بسم الله الرحمن الرحيم

Fundamentals of MBE

Chapter 11: Segregation of Atoms

Segregation and Its Importance

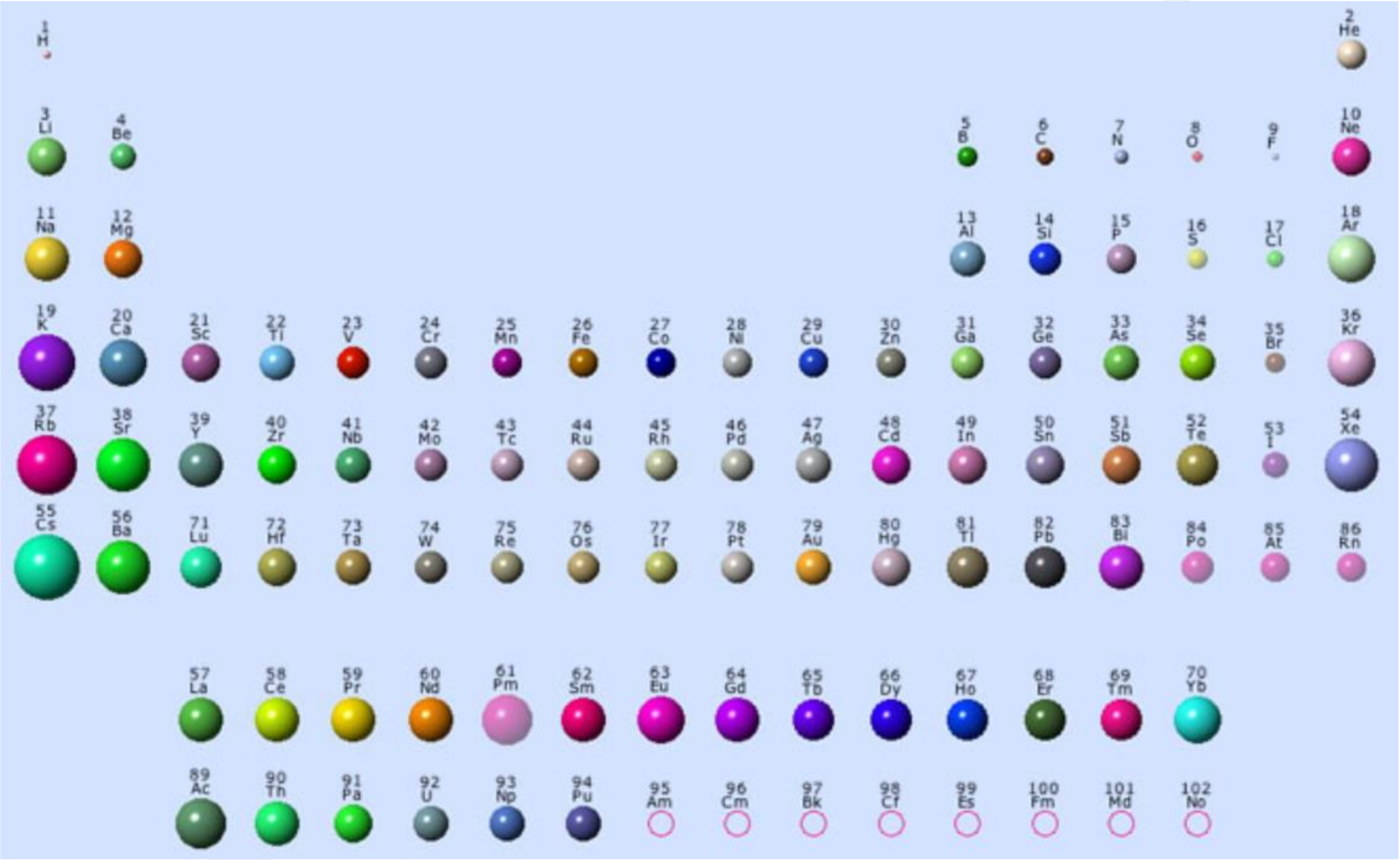
Atomic Segregation

- For low growth temperatures (for example 600^{o}C in AlGaAs/GaAs system), atoms have less chance to rearrange after burial under upcoming layers.
- However, due to the surface mobility, atoms can displace on the growing surface.
- Higher growth temperature leads to the increase of the surface mobility that can result in smoother surface; however, it also causes the so-called surface segregation that is the exchange between the sub-layer atoms with the impinging atoms on the growing surface.
- Several experimental and theoretical studies indicate that both group III and V atoms with weaker bond strength and elastic energy segregate to the surface.

Atomic Segregation

- For example, on the well-known AlGaAs/GaAs QW system, theoretical and experimental results show “Ga” segregation in AlGaAs layer that can cause a composition asymmetry at the normal interface for both AlGaAs/GaAs and GaAs/AlGaAs growths.
- The composition asymmetry at the interfaces results in the change of the energy band alignment of the quantum structures, which alters the optoelectronic properties.
- Therefore, to design an optoelectronic device based on the III-V semiconductor structures, it is important to predict and compensate the concentration profile change due to the segregating of atoms.

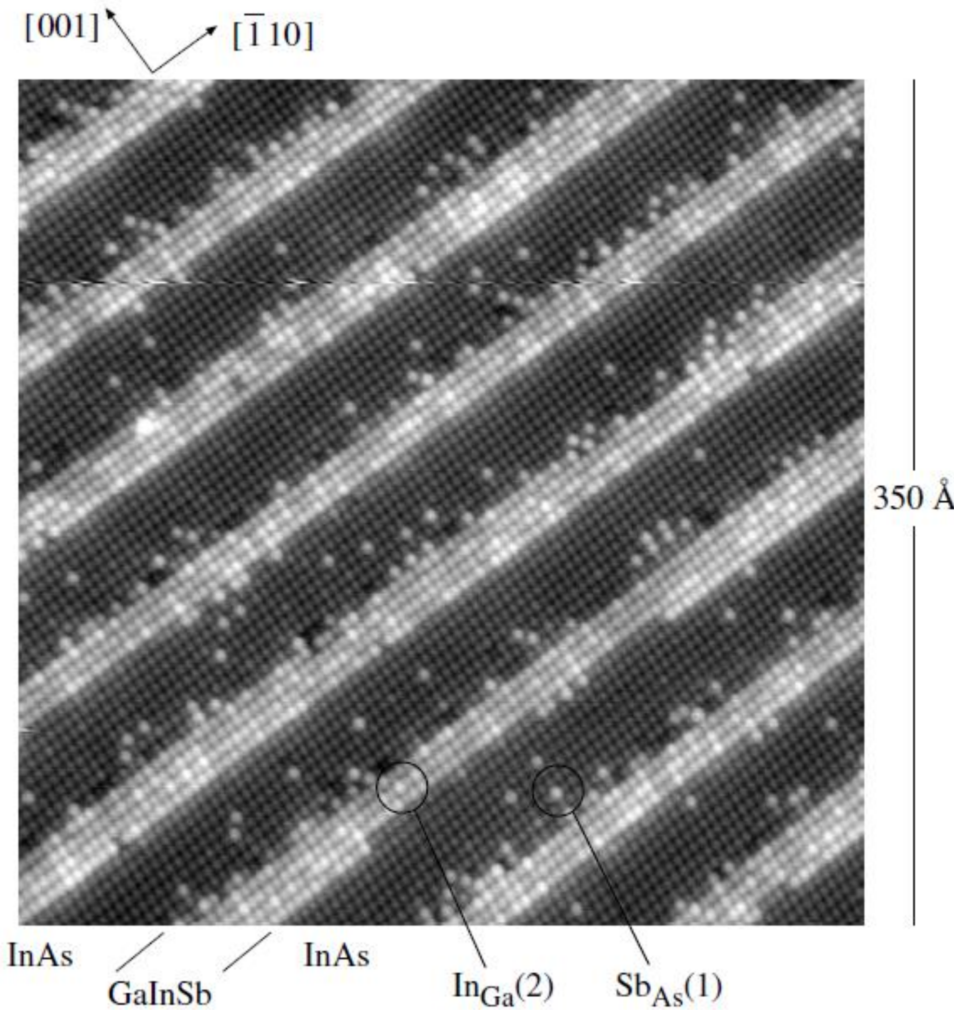
Periodic Table



Segregation Realization in Type II SLS

- Segregation is an inherently asymmetric process that reflects a layer-by-layer competition, during growth, between strain- and/or bond – strength energies that favor expulsion of certain atoms to the surface and entropic factors that account for the tendency to nonetheless incorporate a fraction of these atoms in successively buried epitaxial layers.

- Type of Segregations in this sample:
  1. Sb Segregation
  2. In Segregation



Lattice disorder at interfaces → **No interface abruptness**

Origin of Antimony Segregation in GaInSb/InAs Strained-Layer Superlattices; J. Steinshnider, J. Harper, and M. Weimer; PRL_85_21; 2000

The Driving Force of Segregation

What Is The Driving Force for Segregation?

- Segregation is driven by:
  - 1- Difference in binding energy
  - 2- Difference in elastic energy

- Segregation in III-V compounds results in:
  - 1- Gradual composition
  - 2- Surface enrichment of one of the incorporated group III elements

Dehaese et la., Appl. Phys. Lett. 66 (1), 1995

Does Segregation Depend on The Growth Conditions?

- The profile of the segregating atom in the structure does change with the following growth parameters:

1) Growth Temperature (T_g) $\uparrow$ — Segregation $\uparrow$
2) Growth Rate $\uparrow$ — Segregation $\downarrow$
3) III/V Ratio $\uparrow$ — Segregation $\uparrow$

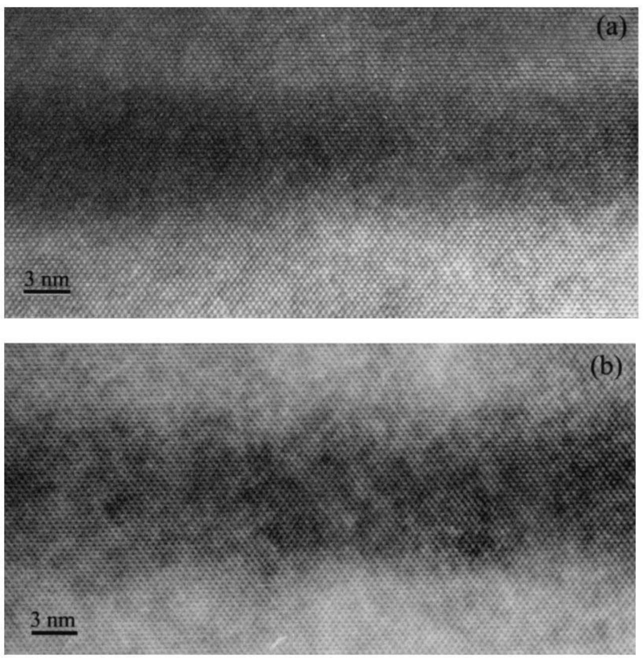
What are the influences of segregation on the characteristic properties of III-V structures?

- Composition of the grown layers changes ➡ Band lineup of the heterostructure changes ➡ Optoelectronic properties of the heterostructure change.
- “Al” atoms segregated in AlGaSb/GaSb QW.

AlGaSb

GaSb

AlGaSb



450°C

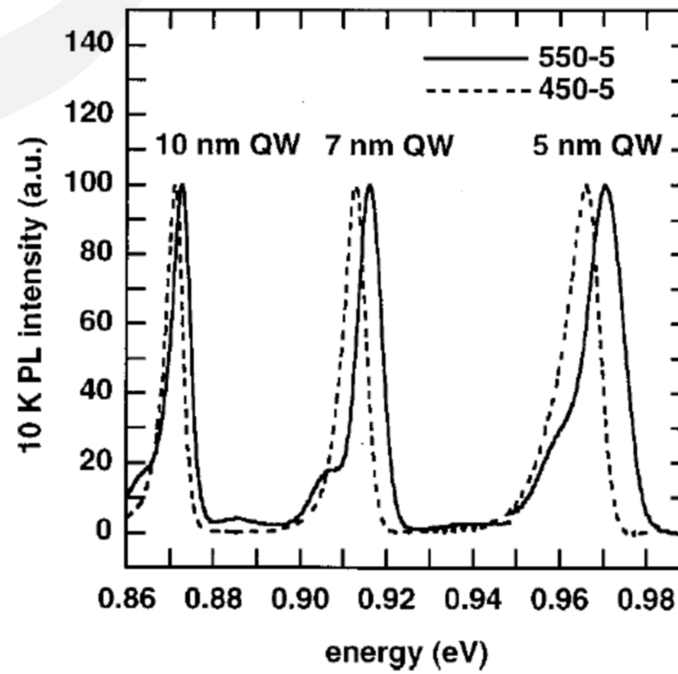
550°C

AlGaSb

GaSb

AlGaSb

➡

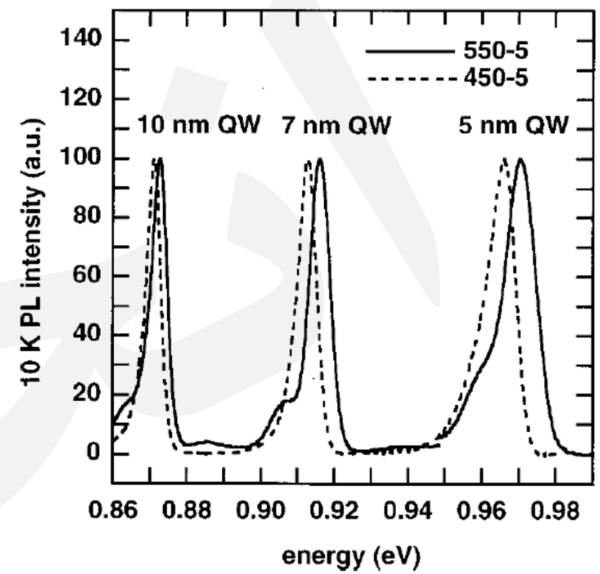


Dehaese et la., Appl. Phys. Lett. 66 (1), 1995

How can we characterize the segregation?

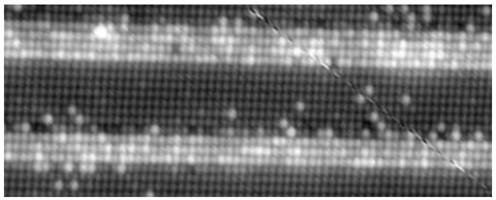
1- Experimental measurements:

- Reflection High Energy Electron Diffraction (RHEED).
- Secondary Ion Mass Spectroscopy (SIMS).
- High Resolution X-ray Diffraction (HRXRD).
- High Resolution Transmission Electron Microscopy (HRTEM).
- Photoluminescence (PL).
- Etc.



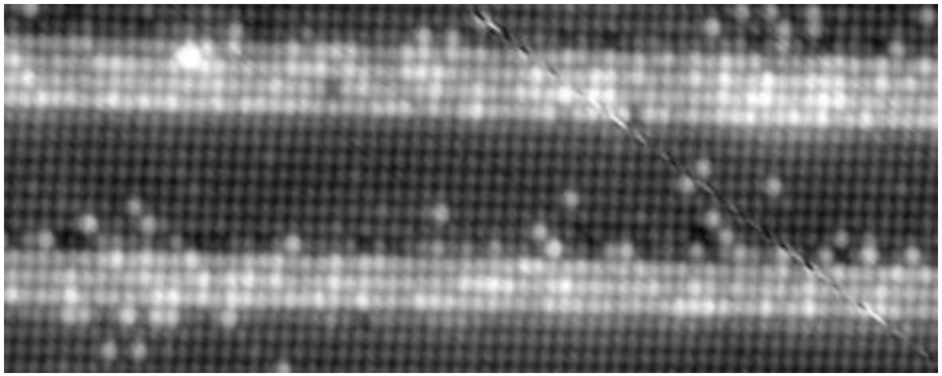
2- Theoretical models:

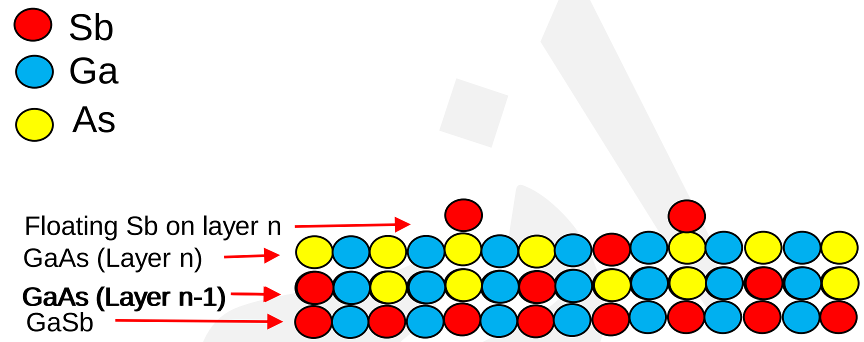
A. Muraki's Model
B. Kinetics Model
C. Kinetics Monte Carlo Simulation(KMC)



A) Muraki's Model

Sb Segregation with no Sb Background Gas





No Background Gas:

- تعداد اتمهایی که در لایه n قرار دارند برابر هستند با R درصد از اتمهای n-1.

$$x_f^n = R x_f^{n-1} \quad \text{(Eq-1)}$$

- تعداد اتمهایی که در لایه n را تشکیل می دهند(X^n_{inc}) برابر هستند با:

$$x_f^{n-1} - x_f^n = x_{inc}^n \quad \text{(Eq-2)}$$

(Eq-1, 2) ⇨ $$x_{inc}^n = x_f^{n-1} - R x_f^{n-1} = x_f^{n-1}(1-R) \quad \text{(Eq-3)}$$

- In which, "X_f" is the floating "Sb", "R" is the segregation ratio of the previous antimony into the next layer, "X_{inc}" is the "Sb" that incorporated to epitaxial growth.

Sb Segregation with Sb Background Gas

- When we have Sb background Gas, Eq-1 become:

$$x_f^n = R\left(x_f^{n-1} + x_o\right) \qquad \text{(Eq-4)}$$

x_o^{sb} = The excessive Sb from the background pressure.

$$\underbrace{\left(x_f^{n-1} + x_o\right)}_{\text{Floating Sb on layer n-1}} - \underbrace{\left(Rx_f^{n-1} + Rx_o\right)}_{\text{The segregated Sb from n-1 to n layer}} = x_{inc}^n \qquad \text{(Eq-5)}$$

$$x_{inc}^n = x_f^{n-1} - Rx_f^{n-1} + x_o - Rx_o = x_f^{n-1}(1-R) + x_o(1-R) \qquad \text{(Eq-6)}$$

$$\boxed{x_{inc}^n = (1-R)\left(x_f^{n-1} + x_o\right)} \qquad \text{(Eq-7)}$$

Sb Segregation with Sb Background Gas

- From Eq-4:

$$x_f^n = R\left(x_f^{n-1} + x_o\right)$$

$$x_f^0 \equiv x_i$$

$$x_f^1 = R\left(x_f^0 + x_o\right) = R\left(x_i + x_o\right) = Rx_i + Rx_o$$

$$x_f^2 = R\left(x_f^1 + x_o\right) = R\left[\left(Rx_i + Rx_o\right) + x_o\right] = R^2x_i + R^2x_o + Rx_o$$

$$= R^2x_i + x_oR(R+1)$$

$$x_f^3 = R\left(x_f^2 + x_o\right) = R\left[\left(R^2x_i + x_oR(R+1)\right) + x_o\right]$$

$$= R^3x_i + x_oR(R^2 + R + 1)$$

$$x_f^n = R^nx_i + x_oR(R^{n-1} + R^{n-2} + \cdots + R + 1) \quad \text{(Eq-8)}$$

- بخشی از رابطه ی فوق $(R^3 + R^2 + R + 1)$ یک سری هندسی است، با مقدار اولیه 1 و قدر نسبت R
- از این سری هندسی داریم:

$$\sum_{k=0}^{n} ar^k = ar^0 + ar^1 + ar^2 + ar^3 + \cdots + ar^n = \frac{a(1-r^{n+1})}{1-r}. \quad \text{(Eq-9)}$$

Sb Segregation with Sb Background Gas

- From Eq-8 and 9:

$$x_f^n = R^n x_i + x_o R \frac{1-R^{n+1}}{1-R} \quad \text{یا} \quad x_f^{n-1} = R^{n-1} x_i + x_o R \frac{1-R^n}{1-R} \qquad \text{(Eq-10)}$$

- From Eq-7 and 10:

$$x_{inc}^n = (1-R)\left(x_f^{n-1} + x_o\right) = (1-R)\left(R^{n-1}x_i + x_o R\frac{1-R^n}{1-R} + x_o\right)$$
$$= (1-R)R^{n-1}x_i + x_o R\,(1-R^n) + x_o(1-R)$$
$$= x_i R^{n-1}(1-R) + x_o R - x_o R^n + x_o - x_o R$$

$$\boxed{x_{inc}^n = \underbrace{x_i R^{n-1}(1-R)}_{\text{Sb Falloff}} + \underbrace{x_o(1-R^n)}_{\text{Sb Background Incorporation}}} \qquad \text{(Eq-11)}$$

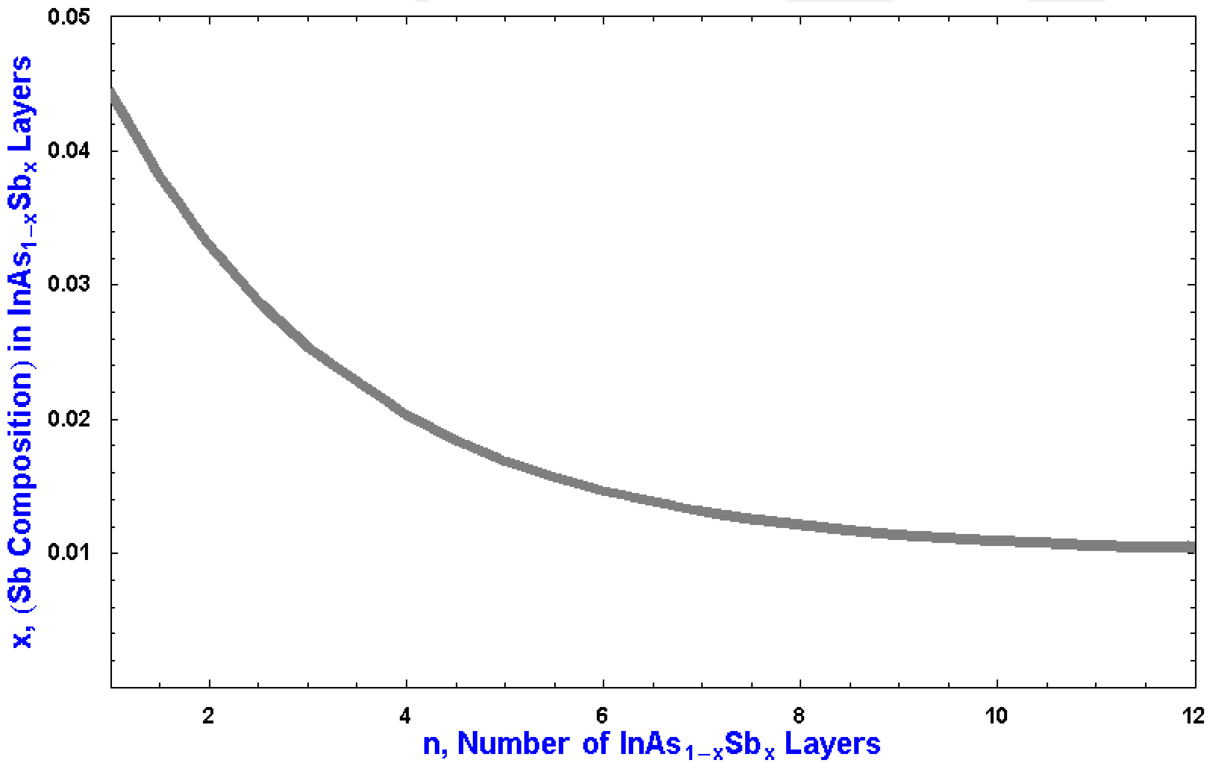
Sb Segregation in Type II SLS

- From Eq-11:

$$x^{Sb}(n) = x_i^{Sb} R^{n-1}(1-R) + x_o^{Sb}(1-R^n)$$

$x^{Sb}(n)$ = The Sb Composition at the n^{th} layer of the InAs.
x_i^{sb} = An initial impurity fraction on the finished GaSb.
x_o^{sb} = The excessive Sb from the background pressure.
R = The segregation ratio of the previous antimony into the next layer .

- "Sb" Incorporation "x" for GaSb/InAs SLS at 400°C with x_i^{Sb}=0.124, x_o^{Sb}=0.010, and R=0.67.



In Segregation in Type II SLS

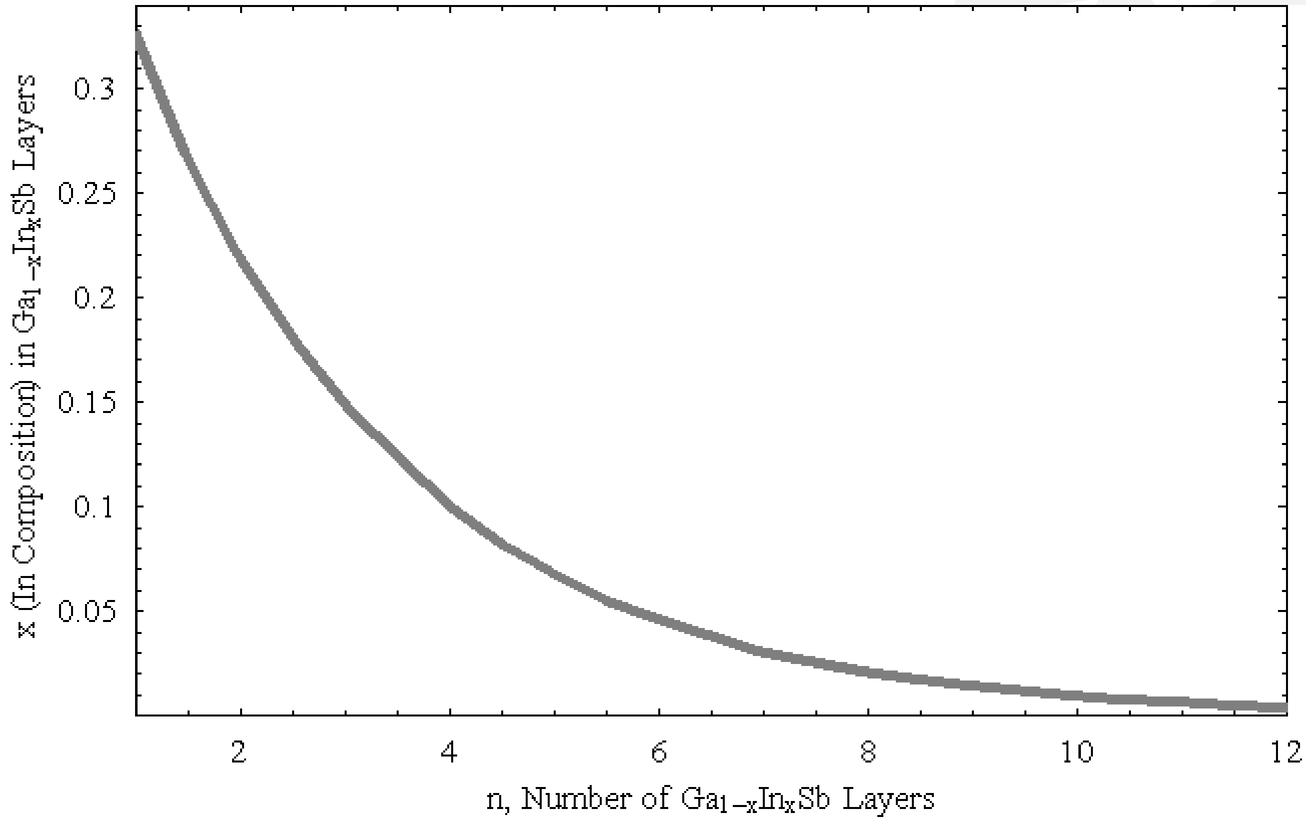
$$x^{In}(n) = x_i^{In} R^{n-1}(1-R)$$

$x^{In}(n)$ = In Composition at the n^{th} layer of the GaSb.

x_i^{In} = The nominal In Composition on the Seed layer.

R = The segregation ratio of the previous layer to the next layer.

- In Incorporation "x" for GaSb/InAs SLS at 400^{o}C with x_i^{In}=1.0, and R=0.66.

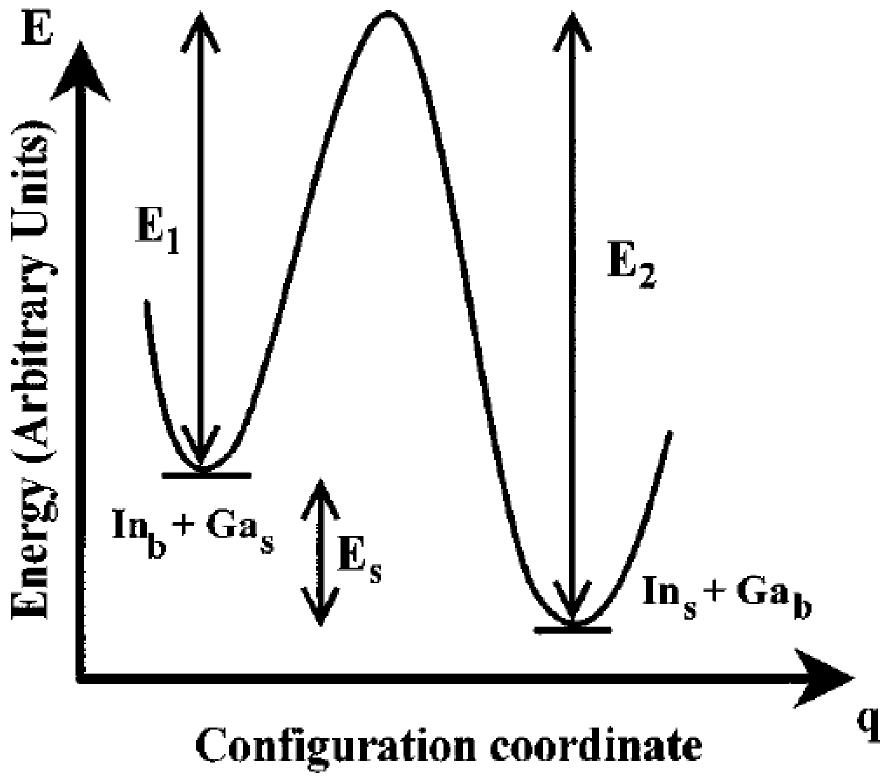


- In Segregation can be detected by RHEED

B) Kinetic Model

What is The Kinetic Model?

- E_1 = Barrier energy for "In" atom segregation to the surface.
- E_2 = Barrier energy for "Ga" atom segregation to the surface.
- E_s = segregation energy.



What is The Kinetic Model?

- Tow exchange process are competing during the growth:

1- Exchange between the atoms in the bulk with the atoms on the surface:

The exchange process is achieved by overcoming an energy barrier E_1 with an exchange rate:

$$P_1 = \nu_1 exp\left(-\frac{E_1}{k_B T}\right)$$

- In which "T" is growth temperature (°K), $"k_B"$ *is* Planck constant "ν" is Effective hopping frequency.

2- Exchange between the atoms on the surface with the atoms in the bulk:

The reverse exchange is also possible but needs to pass over an $E_2 = E_1 + E_s$ energy barrier and has an reverse exchange rate:

$$P_2 = \nu_2 exp\left(-\frac{E_2}{k_B T}\right)$$

What is The Kinetic Model?

- Segregation occurs only due to the exchange process in $A_xB_{1-x}C$/ BC system (A and B = group III, C = group V).
- Segregation driving force (E_s) is determined as:

$$E_s = E_{A/B}^{s\to b} - E_{A/B}^{b\to s}$$

- Assuming that the segregation is only due to the exchange processes, the balance of the incoming to and leaving atoms from the surface gives the evaluation of the number of atom-A on the surface.
- The evolution of the number of "A" surface atoms is given by the balance of incoming and leaving "A" atoms:

$$\frac{dX_A^s(t)}{dt} = \Phi_A + P_{A/B}^{b\to s} X_A^b(t) X_B^s(t) - P_{A/B}^{s\to b} X_A^s(t) X_B^b(t) \qquad \text{(Eq-12)}$$

- In which, Φ_A is the impinging flux of atom-A in ML/s, $X^s{}_A(t)$ and $X^b{}_A(t)$ are the concentration of atom-A at time "t" on the surface or in the bulk, respectively.

What is The Kinetic Model?

- On the other hand, due to the mass conservation for atoms and the fact that $X^b_A(t) + X^b_B(t) = 1$ at any given time "t", we have:

Mass Conservation for atom A in bulk and surface

$$X_A^s(t) + X_A^b(t) = X_A^s(0) + X_A^b(0) + \Phi_A t \qquad \text{(Eq-13)}$$

$$X_B^s(t) + X_B^b(t) = X_B^s(0) + X_B^b(0) + \Phi_B t \qquad \text{(Eq-14)}$$

- Adding Eq-13 with Eq-14, we have:

$$X_A^s(t) + X_A^b(t) + X_B^s(t) + X_B^b(t) = X_A^s(0) + X_A^b(0) + \Phi_A t + X_B^s(0) + X_B^b(0) + \Phi_B t$$

$$X_A^s(t) + X_B^s(t) + \underbrace{X_A^b(t) + X_B^b(t)}_{1} = X_A^s(0) + X_B^s(0) + \underbrace{X_A^b(0) + X_B^b(0)}_{1} + (\Phi_A + \Phi_B)t$$

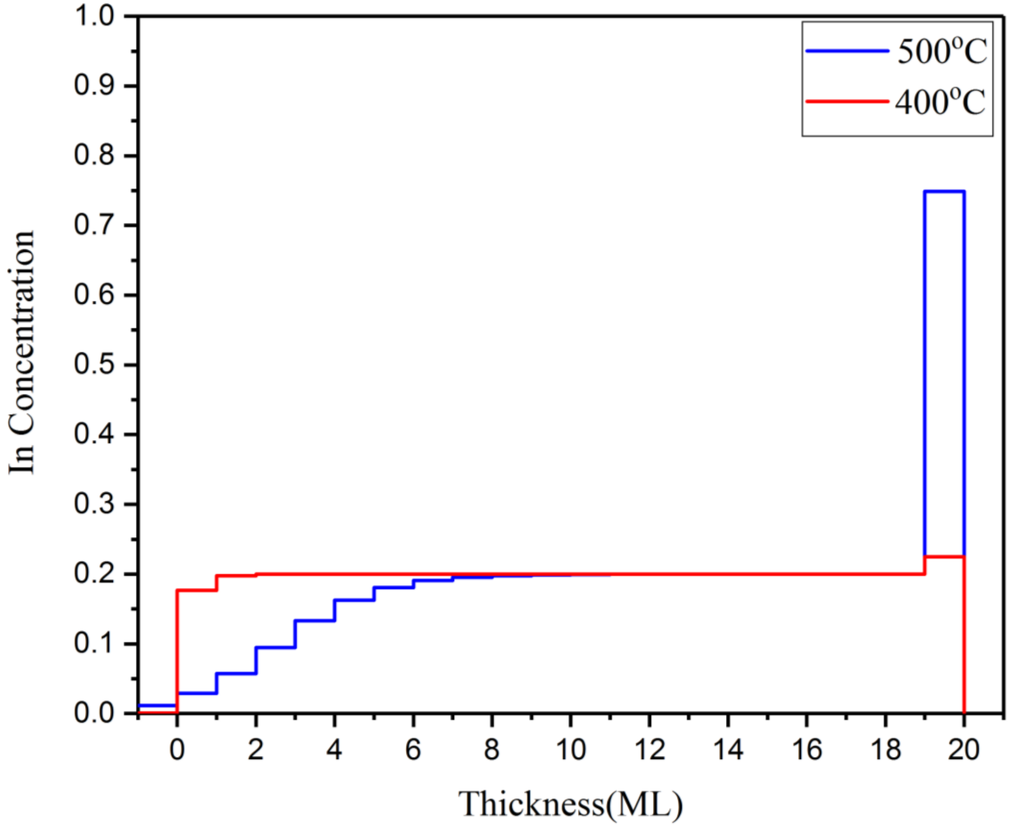
$$\Rightarrow \quad X_A^s(t) + X_B^s(t) = X_A^s(0) + X_B^s(0) + (\Phi_A + \Phi_B)t$$

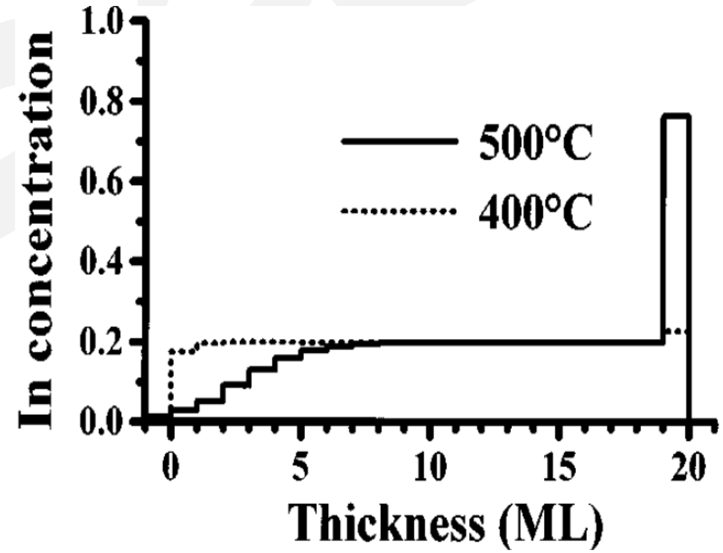
What is The Kinetic Model?

- Using equations (12)-(14), we are able to predict the atomic concentration profile for different growth conditions.

Verification of Simulated Atoms Profiles Due to The Segregation

- Using Kinetics Model, profile of In atoms was calculated in $GaAs/In_{0.2}Ga_{0.8}As$ system:





Verification of Simulated Atoms Profiles Due to The Segregation

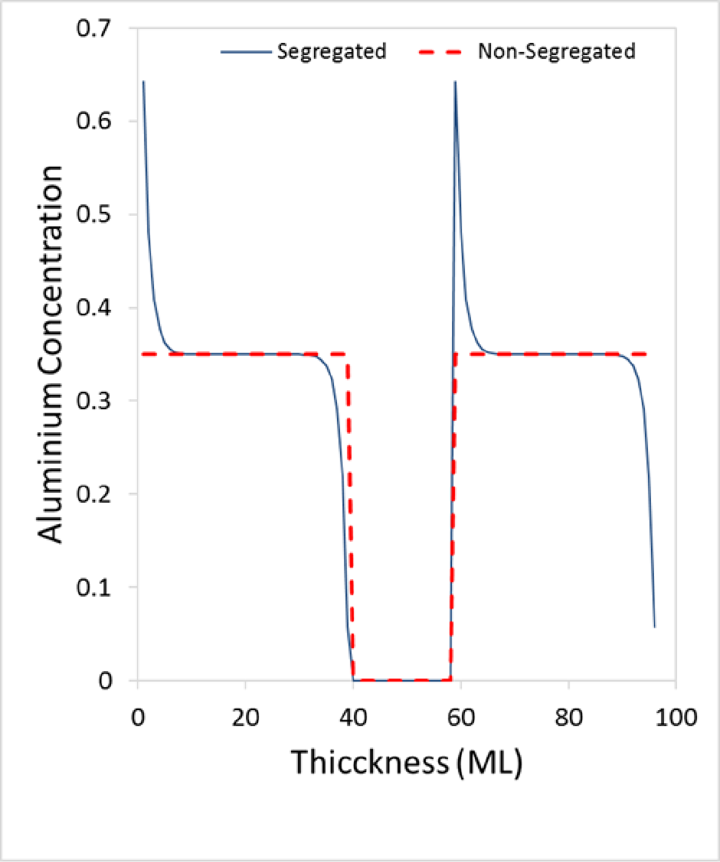
- When we considering "Ga" segregation, based on KM, barrier energy of atoms and growth conditions such as growth temperature and growth rate, can alter the segregation length which is the maximum "Ga" segregation length.
- For example, "In" segregation length in AlSb/InSb system has been reported to be 15 ML at growth temperature of 520^{o}C with a growth rate of 0.5 ML/s.

Ga Segregation in $Al_{0.35}Ga_{0.65}As/GaAs$ System

(808nm Laser)

Ga Segregation in $Al_{0.35}Ga_{0.65}As/GaAs$

- This figure shows the calculated Al concentration profile for both non-segregated and segregated $Al_{0.35}Ga_{0.65}As/GaAs$ at a growth temperature of 710^{o}C and a growth rate of 0.1 ML/s.
- It demonstrates that "Ga" segregation has no effect on GaAs profile, while it alters the AlGaAs profile.
- Based on this calculation, the segregation length in AlGaAs layer is expected to be 7 MLs at growth temperature of 710oC with a growth rate of 0.1 ML/s which is much smaller than "In" segregation length in similar systems.

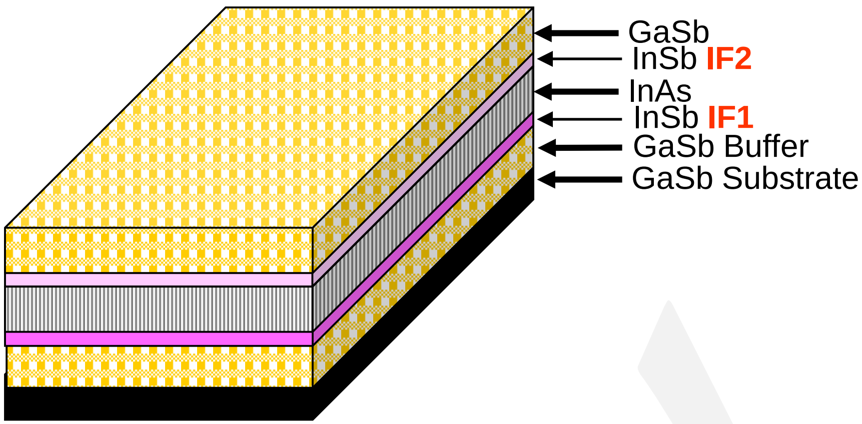


Ga Segregation in $Al_{0.35}Ga_{0.65}As/GaAs$

- Based on KM, reducing growth temperature and/or increasing growth rate can reduce "Ga" segregation and result on an atomic concentration profile closer to non-segregated profile.
- However, lower growth temperature and higher growth rate result on rougher interfaces and broaden energy band gap which is not desirable.
- This is why we need to compensate the segregation effect at high temperature by readjusting the energy bandgap by changing the GaAs well thickness.

Sb Segregation in Type II SLS

Non-Segregated



GaSb

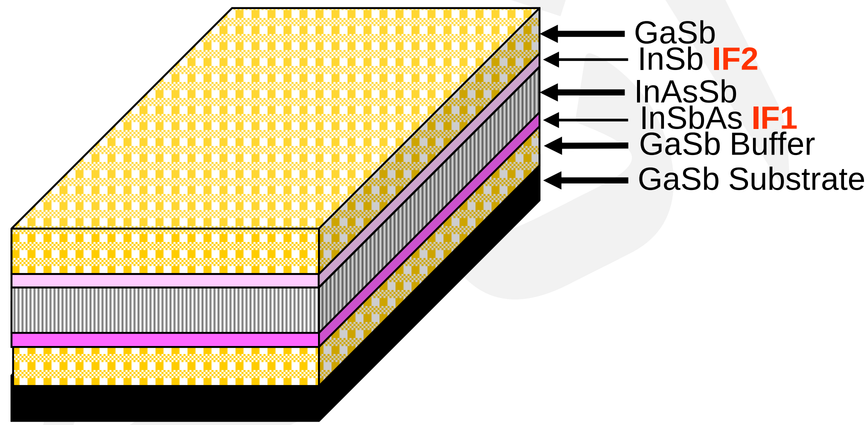
InSb -IF2

InAs

InSb -IF1

GaSb

Sb-Segregated



GaSb

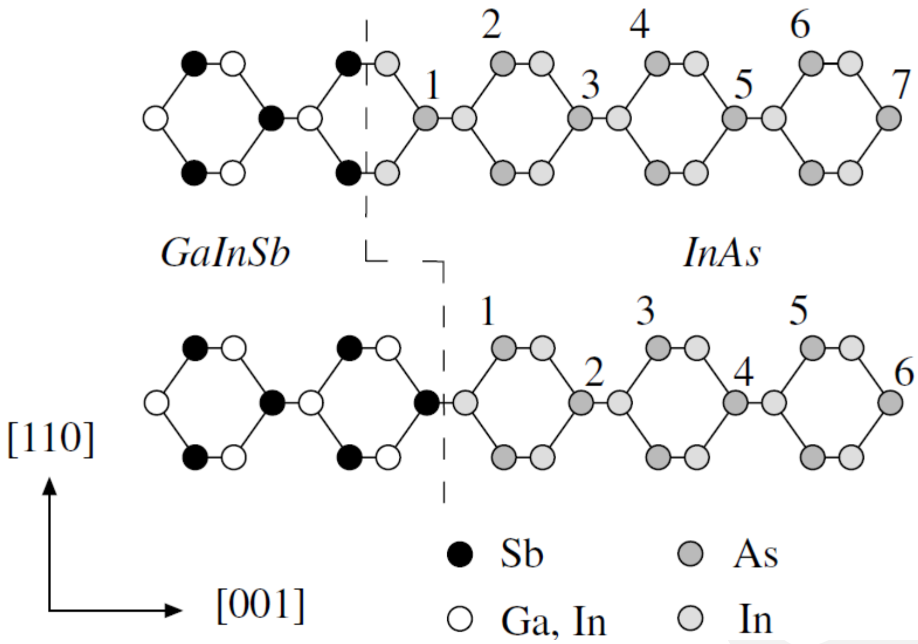
InSb -IF2

InAs (Sb Segregated InAs Layer)

InAsSb (Segregated Interface)-IF1

GaSb

Sb Segregation Can Affect The Individual SLS Layer Thicknesses



- Segregation can add to one layer and/or subtract from another one.
- It can cause adding to GaInSb layer.
- It can cause shifting one mono layer of InAs to the InGaSb layer.
- It can affect the interface composition. The interface can be either InSb or GaAs. It can.

- (001) Is a polar surface that has A or B.

Supporting Slides

Exercise

- In-As bond is stronger than In-Sb bond.
- Compare bond strength and length in:
    1. AlN, GaN, InN,
    2. AlP, GaP, InP
    3. AlAs, GaAs, InAs,
    4. GaSb, InSb, AlSb,
- Plot the results