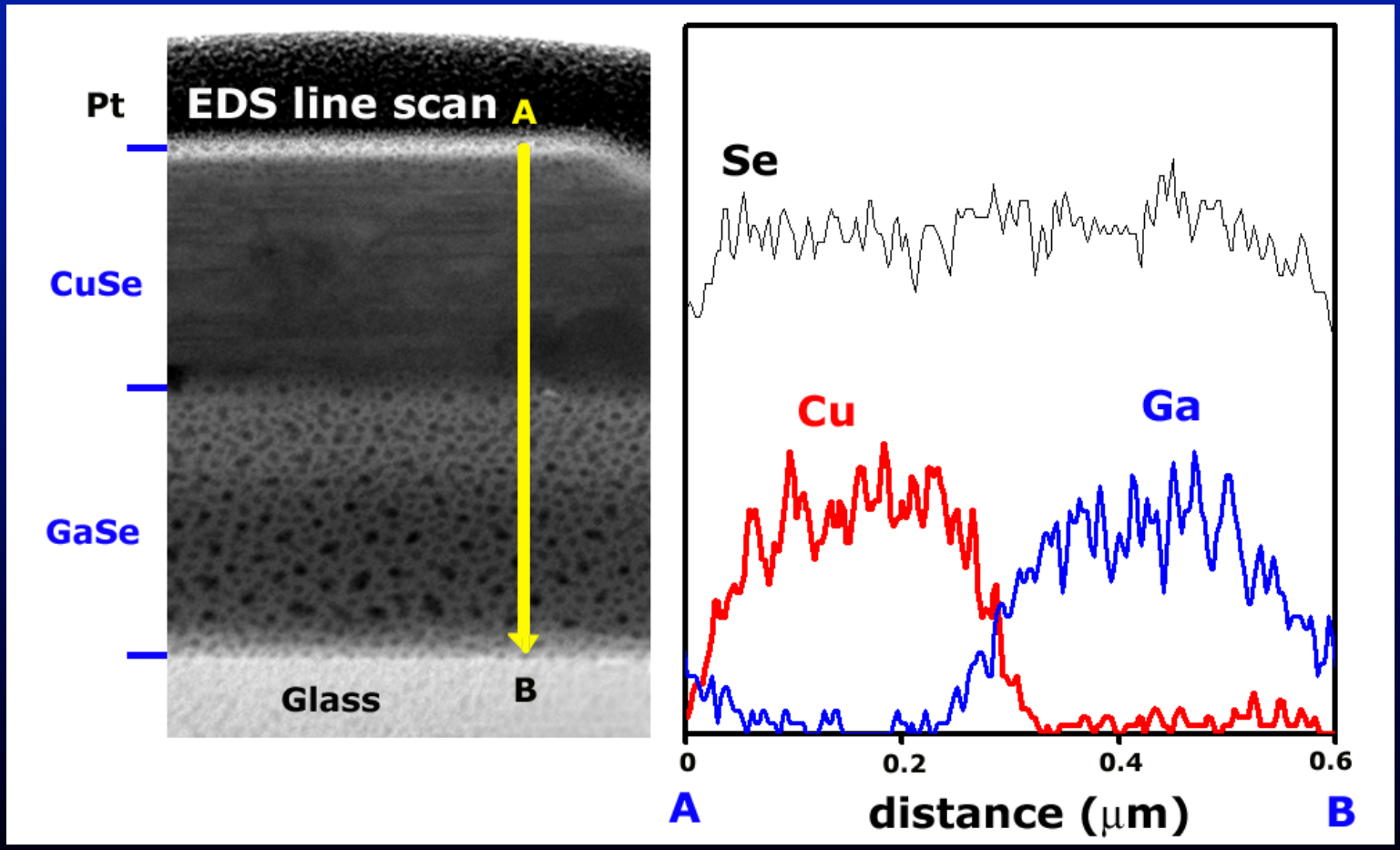

# Isothermal annealing




TEM-EDS

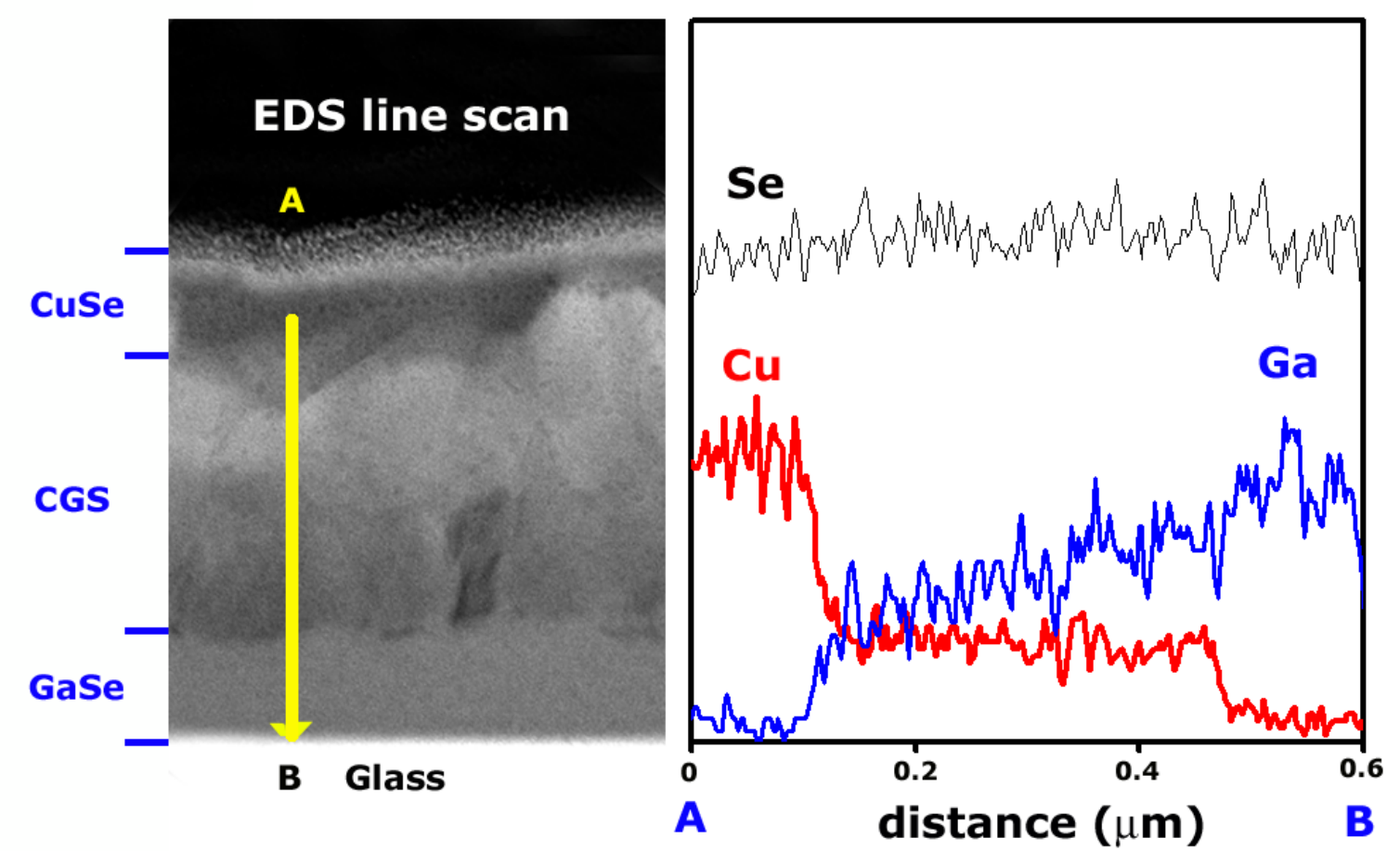
# TEM-EDS Analysis

## Glass/GaSe/CuSe Precursor

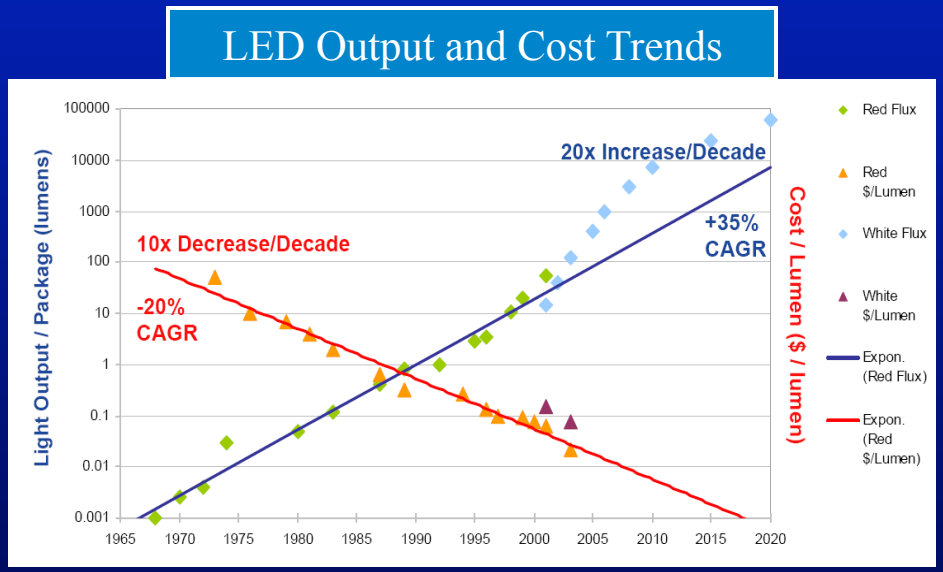


# TEM-EDS Analysis

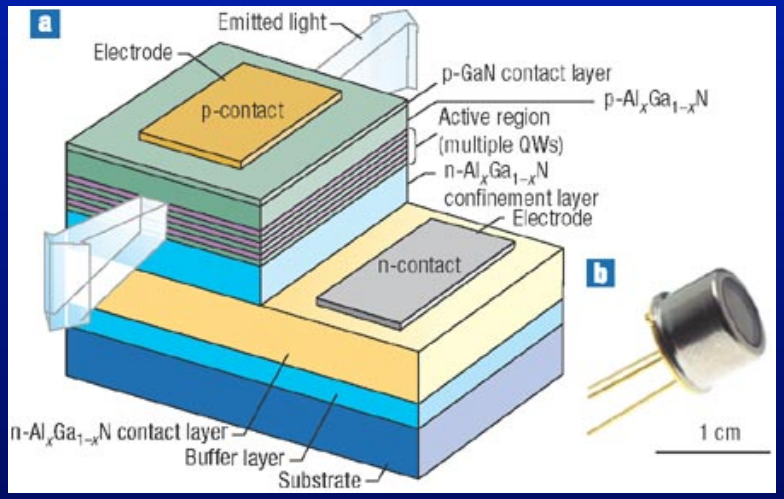
**Glass/GaSe/CGS/CuSe annealed for 30 min, at 300 °C**



# GaN-based LEDs




Source: Haitz & Lumileds




Source: Ultraviolet light-emitting diodes based on group three nitrides A. Khan, K. Balakrishnan, T. Katona *Nature Photonics* **2**, 77 - 84 (2008)

- **Issues with Solid State Lighting**
  - Cost/lumen **too high**, Flux **too low**
  - Topside n-contact limits active area
  - No suitable substrate for GaN

# Motivation for GaN on Si

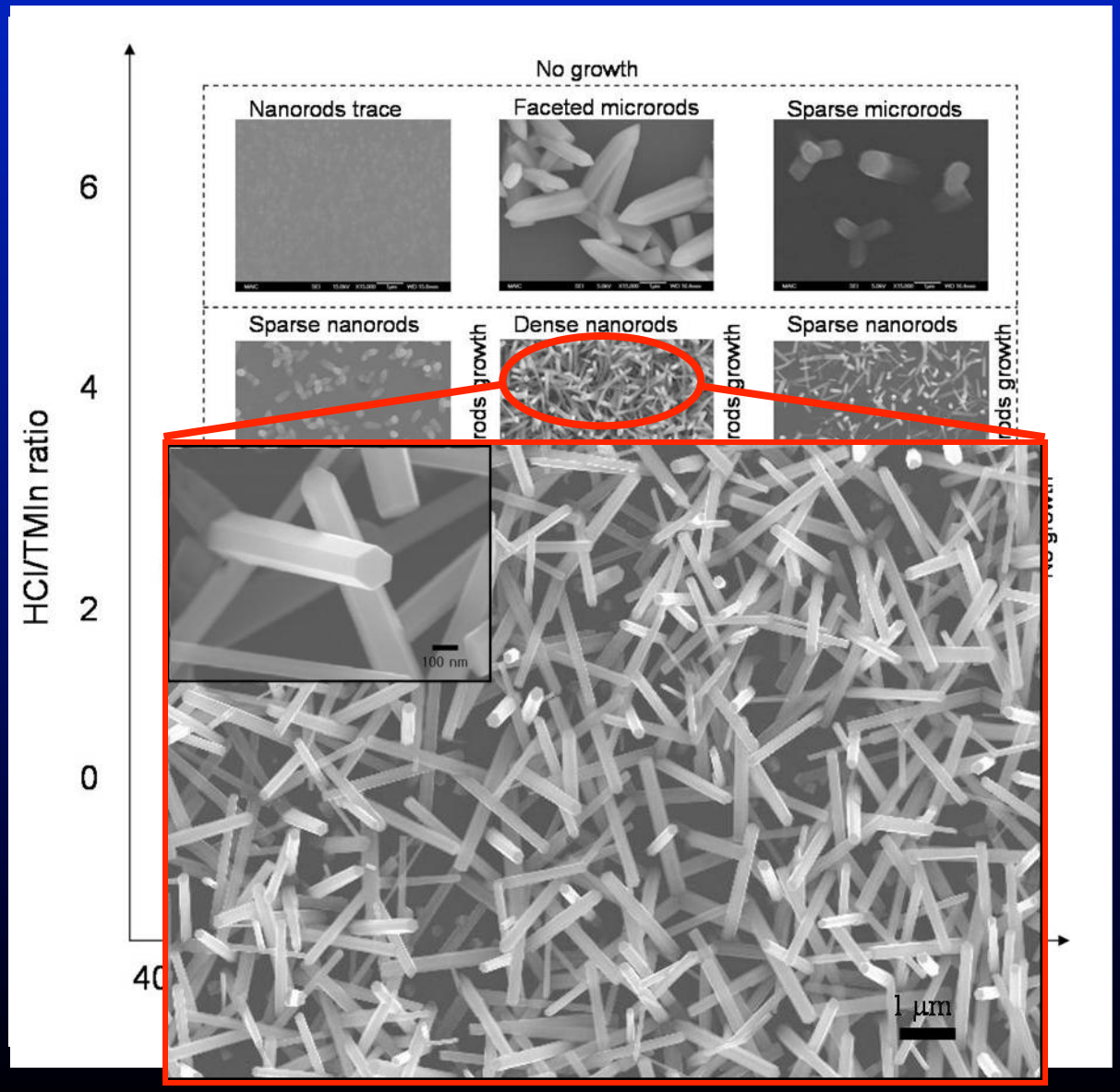
## Advantages

- Low cost
- Large area
- High quality n- and p- wafers
- High electrical & thermal conductivities
- Potential for device integration
- Easily removed

## Challenges

- High dislocation density due large lattice mismatch (17%)
- Cracking due to large thermal coefficient of expansion mismatch (56%)
- Polycrystalline GaN due to $Si_3N_4$ formation at the interface

# Effect of HCl/TMIn and Growth Temperature




**InN nanorods by H-MOVPE: HCl/TMIn vs T**

**V/III= 250**

**Substrate: c-$Al_2O_3$**

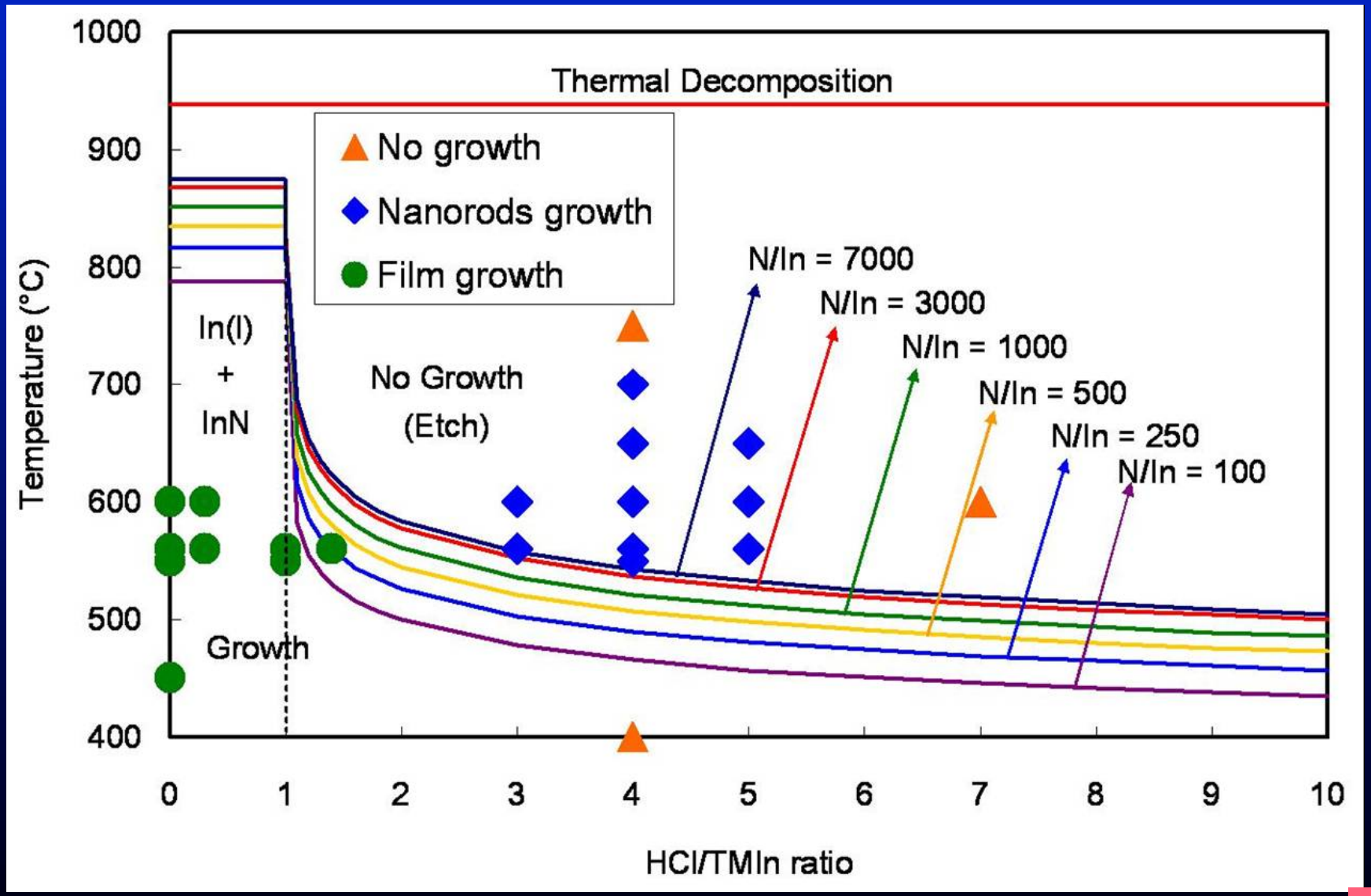
**Optimal Conditions:**

**T = 600 °C**

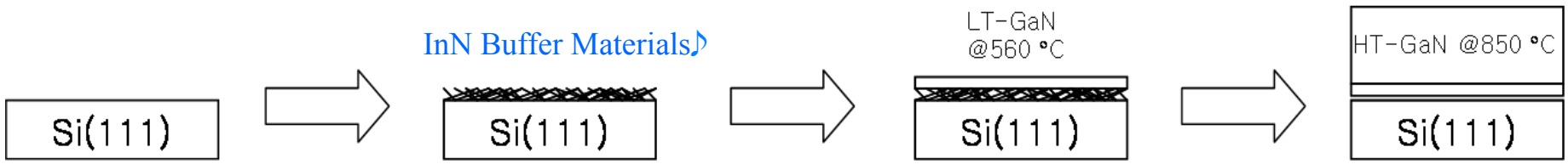
**HCl/TMIn=4**

**V/III=250**

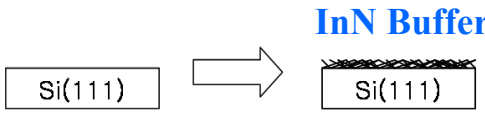
# Comparison with Thermodynamic Analysis



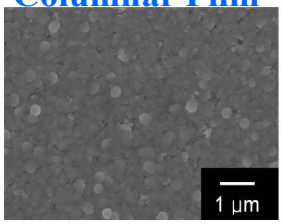
# GaN Growth on Si Using InN Buffer Materials



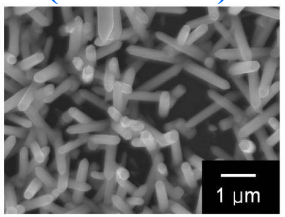
# LT-GaN Growth on Si Using InN Buffer Materials



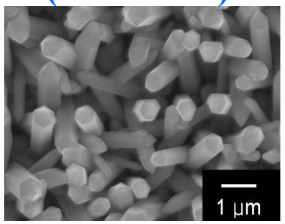

Columnar Film



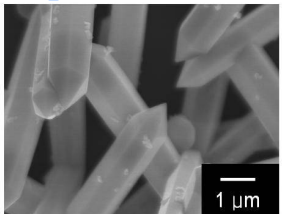

Nanorods (d=250 nm)




Nanorods (d=500 nm)

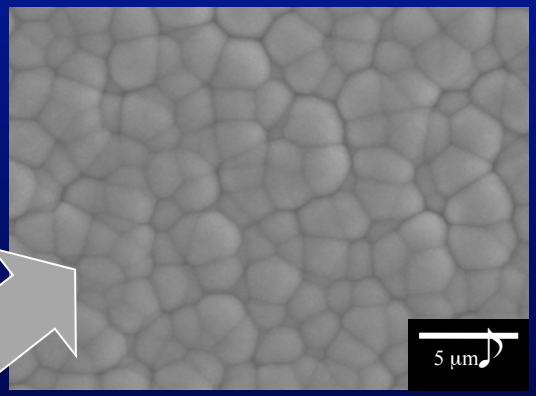


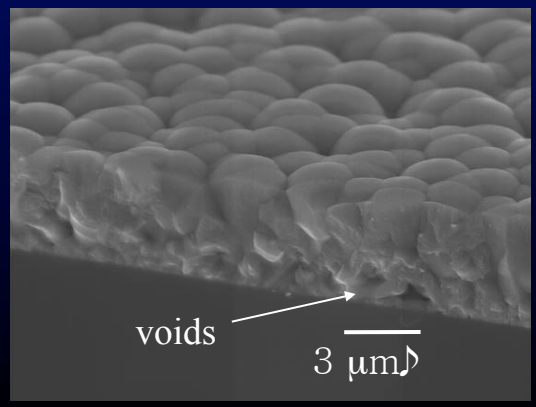

Sparse microrods




| Growth T | CI/III | V/III | Time | Feature |
|---|---|---|---|---|
| 560 °C | 1 | 2500 | 1 hr | Columnar Film |
| 600 °C | 4 | 250 | 20 min | Nanorods d=250nm |
| 600 °C | 4 | 250 | 1 hr | Nanorods d=500nm |
| 650 °C | 5 | 250 | 1 hr | Sparse microrods |

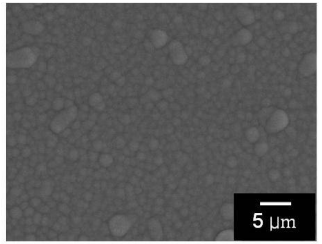
30 min LT-GaN uniformly covered InN nanorods with voids at the interface



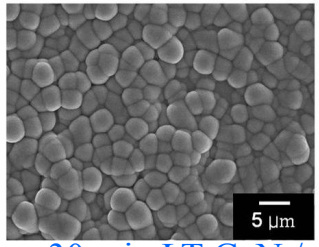



# Thick GaN Growth on Si Using InN Buffer Materials

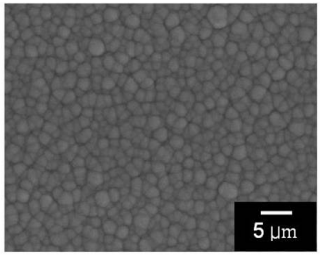
30 min LT-GaN / Columnar Film



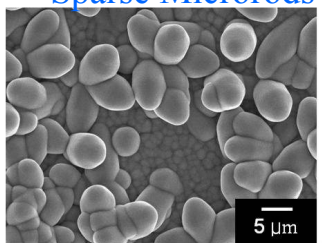

30 min LT-GaN /25 Nanorods

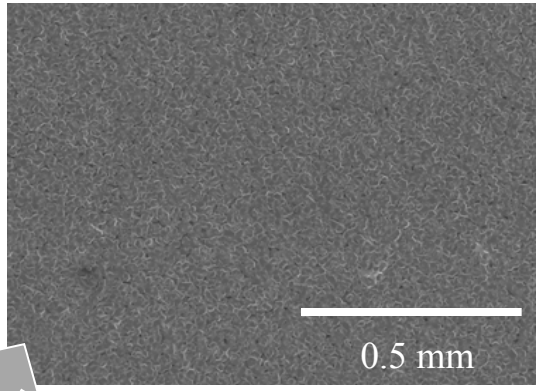


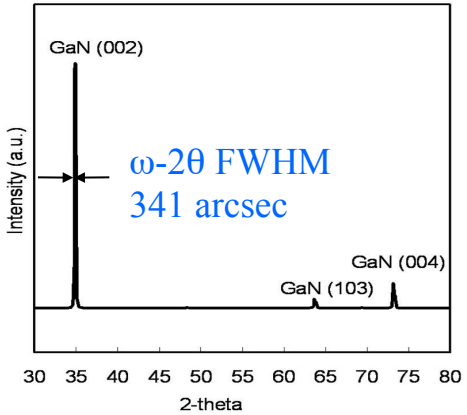

30 min LT-GaN / 500nm Nanorods




30 min LT-GaN / Sparse Microrods

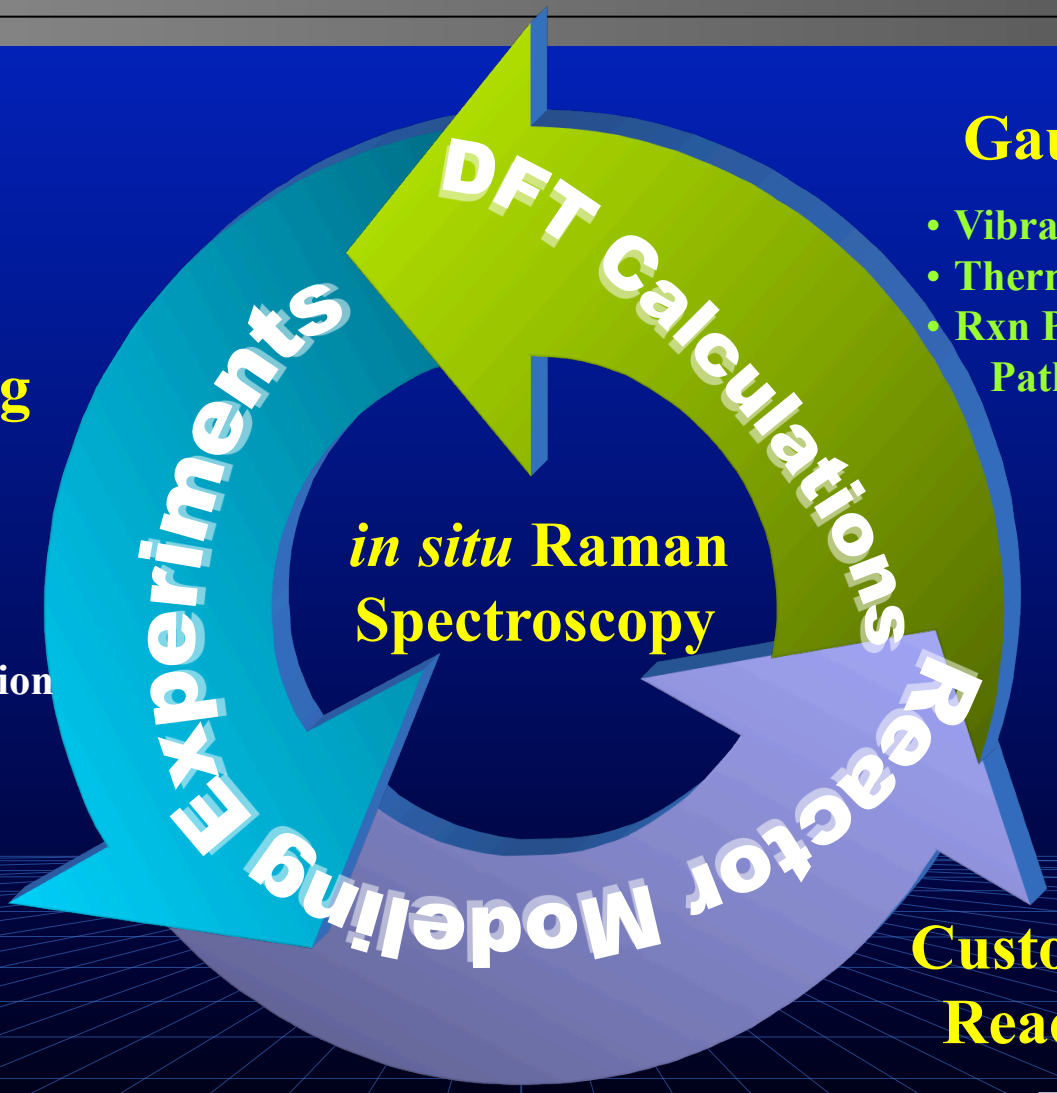



- Crack-free 20 µm thick polycrystalline GaN film was successfully grown on Si using dense InN nanorods (d = 500 nm) as a buffer material

# Approach to Measurement of Kinetics




## Gaussian

- Vibrational Frequencies
- Thermodynamic Properties
- Rxn Parameters and Pathway Screening

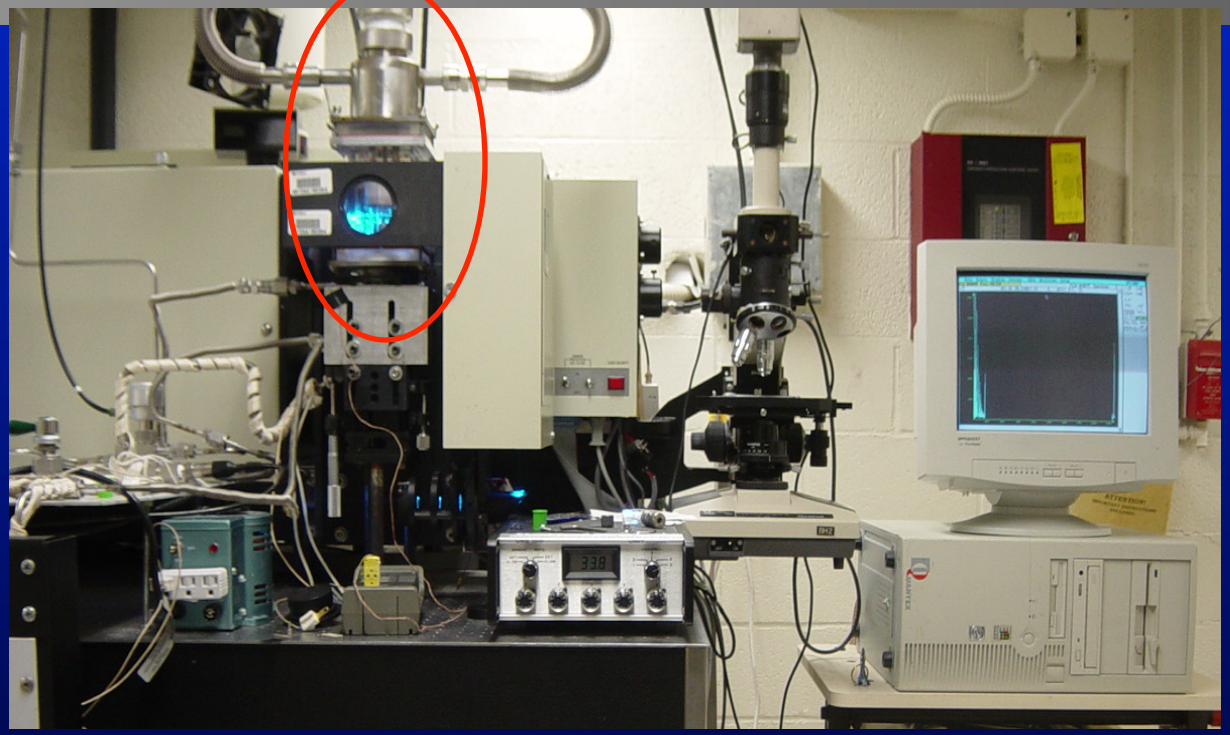
## *in situ* Probing of Gas Phase Chemistry

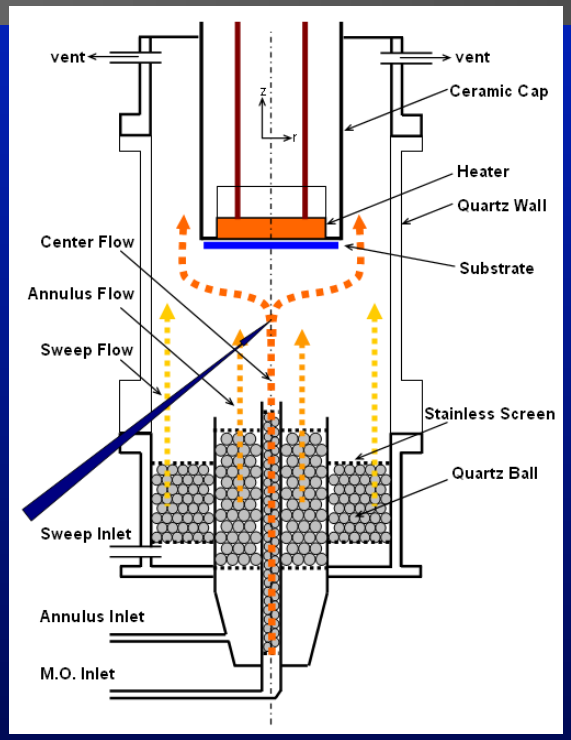
- T, C Measurements
- Intermediate Detection

## Custom FEM Reactor Model

- T and C Profiles

# Experimental Apparatus






- **CVD reactor interfaced with Raman spectrometer**
  - Laser : Nd:YAG (532.08nm)
  - Double additive monochromator (grating:1800 lines/mm)
  - Detectors – photomultiplier tube (PMT) or charge coupled device (CCD)

# Gas Phase Chemistry in $N_2$

$NH_3 + M \longrightarrow NH_2 + H + M$ (M=Ar)

+

TMGa $\longrightarrow$ DMGa $\longrightarrow$ MMGa $\longrightarrow$ Ga

Jacko et al.

$TMGa:NH_3$ $\xrightarrow{\text{intra molecular}}$ $(DMGa:NH_2)_x + xCH_4$

Coates et al.

+

TMGa $\xrightarrow{\text{inter molecular}}$ $DMGa:NH_2\text{-}TMGa + CH_4$

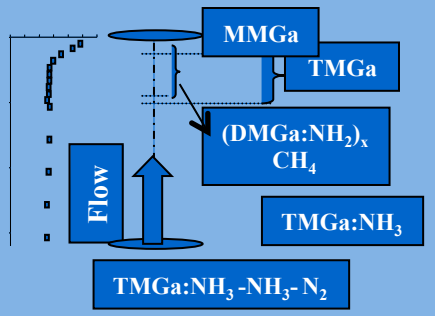
$\downarrow + NH_3$

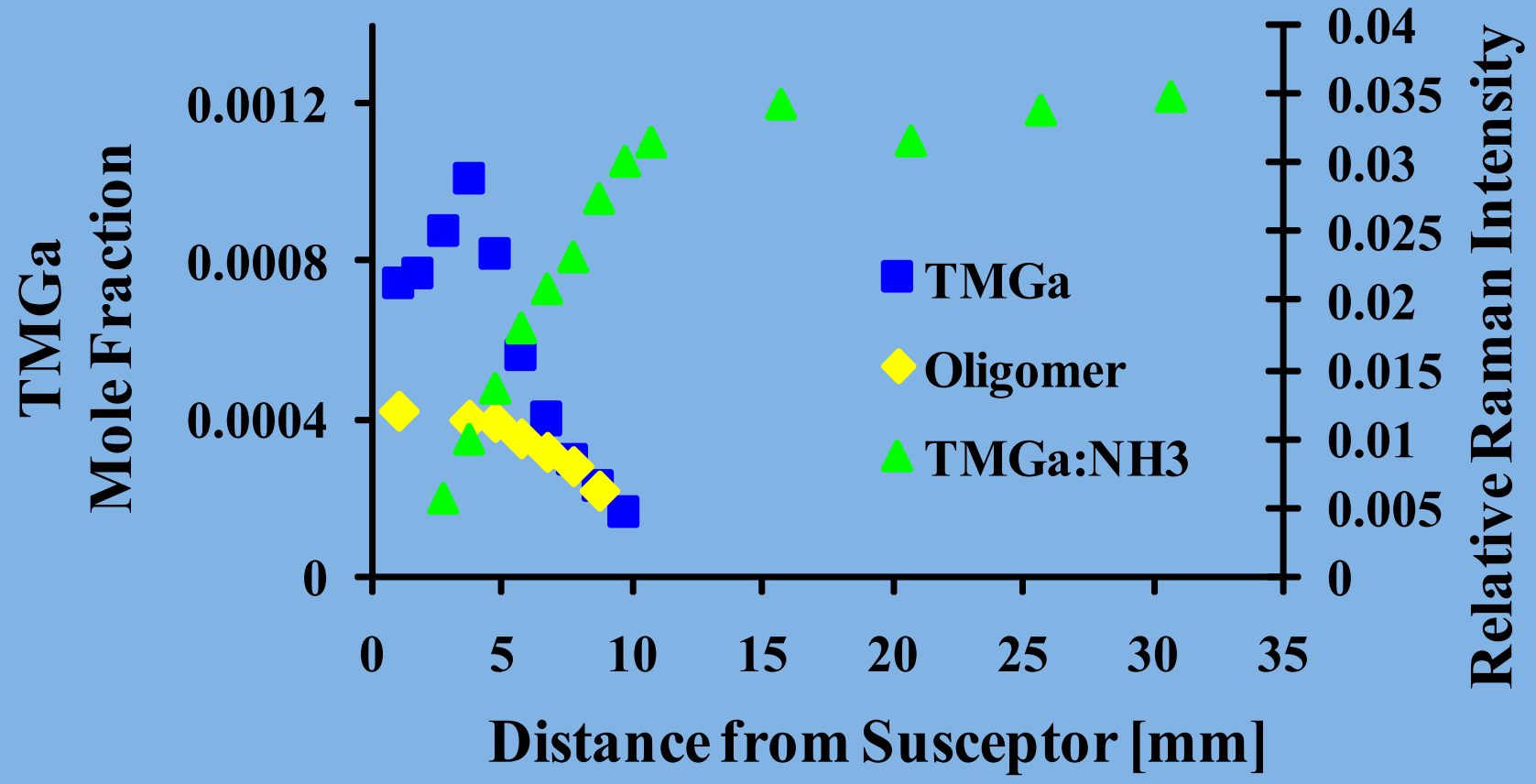
$(DMGa:NH_2)_x + CH_4$

Tachibana et al. (ab inito calculation)

# TMGa:$NH_3$-$NH_3$-$N_2$

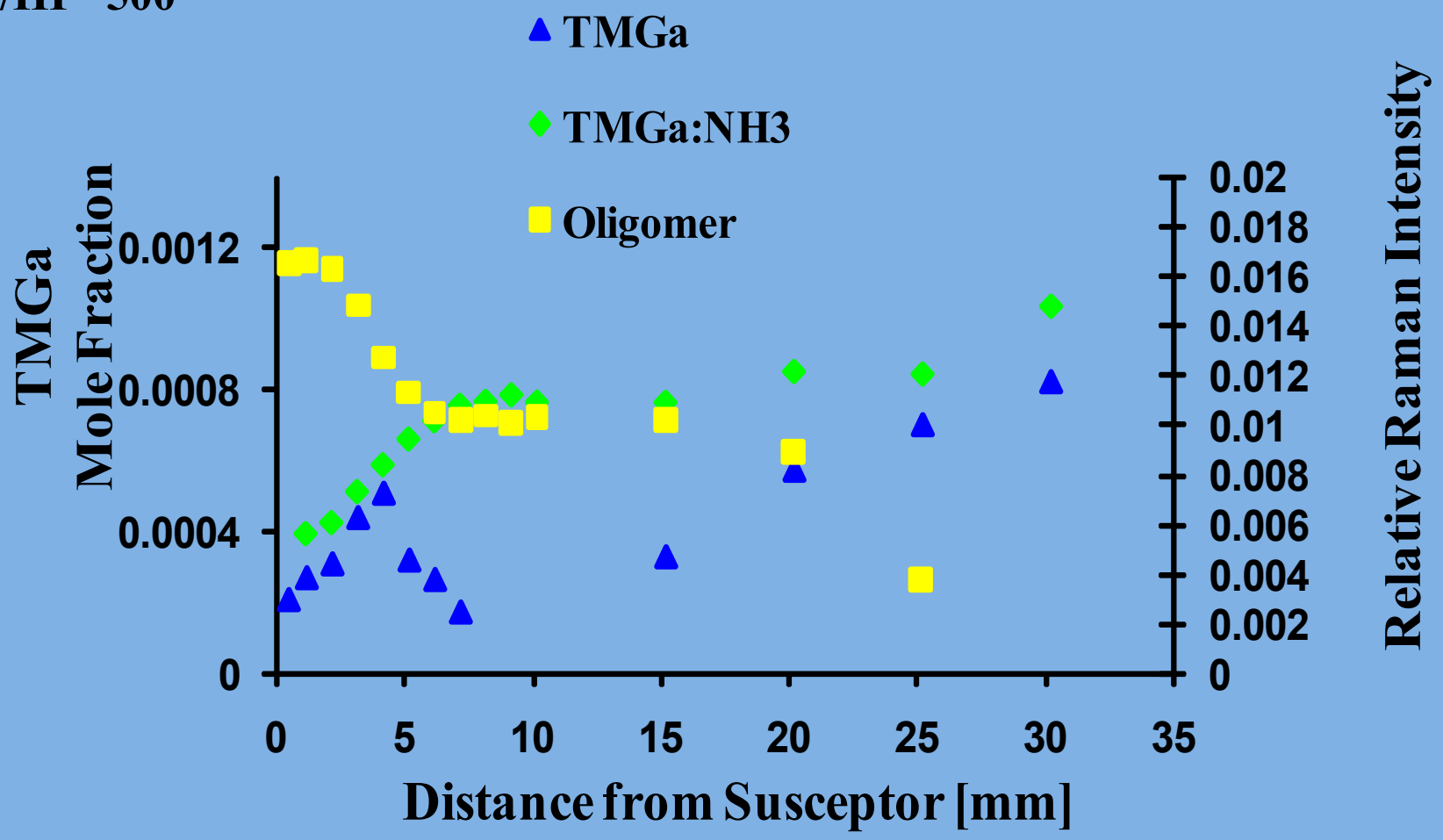
$P_T$ = 1.0 atm
$T_S$ = 1273 [K]
V = 3.0 [cm/s]



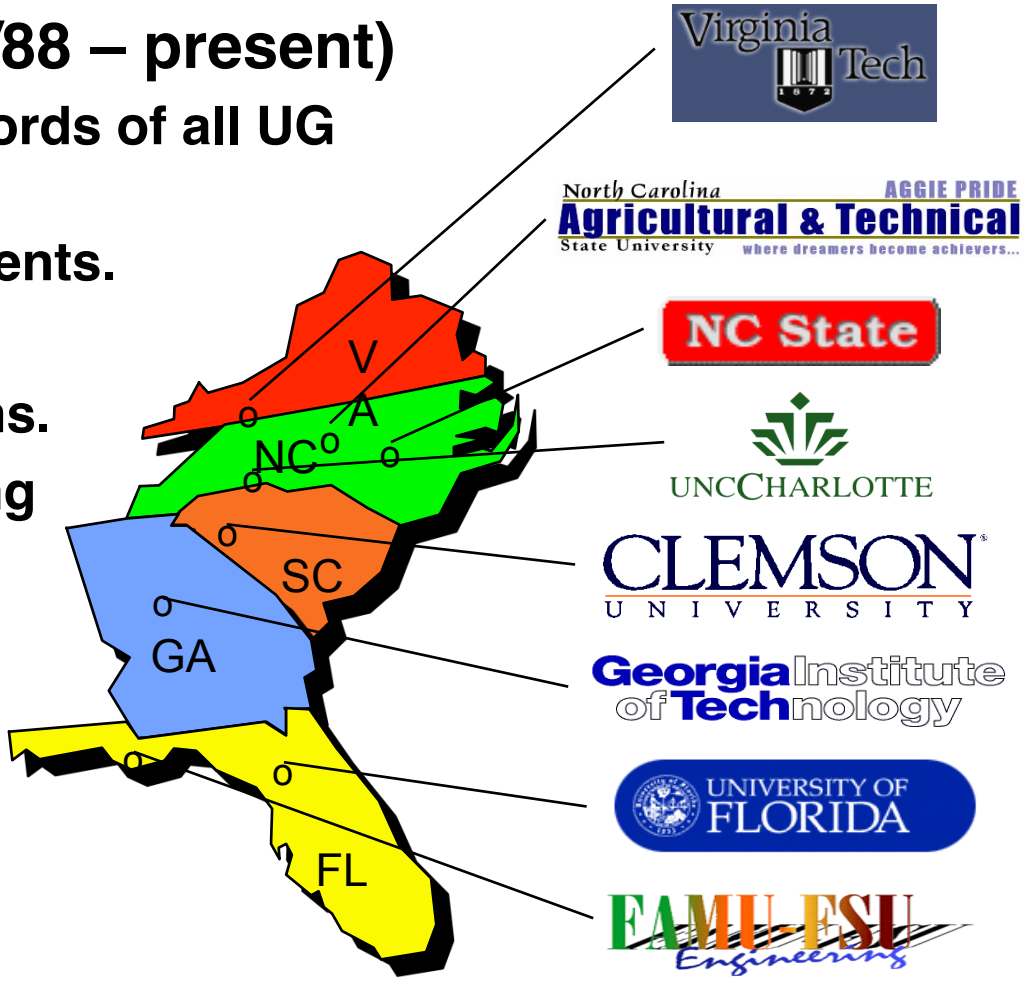
# TMGa-$NH_3$-$N_2$

$P_T$ = 1.0 atm
$T_S$ = 1273 [K]
v = 3.0 [cm/s]
V/III= 500



# Multiple-Institution Database for Investigating Engineering Longitudinal Development (MIDFIELD)

- Longitudinal data (1987/88 – present)
  - 883,020 student-level records of all UG students enrolled.
  - 100,179 engineering students.
  - 6 of the 50 largest U.S. UG engineering programs.
  - 12% of all U.S. engineering UG degrees.
  - 25% of all U.S. African-American eng. B.S. degrees



# Six Significant Core Courses

| MATH | PHYSICS | CHEMISTRY |
|---|---|---|
| Calc 1 | Phys 1 | Introductory Chem |
| Calc 2 | Phys 2 | Chem 1 |
| Calc 3 | Phys 1 Honors | Chem 2 |
| Calc 1 Honors | Phys 2 Honors | Chem 1 Honors |
| Calc 2 Honors | Phys 1 Lab | Chem 1 Lab |
| Calc 3 Honors | Phys 2 Lab | Chem 2 Lab |
| Diff Equations | | |
| Comp. Sci. | | |

**BLUE: Performance in course was significant to retention**

# Odds Ratios and Confidence Intervals for Significant Courses

| Rank | Course | Odds Ratio | 95% Wald CI |
|---|---|---|---|
| 1 | Chem 1 Lab | 1.590 | [1.308, 1.934] |
| 2 | Chem 2 Lab | 1.449 | [1.182, 1.776] |
| 3 | Chem 1 | 1.447 | [1.287, 1.626] |
| 4 | Calc 2 | 1.401 | [1.228, 1.598] |
| 5 | Calc 1 | 1.318 | [1.138, 1.527] |
| 6 | Phys 1 Lab | 1.214 | [1.045, 1.412] |

All other courses had 95% Wald CIs [<1.0, >1.0] (i.e., not significant)

# Student Flow Among Engineering Subfields

**Student flow among engineering subfields. Values are percentage of students beginning in particular subfields that graduate in any (possibly the same) subfield. Total number of beginning engineering students was 20,728.**

| BEGIN / GRAD | *Chemical* | *Civil* | *Computer* | *Electrical* | *Industrial* | *Mechanical/ Aerospace* | *Other Engineering* |
|---|---|---|---|---|---|---|---|
| Chemical | 55.4 | 1.0 | 0.4 | 1.1 | 0.5 | 1.2 | 1.7 |
| Civil | 2.9 | 66.3 | 1.6 | 2.5 | 2.6 | 4.3 | 3.4 |
| Computer | 0.4 | 0.2 | 60.9 | 1.7 | 0.2 | 0.6 | 0.6 |
| Electrical | 1.6 | 1.6 | 12.5 | 62.9 | 1.4 | 3.3 | 2.1 |
| Industrial | 5.4 | 3.1 | 4.3 | 4.6 | 75.6 | 4.8 | 3.1 |
| Mechanical/ Aerospace | 3.0 | 3.6 | 1.8 | 4.2 | 2.6 | 57.7 | 4.9 |
| Other Engineering | 4.1 | 2.4 | 0.2 | 2.4 | 0.8 | 3.9 | 59.8 |
| Total | 72.8 | 78.1 | 81.6 | 79.5 | 83.7 | 75.8 | 75.5 |

# Student Flow
# Engineering to Non-engineering

**Student flow from engineering to non-engineering fields. Values are percentage of students beginning in a given subfield that graduate in a given non-engineering discipline. The total number of beginning engineering students was 20,728.**

| BEGIN / GRAD | *Chemical* | *Civil* | *Computer* | *Electrical* | *Industrial* | *Mechanical/ Aerospace* | *Other Engineering* |
|---|---|---|---|---|---|---|---|
| Biology | 4.0 | 1.0 | 0.9 | 1.2 | 0.5 | 1.2 | 1.7 |
| Business | 4.3 | 6.0 | 4.1 | 4.9 | 9.4 | 6.6 | 5.5 |
| CIS | 0.9 | 0.6 | 7.7 | 3.1 | 0.7 | 1.6 | 1.5 |
| Physical Science | 8.2 | 1.0 | 0.9 | 0.8 | 0.4 | 1.5 | 2.2 |
| Social Science | 1.8 | 2.3 | 2.1 | 2.0 | 1.2 | 3.1 | 2.0 |
| Other Non-Engineering | 8.0 | 11.0 | 2.7 | 8.5 | 4.1 | 10.1 | 11.7 |
| Total | 27.2 | 21.9 | 18.4 | 20.5 | 16.3 | 24.2 | 24.5 |

# Student Flow
# Non-engineering to Engineering

**Student flow from non-engineering to engineering fields. Values are percentage of students beginning in a given non-engineering discipline that graduate in an engineering subfield. The total number of non-engineering students was 76,960.**

| BEGIN / GRAD | *Biology* | *Business* | *CIS* | *Physical Science* | *Social Science* | *Other Non-Engineering* |
|---|---|---|---|---|---|---|
| Chemical | 0.3 | 0.1 | 0.2 | 2.6 | 0.1 | 0.3 |
| Civil | 0.4 | 0.2 | 0.9 | 0.9 | 0.3 | 0.4 |
| Computer | 0.0 | 0.0 | 2.8 | 0.2 | 0.0 | 0.0 |
| Electrical | 0.1 | 0.1 | 2.9 | 1.6 | 0.1 | 0.2 |
| Industrial | 0.5 | 0.9 | 1.7 | 1.2 | 0.2 | 0.3 |
| Mechanical/ Aerospace | 0.4 | 0.2 | 1.0 | 1.8 | 0.1 | 0.3 |
| Other Engineering | 0.6 | 0.3 | 0.6 | 2.0 | 0.3 | 1.2 |
| Total | 2.3 | 1.8 | 10.2 | 10.3 | 1.0 | 2.7 |

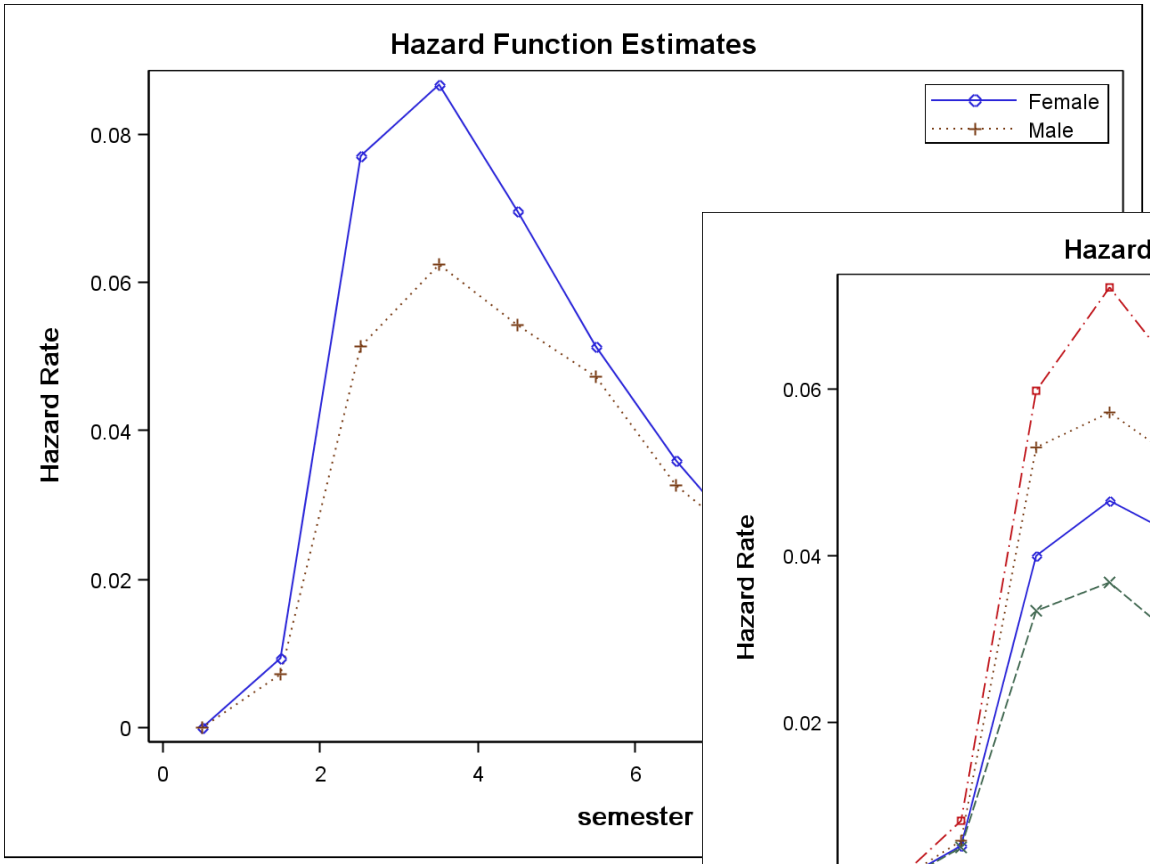
# Pair-Wise Comparisons Among CHE, OENG, SCI and NSCI Groups

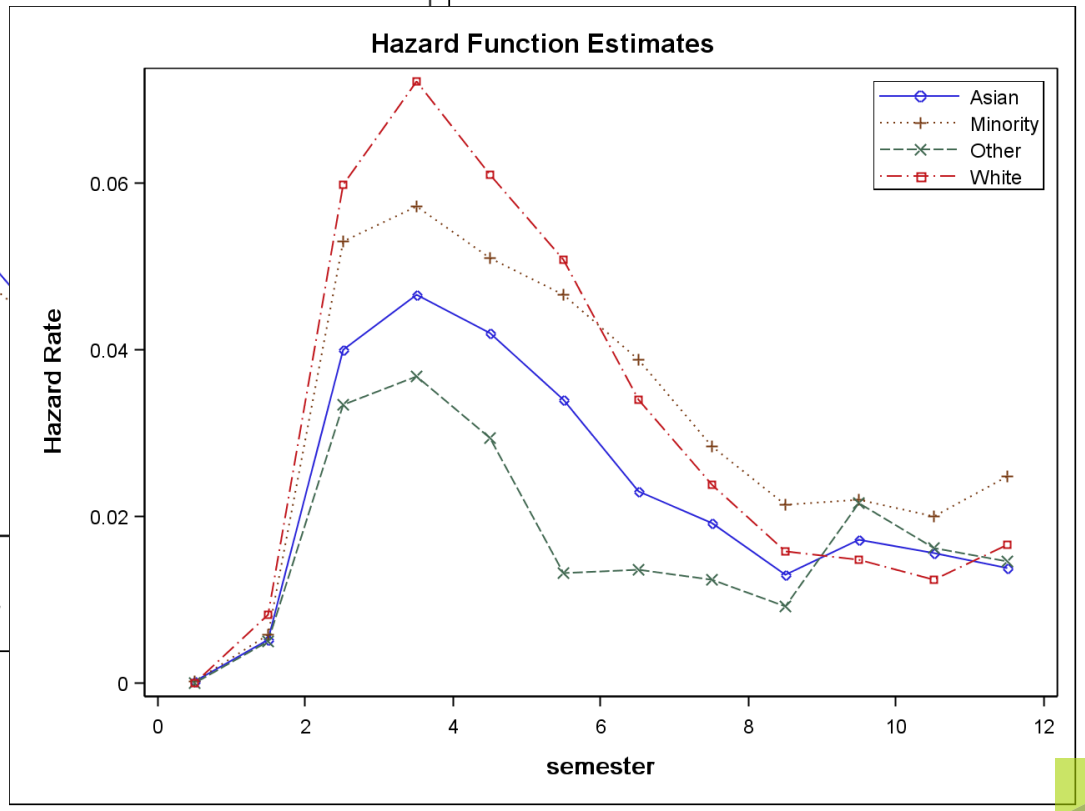
| Variable | Statistic | CHE | OENG | SCI | NSCI |
|---|---|---|---|---|---|
| *SAT math score | M | 645.92[a] | 635.88[b] | 609.11[c] | 533.16[d] |
| | SD | 82.29 | 83.83 | 96.20 | 92.20 |
| *SAT verbal score | M | 533.96[a] | 517.34[b] | 519.66[b] | 490.06[c] |
| | SD | 86.73 | 87.62 | 95.66 | 87.45 |
| **High School GPA | M | 3.72[a] | 3.56[b] | 3.57[b] | 3.31[c] |
| | SD | 0.36 | 0.41 | 0.47 | 0.52 |
| Months to Graduation | M | 53.88[a] | 55.90[b] | 51.77[c] | 51.82[c] |
| | SD | 8.88 | 10.24 | 11.22 | 10.88 |
| Cumulative GPA | M | 3.17[a] | 2.98[b] | 3.04[c] | 2.97[d] |
| | SD | 0.49 | 0.55 | 0.68 | 0.54 |
| # Major Changes | M | 0.63[a] | 0.95[b] | 0.89[c] | 1.29[d] |
| | SD | 0.76 | 0.83 | 0.92 | 1.03 |
| Semesters to Graduation | M | 13.04[a] | 13.87[b] | 11.69[c] | 10.94[d] |
| | SD | 4.07 | 4.35 | 3.62 | 2.62 |
| Cum. Semester Hours | M | 163.35[a] | 168.87[b] | 146.05[c] | 136.11[d] |
| | SD | 38.42 | 42.12 | 36.29 | 26.10 |
| Avg. Semester Hours | M | 13.01[a] | 12.60[b] | 12.84[c] | 12.68[d] |
| | SD | 2.34 | 2.22 | 1.99 | 1.75 |

# Nonparametric Survival Analysis

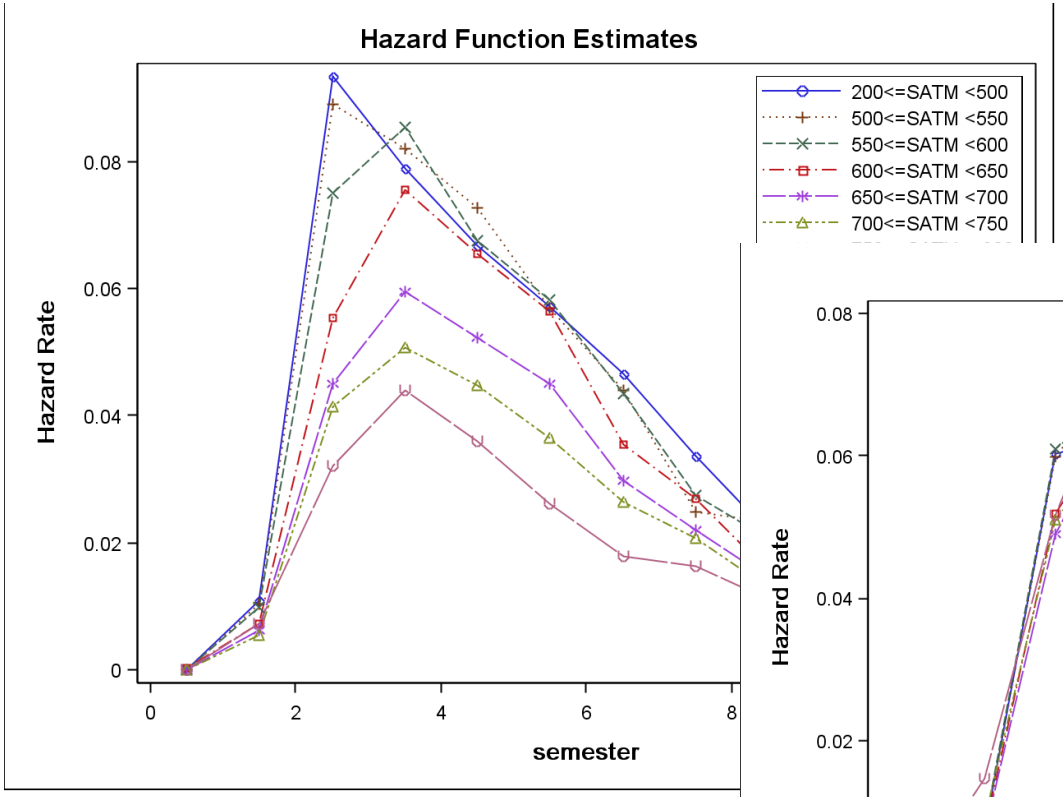
- Class of statistical methods for studying the occurrence and timing of events.
  - Originally used to analyze cancer data.
  - Engineering literature: reliability or failure time analysis
  - Probability of an event occurring at a particular time.
- Definitions
  - A non-failure: A student who did not leave an engineering major, i.e., graduated with an engineering degree or is still enrolled in eng.
  - A failure: A student who left an engineering major, i.e., changed major from engineering to another discipline or left the university.
  - A major change from one engineering major to another one at the same institution or student who leaves engineering but returns to engineering at the same institution do not constitute failure.
- Examined cognitive factors (SAT, HS GPA, college GPA, individual characteristics (gender and ethnicity), and institutional characteristics (institutional type, size)

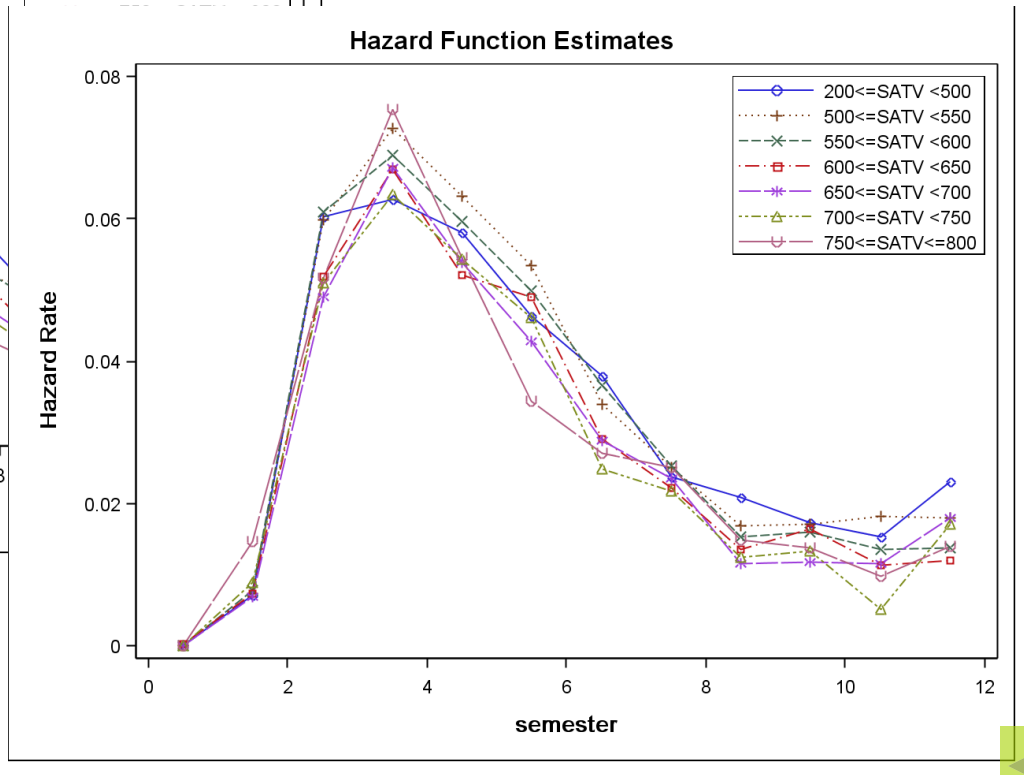
# Hazard Function by Gender and Ethnicity



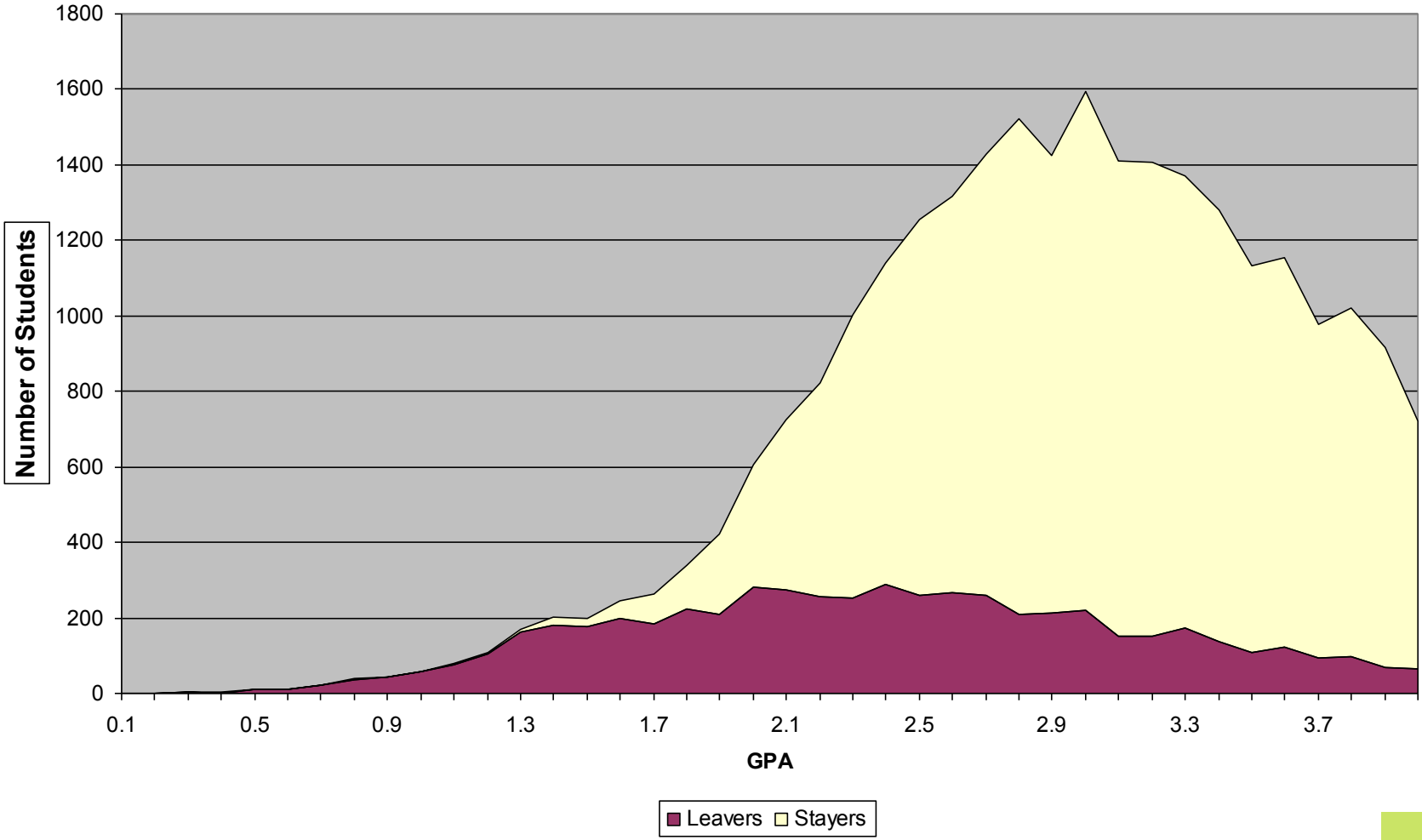



# By SAT Score Group



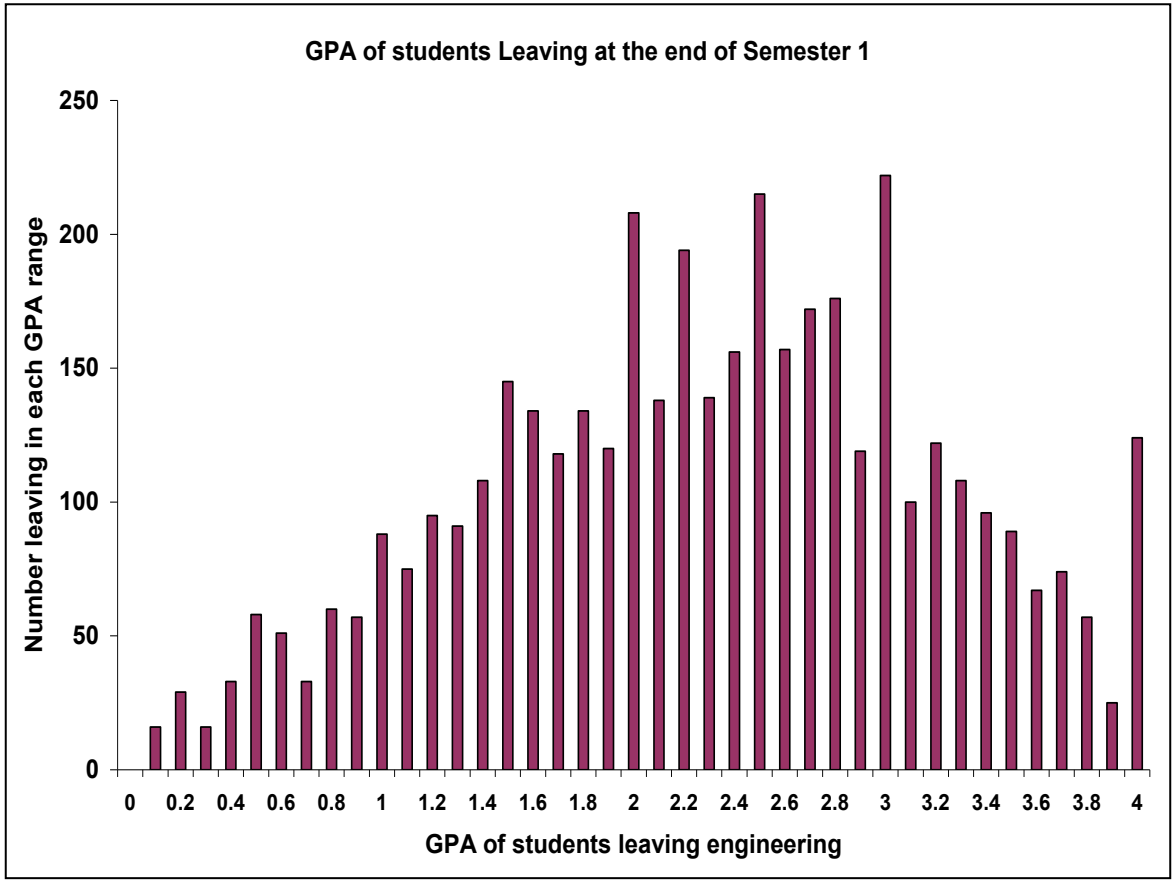



# GPA Distributions of Students Who Leave in Semester 3 and Those Who Remain



# Is GPA a Continuous Variable?

- With fewer credit hours, certain GPAs are more likely
- Effect lasts only 1-2 semesters



# Other Studies

- Is there grade inflation?
  - Is it justified?
- Does block scheduling work?
- Variations among institutional setting?
- What is the effect of a ‘wake-up call’?
- What prerequisites are needed?
- Do performance-based scholarships change student behavior?
- What are the best predictors of success?

# Contributing Researchers

- ✈ **Guili Zhang *(UF PhD, Education)***
- ✈ **Youngkyoung Min *(UF PhD, Education)***
- ✈ **Brian Thorndyke (UF PhD Physics)**
- ❑ **Miguel Padilla *(UF PhD Educational Pyschology)***
- ✈ **Miguel Padilla *(UF PhD Educational Pyschology)***
- ✈ **Steve Chang *(UF Statistics graduate student)***
- ✈ **Russell Long (*Purdue University)***
- ✈ **Matthew W. Ohland (*Purdue University)***

# COMPARISON BETWEEN a CHEMICAL PROCESSING PLANT and an INTEGRATED CIRCUIT

| | *TYPICAL CHEMICAL PLANT* | *TYPICAL INTEGRATED CIRCUIT* |
|---|---|---|
| Raw material source | Many but depleting | Electrical ground |
| Number of species | $10^2$ or more | 2 (electron, hole) |
| Transport | Pipe (10 inch O.D.) | Wire, metal interconnect ($10^{-5}$ cm O.D.) |
| Storage | Tank ($10^6$ moles) | Capacitor ($10^{-10}$ moles) |
| Pump | 10 hp | $10^{-9}$ hp (bipolar transistor) |
| Control | Gate valve | FET |
| | On-off valve | Transistor |
| | Check valve | Diode |
| Reactions | Many | Recombination/generation |
| Flow Rates | $10^3$ moles/s | $10^{-11}$ moles/s |
| Unit operations | $10^4$/mi$^2$ | $10^{18}$/mi$^2$ |
| Cost | \$$10^8$ (\$$10^9$/mi$^2$) | \$$10^2$ (\$$10^9$/mi$^2$) |
| Diffusion coefficient | $10^{-2}$ to $10^{-5}$ cm$^2$/s | 10 to $10^3$ cm$^2$/s |
| Reaction Rate | $10^6$ 1/moles/s | $10^{16}$ 1/moles/s |

# Acknowledgements


- U.S. Department of Energy (support through SAI and F-PACE awards)
- Oak Ridge National Laboratory (HTML, CNMS, and SHARE User Program)
- NREL (R. Noufi)