

Metal Organic Vapor Phase Growth of Complex Semiconductor Alloys

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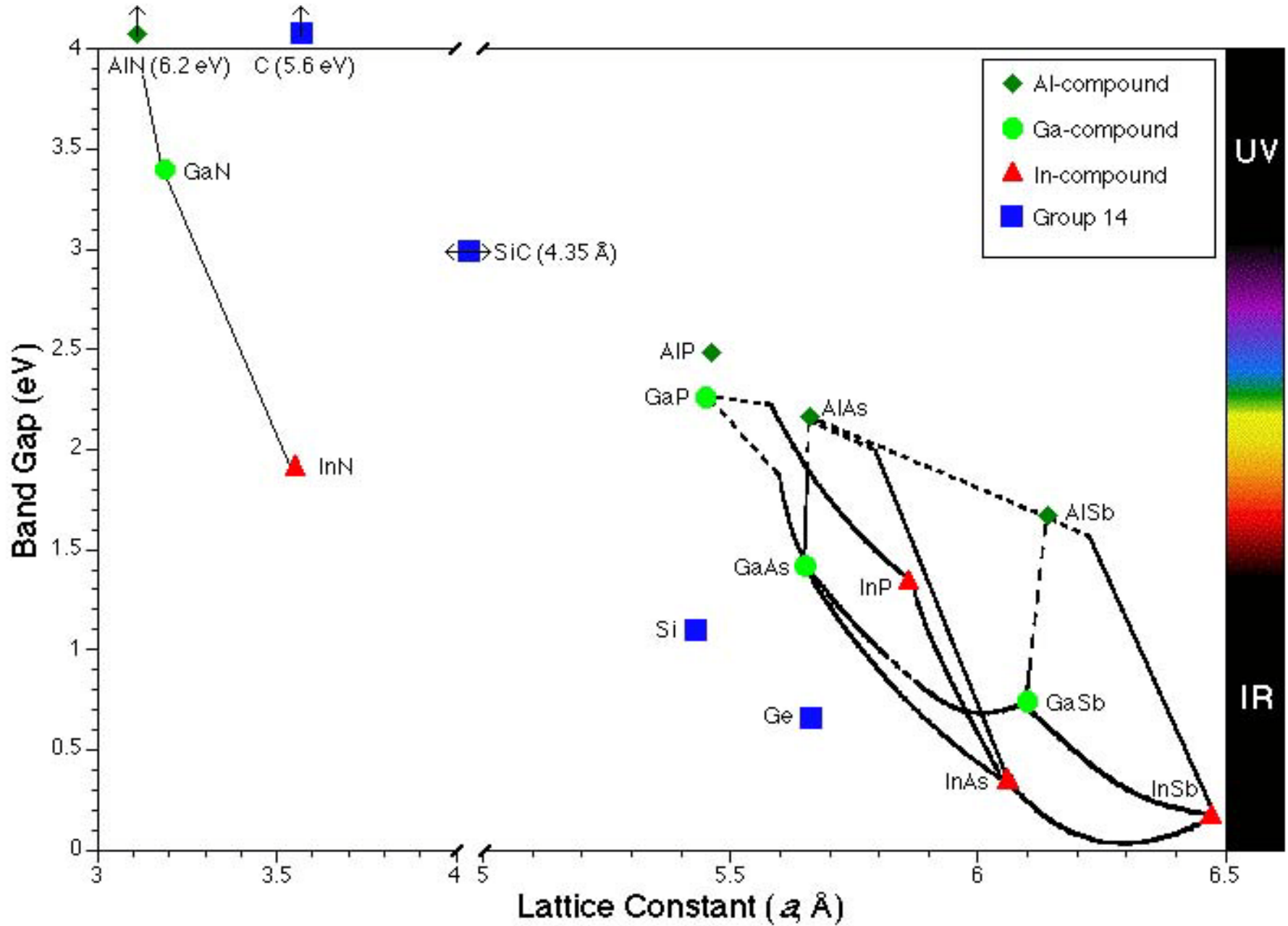
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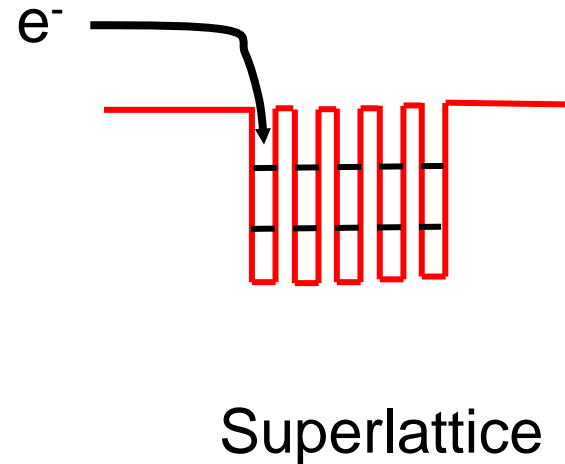
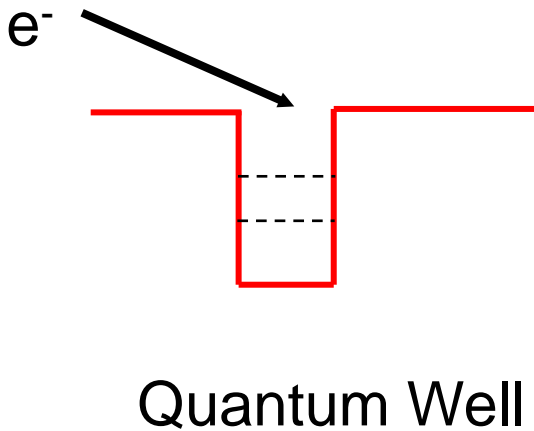
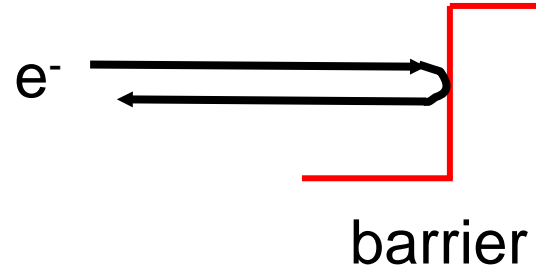
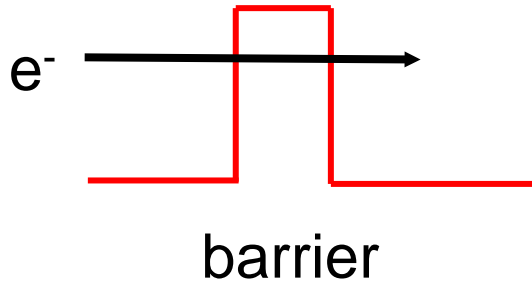
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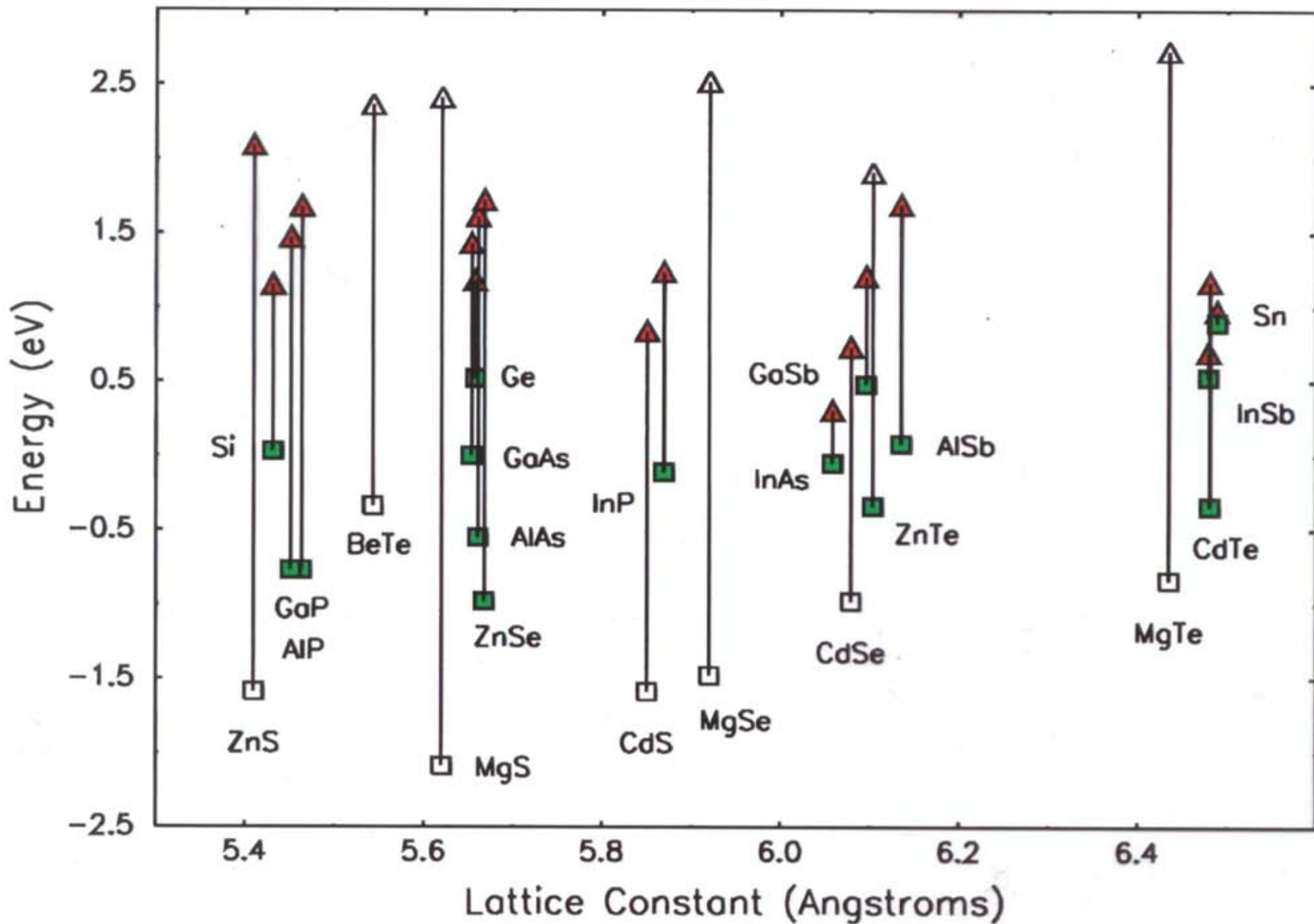


What we need:

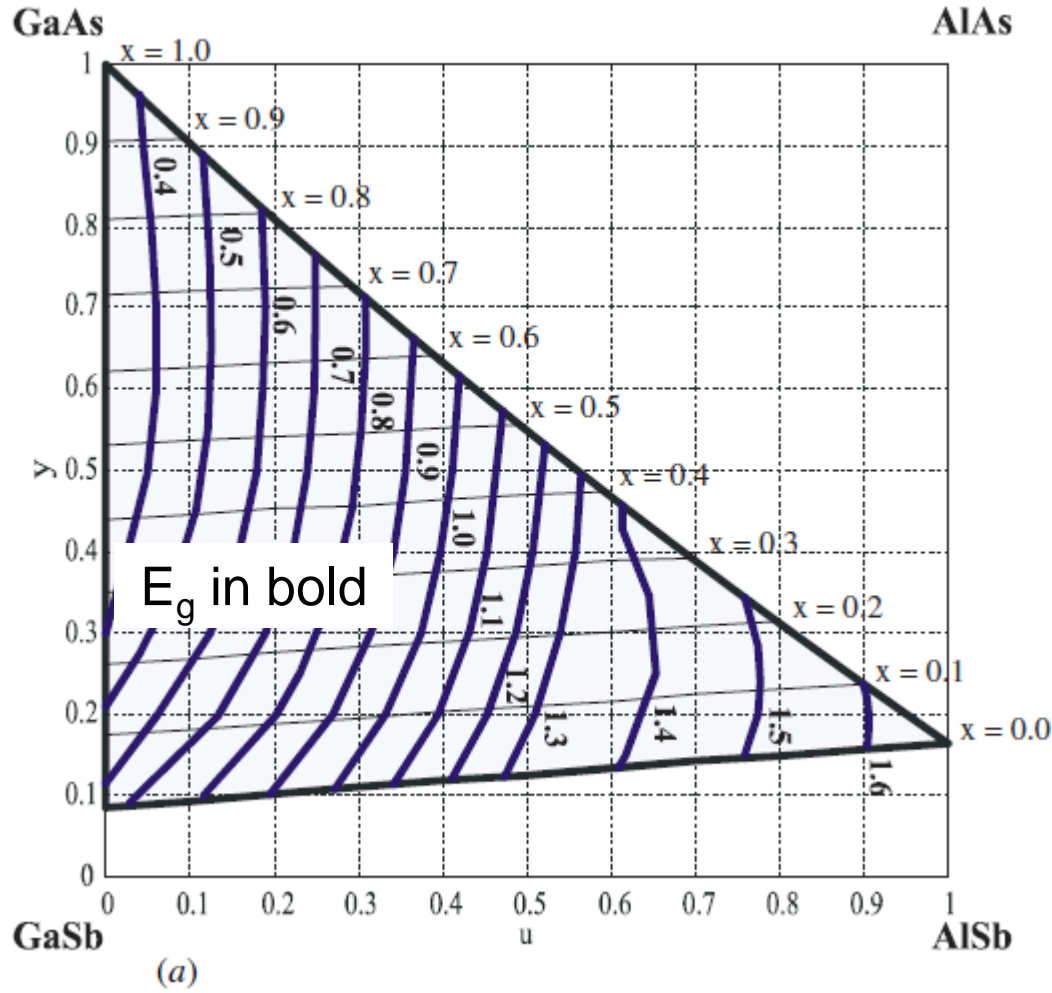
Electron Structure Engineering through modifications to the composition during growth



McCaldin Diagram



Materials Issues: Phase Stability



Wide gap
adjustability
with unusual
band line-ups

Relatively Unexplored Materials

$\text{InAs}_{1-x}\text{Sb}_x$, $\text{InAs}_{1-x}\text{Bi}_x$, $\text{In}_{1-x}\text{Tl}_x\text{Sb}$, $\text{InSb}_{1-x}\text{Bi}_x$

Quaternary alloy systems: e.g. $\text{InAs}_{1-x-y}\text{Sb}_y\text{Bi}_x$

Pentenary alloy Systems: e.g. $(\text{Ga},\text{In})\text{As}_y\text{Sb}_{1-y-z}\text{N}_z$

$\text{InSb}_{1-x}\text{Bi}_x$

Reported maximum solid solubility
limit is 2.6 mol% InBi

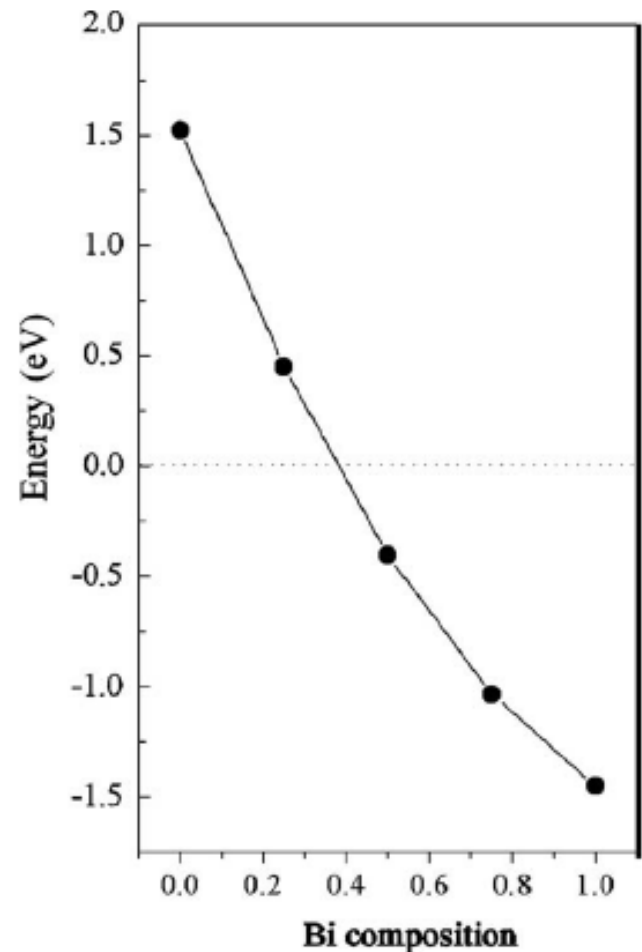
Band Gap: 0.18 to -1.5eV

$\text{GaAs}_{1-x}\text{Bi}_x$

Reported maximum solid solubility
limit is 2.6 mol% InBi

Band Gap: 1.5 to -1.5eV

Madouri , et al., Comp. Mater.
Sci., 43 (2008) 818 -22



Example of Multinary metastable materials

- **InGaAsSbP(N)** Quinternary dilute-nitride compounds are largely unexplored → many potential device applications, solar cells, photodetectors, and lasers
- **GaAsBiN** compounds: very narrow bandgap materials giant spin-orbit splitting → reduced nonradiative Auger recombination for far-infrared emitters, and spintronics

Key Issues to address:

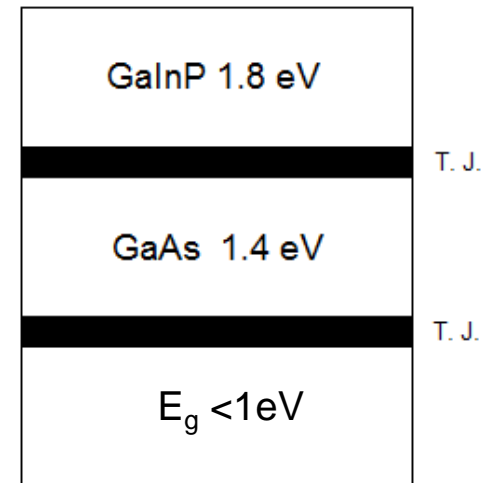
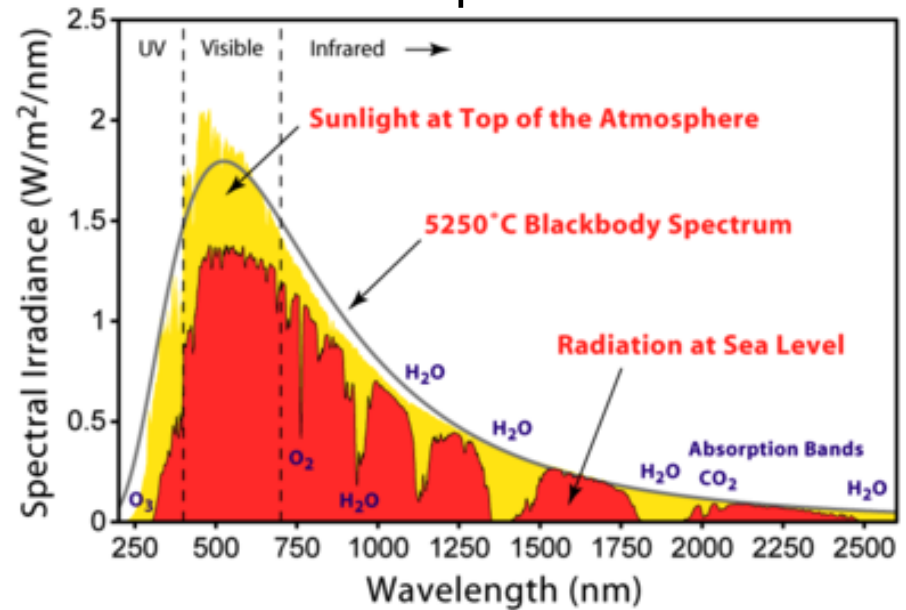
- Control of composition: material growth
- Prediction of accessible bandgap energies and lattice constants
- Prediction of conduction and valence band offsets
- Structural uniformity
- Lattice mis-matched and strained-layer quantum well materials
- Electronic and optical properties: minority carrier lifetime

Example application: High Efficiency (>50%) Multi-junction solar cell

Need: Low defect density materials with $E_g < 1\text{eV}$, which can be deposited monolithically on conventional GaAs substrates.

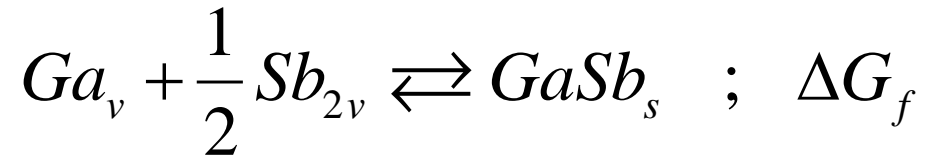
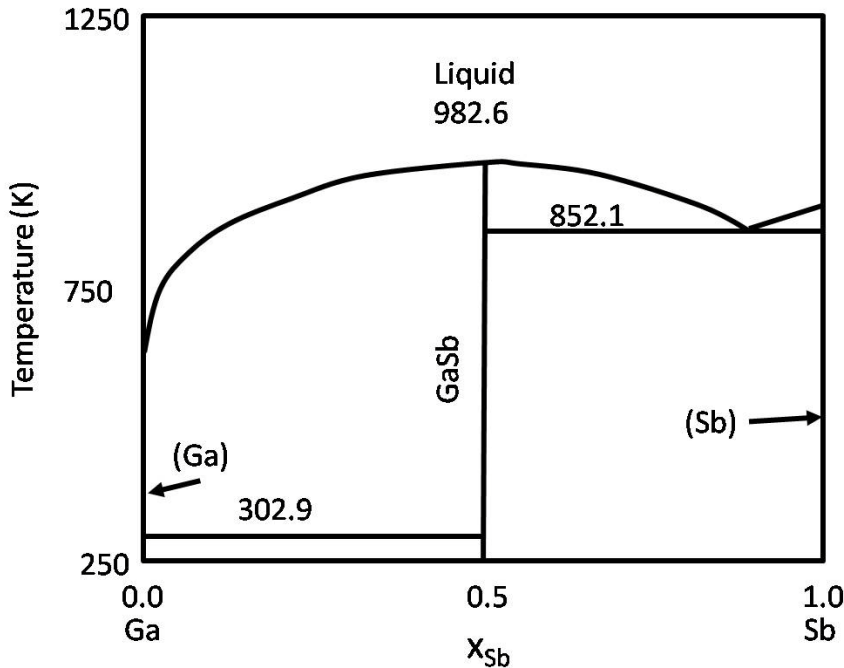
- Flexibility in designing optimal bandgap energy **and** lattice constant → potential for device efficiencies > 50%
- Completely monolithic approach: simplifies growth of solar cell

Solar spectrum



Triple junction solar cell

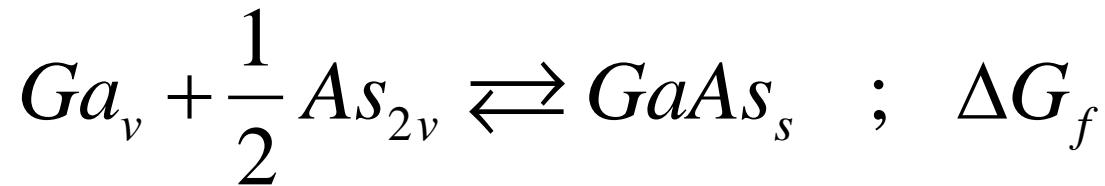
Binary Systems: Thermodynamics



The Enthalpies of formation for the Binary compound semiconductors

	$\Delta H_{f,298}^0$		$\Delta H_{f,298}^0$		$\Delta H_{f,298}^0$
AlN	-320	GaN	-129.3	InN	-28.6-31.8
AlP	-166.5	GaP	-102.5	InP	-92.0
AlAs	-148.1	GaAs	-84.9	InAs	-54.4
AlSb	-105.8	GaSb	-41.0	InSb	-41.84

The Range of Stability



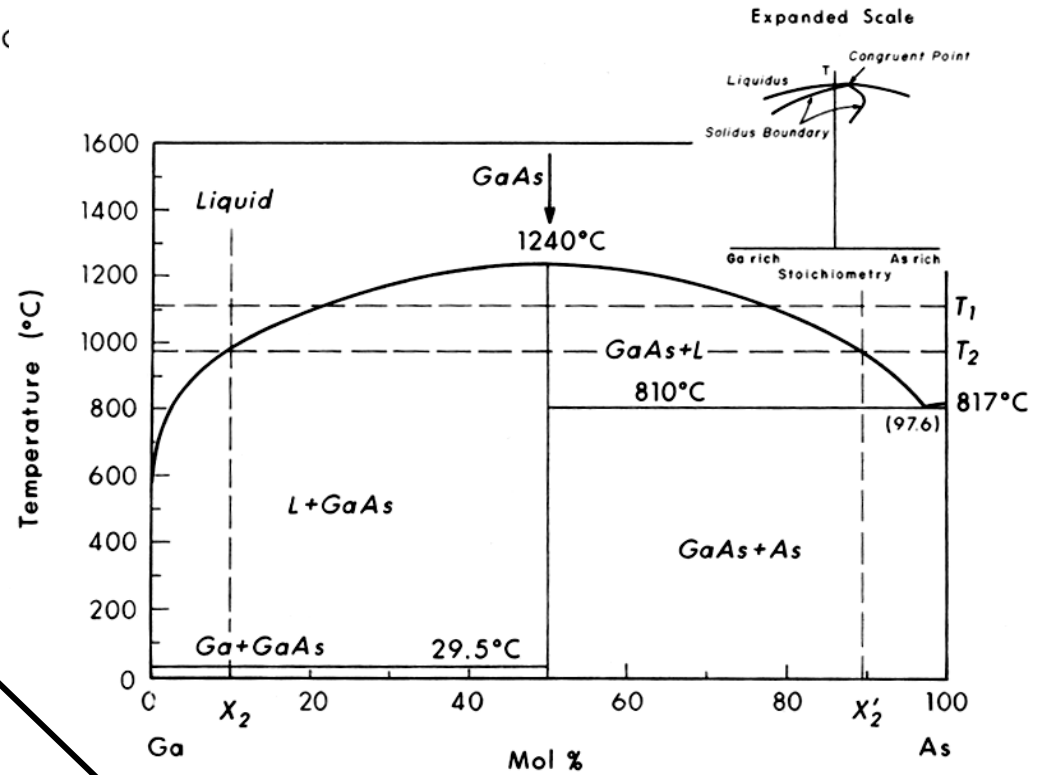
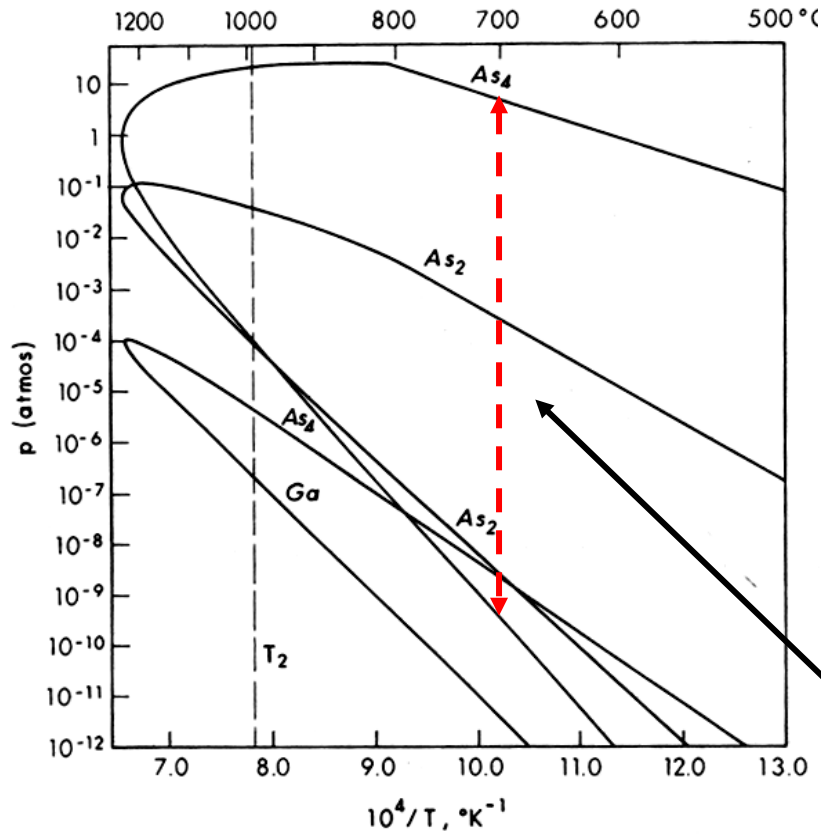
$$K_a = e^{-\frac{\Delta G_f}{RT}} = \frac{a_{GaAs}}{a_{Ga_v} a_{As_{2v}}^{1/2}} \quad a_{GaAs} \approx 1$$

$$K_a = P_{Ga}^0^{-1} \left(P_{As_2}^0 \right)^{-1/2} = \prod P_i^{\nu_i}$$

$$\nu_{Ga} = -1, \quad \nu_{As_2} = -1/2, \quad \nu_{GaAs} = 1$$

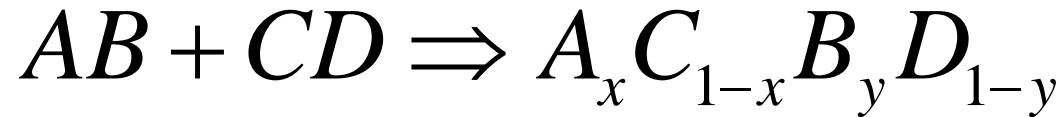
$$P_{Ga} \left(P_{As_2} \right)^{1/2} > P_{Ga}^0 \left(P_{As_2}^0 \right)^{1/2} \quad \text{For growth}$$

Growth Behavior: Thermodynamics of GaAs



Range of As_4 allowed during growth

Extension to Alloy Systems



How do materials form stable alloys?

We need to have the energy of the alloy system be less than the energy of the system (phase) separated .

$$\Delta G_{alloy} < x\Delta G_1 + (1-x)\Delta G_2$$

Non-ideal Solutions:

We define free energy of mixing as the deviation of the free energy from that of an ideal solution.

$$\Delta G_{mix} \equiv \Delta H_{mix} - T \Delta S_{mix}$$

Such that

$$G = G^{ideal\ solution} + \Delta G_{mix} = \sum_i x_i G_i + RT \sum_i x_i \ln x_i + \Delta G_{mix}$$

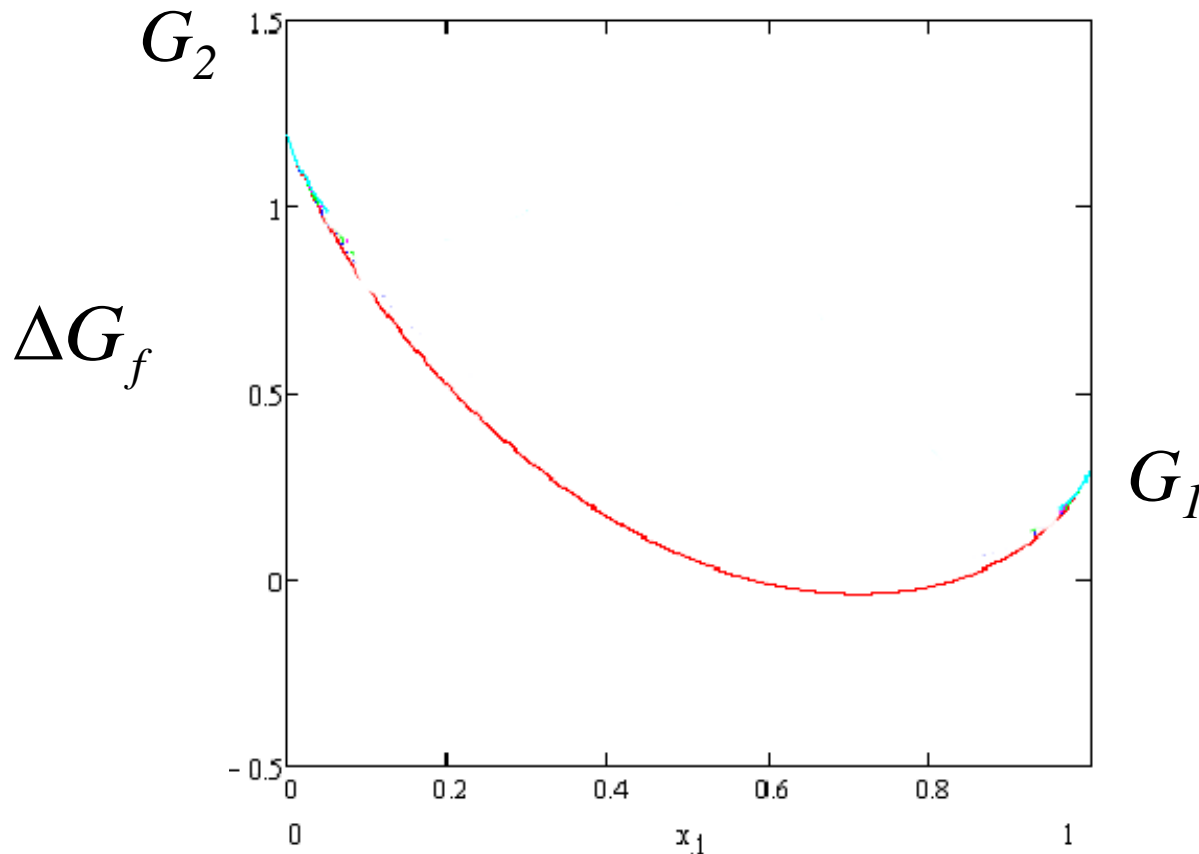
All deviations from ideal behavior is in this free energy of mixing (which contains any excess free energy).

$$\Delta H_{mix} = f(x_1, x_2, \dots, T) \quad \Delta S_{mix} = f(x_1, x_2, \dots, T)$$

Ideal Solutions: Alloys

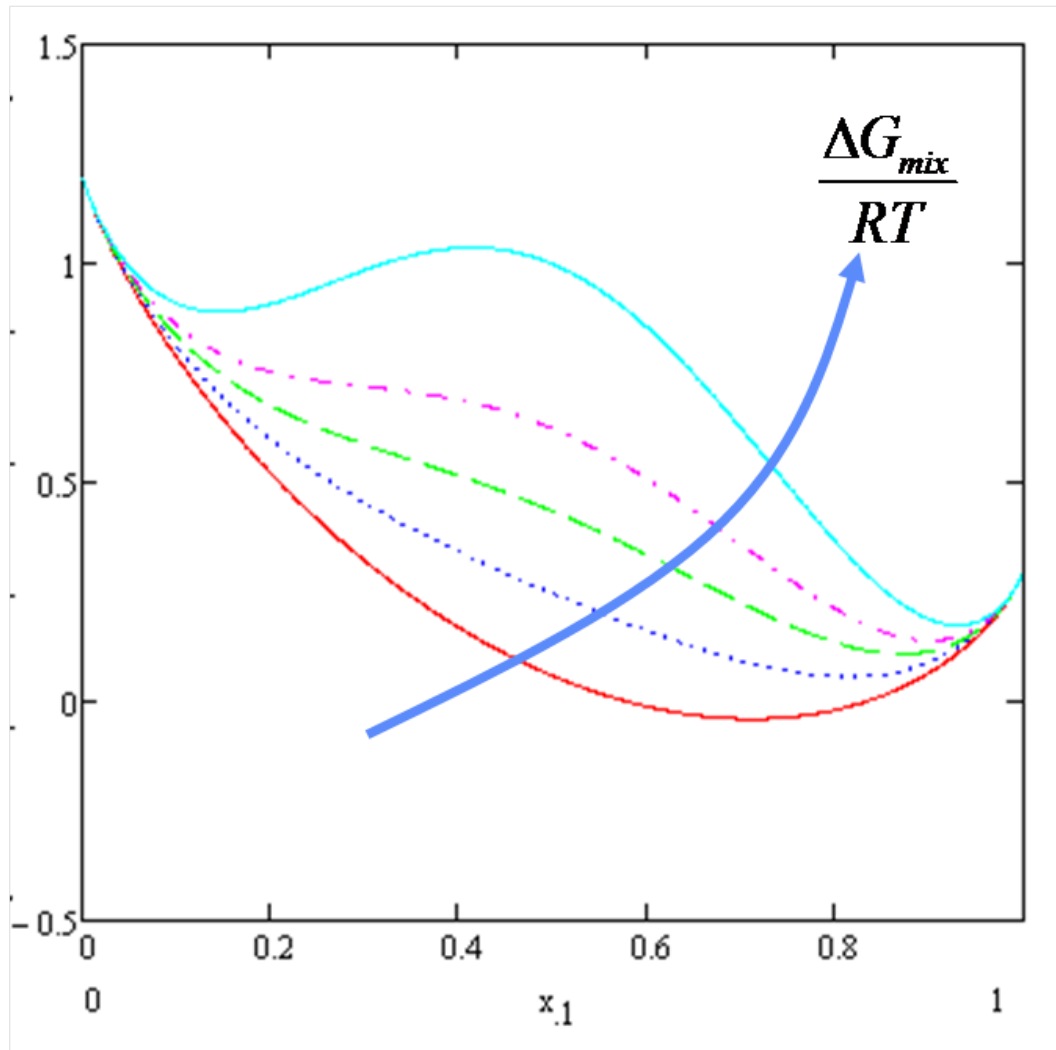
$$G = G^{ideal\ solution} + \Delta G_{mix} = \sum_i x_i G_i + RT \sum_i x_i \ln x_i$$

G_1 & $G_2 \Rightarrow$ Free energy of the binaries



Free energy and phase equilibria:

$$G = \sum_i x_i G_i + T \sum_i x_i \ln x_i + \Delta G_{mix}$$



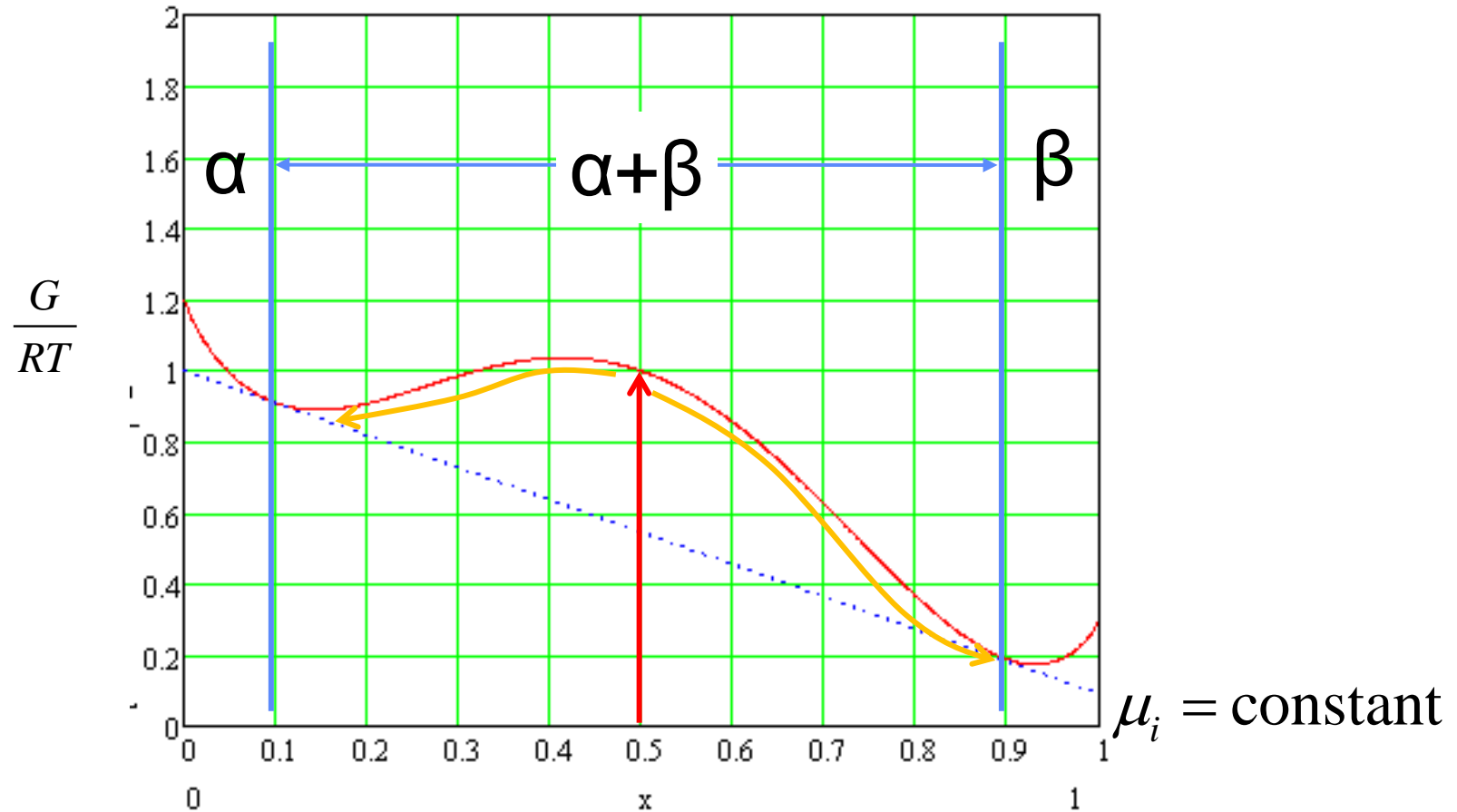
e.g. Stringfellow's
delta lattice
parameter model
for ternary alloys

$$\Delta H_{mix} = X_A X_B \Omega_{AB}$$

$$\Omega_{AB} = 4.375K \frac{\Delta a_0^2}{a^{4.5}}$$

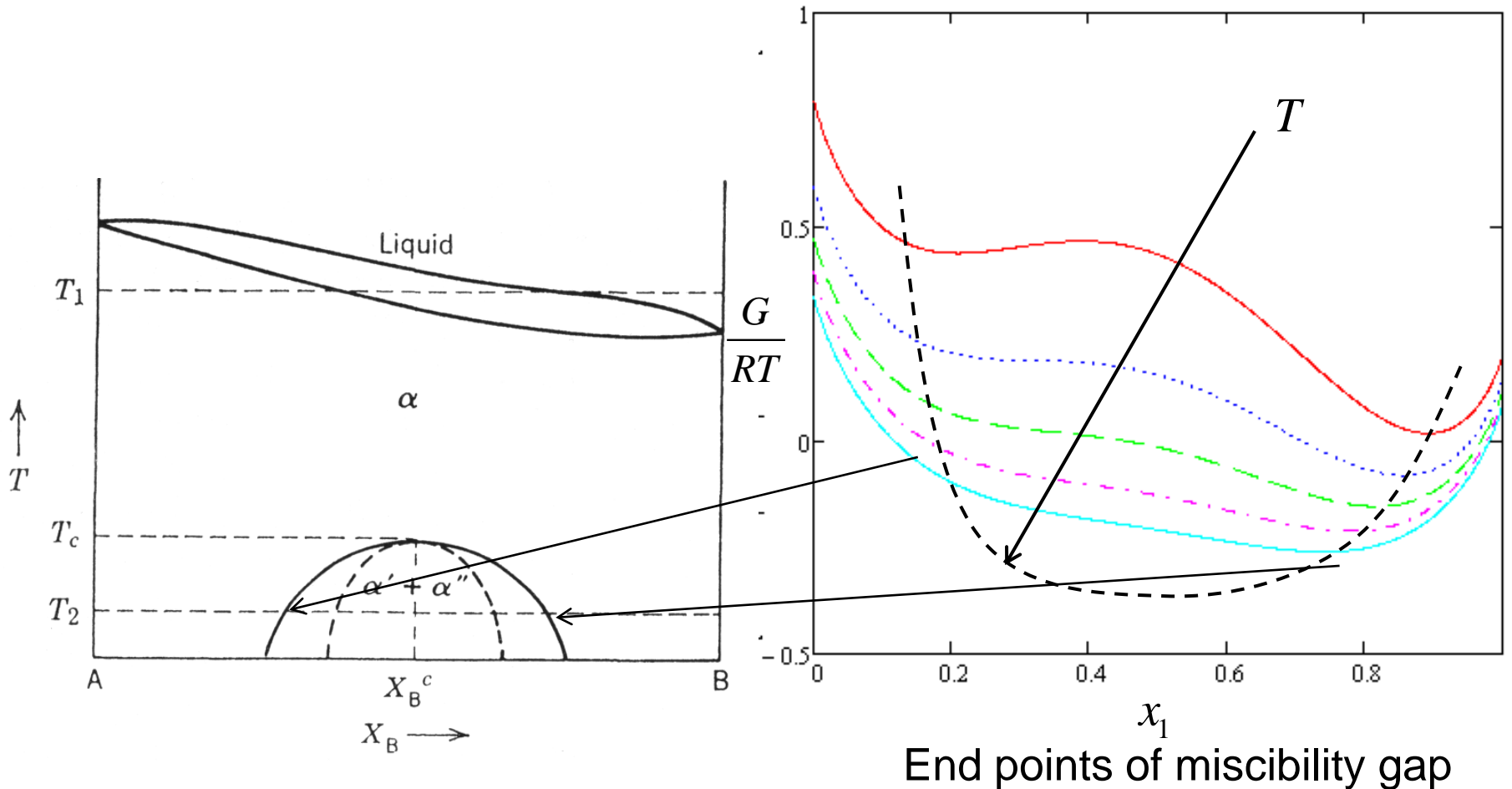
Difference in atomic size,
bonding ...

Free energy and phase equilibria:

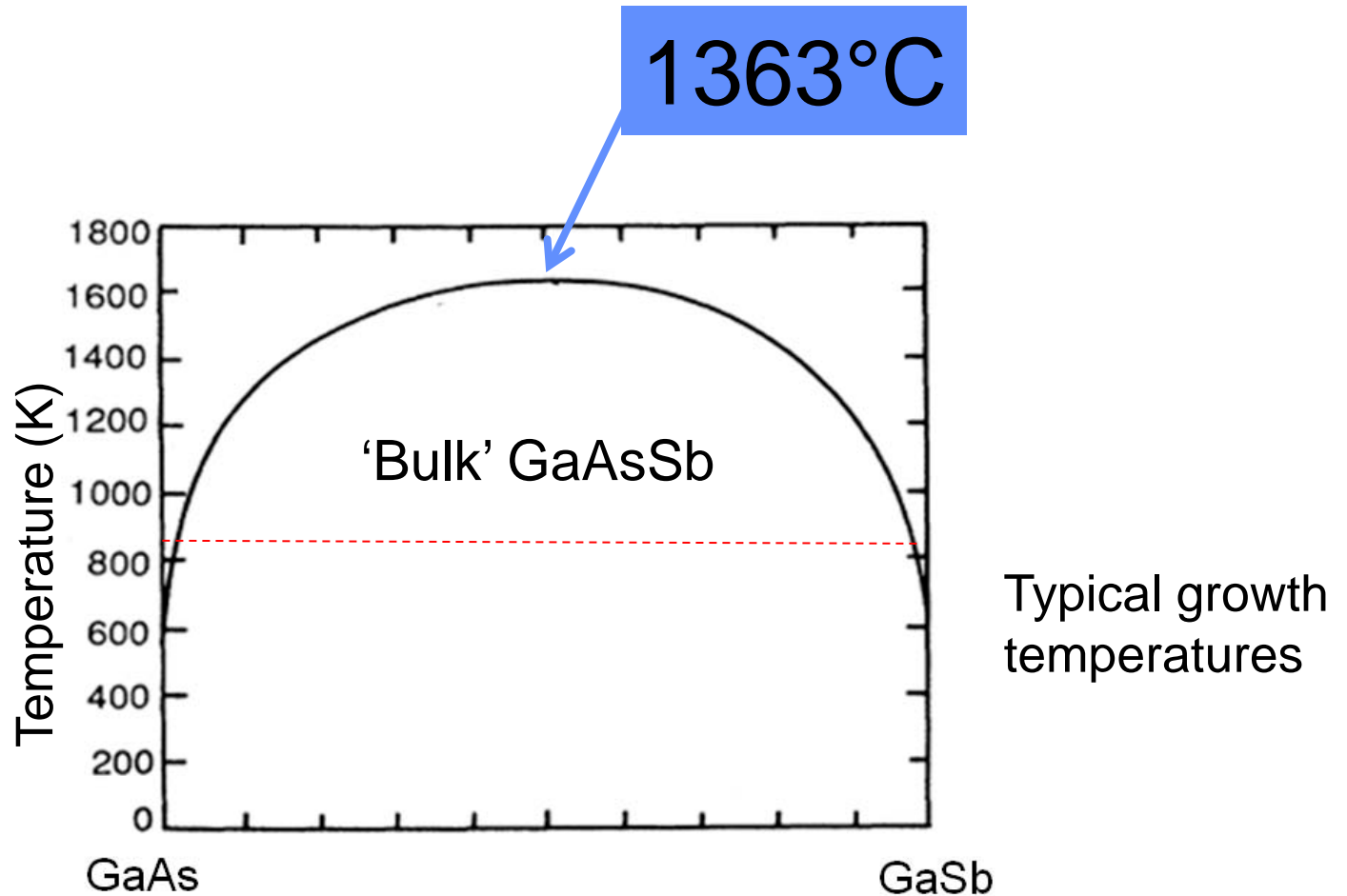


Free energy and phase equilibria:

We can plot out the immiscibility regions from the free energy.

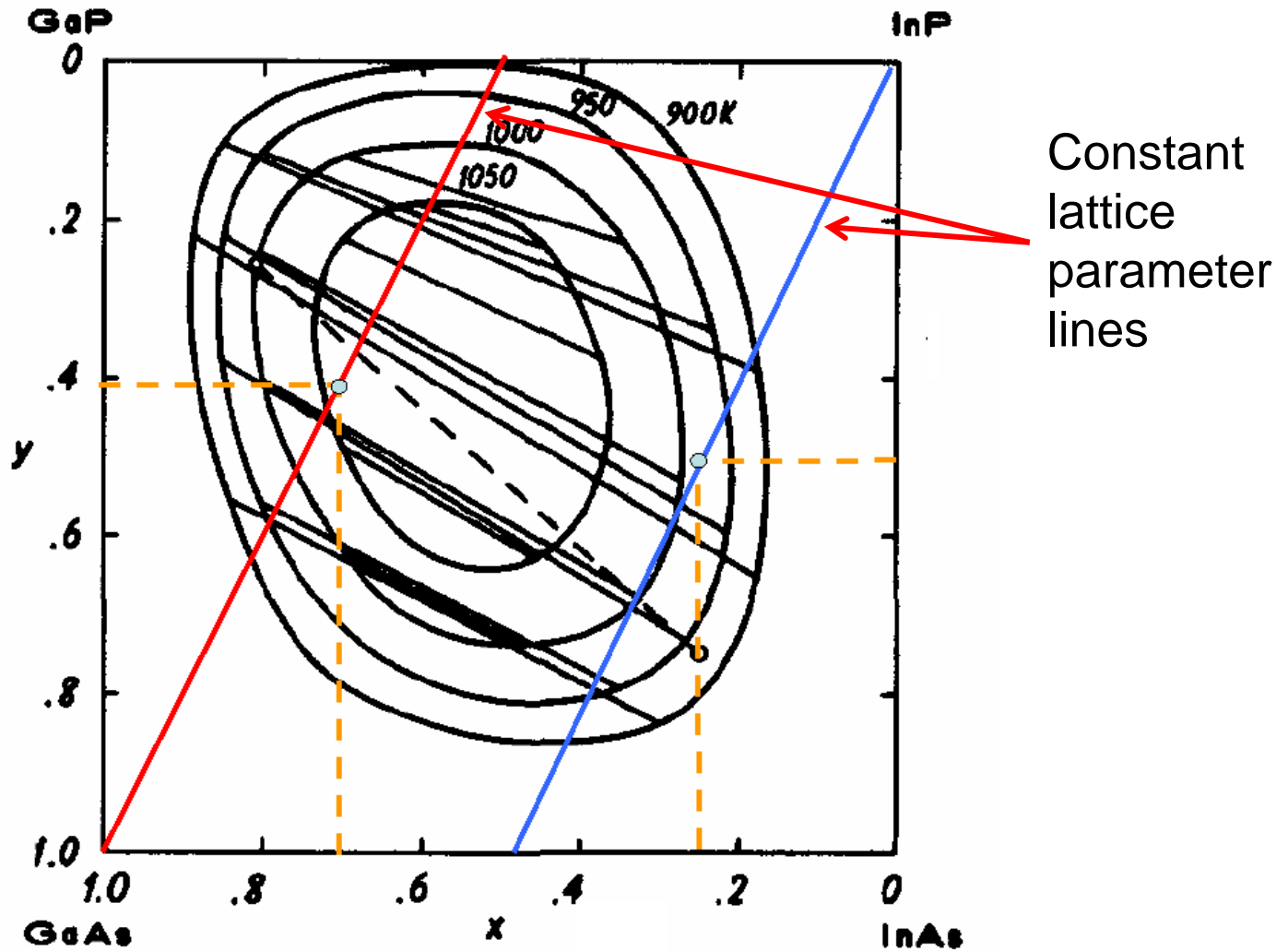


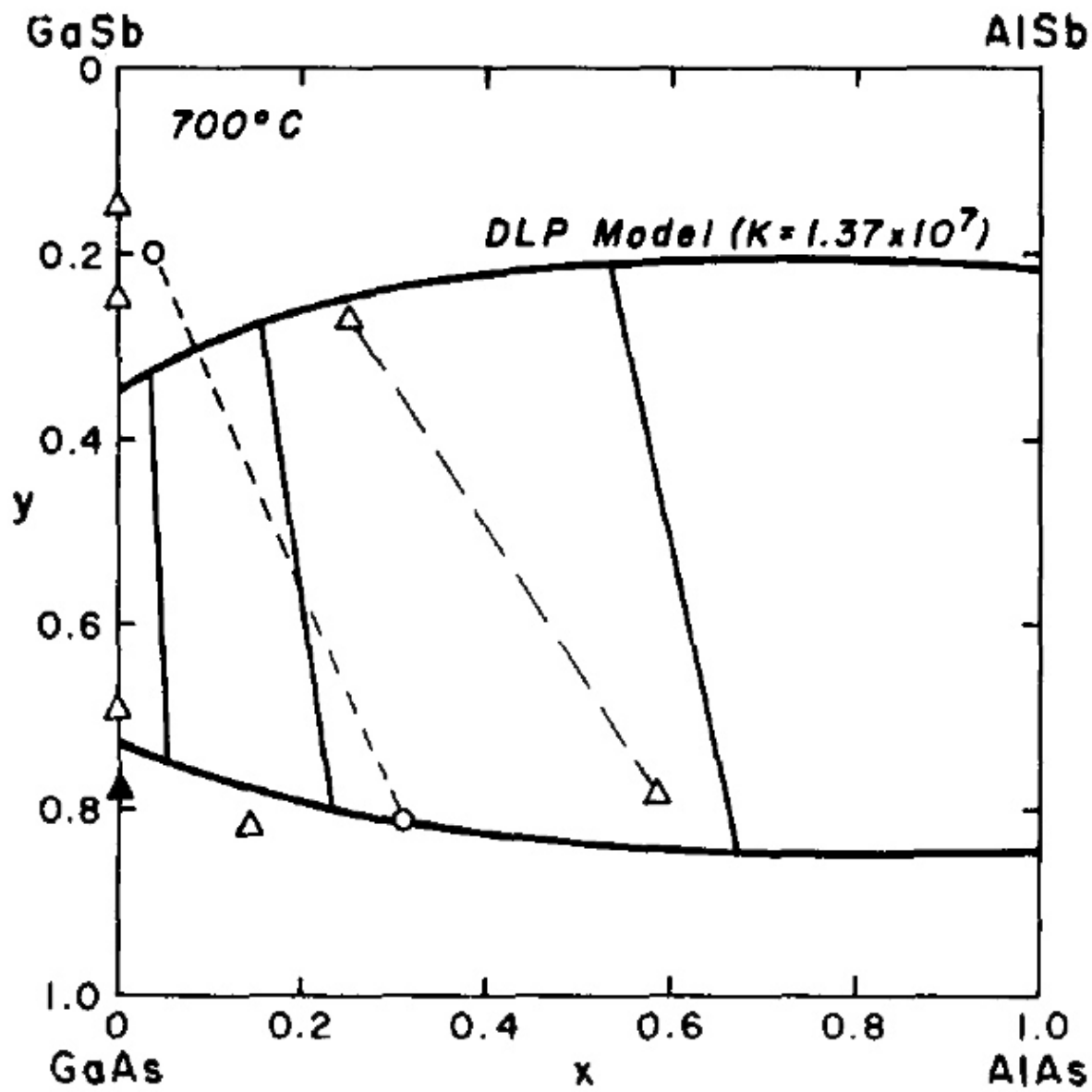
GaAsSb as a thermodynamic and growth system



Wood and Zunger, Phys. Rev B40 (1989) 406.

InGaAsP

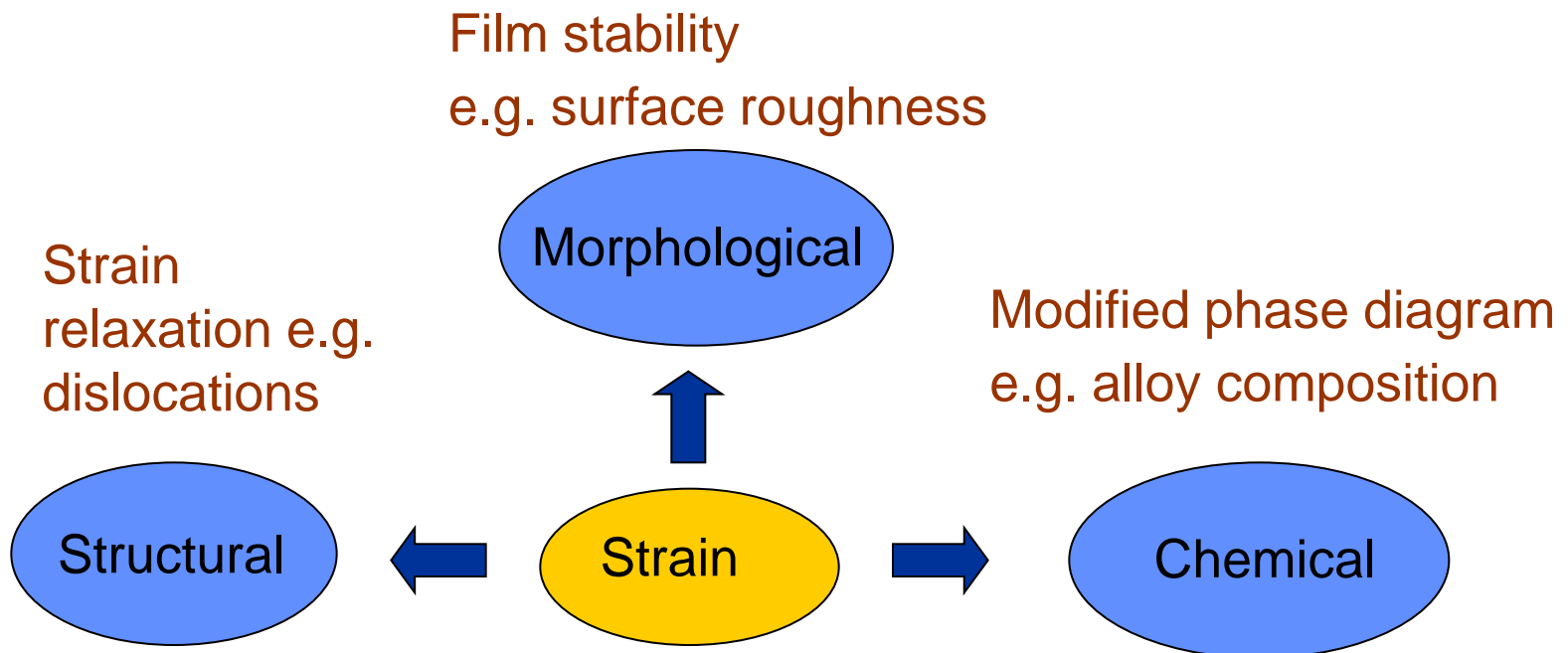




$(\text{Ga,Al})(\text{As,Sb})$

Heteroepitaxy: strain effects

- Dissimilar film and substrate
 - Different crystal structure and/or lattice constant
- Film reproduces the substrate in-plane crystal structure
- Lattice-mismatch derived strain
 - Undesirable modifications to the film crystal lattice

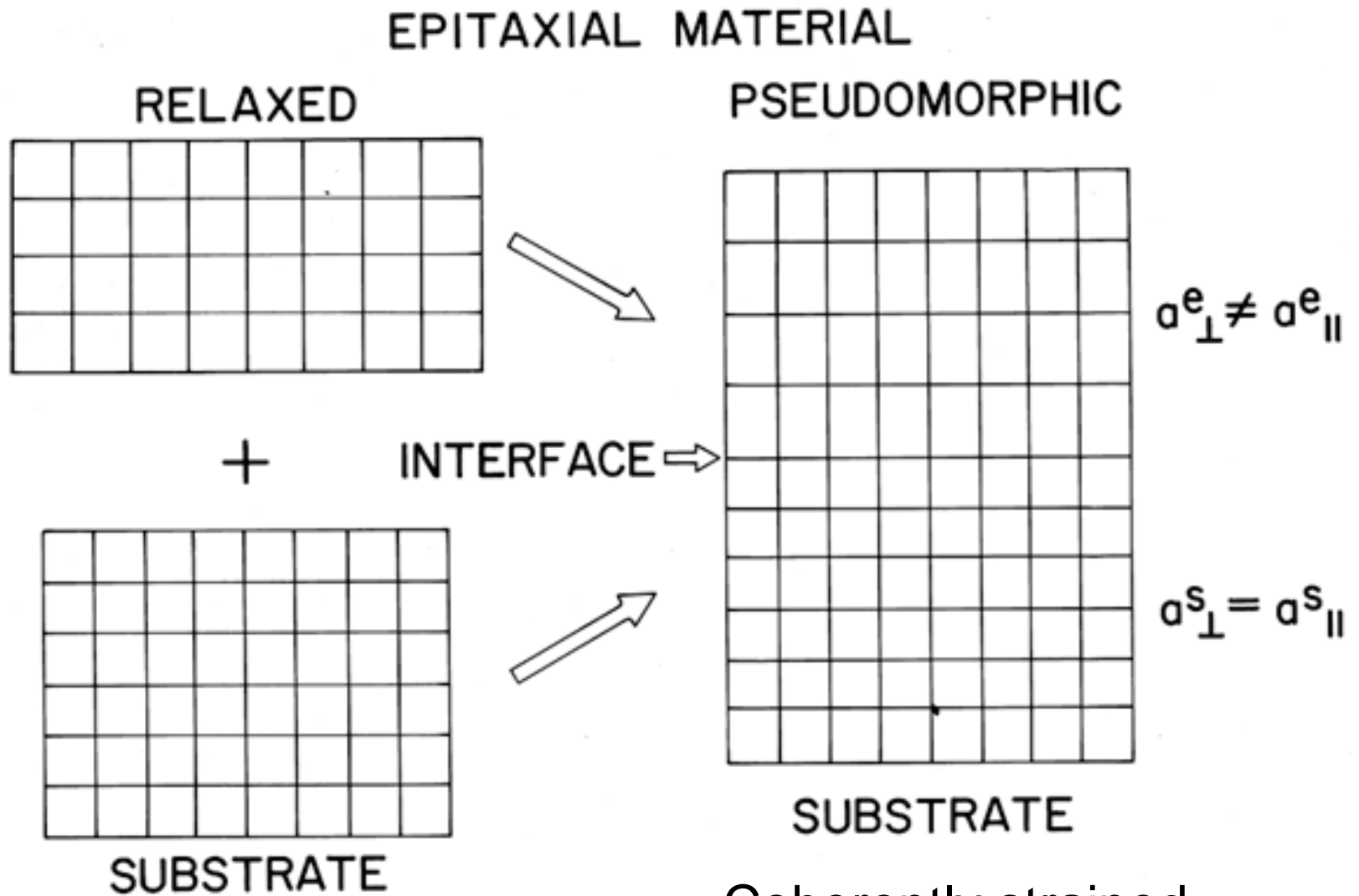


What if there is strain?

$$\begin{aligned} G &= G^{ideal\ solution} + \Delta G_{mix} + \Delta G_{strain} \\ &= \sum_i x_i G_i + RT \sum_i x_i \ln x_i + \Delta G_{mix} + \Delta G_{strain}(c_{ij}, \sigma, \varepsilon) \end{aligned}$$

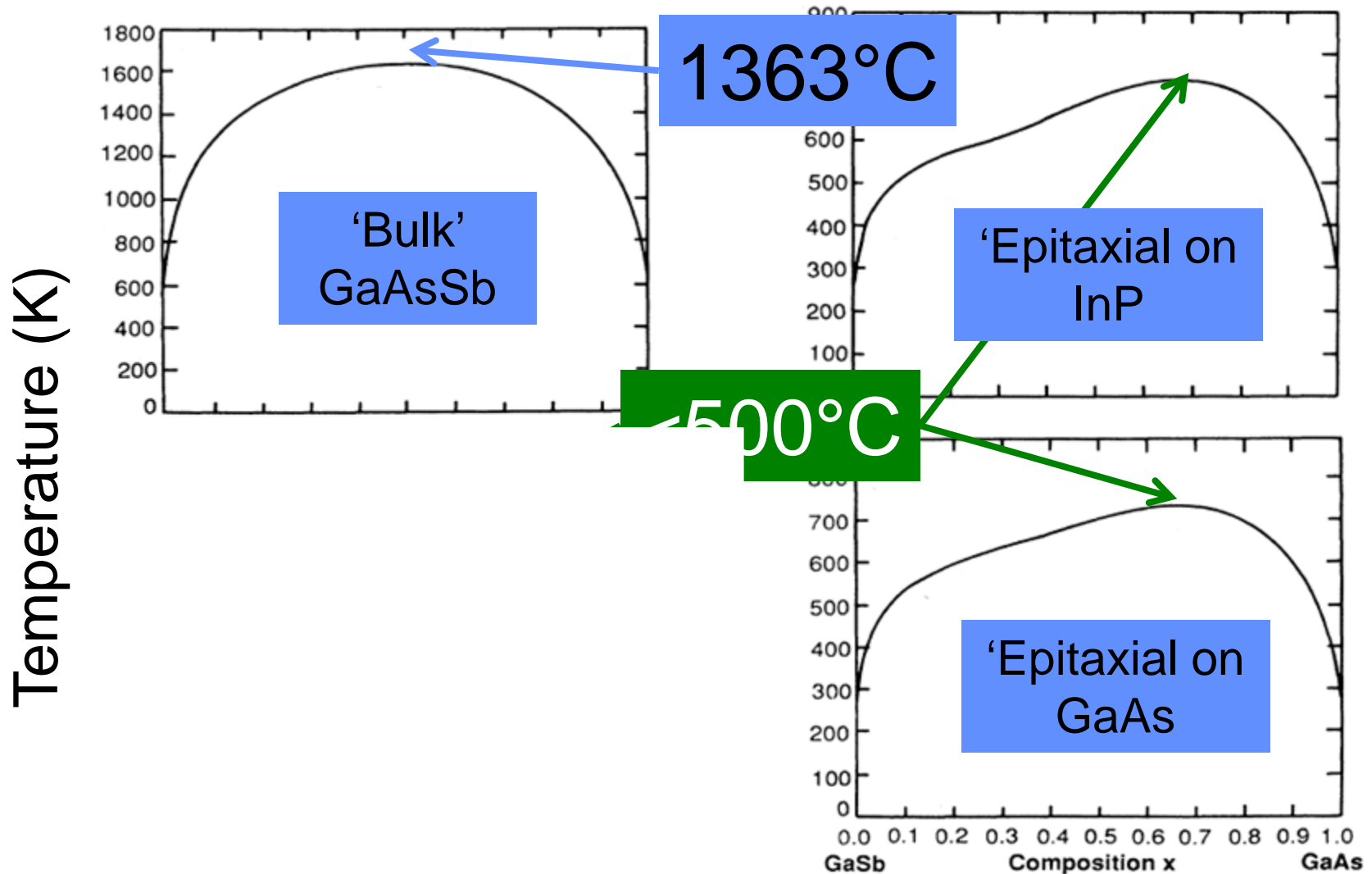
Phase diagrams can be modified through the presence of strain: epitaxial coherent strain effects

What if there is strain?



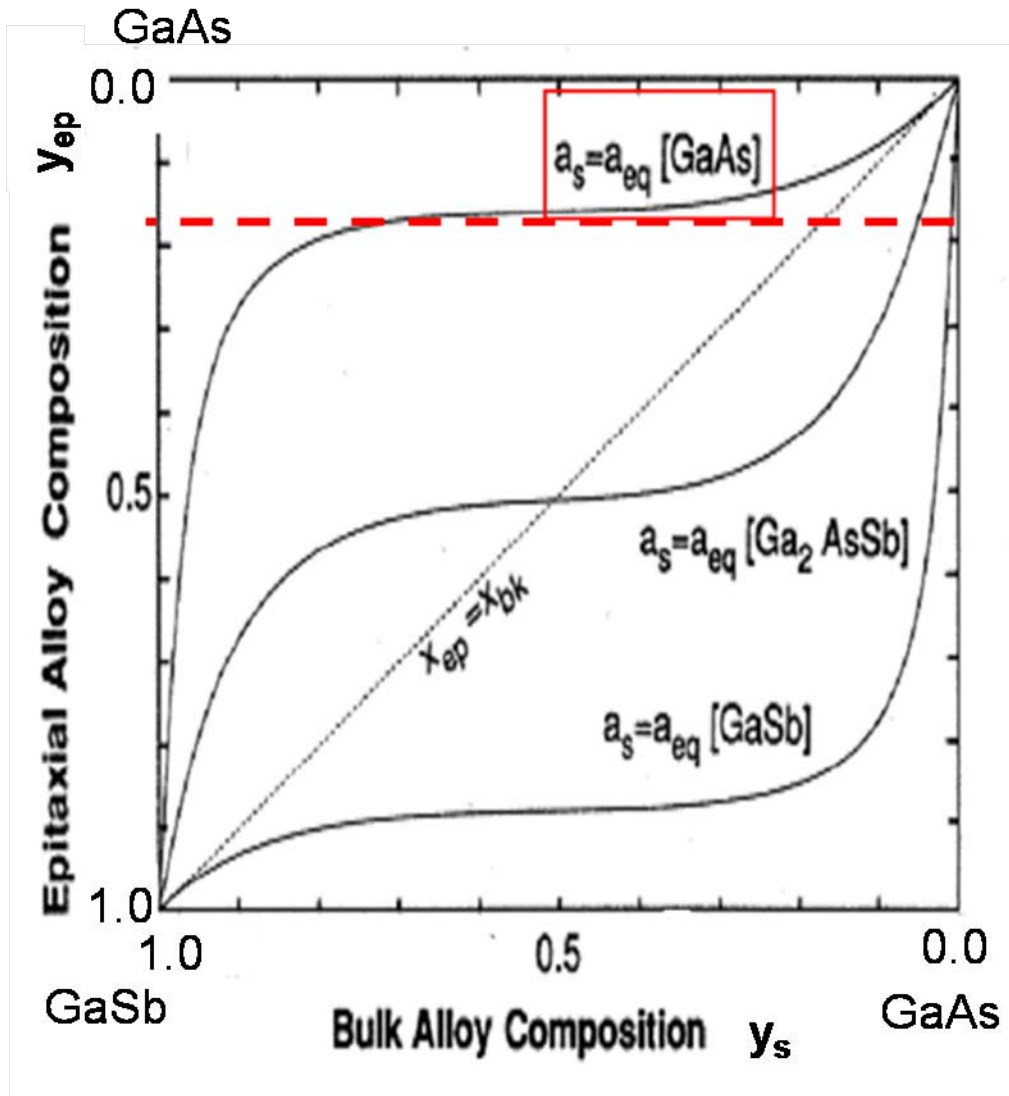
Coherently strained

Strain-dependent phase diagram



Materials Issues:

Strain modified Phase Stability



The composition is pinned over a substantial compositional range: 'lattice-latching'

Background:

- Miscibility gaps exist (probably the rule at T_{gr})
- Strain can modify this behavior
- Ranges of stability exist which must be maintained during growth

Growth and forming these materials despite some thermodynamic constraints

- Use Metal Organic Vapor Phase Epitaxy as example
- Look to the forming some models systems to Identify the possible approaches

Metal-organics - not just compound semiconductors

Metals: Nickel - $\text{Ni}(\text{CO})_6$

Insulators: SiO_2 - Tetraethyl orthosilicate,
 $\text{Si}(\text{OCH}_2\text{CH}_3)_4$
 B_2O_3 - Trimethyl Borate, $2\text{B}(\text{OCH}_3)_3 + 9\text{O}_2$
 BaTiO_3 ,
 HfO_2

Semiconductors: GaAs, InP, $\text{Al}_x\text{Ga}_{1-x}\text{As}$,

Metal-organics are used CVD – ALD, sol-gel, ..

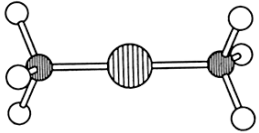
MOVPE Growth Precursors

- An ideal source should have an adequate vapor pressure
- Suitable purification routes
- Appropriate chemical reaction pathways

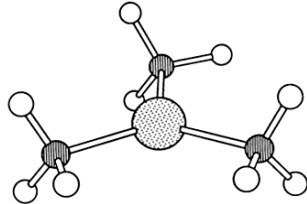
<u>Cation Source</u>	<u>Anion Source</u>	<u>Compound Semiconductor</u>
$Ga(CH_3)_3$	AsH_3	GaAs
$Ga(C_2H_5)_3$	$As(CH_3)_3$	$Al_xGa_{1-x}As$
$(C_2H_5)_2GaCl$ +	PH_3	$\rightarrow GaAs_yP_{1-y}$
$Al(CH_3)_3$	$(CH_3)_3PH_2$	$Al_xGa_{1-x}P$
$In(CH_3)_3$	$Sb(CH_3)_3$	$In_xGa_{1-x}Sb$

MOVPE Chemistry: The Sources

Typical examples



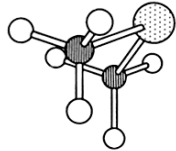
Dimethyl Zinc
 $(\text{CH}_3)_2\text{Zn}$



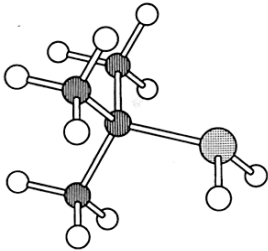
Trimethyl Ga - $(\text{CH}_3)_3\text{Ga}$



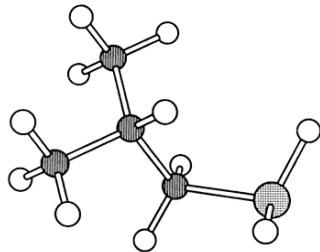
Arsine - AsH_3



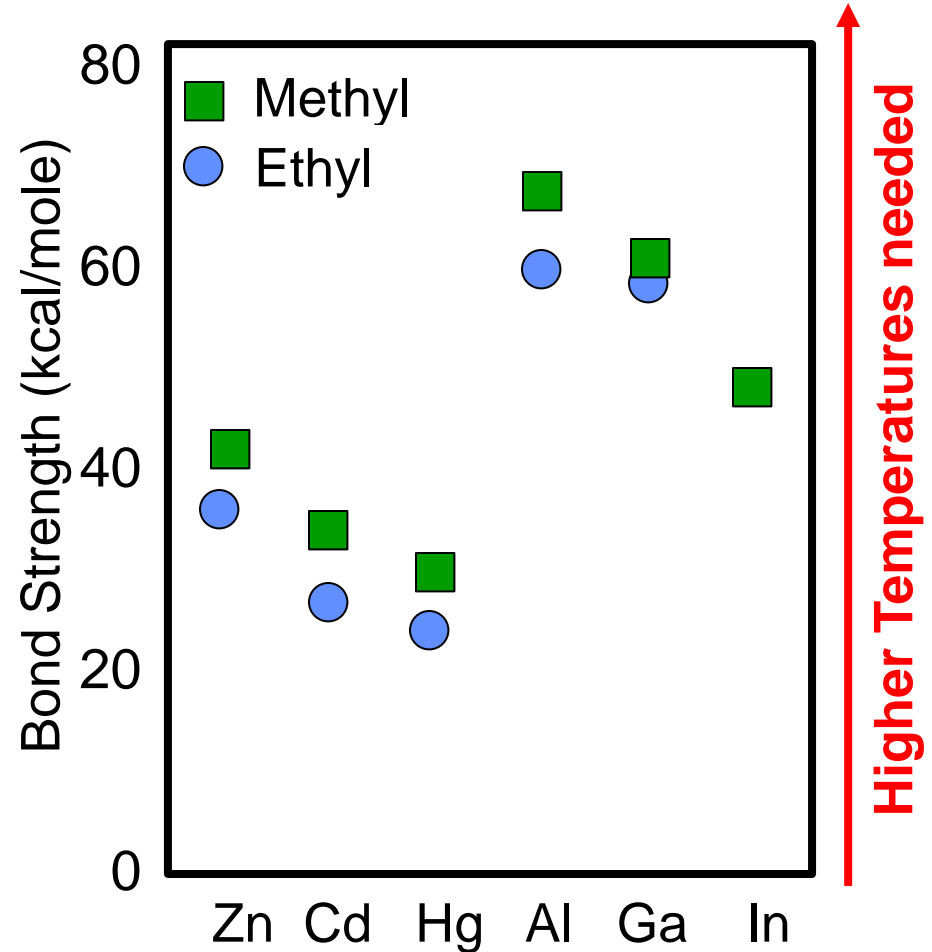
Dimethyl Te - $(\text{CH}_3)_2\text{Te}$



Tertiarybutyl As
 $\text{C}_4\text{H}_9\text{As}$

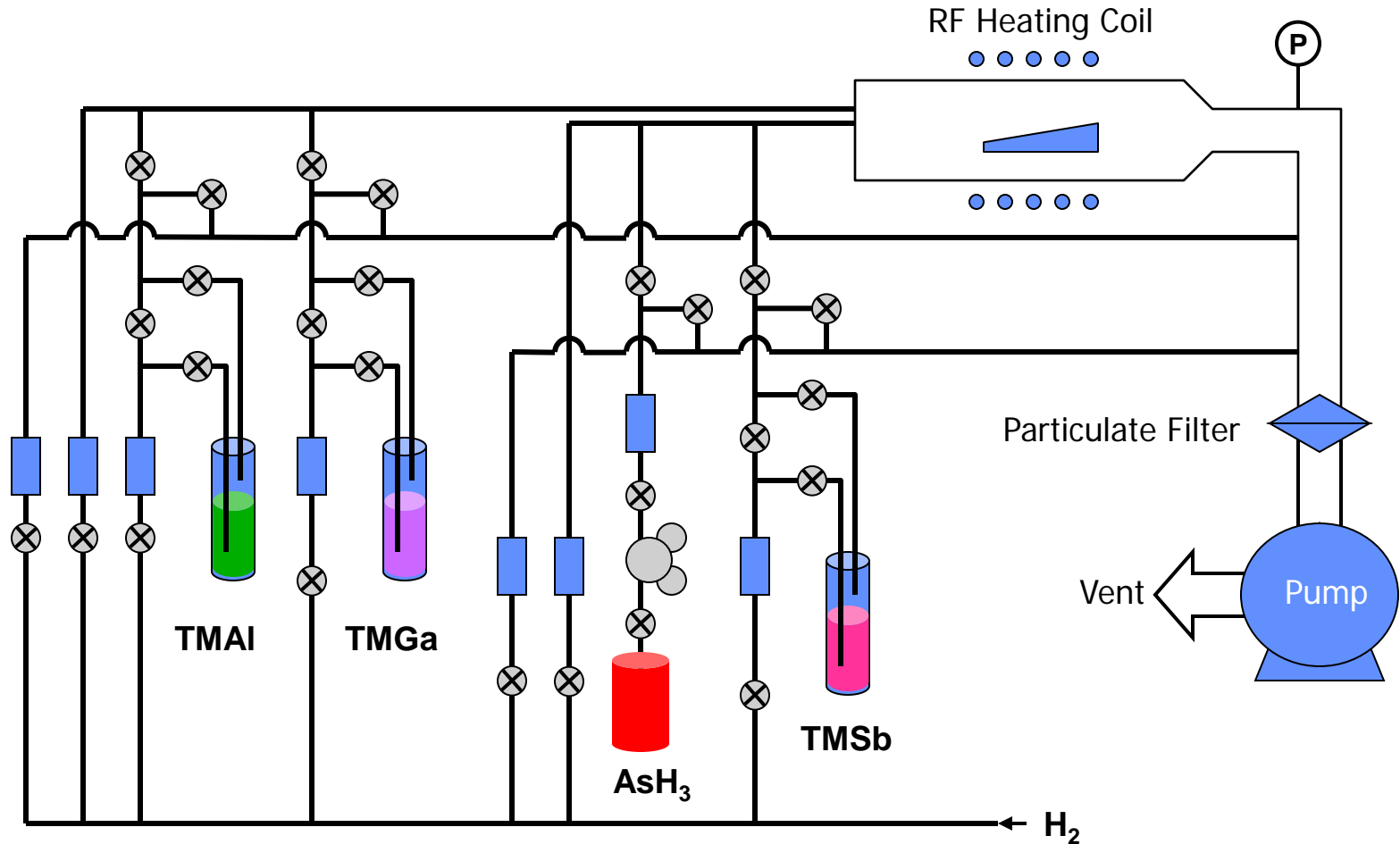


Isobutyl P
 $\text{C}_4\text{H}_9\text{P}$



MOVPE Background

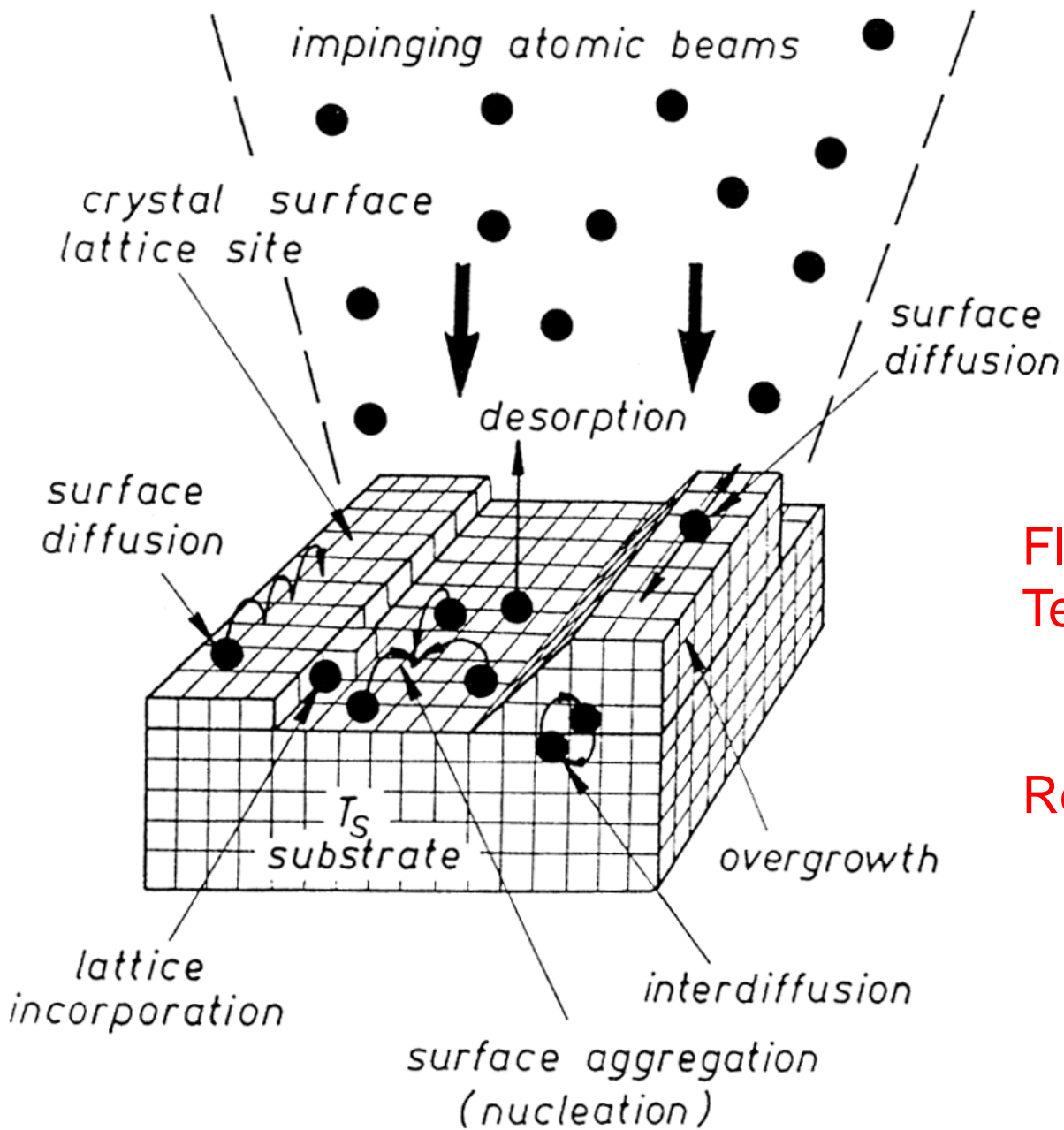
Simplified Reactor Diagram



Thin film formation: general issues

Requirements:

- Flux to the growth front
- Sufficient supersaturation
- Sufficient atomic mobility
- Epitaxial growth:
 - crystal orientation
 - lattice parameter
 - chemical bonding (wetting)



What processes can be altered to control the phase separation?

Flux to surface: Rate

Temperature:

surface mobility

solid state diffusion

Reactants:

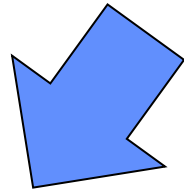
modify adsorption

Diffusion

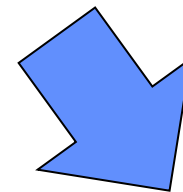
incorporation

Growth of complex alloys therefore needs:

Stabilization of the compositions against phase separation



Thermodynamically
stabilized phases by
→ temperature
→ strain

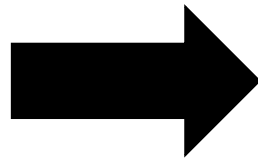
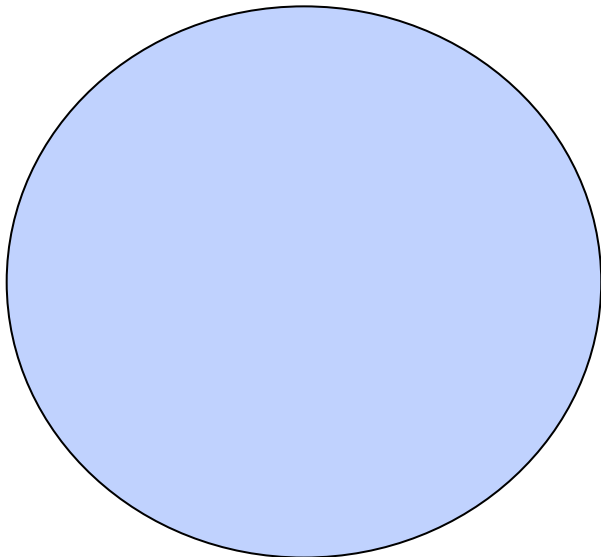


Kinetically stabilized

Prevent nucleation
and growth of the
separate phases

Kinetic stabilization: Prevention nucleation and the growth of the separate phases

Homogeneous but thermodynamically unstable



Nucleation of separate phases requires local mass transport and generation of inter-phase boundaries



Kinetic stabilization:

Prevent nucleation and the growth of the separate phases

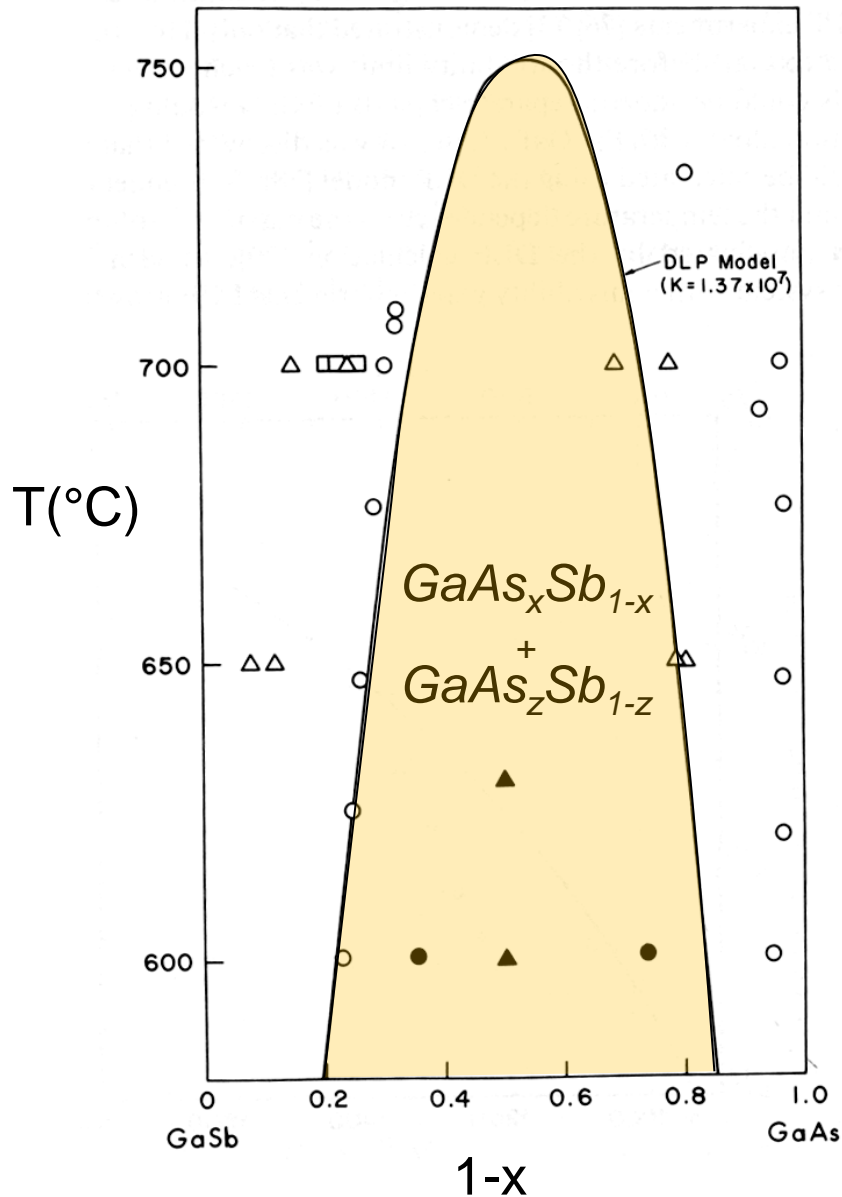
Nucleation - requires formation of phase boundaries and interphase surfaces

Solid Phase Mass transport – requires ‘defects’, temperature-activation, diffusion

Approaches for kinetic stabilization:

1. Low temperatures – reduce mass transport:
 - Lower solid state diffusion
 - Lowersurface diffusion
2. High growth rates - Minimize time for surface diffusion
3. Use of **surface chemistry**
 - Control surface reaction rates
 - Provide a limiting reactant
 - Alter surface diffusion pathways and rates
 - ‘surfactants’

Example: $GaAs_xSb_{1-x}$

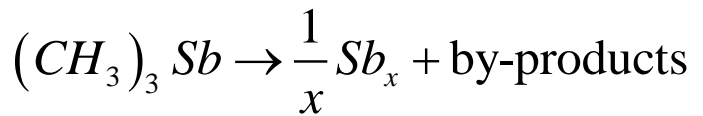
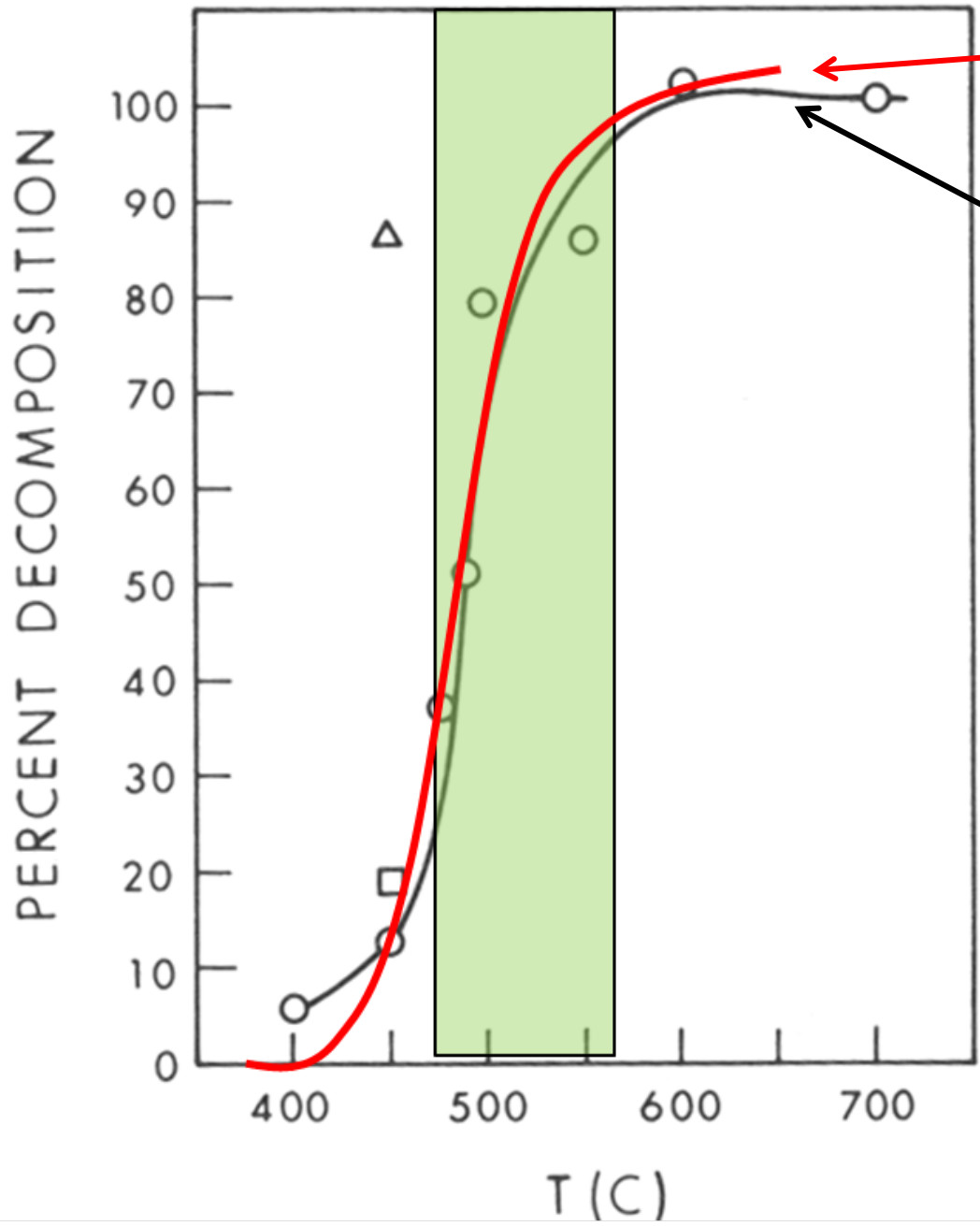


Due to the difference in bonding and anion size, the solid solution of $GaAs_xSb_{1-x}$ is not thermodynamically stable.

There exists, at equilibrium a two phase region at temperature used for the growth of the materials.

$$\Delta H_{f, GaAs}^0 = -20 \frac{\text{kcal}}{\text{mole}}$$

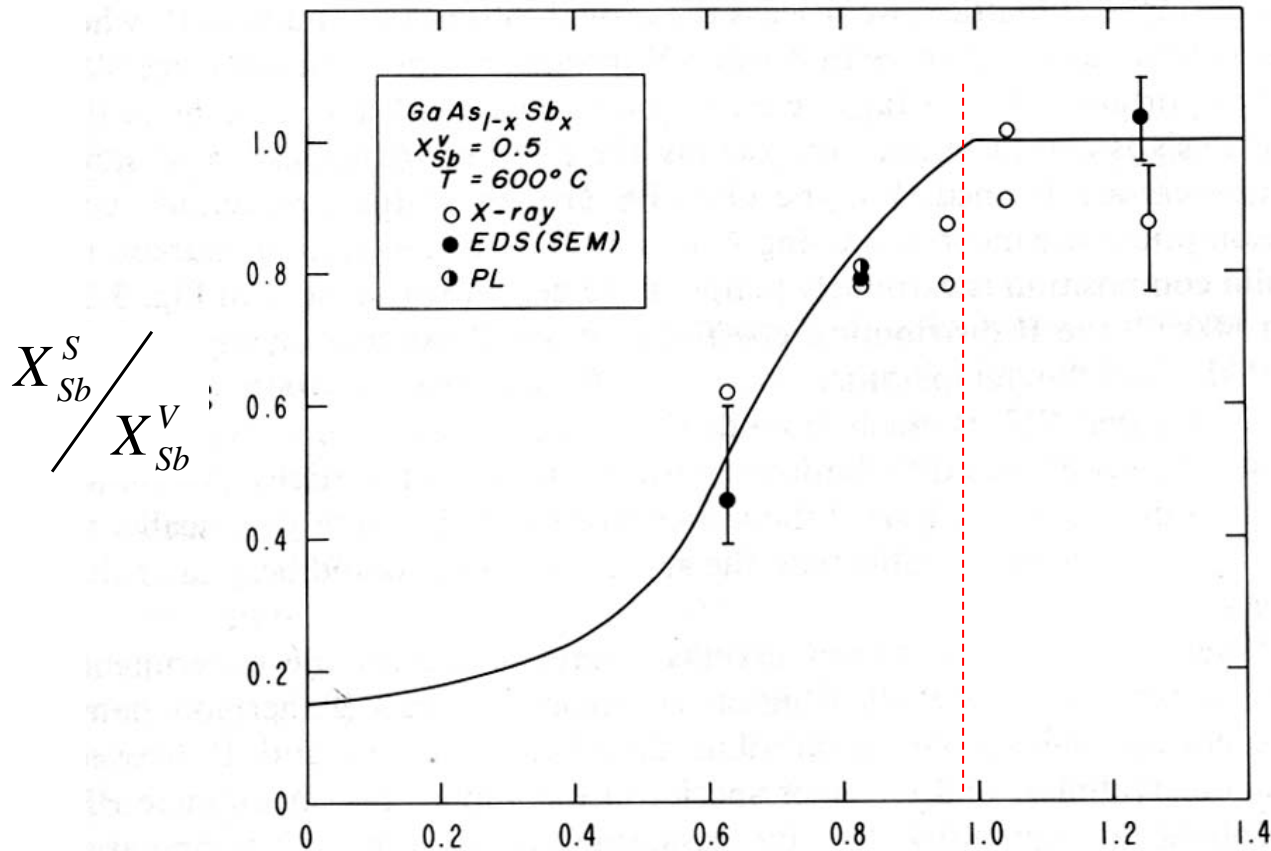
$$\Delta H_{f, GaSb}^0 = -9.5 \frac{\text{kcal}}{\text{mole}}$$



The reactants both decompose, either heterogeneously or homogeneously, at the growth temperature providing a ready supply of nutrients at the surface.

It would be expected that since Sb is less volatile, it would be preferentially incorporated. This behavior is not seen.

Immiscible Systems



Many Sb-based alloys exhibit complicated behavior in growth due to the interplay of kinetics and thermodynamics

As is preferentially incorporated over Sb.

$$\frac{V}{III} = \frac{[Sb]_v + [As]_v}{[Ga]_v}$$

Thermodynamic analysis of growth

$$\left. \begin{aligned} \frac{a_{GaSb}}{p_{Ga}^i (p_{Sb_4}^i)^{1/4}} &= K_{GaSb} \\ \frac{a_{GaAs}}{p_{Ga}^i (p_{As_4}^i)^{1/4}} &= K_{GaAs} \end{aligned} \right\} \text{Thermodynamic equilibrium at the interface}$$

$$\Delta H_{f,GaAs}^0 = -20 \frac{\text{kcal}}{\text{mole}}$$

$$\Delta H_{f,GaSb}^0 = -9.5 \frac{\text{kcal}}{\text{mole}}$$

$$x = \frac{(p_{Sb_4}^* - p_{Sb_4}^i)}{p_{Sb_4}^* - p_{Sb_4}^i + p_{As_4}^* - p_{As_4}^i}$$

Constraint on composition

$$p_{Ga}^* - p_{Ga}^i = 4(p_{Sb_4}^* - p_{Sb_4}^i + p_{As_4}^* - p_{As_4}^i)$$

Constraint on Stoichiometry

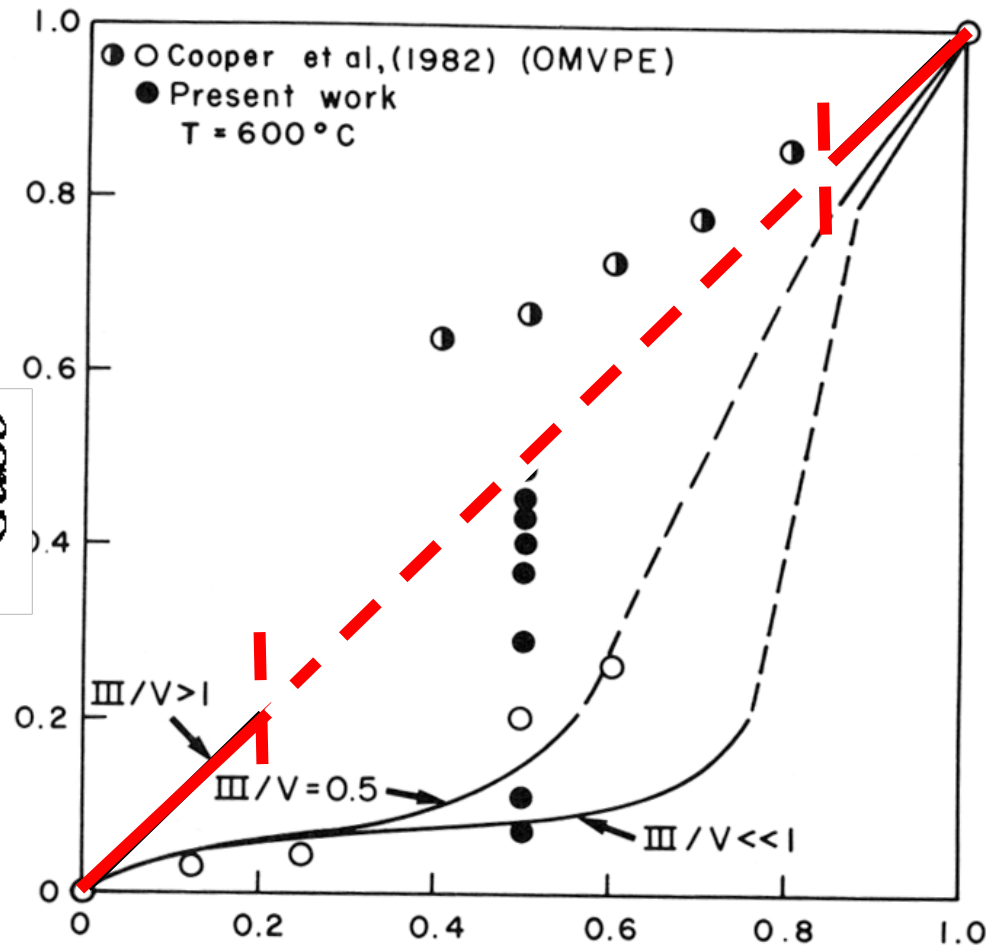
$p_{species}^*$ \Rightarrow value at the reactor inlet

$p_{species}^i$ \Rightarrow value at the interface

4 equations, 4 unknowns

$x, p_{Ga}^i, p_{As_4}^i, p_{Sb_4}^i$

Growth of $\text{GaAs}_y\text{Sb}_{1-y}$



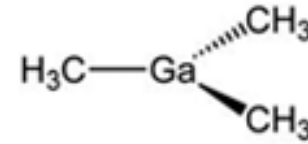
$$\frac{P_{\text{Sb}}^0}{P_{\text{Sb}}^0 + P_{\text{As}}^0}$$

Since GaAs is more stable than GaSb and all reactive species are in ready supply, **thermodynamic influences** can determine the composition.

This is shown in red:
 $\text{V}/\text{III} > 1$

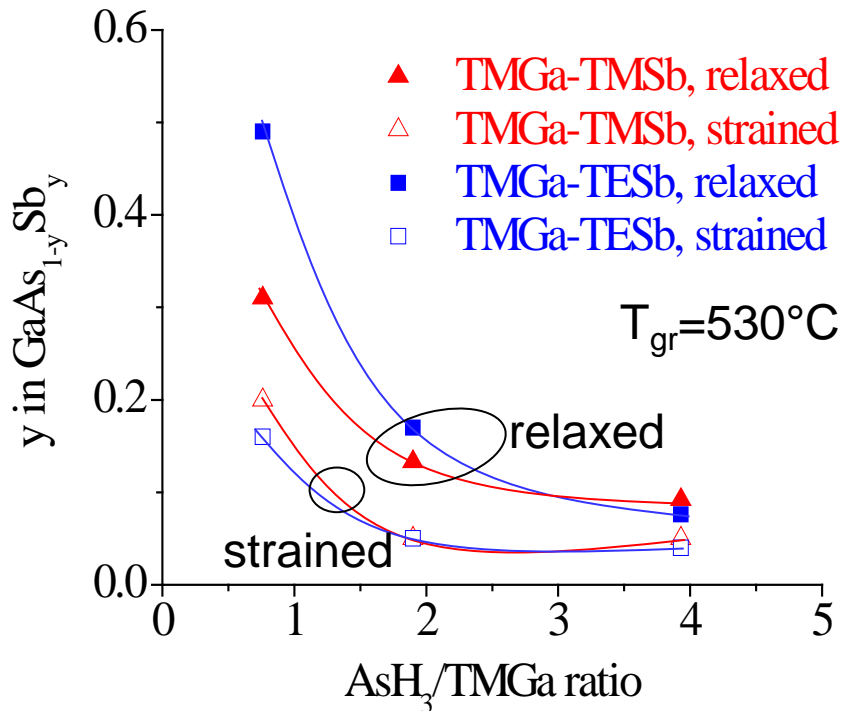
The complete range of compositions can be formed if the $\text{V}/\text{III} < 1$. This means the deposition of the anions proceed and the material is limited by the arrival of Ga.

Chemical influences: $(\text{CH}_3)_3\text{Ga}$ Growth



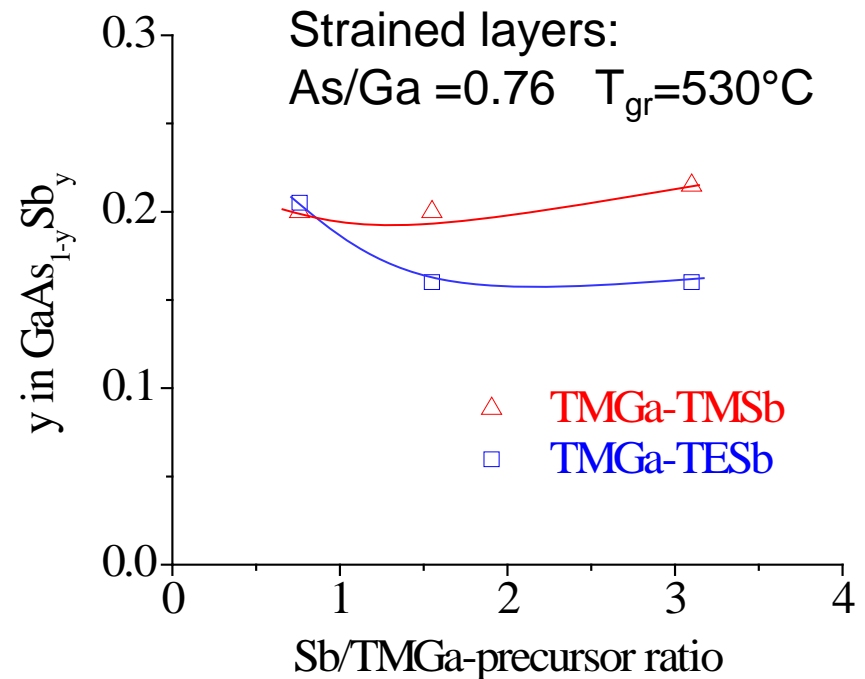
Effect of AsH_3/TMGa ratio

- Sb-mole fraction decrease monotonically for strained and relaxed layers
- $y = 0.05$ for all $\text{AsH}_3/\text{TMGa} > 1$

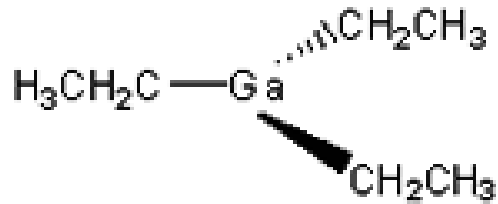


Effect of Sb/TMGa-precursor ratio

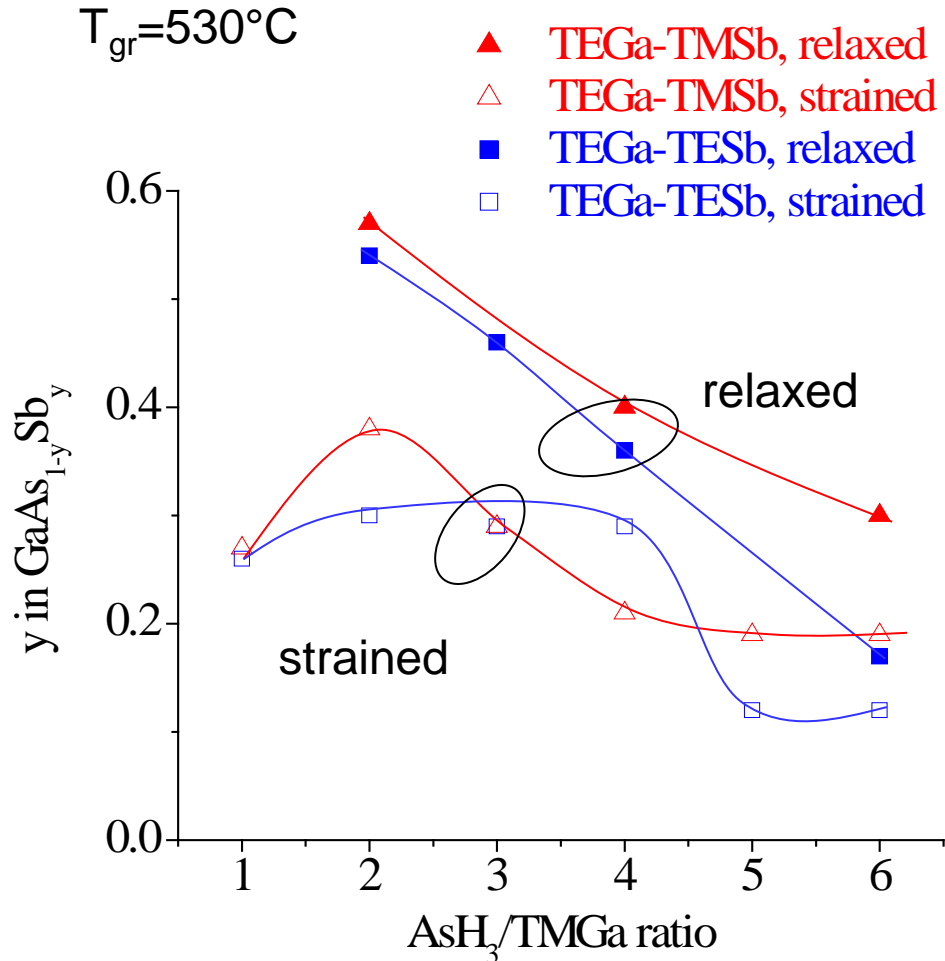
- Almost constant Sb-mole fraction with the Sb-flux variation



Chemical influences: $(C_2H_5)_3Ga$ Growth



$T_{gr}=530^\circ C$



Effect of $AsH_3/TEGa$ -ratio

- Sb-mole fraction in the relaxed $GaAs_{1-y}Sb_y$ layers decreases monotonically
- Higher Sb-incorporation compared to the TMGa-case

Effect of Sb/TEGa-ratio

- Sb-mole fraction increases almost linearly with Sb/TEGa-ratio
- No saturation behavior for Sb-incorporation

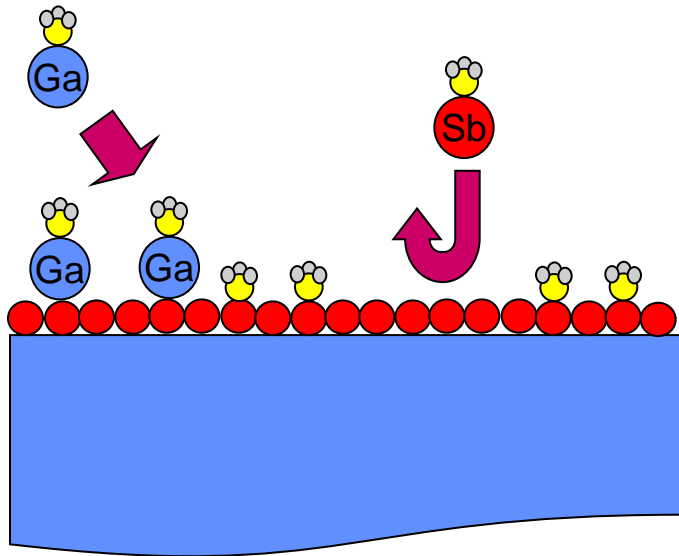
Observations

- Sb-mole fractions are limited to $y \leq 0.2$ in strained $\text{GaAs}_{1-y}\text{Sb}_y$ layers grown using **methyl-** Ga and Sb precursors *not ethyl* sources
- Thermodynamic limitations on the Sb-incorporation can be bypassed by controlling the MOVPE growth kinetics
- Ga- and Sb- precursor chemistry and growth temperature alters the Sb-incorporation efficiency for strained and relaxed $\text{GaAs}_{1-y}\text{Sb}_y$ layers.

TMG-based chemistries: $(CH_3)_3Ga$ decomposition to Ga requires dissociative surface adsorption as CH_3Ga



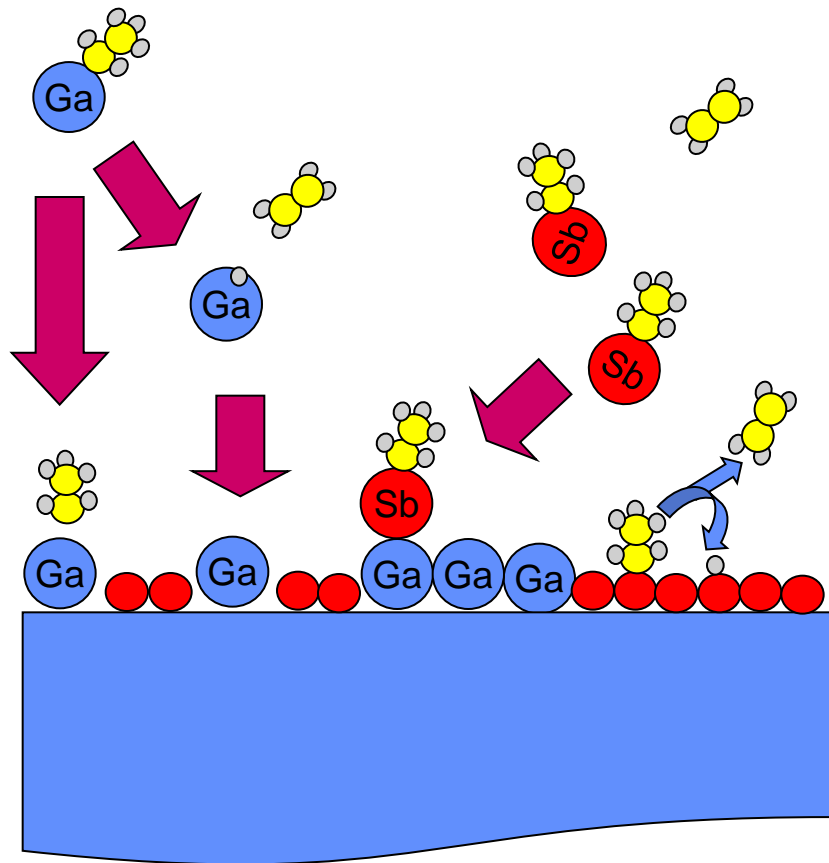
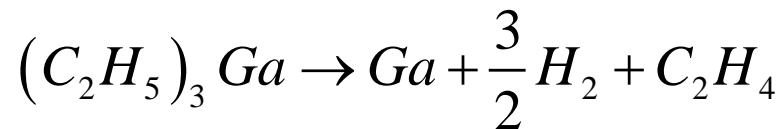
Strained-layer growth, surface segregated Sb saturates but at different levels depending on Sb-precursor



- Thermodynamic limit Sb to $y \sim 0.2$ – Sb segregation
- Sb increase with growth temperature
- Sb overlayer slows adsorption and decomposition of Sb source
- Sb- trapping evident

TEG-based chemistries:

Gas-phase decomposition of TEGa to elemental Ga via β -hydride elimination reaction



- Ethyl groups completely removed at $<350^\circ\text{C}$
- Higher Ga-surface coverage, independent of Sb-coverage
 - Provides sites for Sb incorporation

Methyl Sources

- High decomposition temperatures
- Heterogeneous reactions requiring surface reaction site
- Steady-state Sb coverage (requiring growth interruptions and procedures)

Ethyl Sources

- Low decomposition temperatures – leaves elemental Sb and Ga on surface
- Reactivity and hence Sb incorporation is not limited by the heterogeneous reactivity of the source

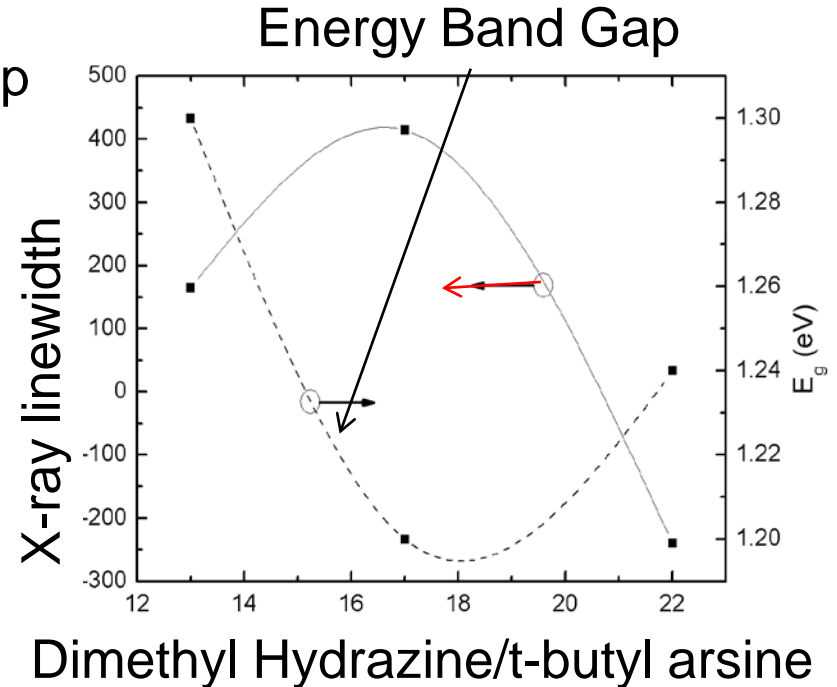
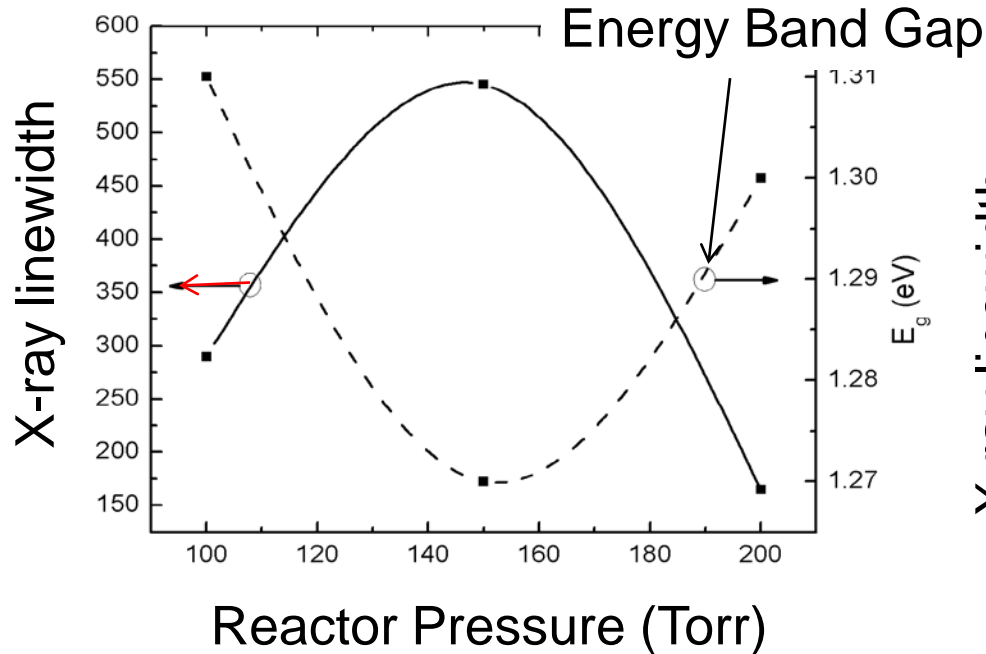
- *Thermodynamic influences alone are insufficient to describe all results: surface chemistry can alter the composition and surface compositions*
 - Lattice-latching should limit composition at equilibrium in strained growth
 - Wide miscibility gap in relaxed growth
- *Excess Sb-layer on growth surface (~0.8 ML) due to Sb-surface segregation¹*
 - Higher Sb surface coverage for strained GaAs_{1-y}Sb_y layers due to the lower incorporation rate

¹R. Kaspi and K. R. Evans, J. Crystal Growth 175-1762, 838 (1997)

GaSbN - Growth

- GaSbN grown on GaSb substrates:
 - MBE (QinetiQ Ltd.), JCG **278** (2005) 188
 - LPE (Univ. Calcutta), JCG **297** (2006) 4
 - MOVPE (this work)
- GaAsSbN grown by MOVPE:
 - GaAs sub (Sandia), JCG **261** (2004) 398
 - InP sub (UW-Madison), JCG **310** (2008) 2382
 - GaSb sub (this work)

GaInNAsSb – Balancing Strain in Multinaries



- Optimal reactor pressure ~150 Torr
- DMHy/TBAs – figure of merit for N incorporation*
 - Reduce TBAs molar flow
 - III, Sb mol fraction constant

- Optimized DMHy/TBAs is 17-18 for $P = 150$ Torr
- GaInNAsSb films for DMHy/TBAs ≥ 21 **



*Volz, K. et al. *J. Cryst. Growth*, vol. 311, (2009) p. 2418-2426
 **Geisz, J. F., Friedman, D. J., *Semicond. Sci. Technol.*, vol. 17, (2002) p.769-777

Summary of MOVPE Growth Chemistry Issues:

Simple Binary semiconductors: the metal source decomposes rapidly, the anion is in excess

Mixed Cation systems, $\text{Al}_x\text{Ga}_{1-x}\text{As}$, $\text{In}_x\text{Ga}_{1-x}\text{As}$, $\text{In}_x\text{Ga}_{1-x}\text{P}$, ..., are easily grown with the solid and gas phase compositions being equal.

Mixed Anion systems, $\text{GaAs}_x\text{P}_{1-x}$, $\text{GaAs}_x\text{Sb}_{1-x}$, $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$, ..., are more complex with both kinetic and thermodynamically-limited alloy formation seen.

Conclusions: New complex multinary alloys can be formed through an understanding of the chemical and physical processes of crystal growth

Thermodynamic influences involving strain can lead to phase stable alloys under some conditions

- Accurate phase diagrams for multinary alloys need to be developed
- Modifications to these diagrams due to epitaxy related strains are known only for a few systems

Kinetic stabilization can produce metastable alloys

- low temperatures
- High flux rates
- Chemical considerations

Dilute-nitride materials “lattice matched” to GaAs

- Historically, III/V semiconductor compounds containing dilute amounts of nitrogen (~2-3% N) have high background hole concentrations due to unintentional incorporation of carbon.
- Result of N incorporation:
 - Thin depletion widths¹
 - Low luminescent properties¹
 - Deep level defects¹
- Quaternary materials
 - No prior reports of GaInAsSbP(N) materials
 - LPE growth of GaInAsSbP/GaSb for mid-infrared light sources and detectors^{2,3}

1. Geisz, J. F., Friedman, D. J., *Semicond. Sci. Technol.*, vol. 17, (2002) p.769-777.

2. A. Krier, et al., *Appl. Phys. Lett.*, **91** (2007) 082182.

3. A. Krier, et al., *Appl. Phys. Lett.*, **90** (2007) 211115.