
بسم الله الرحمن الرحيم

Segregation and Its Importance

Atomic Segregation

- For low growth temperatures (for example 600°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.

- مهاجرت اتم ها به معنی جا به جایی اتم های بالک و سطح به صورت یک طرفه است.
- این پدیده با thermal intermixing که در دو جهت و در دماهای خیلی بالا اتفاق میفتد نباید اشتباه گرفته شود.

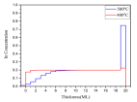
Atomic Segregation

- Heterojunctions between two given binary materials “A” and “B” are abrupt or not in composition, depending on the growth sequence (“A” grown on “B” or “B” grown on “A”).
- For one sequence (when one atom segregates), the top monolayer of the base material is gradually distributed in the growing over layer.
- For group III arsenide material, the segregation tendency can be summarized as In>Ga>Al.
- This means the surface composition of the ternary arsenide $Ga_{0.7}Al_{0.3}As$ is found to be Ga-rich and $Ga_{0.5}In_{0.5}As$ and $Al_{0.5}In_{0.5}As$ alloys to be In-rich.
- This should not get confused with thermal intermixing which is happening in both up and down growth directions and above 600^{o}C for arsenide material.

Atomic Segregation

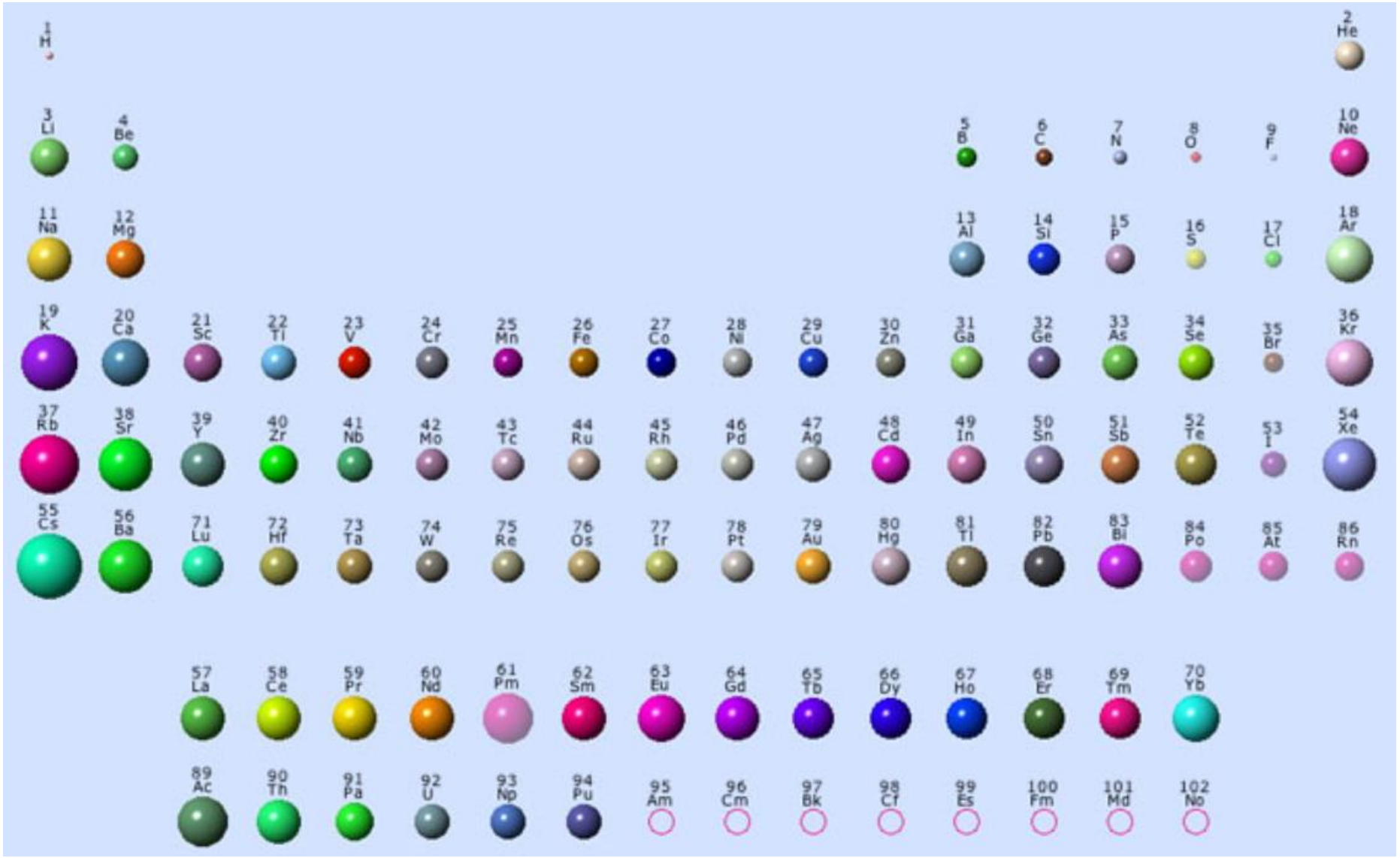
- For example, on the well-known AlGaAs/GaAs QW system, theoretical and experimental results show "Ga" segregation in AlGaAs layer that can cause a composition asymmetry at the normal interface for both AlGaAs/GaAs and GaAs/AlGaAs growths.
- The composition asymmetry at the interfaces results in the 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.
- Segregation may also prevent dopant atoms from getting correctly incorporated during the growth, or redistribute impurities like carbon.

Segregation Effects



1) Geometrical accuracy of the structure.
2) Interface abruptness: Considering segregation, for a binary heterostructure, the two interfaces behave differently as in one case we may see a ternary material while the other one will remain binary with no segregation.
3) Energy bandgap deformation.
4) High doping level: Segregation can lead to a very high doping level if the segregation atoms acts as dopants.
   - For example, if segregation of substrate atoms leaves 0.001 ML of substrate atoms to be incorporated in each growing monolayer, the supply is exhausted after a 0.3 um growth, but the resulting over layer has a doping level of $3X10^{19}$ cm^{-3}.

Periodic Table



تمایل مهاجرت اتم ها

- برای اتم های گروه III تمایل مهاجرت به شکل زیر خلاصه می‌شود.

In>Ga>Al

- که همین ترتیب را در طول باند و Bonding-Energy نیز می‌توانیم مشاهده کنیم:

- Bonding Energy:

  III-As Materials: In-As(1.41eV) < Ga-As (1.59eV) < Al-As (1.98 eV)

  III-Sb Materials: Ga-Sb (1.50eV) < Al-Sb(1.79 eV)

- Bonding Length:

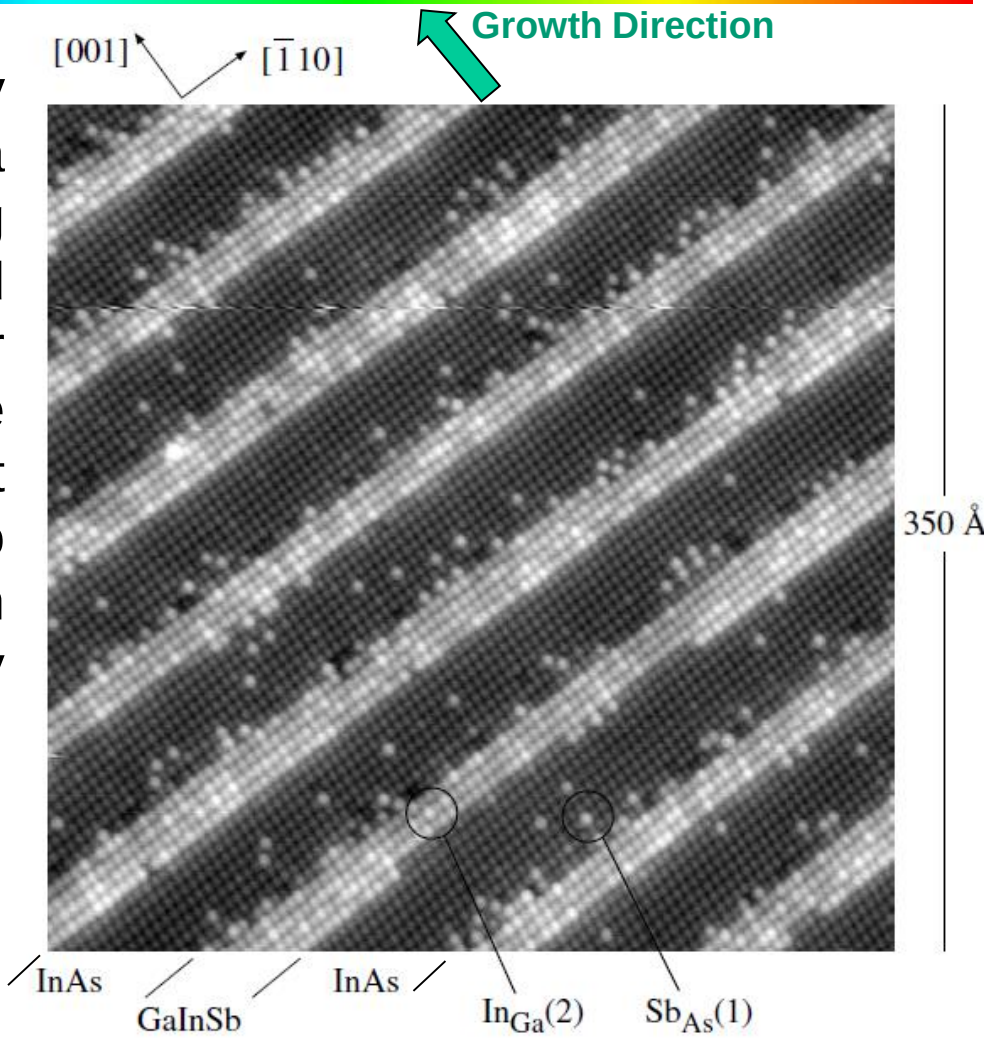
  III-As Materials: In-As(2.62 Å) > Ga-As (2.45 Å) ≈Al-As(2.45 Å)

  III-Sb Materials: Ga-Sb (2.64 Å) <Al-Sb (2.66 Å)

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**

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; which is the mechanical potential energy stored in the configuration of a material or physical system as it is subjected to elastic deformation by work performed upon it.

- Segregation in III-V compounds results in:

  1- Gradual composition.

  2- Surface enrichment of one of the incorporated group III elements.

  3- Energy band structure deformation.

  4- Doping level deformation.

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

Does Segregation Depend on The Growth Conditions?

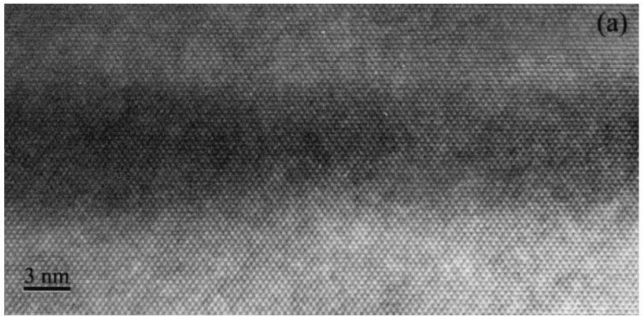
- The profile of the segregating atom in the structure does change with the following growth parameters:

1) Growth Temperature (T_g) ↑ Segregation ↑
2) Growth Rate ↑ Segregation ↓
3) III/V Partial Pressure Ratio ↑ Segregation ↑
4) Growth Pressure ↑ Segregation ↓
5) Interruption Time ↑ Segregation ↑

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

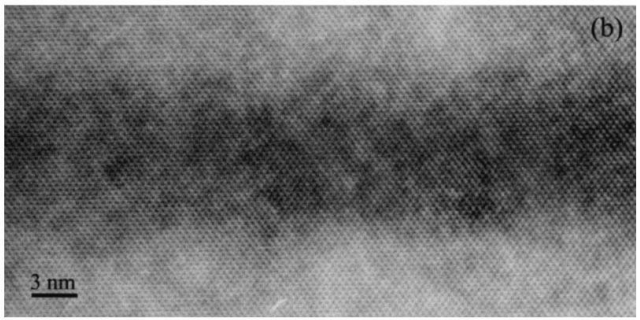
- Composition of the grown layers changes ⇒ Band lineup of the heterostructure changes ⇒ Optoelectronic properties of the heterostructure change.
- "Al" atoms segregated in AlGaSb/GaSb QW.

AlGaSb / GaSb / AlGaSb

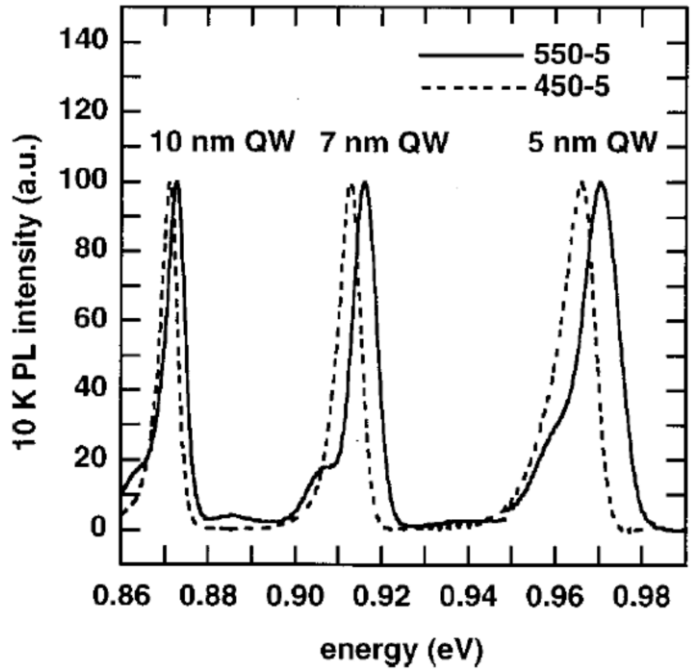


450°C

AlGaSb / GaSb / AlGaSb

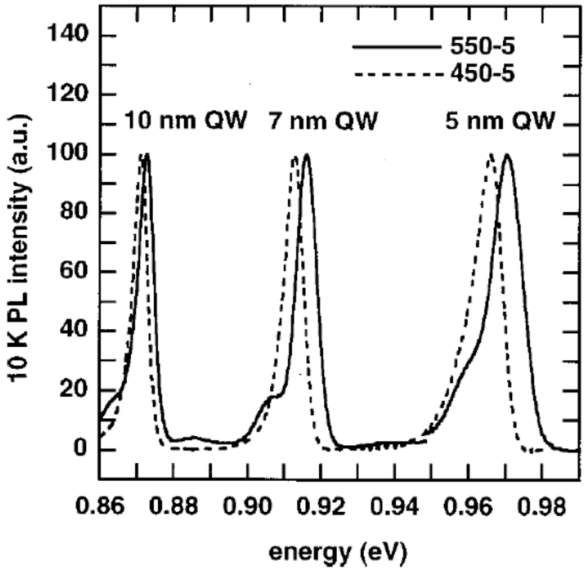


550°C



How can we characterize the segregation?

- Experimental measurements:
  - Reflection High Energy Electron Diffraction (RHEED).
  - Rutherford Backscattering Spectroscopy (RBS).
  - Electron Energy Loss Spectroscopy (EELS).
  - Secondary Ion Mass Spectroscopy (SIMS).
  - High Resolution X-ray Diffraction (HRXRD).
  - X-ray Photoelectron Spectroscopy (XPS).
  - UV Photoelectron Spectroscopy (UPS).
  - Auger Electron Spectroscopy (AES).
  - Photoluminescence (PL).
  - Raman Spectra (RS).
  - High Resolution Transmission Electron Microscopy (HRTEM).
  - Etc.

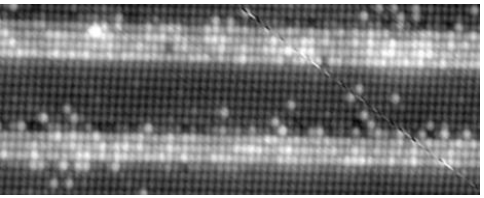


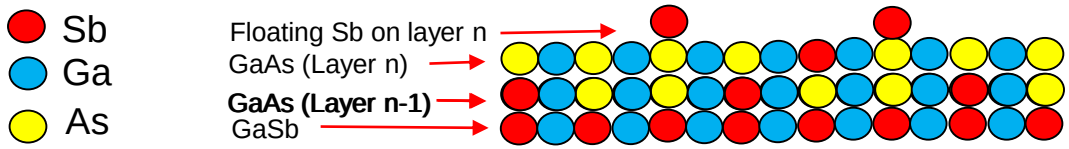
Segregation Theoretical Models

1) Muraki's Model
2) Sigmoidal
3) Kinetics Model
4) Sigmoidal Model
5) Fluid Three-layer Exchange Model
6) Kinetics Monte Carlo Simulation(KMC)

1) Muraki's Model

Sb Segregation with no Sb Background Gas





No Background Gas:

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

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

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

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

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

- 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.

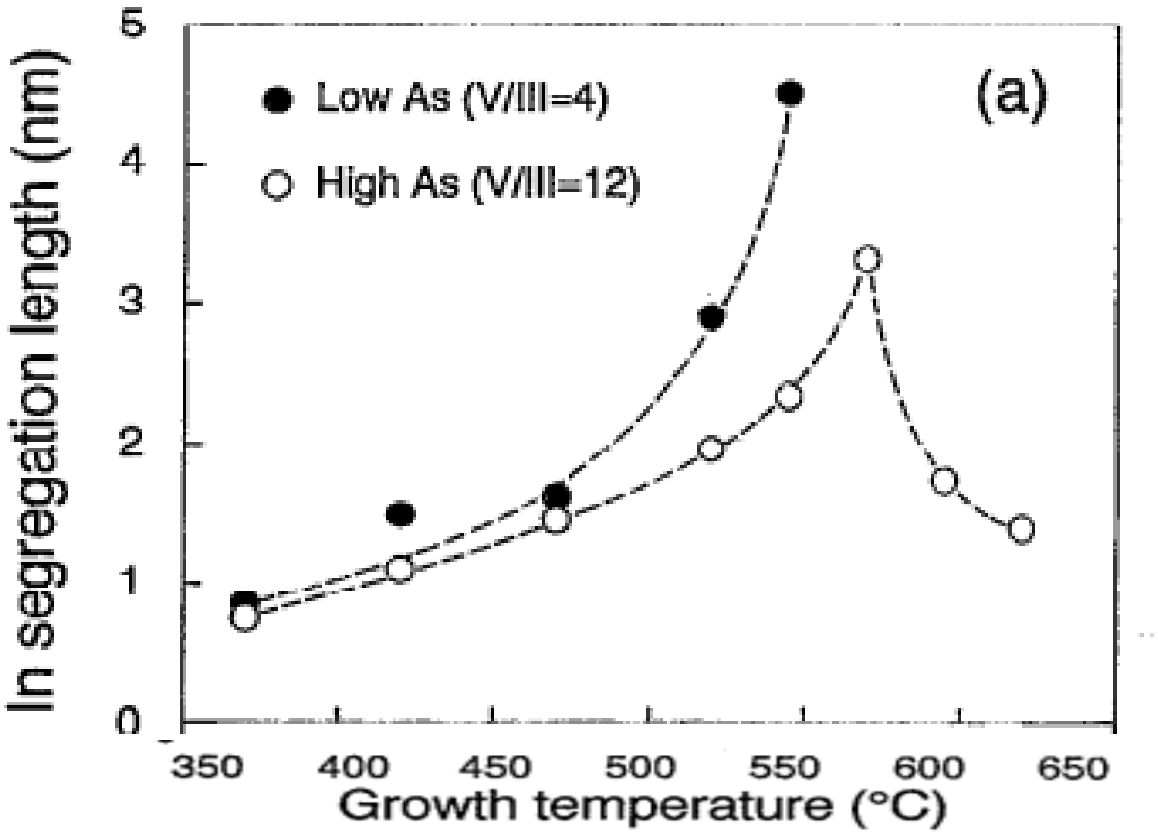
Sb Segregation with no Sb Background Gas

- In general we have:

$$R = e^{-\frac{d}{\lambda}}$$

- In which “d” is half the lattice constant, “λ” is the segregation length which can be obtained from SIMS profile.
- R for different material of group III can be found in PRB_40_6149.

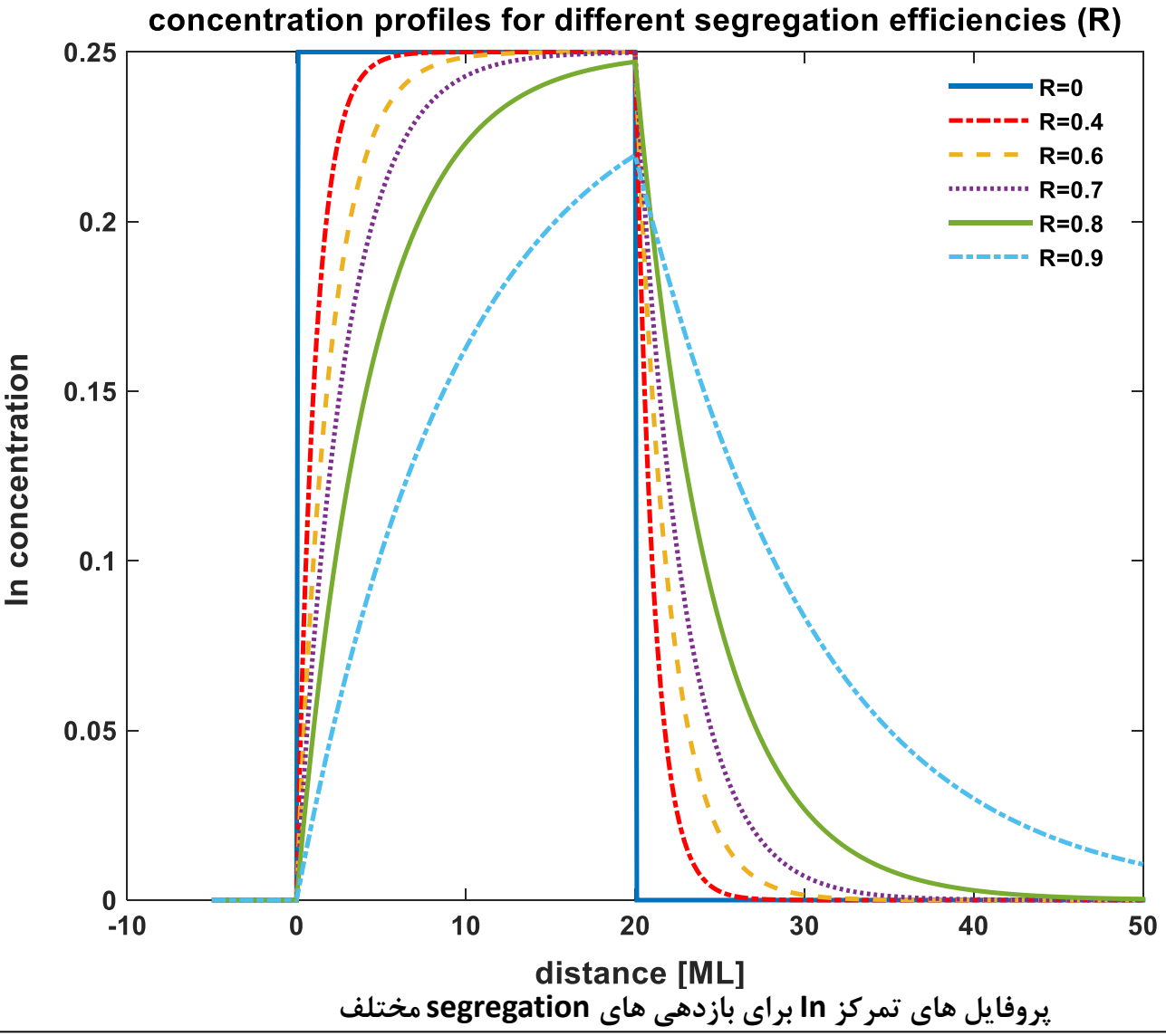
Supporting Length



وابستگی طول مهاجرت Inبه سطح به دمای رشد

- وابستگی طول مهاجرت Inدر سطح به دمای رشد بدست آمده از SIMSدر شکل مقابل خلاصه شده است.
- طول تفکیک با کاهش دمای رشد، کاهش میابد. این امر به این دلیل است که تفکیک سطح، به عبارت دیگر ، تبادل اتم بین سطح و فاز bulk از نظر جنبشی با کاهش دما محدود می شود.

"R" Effect on Supporting Length



پروفایل های تمرکز In برای بازدهی های segregation مختلف

- پروفایل تمرکز In از چاه کوانتومی برای ساختار نامتناجس InGaAs/GaAsبرای بازدهی‌های مهاجرت مختلف با استفاده از مدل موراکی و نرم افزار MATLABشبیه سازی شده و در شکل مقابل نشان داده شده است.
- همان طور که مشاهده میشود هرچه قدر مقدار R بیشتر باشد اتم ها در طول بیشتری در لایه بعدی مهاجرت میکنند.

Sb Segregation with Sb Background Gas

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

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

x_o = The excessive Sb from the background pressure.

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

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

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

Sb Segregation with Sb Background Gas

- From Eq-4 we have: $x_f^n = R\left(x_f^{n-1} + x_o\right)$ therefore:

$$x_f^0 \equiv x_i$$

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

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

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

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

- 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:

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

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:

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

$$x_{inc}^n = x_i R^{n-1}(1-R) + x_o(1-R^n) \qquad \text{(Eq-11)}$$

Sb Falloff

Sb Background Incorporation

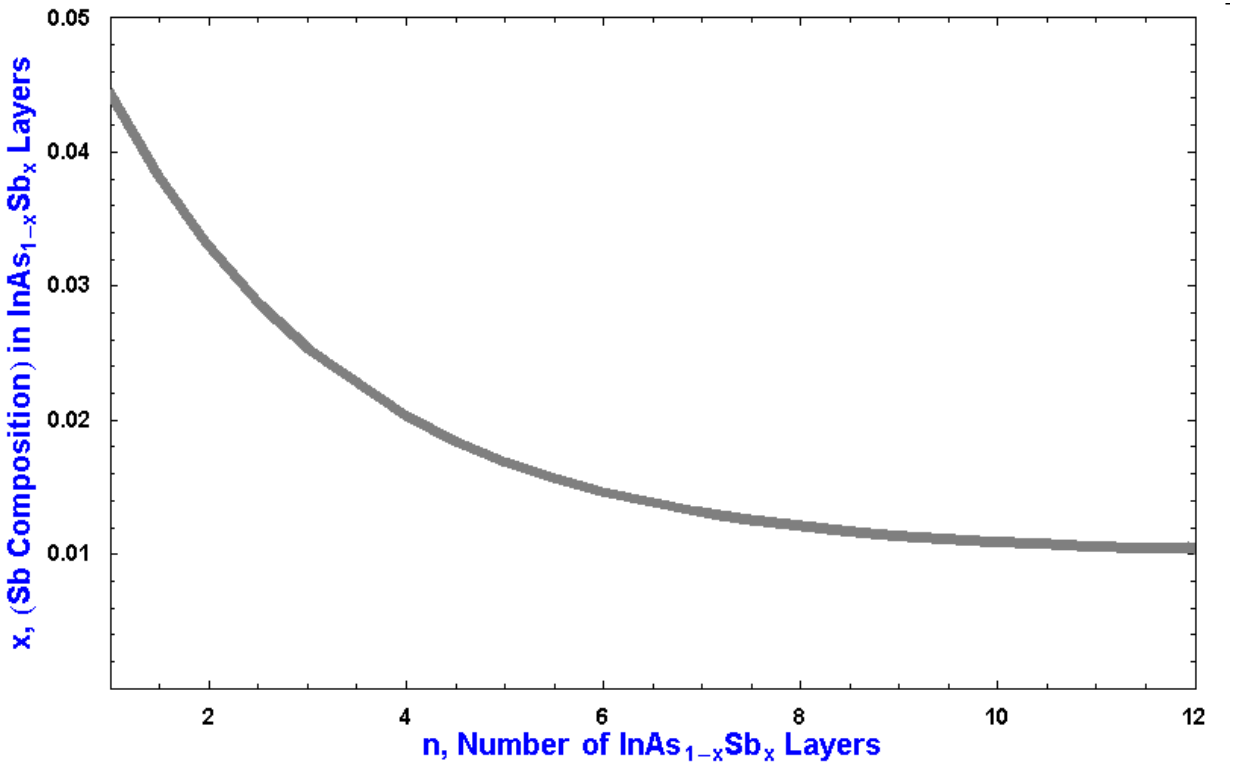
Muraki's Model Examples

Sb Segregation in Type II SLS

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

$x^{Sb}(n)$ = 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

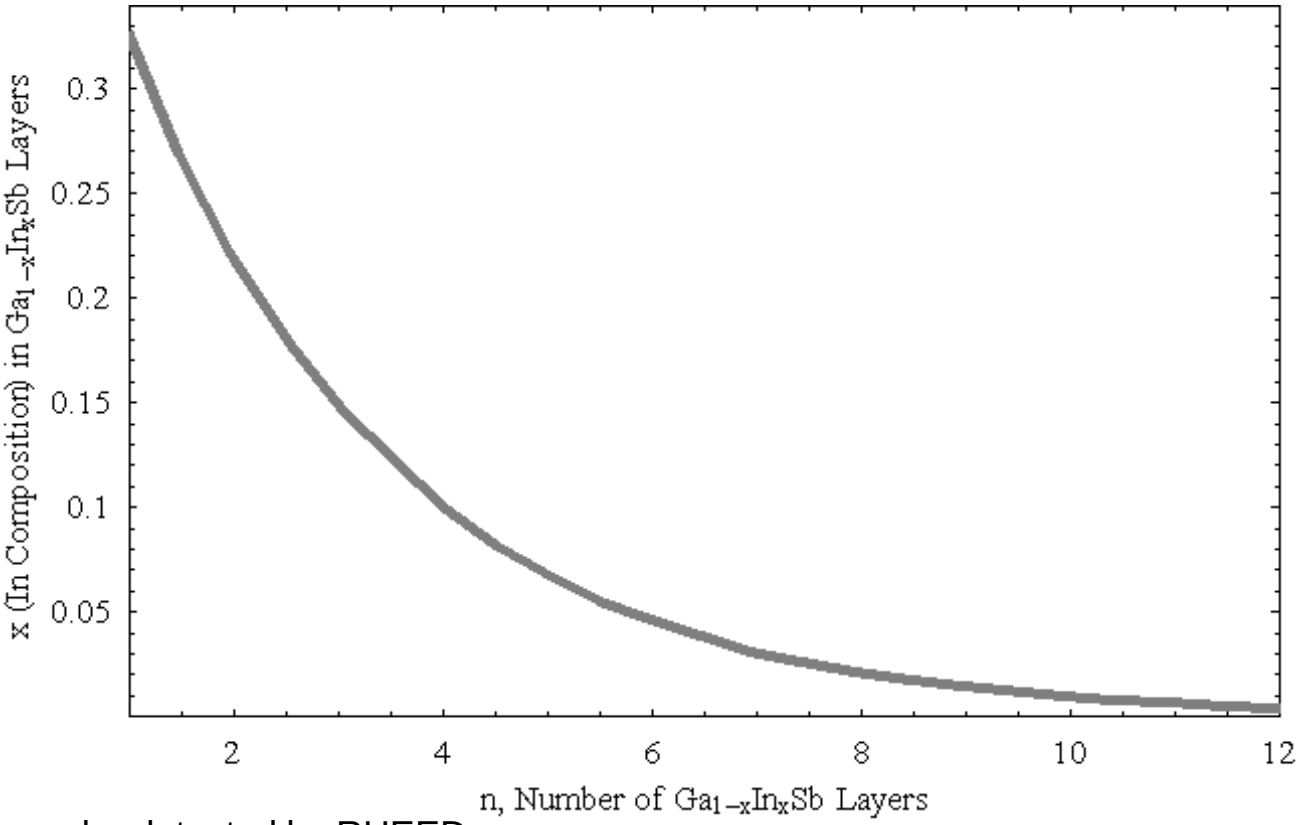
$$x^{In}(n) = x_i^{In} R^{n-1}(1-R)$$

$x^{In}(n)$ = 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°C with x_i^{In}=1.0, and R=0.66.



- In Segregation can be detected by RHEED

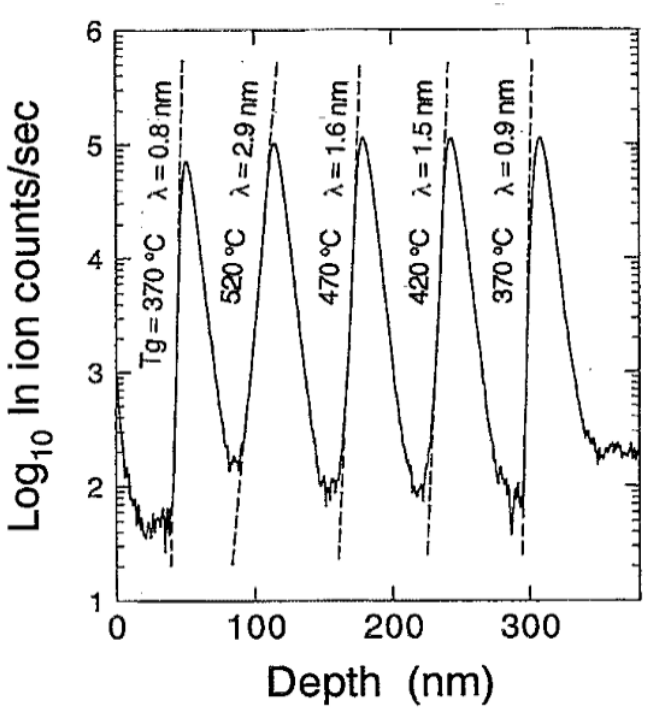
Muraki's Model for In Segregation

- System: $In_x Ga_{1-x}As/GaAs$
  - R=0.91 at T=520(℃)
  - R=0.70 at T=370(℃)

$$R = e^{-\frac{d}{\lambda}}$$

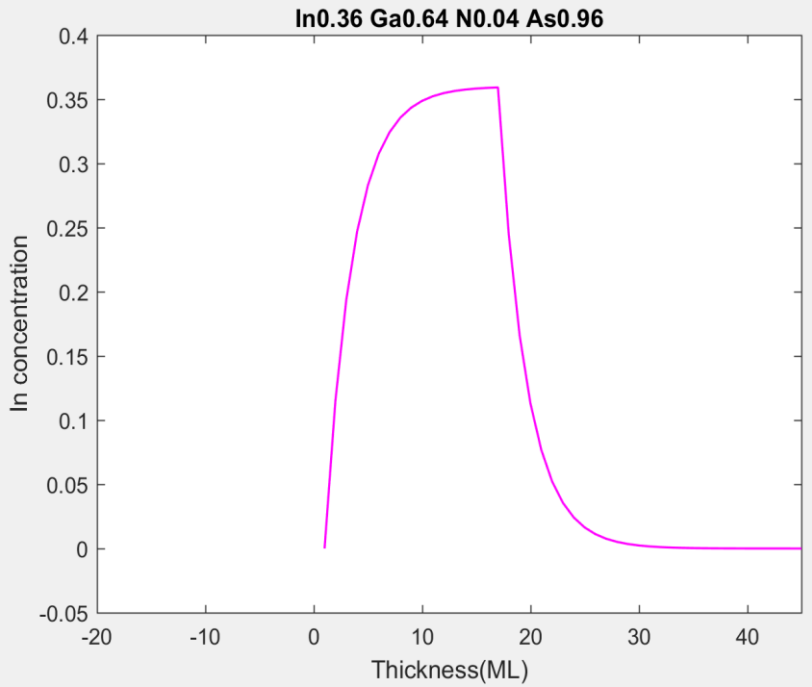
- In which "d" is half the lattice constant of GaAs (2.83 Å), "λ" is the segregation length which can be obtained from SIMS profile

temperature(℃)	370	420	470	520
R	0.70	0.82	0.83	0.91

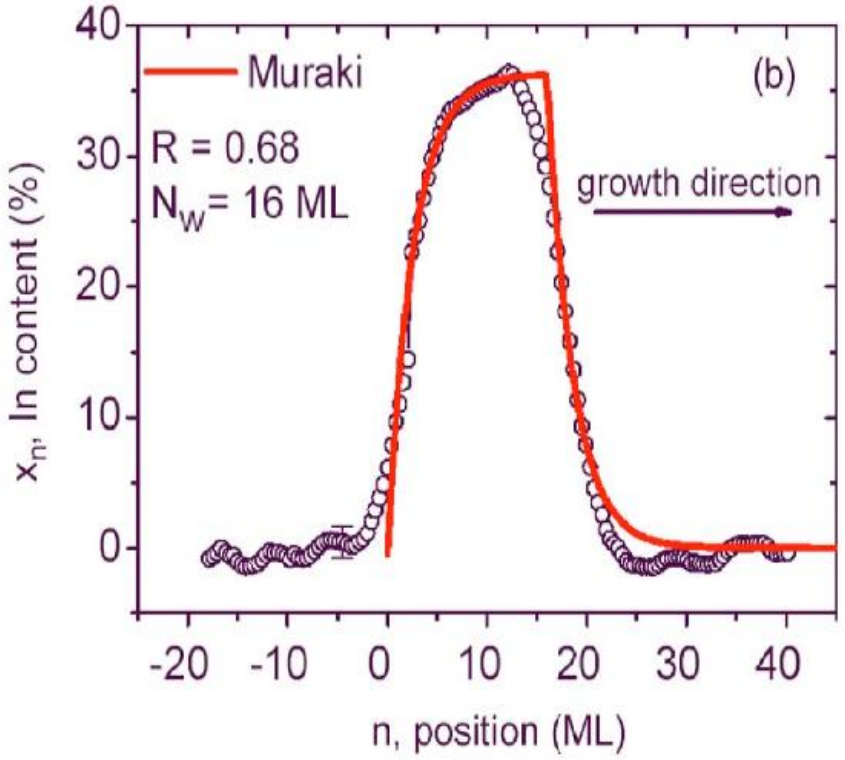


Muraki's Model for In Segregation

System: $In_{0.36}\ Ga_{0.64}\ N_{0.04}\ As_{0.96}$ /GaAs



Mr. Mokhtari's Simulation



2) Sigmoidal Model

Sigmoidal Model

- In 2008, a new model was introduced by Luna which helped Muraki's model to fit better the experimental data. APL_2_141913

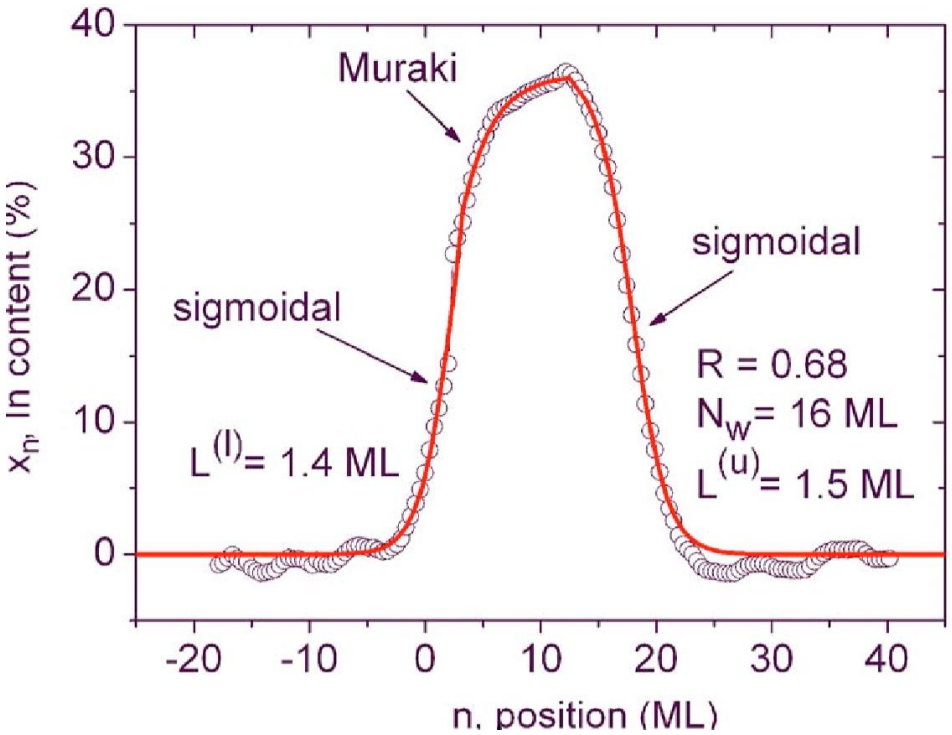
معادلات Sigmoidal

$$x_n = \frac{x_0^{(l)}}{1+e^{-(n+\frac{N_W}{2})/L^{(l)}}}$$

for n<0 (Lower Interface)

$$x_n = x_0^{(u)} - \frac{x_0^{(u)}}{1+e^{-(n-\frac{N_W}{2})/L^{(u)}}}$$

for n>0 (Upper Interface)



- در این معادلات x_n همان معنا را در معادلات موراکی داردو N_w تعداد لایه های Well است.
- $L^{(u)}$ و $L^{(l)}$ دو پارامتر هستند که به کمک تطبیق باید اندازه گرفته شوند و محل تفاوت مدل موراکی و سیگمویدال است.
- $x_0^{(u)}$ و $x_0^{(l)}$ درصد اتم های ایندیوم در محل تغییر بالا و پایین است.