Growth of nanowires

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GdR PULSE, Summer School, Porquerolles, Sept 17th 2015

This lecture will focus on:

Semiconductor nanowires (III-V mainly)

(other types of nanowires: metallic, dielectric)

elaborated by CVD or MBE

(other methods: laser ablation, HVPE, wafer annealing, low temperature solution, electrochemical deposition…)

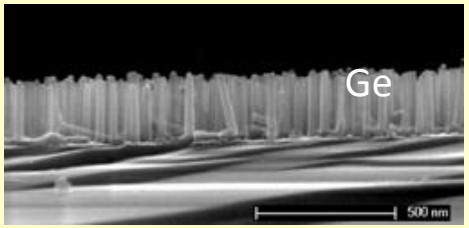
via the catalyst-assisted vapor liquid solid (VLS) mechanism

(other mechanisms: catalyst free growth, selective growth, dislocation- mediated growth, ligand-aided solid-solution growth…)

Nanowires of semiconductors

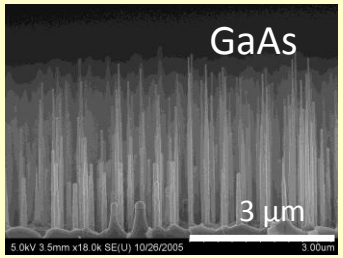
Au-assisted growth

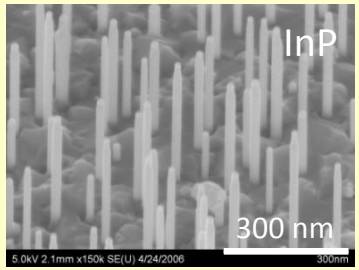
IV

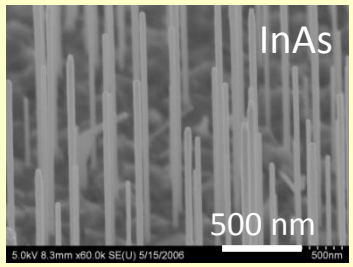


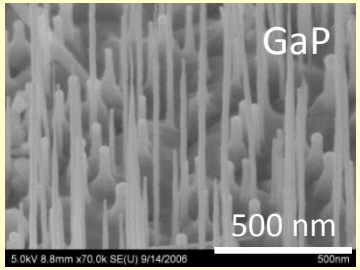
IEF, Orsay

III-V



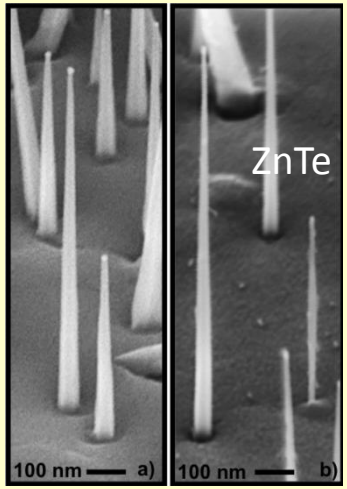






LPN, Marcoussis

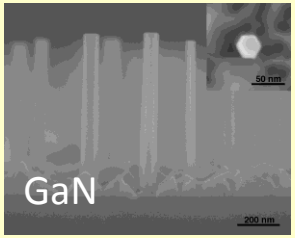
II-VI



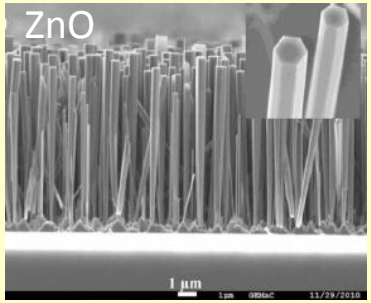
Institut Néel, Grenoble

Rueda et al, Nano Lett. 14, 1877 (2014)

Catalyst-free growth



LPN, Marcoussis

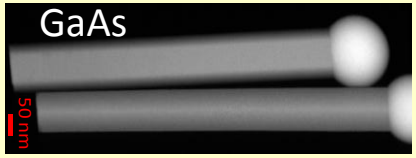


GEMAC, Versailles

Amiri et al, Phys. Stat. Sol. B 250, 2132 (2013)

Self-catalyzed growth

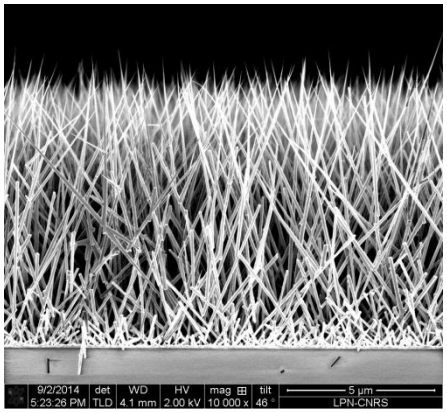
F. Jabeen et al, Nanotechnol. 19, 275711 (2008)
C. Colombo et al. PRB 77, 155326 (2008)



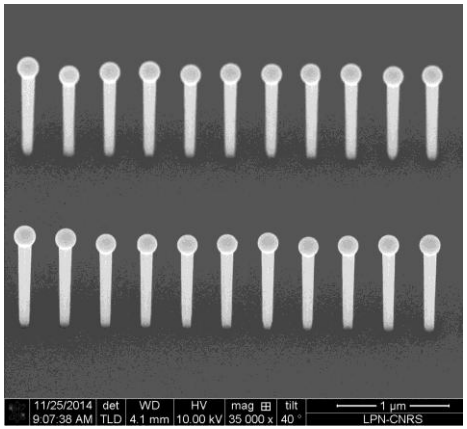
LPN, Marcoussis

Typical diameter ranges between a few nm and several 100 nm
Typical length from < 1 µm to several 100 µm

Nanowires of semiconductors: various objects, flexible growth



MBE, GaAs NWs grown on glass
LPN Marcoussis, T. Jegorel



MBE, GaAs NWs grown on patterned Si
LPN Marcoussis, F. Oehler

HVPE, very long GaAs NWs (R_g = 170 µm/h)
Institut Pascal, Clermont Ferrand

Ramdani et al, Nano Lett. 10, 1836 (2010)

Outline

- Generalities on catalyst-assisted nanowire growth
- Kinetics of nanowire growth
- Nucleation in VLS growth
- Formation of heterostructures in nanowires

Why is Au such a successful catalyst?

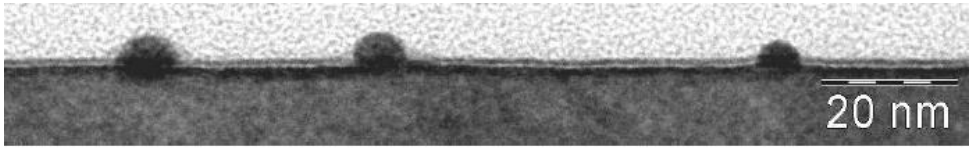
✓No oxidation in air

✓Au forms eutectic alloys
with Si, Ge, Ga, In, Al, Zn, Cd…

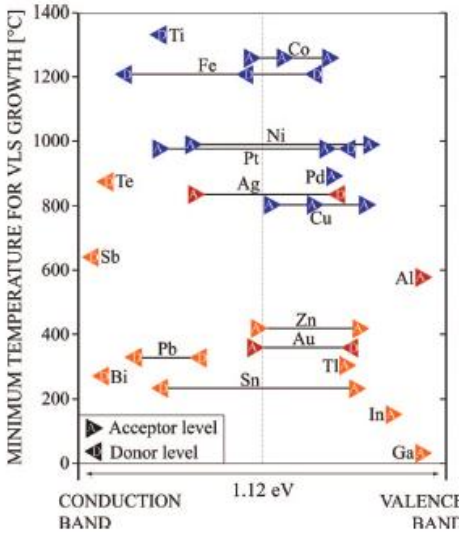
→VLS growth is possible

Eutectic temperatures	
Au-Si	363°C
Au-Ge	361°C
Au-Al	525°C
Au-Ga	349°C
Au-In	224°C
Au-Zn	403°C
Au-Cd	309°C

✓Small droplets are easily obtained
Colloïds
Thin film deposition + dewetting



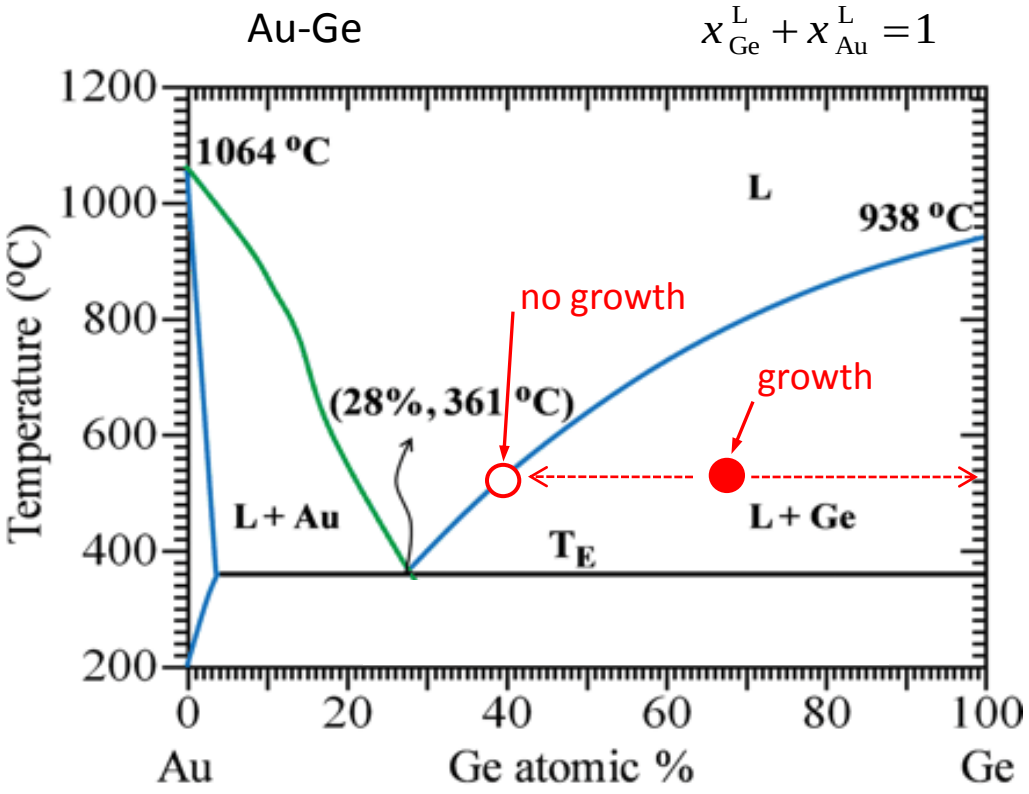
Au ≡ Deep level



Metal catalysts for Si NW growth

Schmidt et al, Chem. Rev. 110, 361, 2010

The catalyst is a reservoir of NW constituents

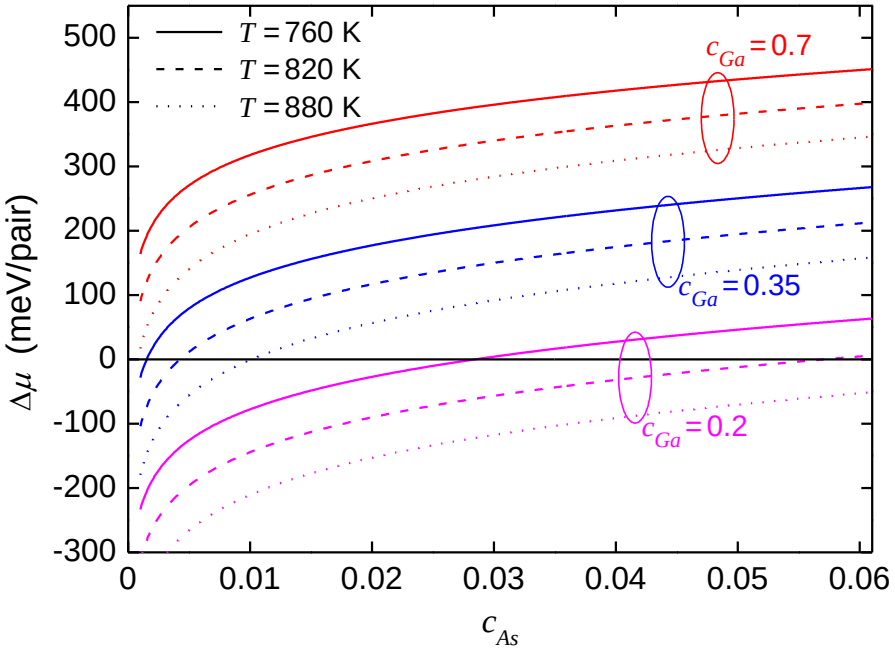


x^{L}_{Ge} must be higher than the equilibrium concentration to start growing

Case of III-V compounds

Both group III and group V atoms must dissolve in the catalyst

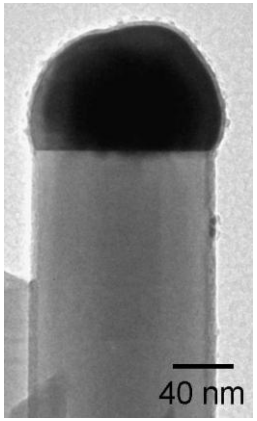
AuGaAs liquid catalyst $x_{Ga}^{L} + x_{As}^{L} + x_{Au}^{L} = 1$



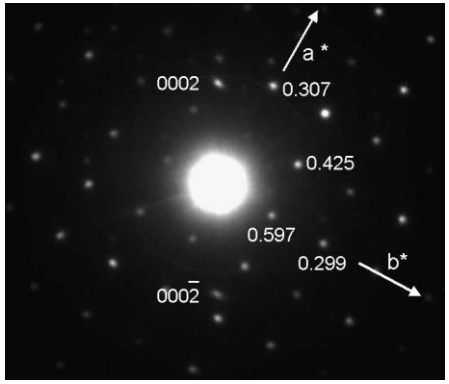
$$\Delta\mu(x_{Ga}^{L}, x_{As}^{L}, T)$$

Group III atoms are much more soluble than group V atoms

Catalyst composition after GaAs NW growth



$Au_{0.5}Ga_{0.5}$ phase



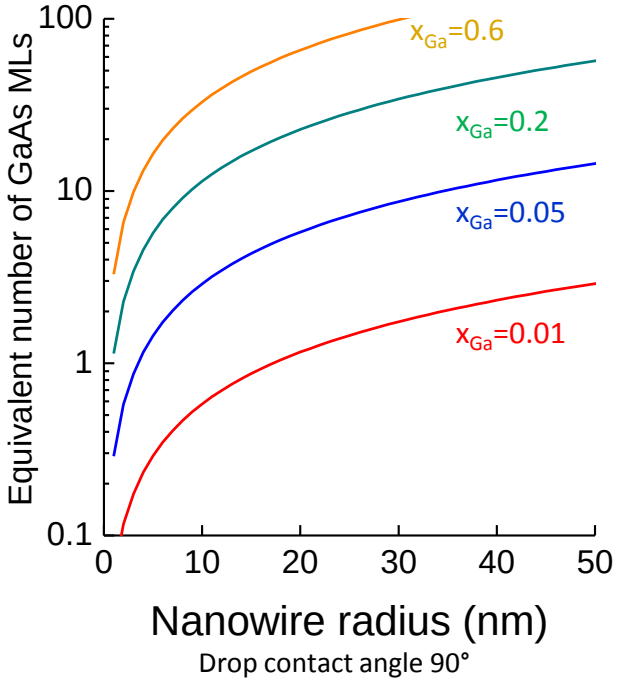
Glas, J. Appl. Phys. 108, 073506 (2010)

How much of each constituent in the reservoir?

During growth

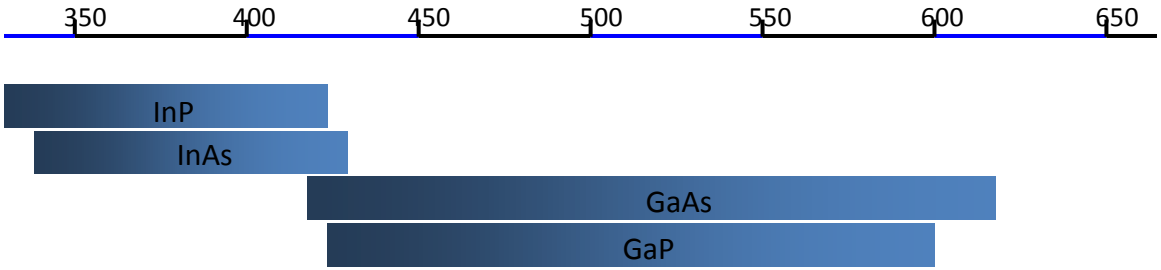
Ga composition: several 10% ≡ tens to hundreds of monolayers of solid NW

As composition: not more than a few % ≡ a few monolayers of solid NW (can be less than 1ML)



To fabricate heterostructures, it is more favorable to commute group V atoms (less soluble → faster to purge)

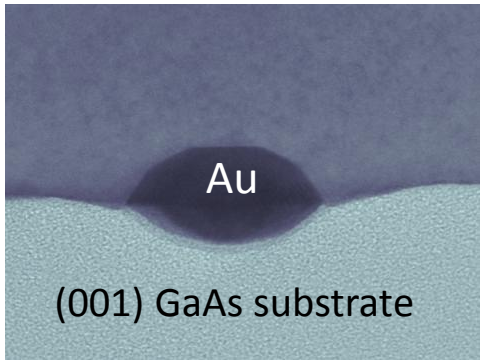
Compounds with same group III atoms have comparable ranges of growth temperature

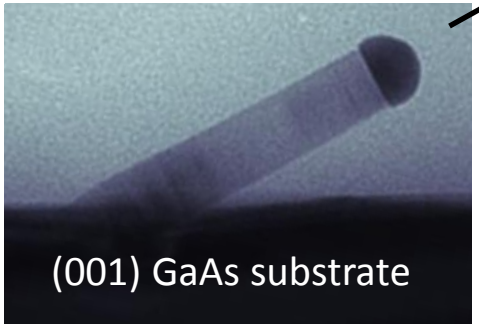


Temperature range for NW growth by MBE of different III-V compounds

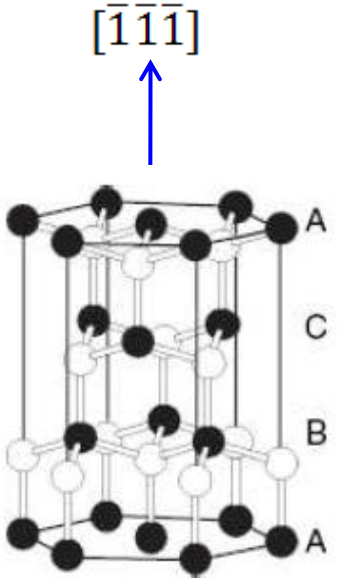
Preferential growth axis

Au-catalyzed semiconductor nanowires

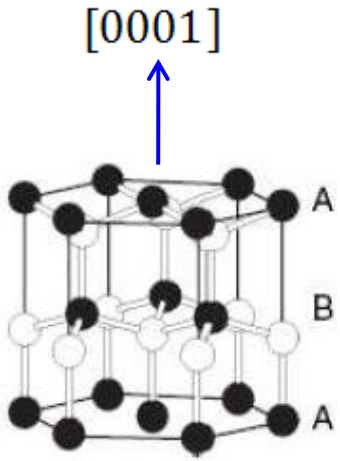




$[\bar{1}\bar{1}\bar{1}]$



Cubic
(Zinc Blende)



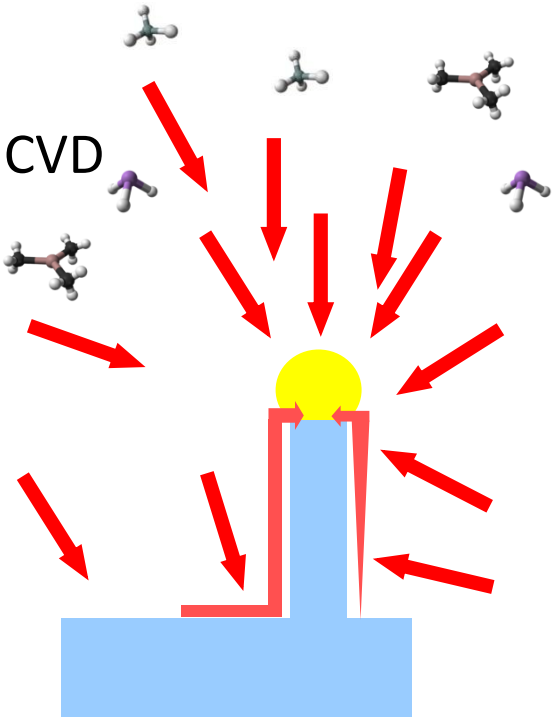
Hexagonal
(Wurtzite)

In most cases, the growth axis is [-1-1-1] for cubic phase or [0001] for hexagonal phase

Outline

- Generalities on catalyst-assisted nanowire growth
- **Kinetics of nanowire growth**
- Nucleation in VLS growth
- Formation of heterostructures in nanowires

Why is growth faster under the metal drops ?

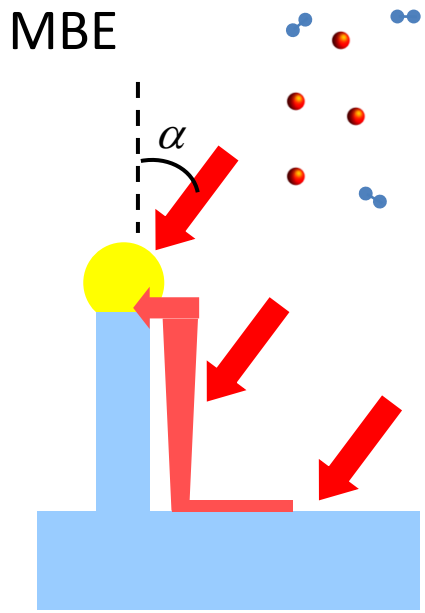


Precursors are gas molecules ($TMGa$, AsH_3, SiH_4…)

The metal droplet can promote their decomposition

« Chemical catalyst »

Precursor flow from the vapor to the droplet

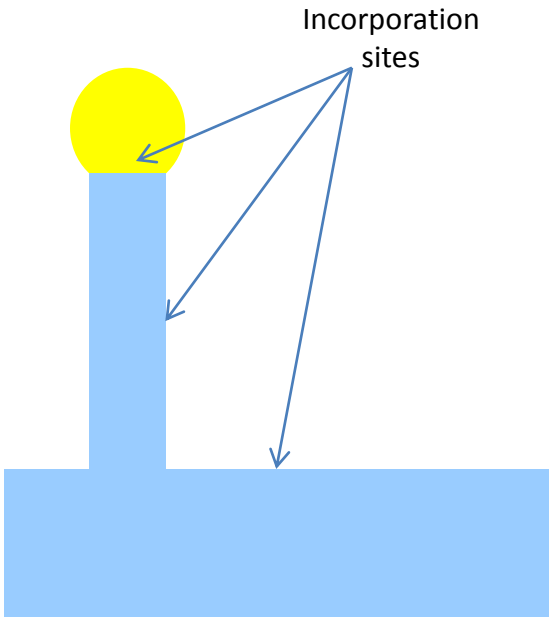


Constituents are brought as directional beams of atoms or simple molecules (Si , Ge, Ga, In, P_2, As_4…)

no chemical reaction needed

The metal droplet promotes incorporation of atoms in the solid phase

« Physical catalyst »



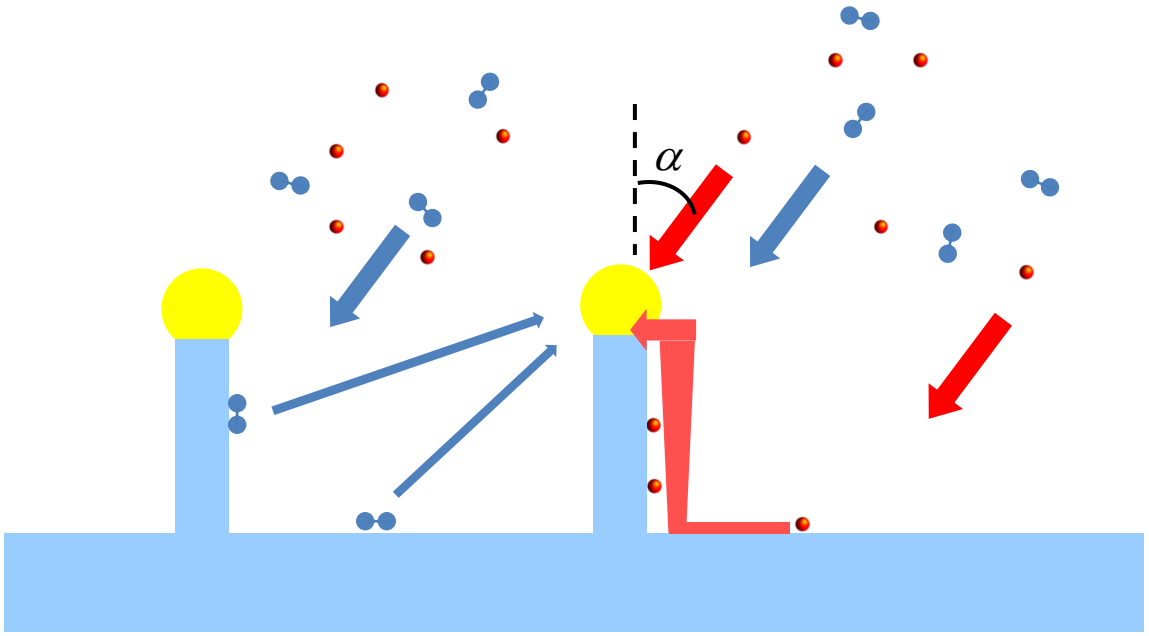
The liquid drop is a dense phase:

Aggregation of atoms to form solid nuclei is faster at liquid/solid interface than at vapor/solid interface

Faster consumption induces surface diffusion of adatoms to the droplet

Case of III-V NW growth by MBE

Different pathways to the droplet for group III or group V atoms



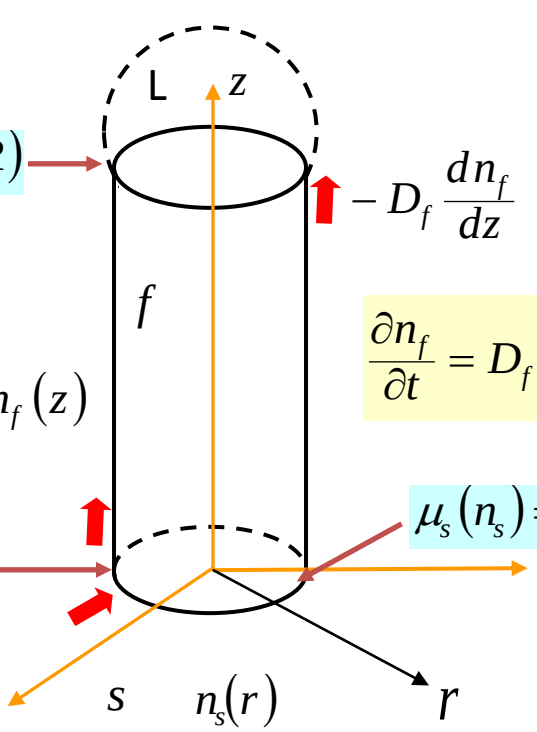
Group V : sticking coefficient <<1
Surface adsorption + reemission in the vapor phase

Group V atoms reach the droplet by
-direct impingement
-reemission

Group III : sticking coefficient =1
Surface adsorption + surface diffusion

Group III atoms reach the droplet by
-direct impingempent
-surface diffusion

Surface diffusion of adatoms



$$\mu_f(n_f) = \mu_L(T, x_L, \ldots, R)$$

$$-D_f \frac{dn_f}{dz}$$

$$\alpha \qquad J$$

$$\frac{\partial n_f}{\partial t} = D_f \frac{\partial^2 n_f}{\partial z^2} + \frac{1}{\pi} J \sin\alpha - \frac{n_f}{\tau_f} = 0$$

$$D_s \frac{dn_s}{dr} = -D_f \frac{dn_f}{dz}$$

$$\mu_s(n_s) = \mu_f(n_f)$$

$$\mu_f(n_f) = \mu_f(n_f^0) + k_B T \ln \frac{n_f}{n_f^0}$$

$$\left.\frac{dn_s}{dr}\right|_{r\to\infty} = 0$$

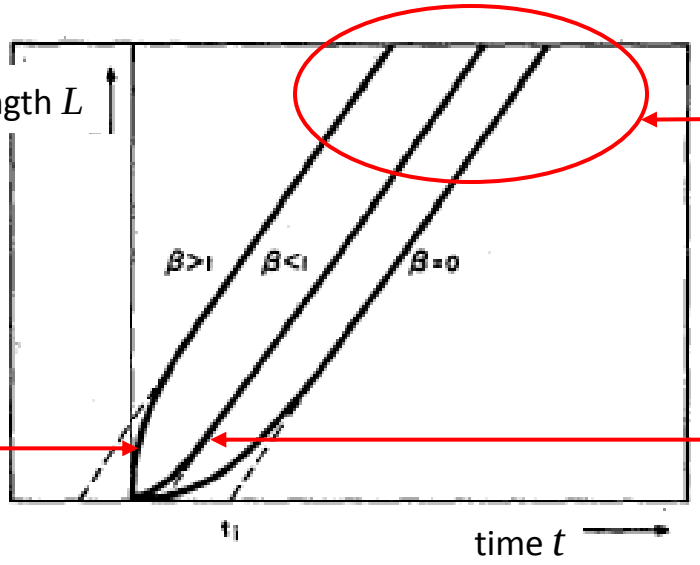
$$\frac{\partial n_s}{\partial t} = D_s \Delta n_s + J\cos\alpha - \frac{n_s}{\tau_s} = 0$$

Diffusion equations may be solved.... if μ_L is known

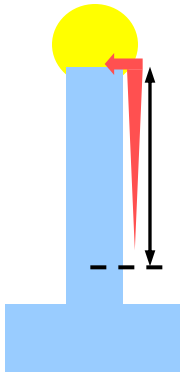
$\rightarrow$ Diffusion flux into the drop

Elongation rate is not constant

Assume μ_L is known



$L(t) >> \lambda_f$



$\sim \lambda_f$

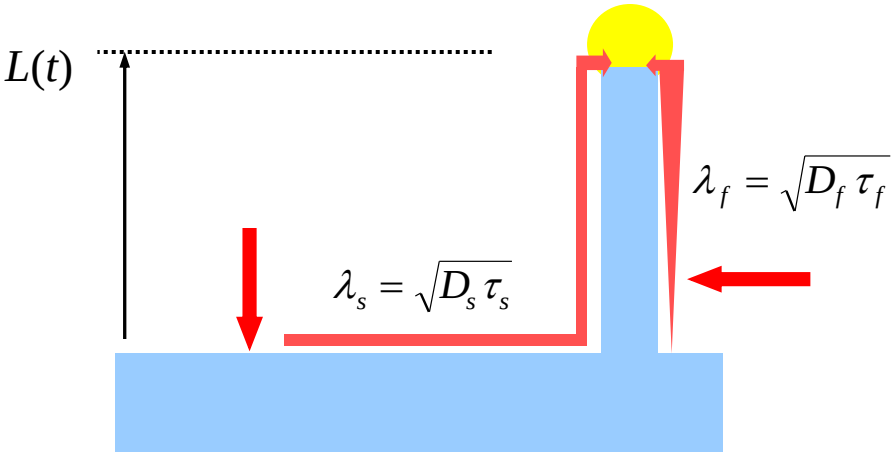
λ_s large

substrate Contribution dominates

λ_f large

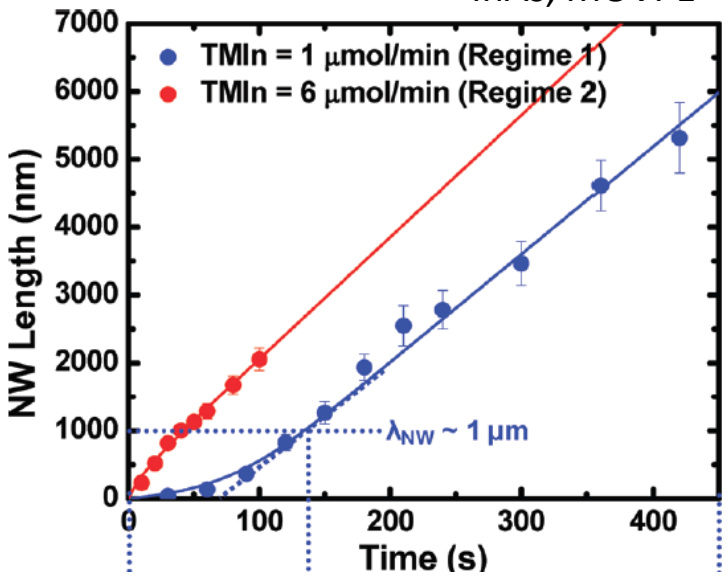
sidewall contribution dominates

Ruth and Hirth, J. Chem. Phys. 41, 3139 (1964)



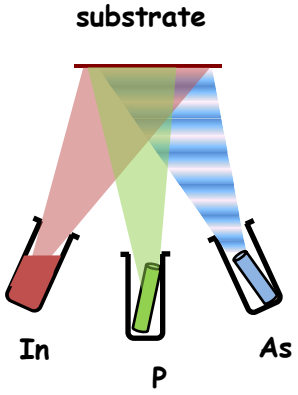
(case of no growth on substrate or sidewalls)

InAs, MOVPE

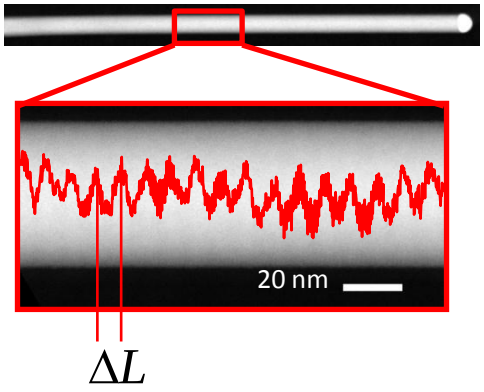


Dayeh, Yu, Wang, Nano Lett. 9, 1967 (2009)

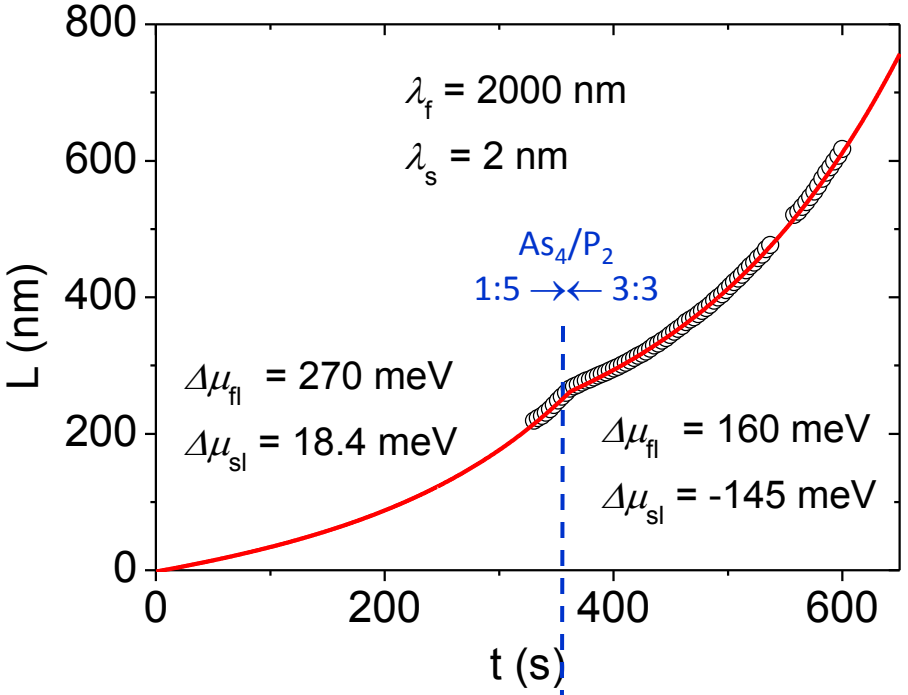
Case study: InAsP nanowires grown by MBE

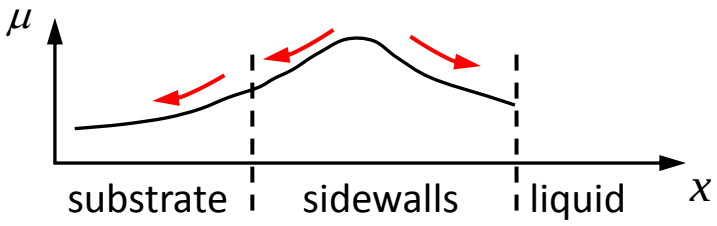


Modulation period τ



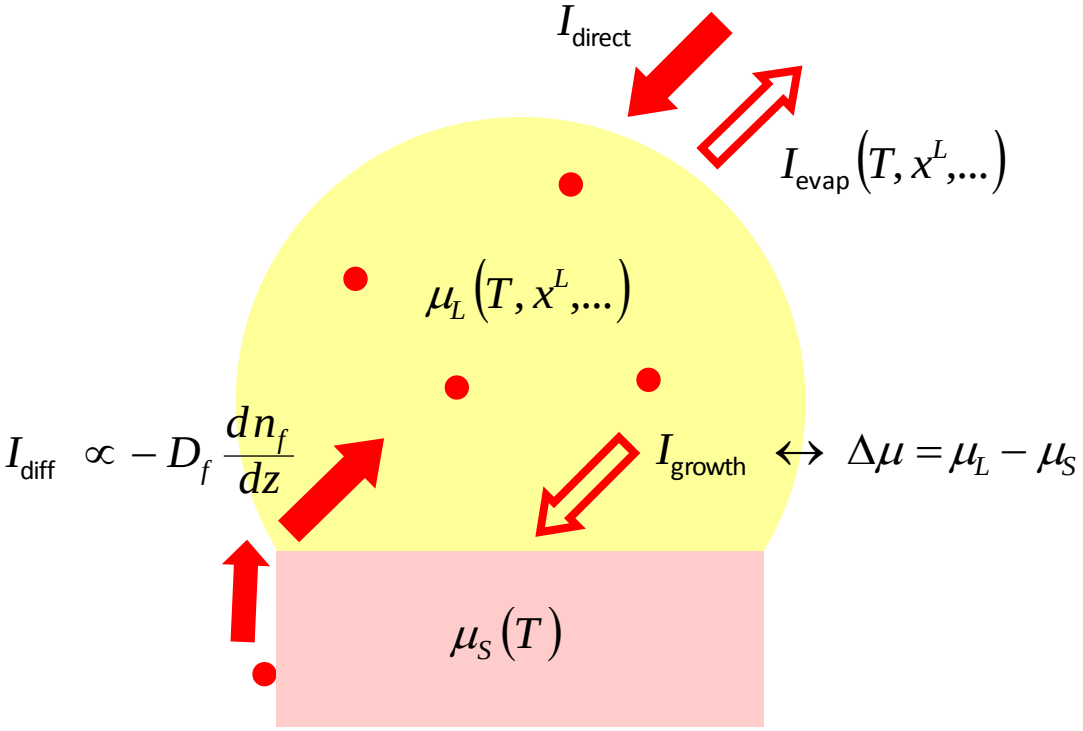
Instantaneous elongation rate $\frac{\Delta L}{\tau}$





*Harmand, Glas, Patriarche, Phys. Rev. B **81**, 235436 (2010)*

Coupling between diffusion and incorporation

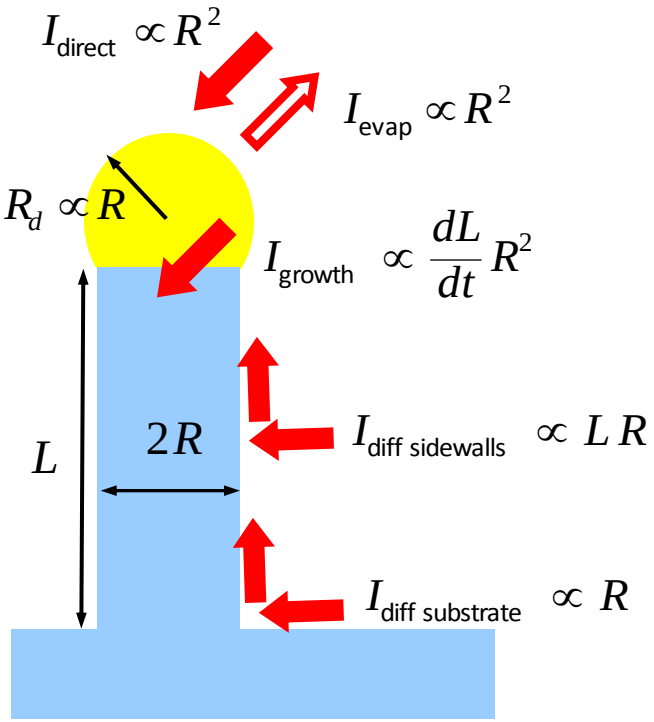


- Material balance $I_{\text{direct}} + I_{\text{diff}} = I_{\text{growth}} + I_{\text{evap}}$ ⟶

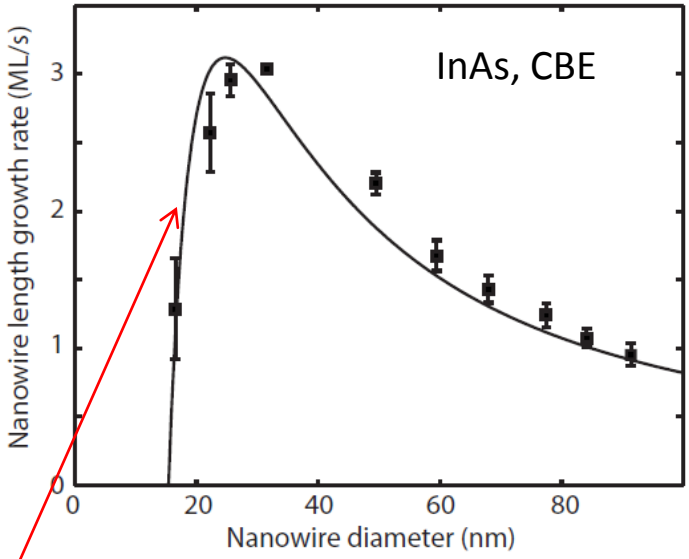
  self-consistent determination of x^L and growth rate possible in principle in simple sytems

- Feedback $I_{\text{growth}} \uparrow \Rightarrow x^L \downarrow \Rightarrow \Delta\mu \downarrow \Rightarrow I_{\text{in}} \uparrow \Rightarrow x^L \uparrow$

Length / radius dependence

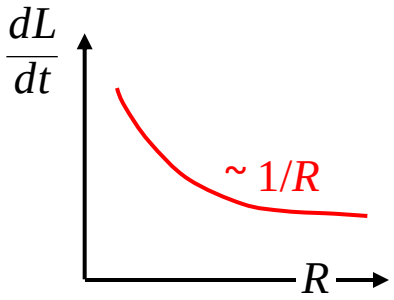


μ^L treated as a fitting parameter



Gibbs Thomson effect

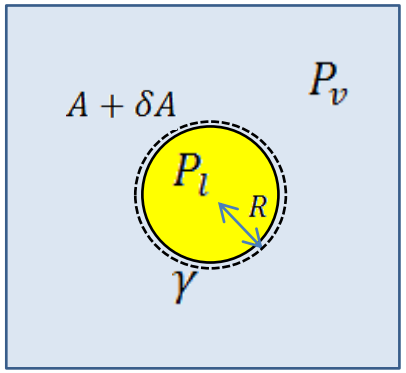
$$\frac{dL}{dt} = A + \frac{B}{R}$$



Fröberg et al., Phys. Rev. B 76, 153401 (2007)

Gibbs Thomson effect in a spherical droplet

The Gibbs Thomson effect describes the increase of chemical potential in a particular phase due the Laplace pressure which results from curvature effects



Laplace pressure

$$dF = \gamma dA - P_l dV_l - P_v dV_v$$

$$dV_v = -dV_l$$

$$dF = 0 \Rightarrow (P_l - P_v) = \gamma \frac{dA}{dV}$$

For a sphere

$$V = \frac{4}{3}\pi R^3 \qquad dV = 4\pi R^2 dR$$

$$A = 4\pi R^2 \qquad dA = 8\pi R dR$$

$$\frac{dA}{dV} = \frac{2}{R}$$

$$P_l - P_v = \frac{2\gamma}{R}$$

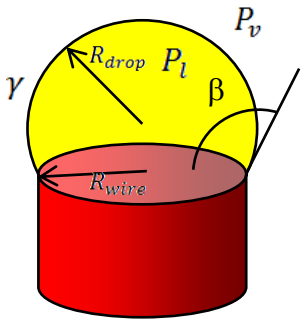
$$for\ a\ \ 10\ nm\ radius\ Au\ droplet\ (\gamma_{Au} = 0.91\ J.m^{-2})$$

$$P_l - P_v \approx 2000\ atm$$

Nanodroplets are under very high pressures

GT effect in the catalyst droplet of a nanowire

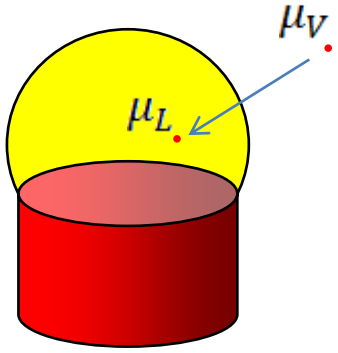
Generally, the shape of the catalyst is a truncated sphere on top of the nanowire of radius R_{wire}



Although the geometry has changed, we still have: $\frac{dA}{dV} = \frac{2}{R}$ with $R = R_{drop}$

$$P_l - P_v = \frac{2\gamma}{R_{drop}}$$

Change of free enthalpy after transferring one atom from the vapor to the liquid droplet



$$\delta G = \mu_L - \mu_V = \mu_L^{\infty} + \gamma \delta A - \mu_V$$

$$\delta A = \frac{2\delta V}{R_{drop}} = \frac{2\Omega_L}{R_{drop}}$$

Ω_L *atomic volume in the liquid*

$$\mu_L = \mu_L^{\infty} + \frac{2\gamma}{R}\Omega_L$$

For a Si atom dissolved in an Au droplet on top of a NW of 10 nm radius

$$\mu_L - \mu_L^{\infty} = 21\ meV$$

Kelvin effect: Equilibrium partial pressure is higher (desorption from the drop is higher)

$$P = P^{\infty} \exp \frac{2\gamma\Omega_L}{R k_B T}$$

for a NW of 10 nm radius

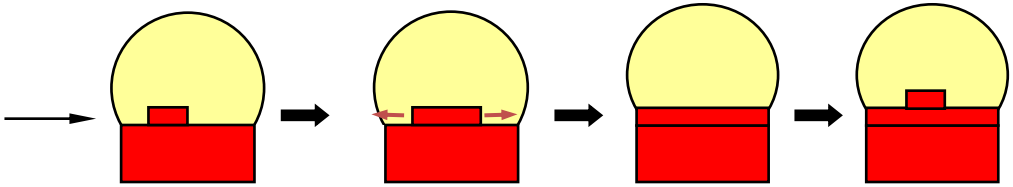
$$P \approx 1.33\ P^{\infty}$$

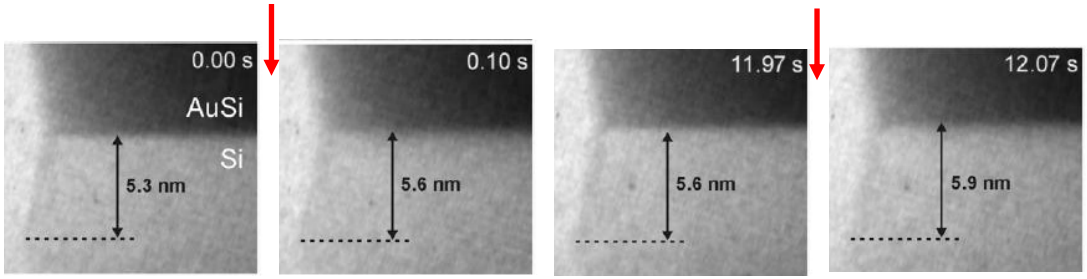
Outline

- Generalities on catalyst-assisted nanowire growth
- Kinetics of nanowire growth
- **Nucleation in VLS growth**
- Formation of heterostructures in nanowires

How does VLS growth proceed

- Monolayer by monolayer (1ML = 2 atomic planes)

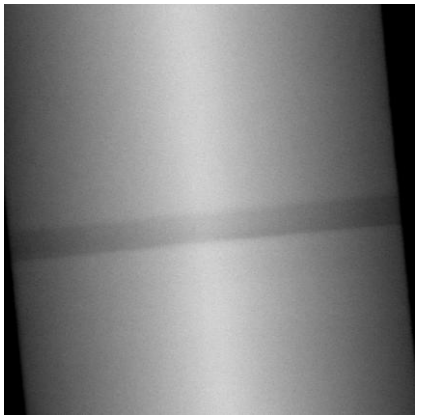




Si NW growth in a TEM

Wen et al., Science 326, 1247 (2009)

Flat heterointerfaces



AlGaAs insertion in GaAs NW

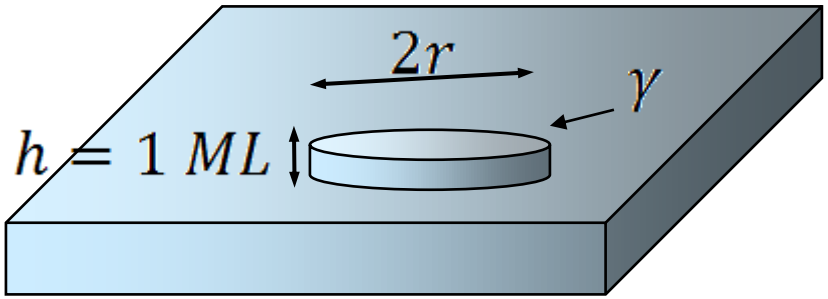
- At least one new 2D nucleus is needed for each ML
- If top facet is narrow enough, mononuclear regime

1 ML ↔ 1 nucleation event

Classical 2D nucleation theory

Supersaturated phase (gas, liquid, adatoms) $\Delta\mu > 0$

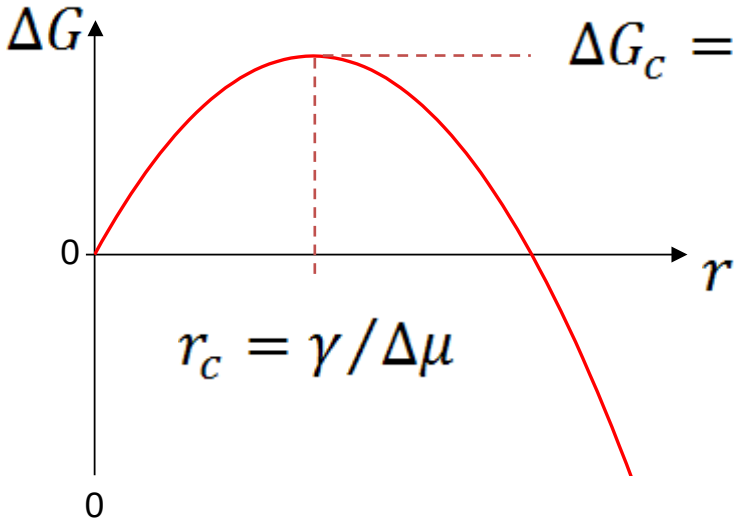
Venables et al, Rep. Prog. Phys. 47, 399 (1984)



Gibbs free energy of nucleus formation

$$\Delta G = -\pi r^2 h \Delta\mu + 2\pi r h \gamma$$

Nucleation barrier



$$\Delta G_c = \pi h \gamma^2 / \Delta\mu$$

$$r_c = \gamma / \Delta\mu$$

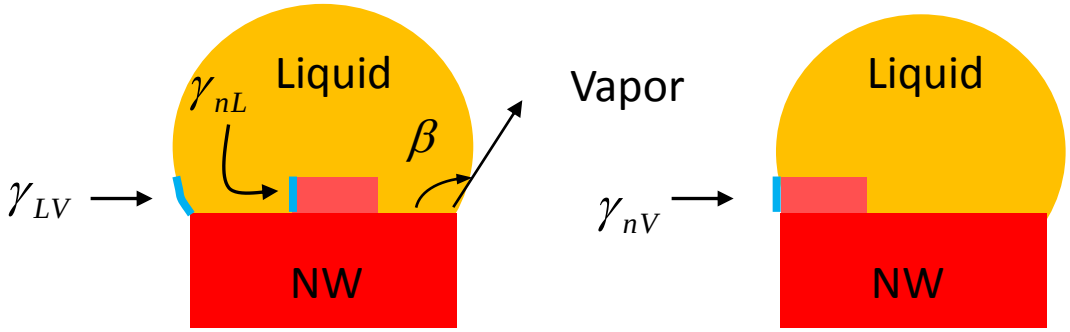
Nucleation rate:
Probability of forming a 2D nucleus
/(unit time x unit area)

$$J \propto \exp\left(\frac{-\Delta G_c}{k_B T}\right)$$

$r<r_c$ nuclei decompose easily

$r>r_c$ nuclei can extend by step flow

Where ?



Nucleus entirely surrounded by liquid

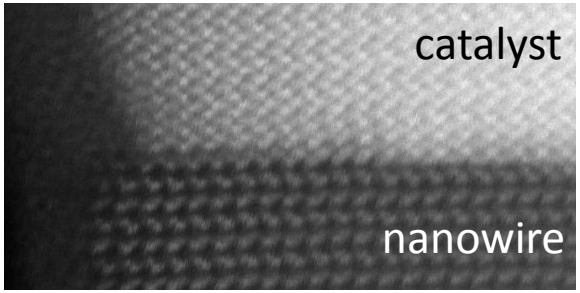
Nucleus at the periphery

Nucleation at the triple phase line if $\gamma_{nV} < \gamma_{nL} + \gamma_{LV} \sin\beta$

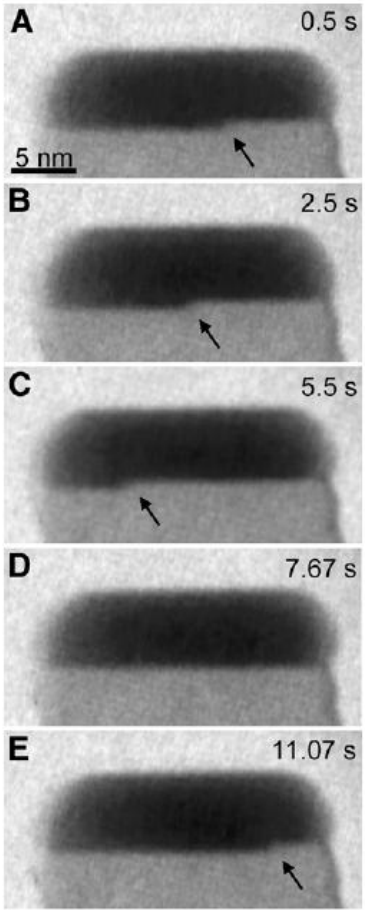
Easily satisfied for β ~90°

F. Glas et al., Phys. Rev. Lett. 99, 146101 (2007)

Some experimental indications of nucleation at TPL

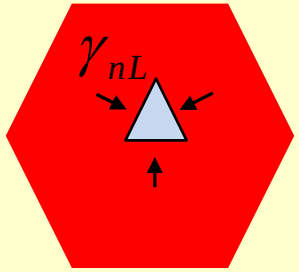


Wen, Science 326, 1247 (2009)
VSS growth of Si NW in UHV TEM
AlAu catalyst



Impact of nucleation at the TPL on the crystal phase

Nucleus
surrounded by liquid

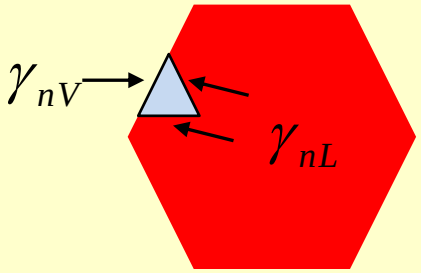


$$\gamma_{\text{eff}} \approx \gamma_{nL} \qquad \gamma_{eff}^{WZ} \approx \gamma_{eff}^{ZB}$$

In this case, the ZB nucleus is the stabler (like in bulk III-Vs)

Difference of cohesion energy: $\delta E_{coh} = E^{ZB} - E^{WZ} \approx 24\,meV / GaAs\,pair$

Nucleus at the periphery



$$\gamma_{\text{eff}} \approx \frac{2}{3}\gamma_{nL} + \frac{1}{3}(\gamma_{nV} - \gamma_{LV}\sin\beta) \qquad \gamma_{eff}^{ZB} - \gamma_{eff}^{WZ} \approx \frac{1}{3}(\gamma_{nV}^{ZB} - \gamma_{nV}^{WZ})$$

And we have $\gamma_{nV}^{ZB} > \gamma_{nV}^{WZ}$

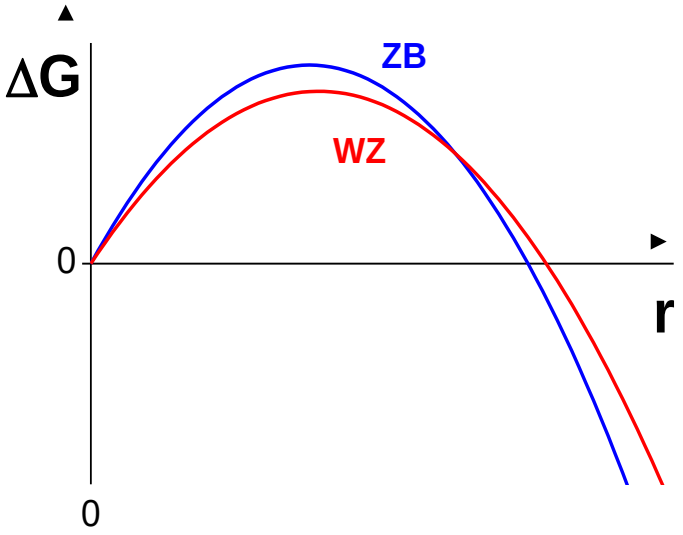
See DFT calculations by
Pankoke, Phys. Rev. B 84 , 075455 (2011)

In this case the nucleation barrier can be lower for the WZ nucleus

Zinc blende / wurtzite polytypism

Different barriers to form a ZB or WZ nucleus

$$\Delta G_c^{ZB} = gh\frac{\gamma_{eff}^{ZB\,2}}{\Delta\mu} \qquad \Delta G_c^{WZ} = gh\frac{\gamma_{eff}^{WZ\,2}}{\Delta\mu - \delta E}$$



We have $\Delta G_c^{WZ} < \Delta G_c^{ZB}$

when $\Delta\mu > \dfrac{\gamma_{eff}^{ZB\,2}}{\gamma_{eff}^{ZB\,2} - \gamma_{eff}^{WZ\,2}}\delta E$

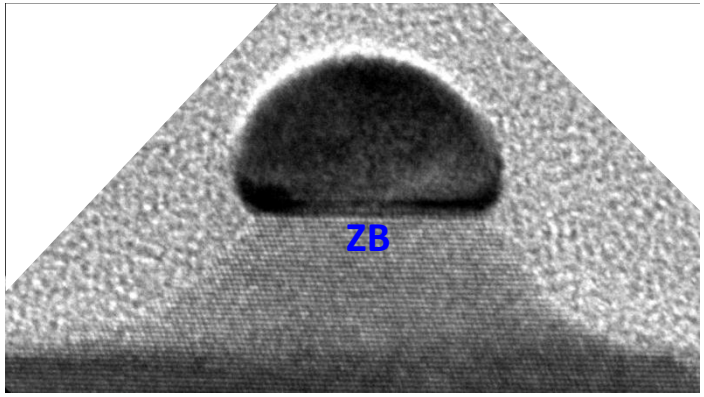
Glas, Harmand, Patriarche, Phys. Rev. Lett. 99, 146101 (2007)

$\Delta\mu \uparrow$, critical nucleus becomes smaller, edge energy weighs more, favorable to WZ

$$r_c = \gamma/\Delta\mu$$

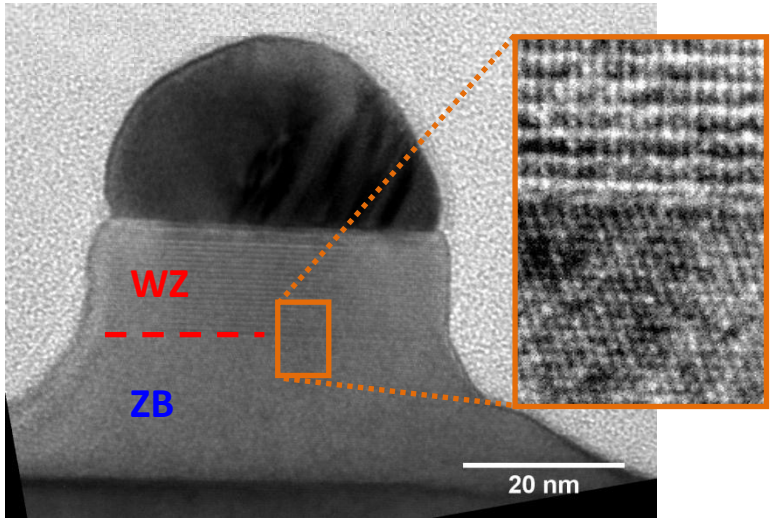
Experimental evidence of phase transitions

Beginning of growth

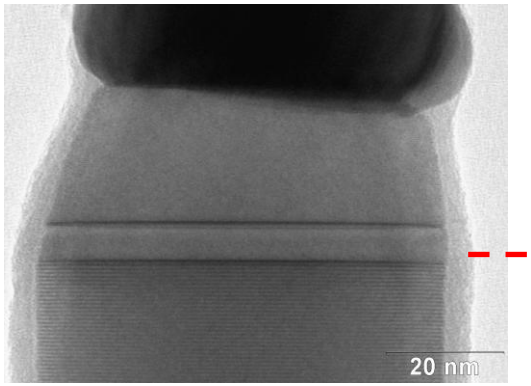


Phase transition when
$\Delta\mu > \Delta\mu_c$

$\Delta\mu \uparrow$



End of growth under As
The drop is purged
Reverse transition when $\Delta\mu < \Delta\mu_c$

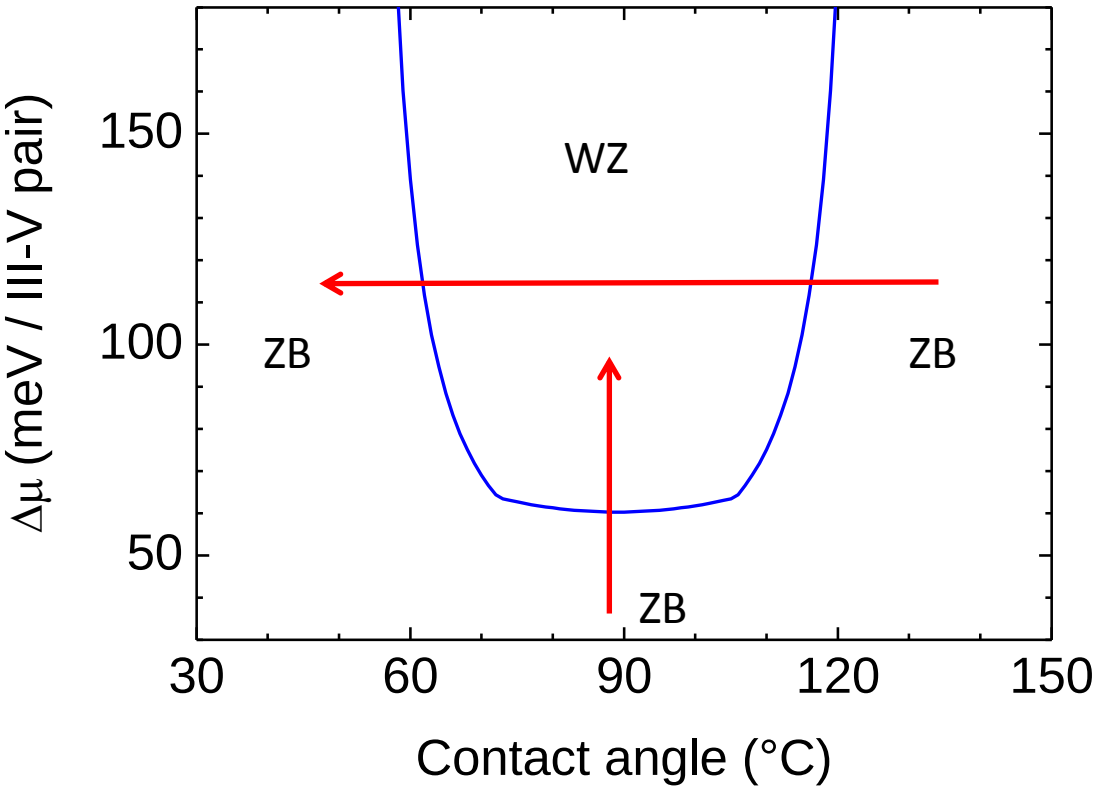


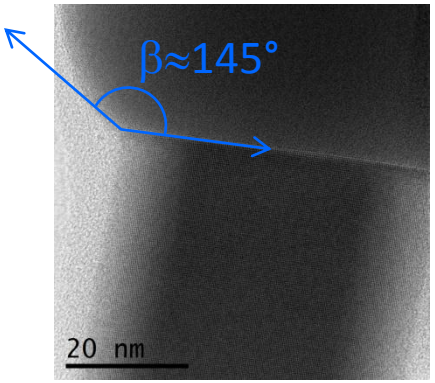
$\Delta\mu \downarrow$

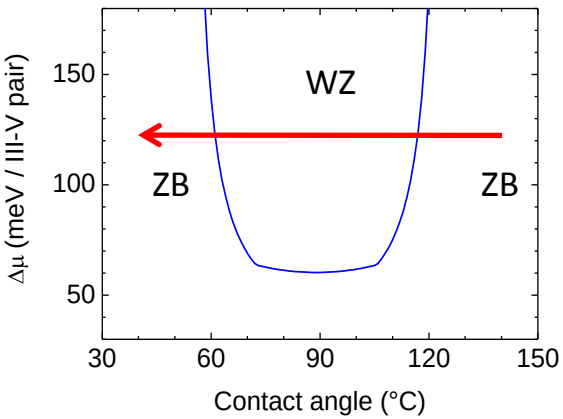
Role of the contact angle β

The critical supersaturation depends on β

$$\Delta\mu_c = \frac{\gamma_{eff}^{ZB\,2}}{\gamma_{eff}^{ZB\,2} - \gamma_{eff}^{WZ\,2}}\,\delta E_{coh} \qquad \gamma_{eff}^{WZ} \approx \frac{2}{3}\gamma_{nL}^{WZ} + \frac{1}{3}\left(\gamma_{nV}^{WZ} - \gamma_{LV}\sin\beta\right)$$







ZB

Faulted WZ

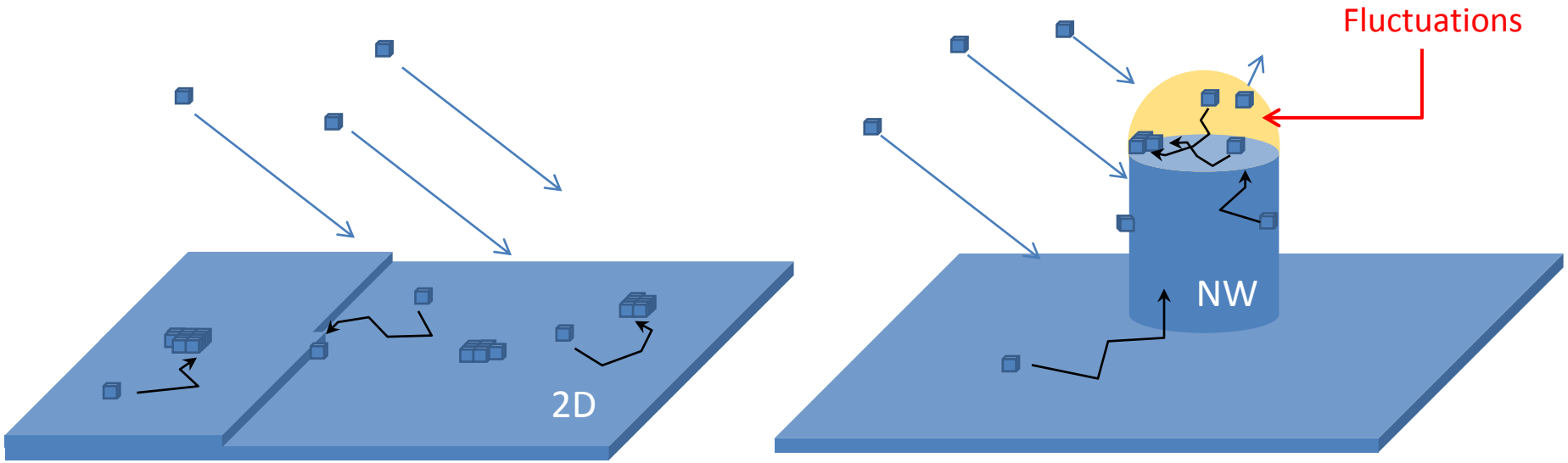
WZ

Faulted WZ

Faulted ZB

ZB

Comparing 2D and NW growth



Formation of 1 ML

Infinite surface
infinite parent phase

- Many nuclei
- Step flow
- Coalescence

Time to form 1ML = cst

Statistics of nucleation events is hidden

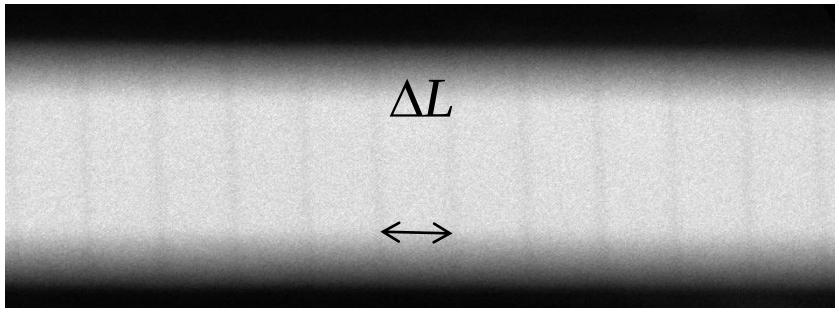
Limited surface area
parent phase ≡ finite and open nanovolume

- 1 nucleation event is needed at each new ML
- Extension by step flow until the ML is completed
- Composition of the parent phase may fluctuate

Time to form 1ML ≠ cst

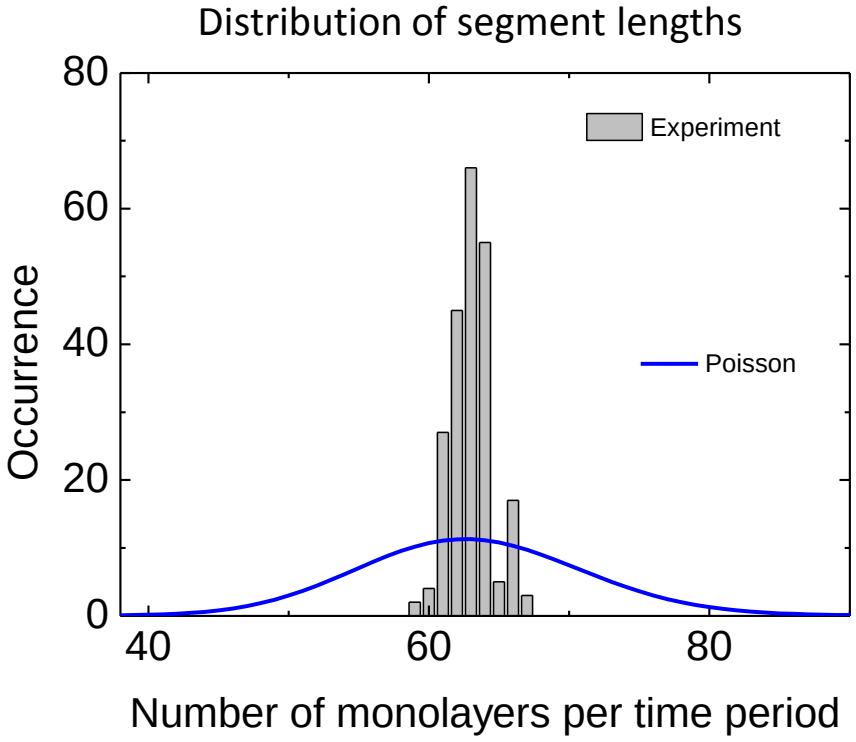
Depends on nucleation statistics

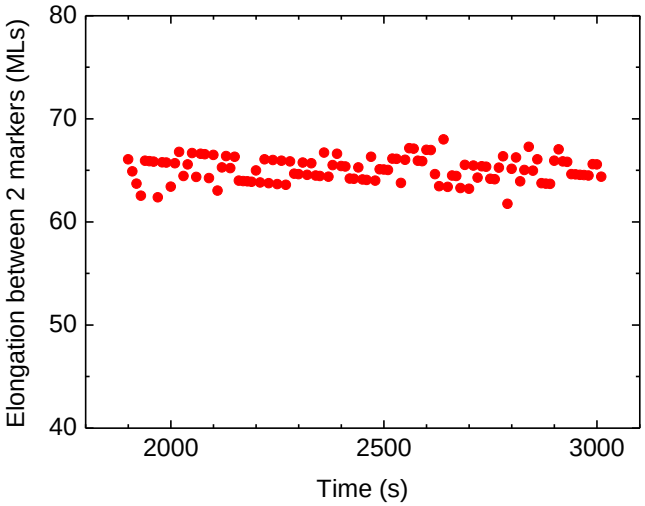
Nucleation statistics



Use of chemical markers (here AlGaAs in GaAs NW) introduced periodically (period τ) during growth

For each period, elongation ΔL is measured
= number of MLs grown in the time period τ
= number of nucleation events during τ
if growth regime is mononuclear

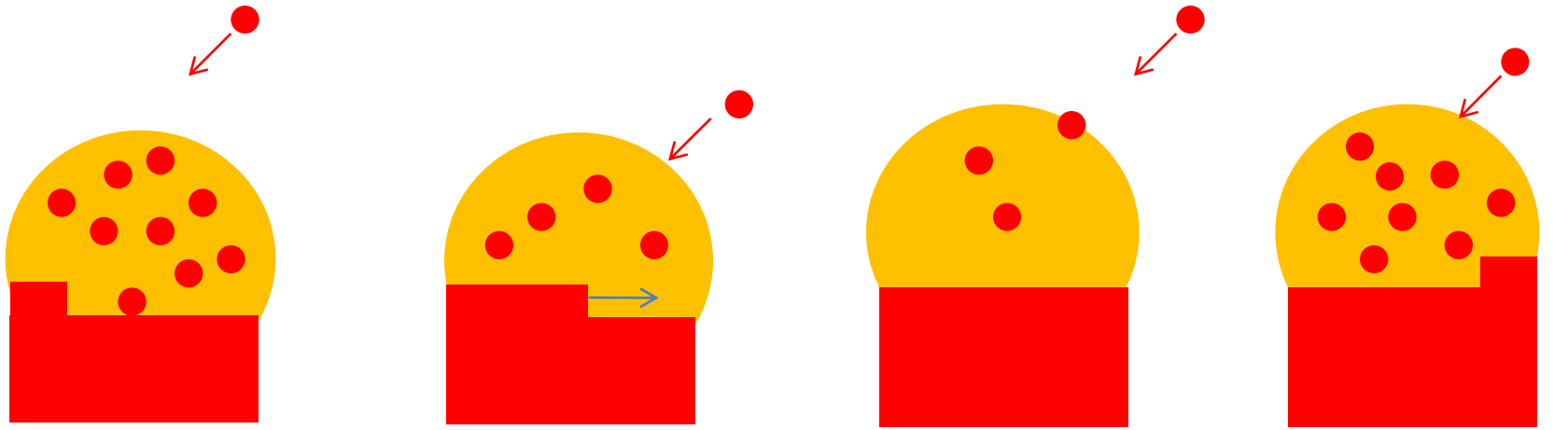




→ Sub-poissonian statistics
→ Probability of nucleation varies with time

*Glas, Harmand, Patriarche PRL **104**, 135501 (2010)*

Self-regulated growth



Nucleation

Rapid depletion of the reservoir

Time for refilling

New nucleation

Concentrations of the NW constituents vary with time:

→ Rapid decrease when a ML forms after a nucleation event
→ Slow refilling rate between two nucleations

This mechanism regulates the nucleation events which become anti-correlated.

Model

*Glas, Harmand, Patriarche PRL **104**, 135501 (2010)*

Nucleation probability

$$P \propto exp[-\Delta G_c/(k_B T)] \quad \text{with} \quad \Delta G_c = A/\Delta\mu \quad \text{and} \quad A = g\Omega h\gamma^2$$

Expanding $\Delta\mu$

$$\Delta\mu = \overline{\Delta\mu} + \alpha_{III}\frac{\delta c_{III}}{\bar{c}_{III}} + \alpha_V\frac{\delta c_V}{\bar{c}_V} \quad \text{with} \quad \alpha_i = \bar{c}_i\left(\frac{\partial\Delta\mu}{\partial c_i}\right)_{\bar{c}_{III},\bar{c}_V} \quad \text{and} \quad \delta c_i = c_i - \bar{c}_i$$

$$P \approx \bar{P}\, exp\left[\frac{A}{\overline{\Delta\mu}^2}\left(\frac{\alpha_{III}}{k_B T}\frac{\delta c_{III}}{\bar{c}_{III}} + \frac{\alpha_V}{k_B T}\frac{\delta c_V}{\bar{c}_V}\right)\right]$$

Self catalyzed growth: Ga droplet with a small concentration of As
We use parameters extracted from a study of self-catalyzed growth kinetics

Ramdani, Harmand, Glas, Patriarche, Travers, Cryst. Growth & Des. 13, 91 (2013)

Glas, Ramdani, Patriarche, Harmand, Phys. Rev. B 88, 195304 (2013)

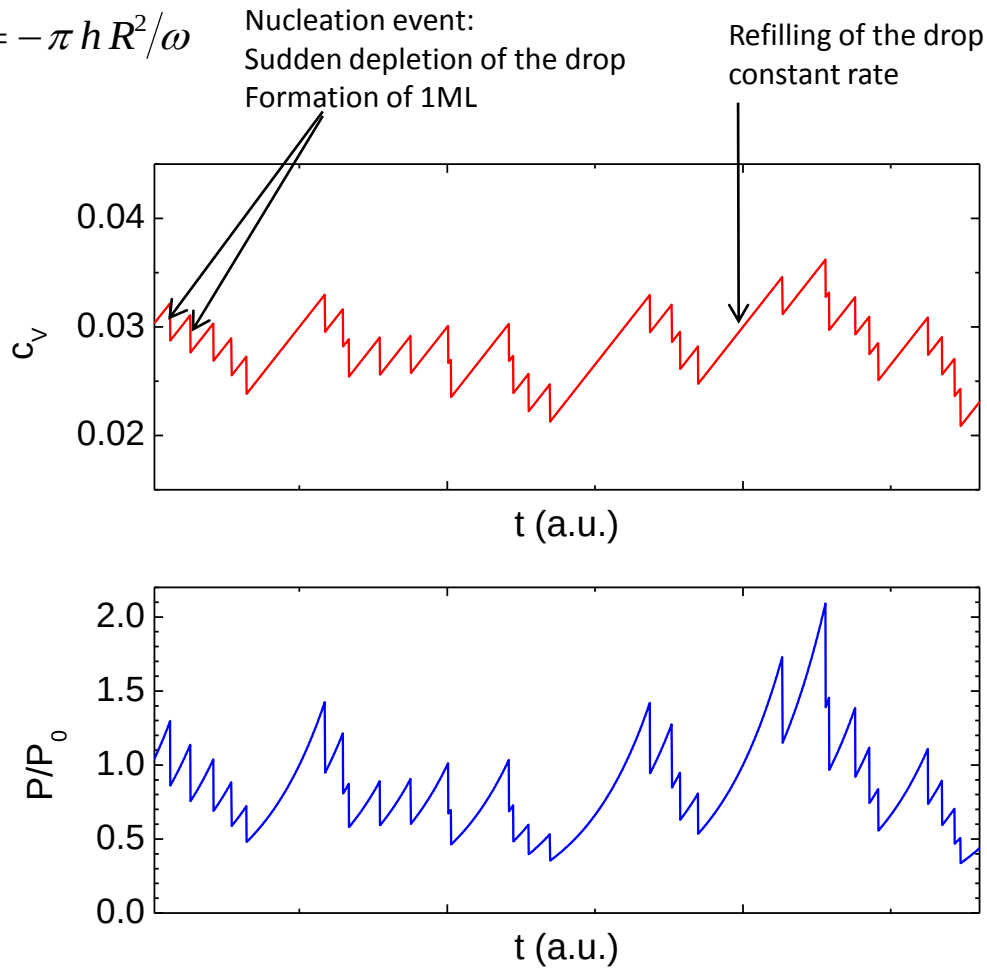
$\overline{c_{III}} = 0.987 \quad \overline{c_V} = 0.013$

After 1 ML completion in a NW with $R = 32\ nm \quad \beta = 125$

$|\delta c_{III}/\overline{c_{III}}| = 0.002 \quad |\delta c_V/\overline{c_V}| = 0.159$

Simulation of a sequence of nucleations

$$\delta N_{III} = \delta N_V = \delta N_{ML} = -\pi h R^2/\omega$$

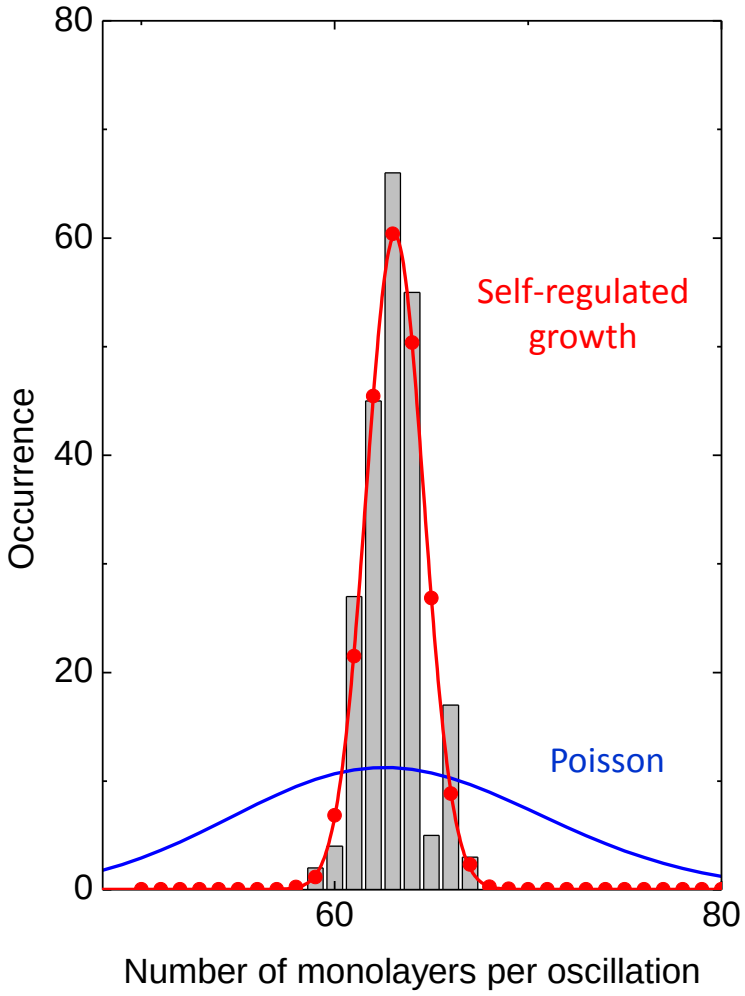


$$\delta N_{III}/\delta t = \delta N_V/\delta t$$

→ The regulation effect is due to the low concentration of group V atoms in the droplet

→ The thinner the NW, the larger the effect

Modeling the nucleation statistics



Set of parameters

Simulation

$c_{As} = 0.013$

$\overline{\Delta\mu} = 145$ meV

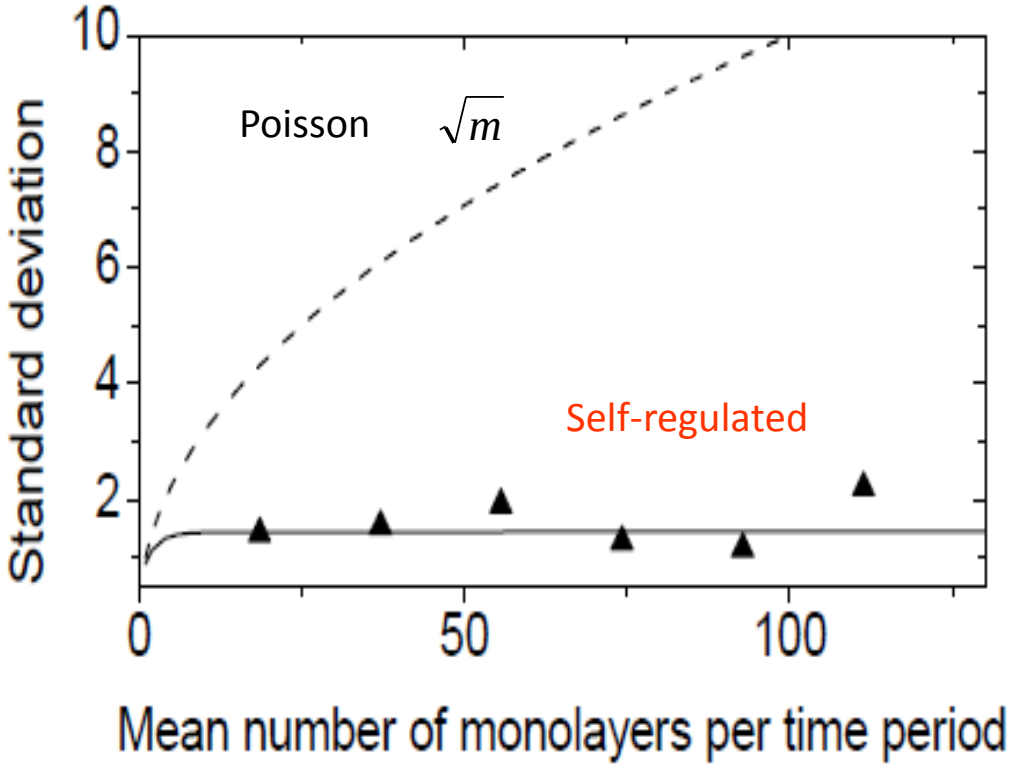
$\gamma_e = 0.155\ Jm^{-2}$

Growth kinetics of these NWs was fitted with very similar values…

Ramdani et al, Cryst. Growth & Des. 13, 91 (2013)

Glas et al, Phys. Rev. B 88, 195304 (2013)

Saturation of the standard deviation



The lengths of NWs grown from identical droplets can be very uniform

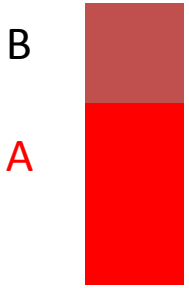
*Glas, Harmand, Patriarche PRL **104**, 135501 (2010)*

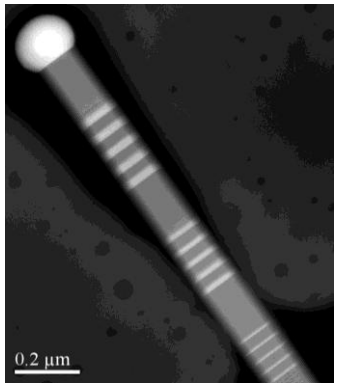
Outline

- Generalities on catalyst-assisted nanowire growth
- Kinetics of nanowire growth
- Nucleation in VLS growth
- **Formation of heterostructures in nanowires**

Heterostructures in NWs

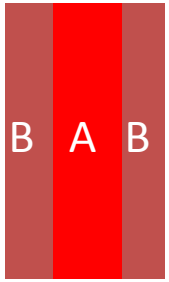
Axial

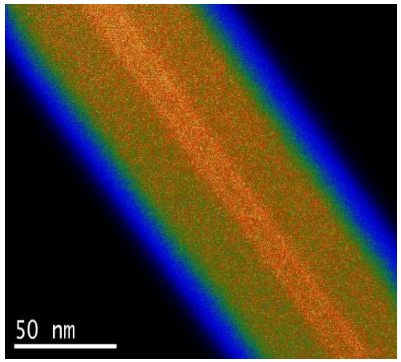




GaP/GaAs superlattices
G. Priante (LPN)

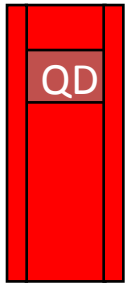
Radial (core-shell)

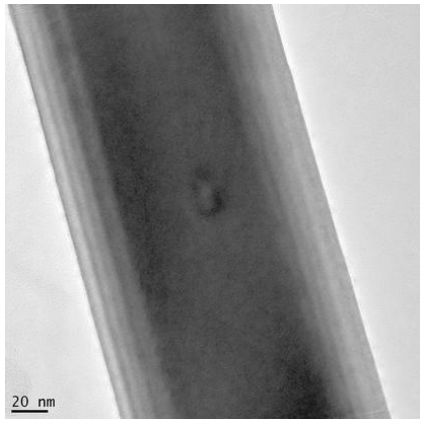




In(P,As)/InP core-shell
L. Liu (LPN)

Axial + radial

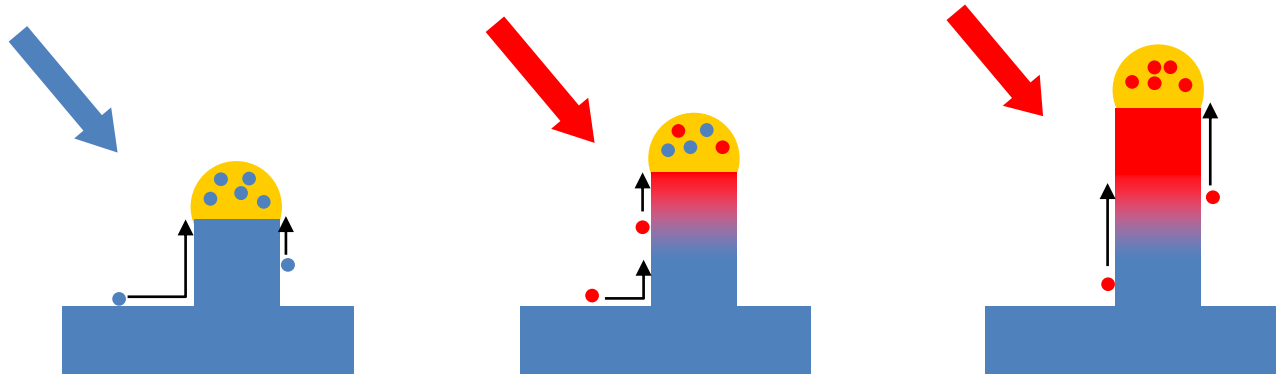




In(P,As) QD
in InP NW (LPN)

- Control of dimensions via NW seed or mask pattern and growth time
- Strain accommodation easier in NWs than in 2D layers

The reservoir effect in axial heterostructures

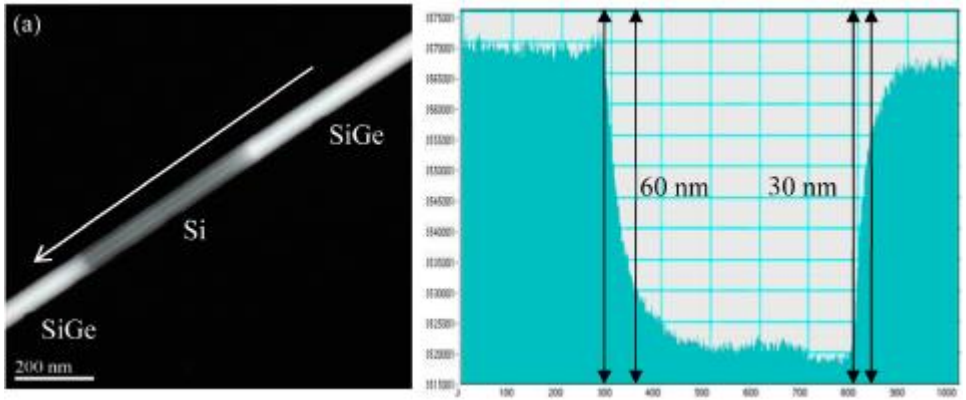


Length of graded composition ~R

The reservoir effect is critical for the constituents which are highly soluble in the catalyst

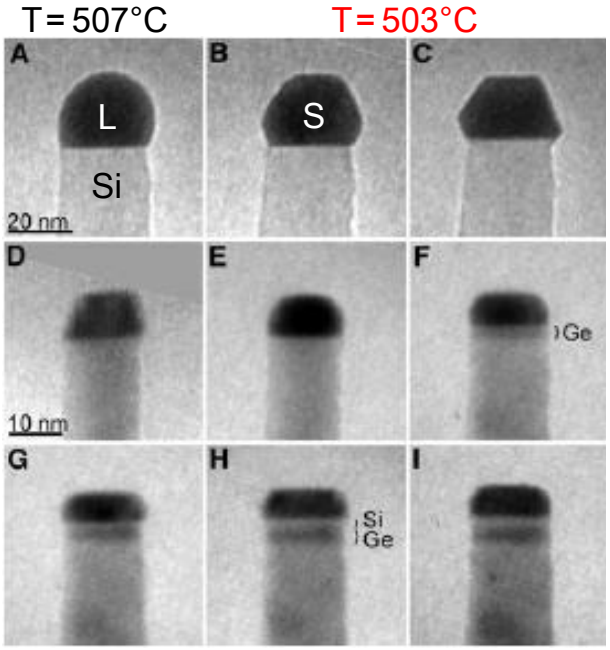
Au catalyst:
Si/Ge heterostructures
GaAs/InAs, GaAs/AlAs

Au catalyzed Si/SiGe NWs *Periwal et al, Nano Lett. 14, 5140 (2014)*

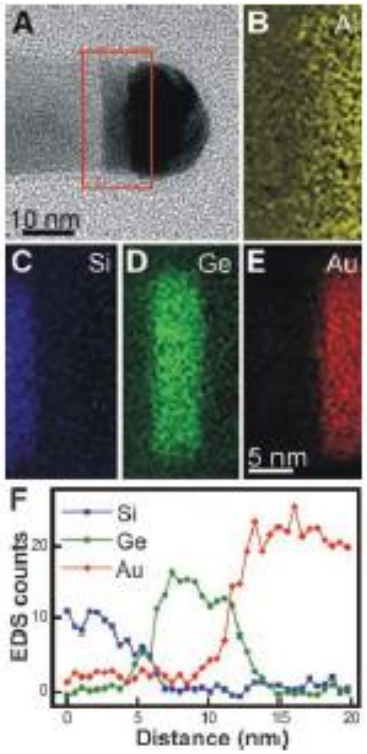


Getting around the reservoir effect

Solid reservoir: VSS growth



Wen et al., Science 326, 1247 (2009)

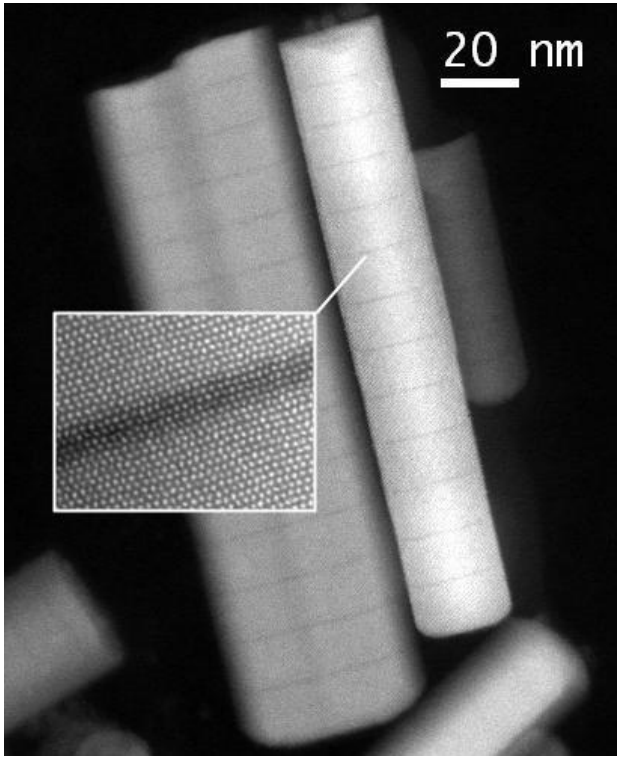


Solubility of NW element(s) is much lower in a solid catalyst

Sharp interfaces... but VSS growth is very slow

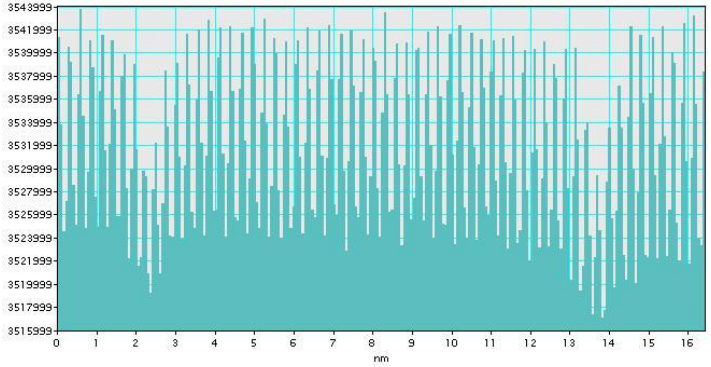
Getting around the reservoir effect

No reservoir: Catalyst-free growth



E. Galopin et al, Nanotechnology 22, 245606 (2011)
LPN, Marcoussis

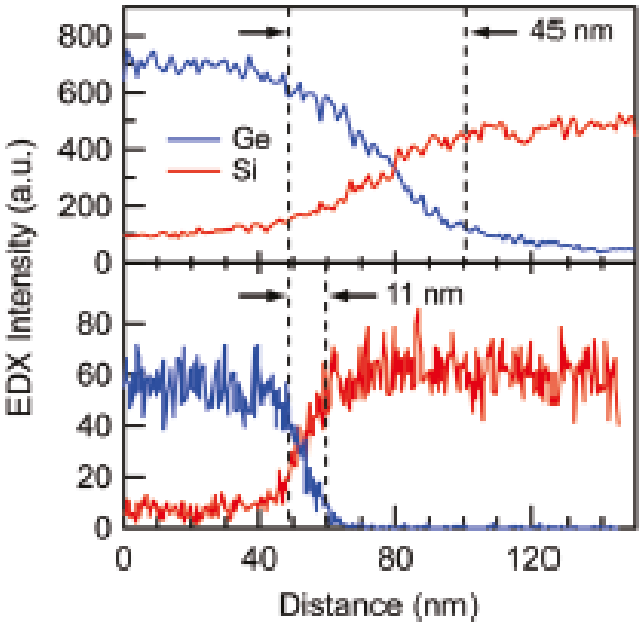
GaN/AlN heterostructures



Getting around the reservoir effect

Modify the catalyst to lower the solubility of NW constituent

Si/Ge heterostructures



Au catalyst

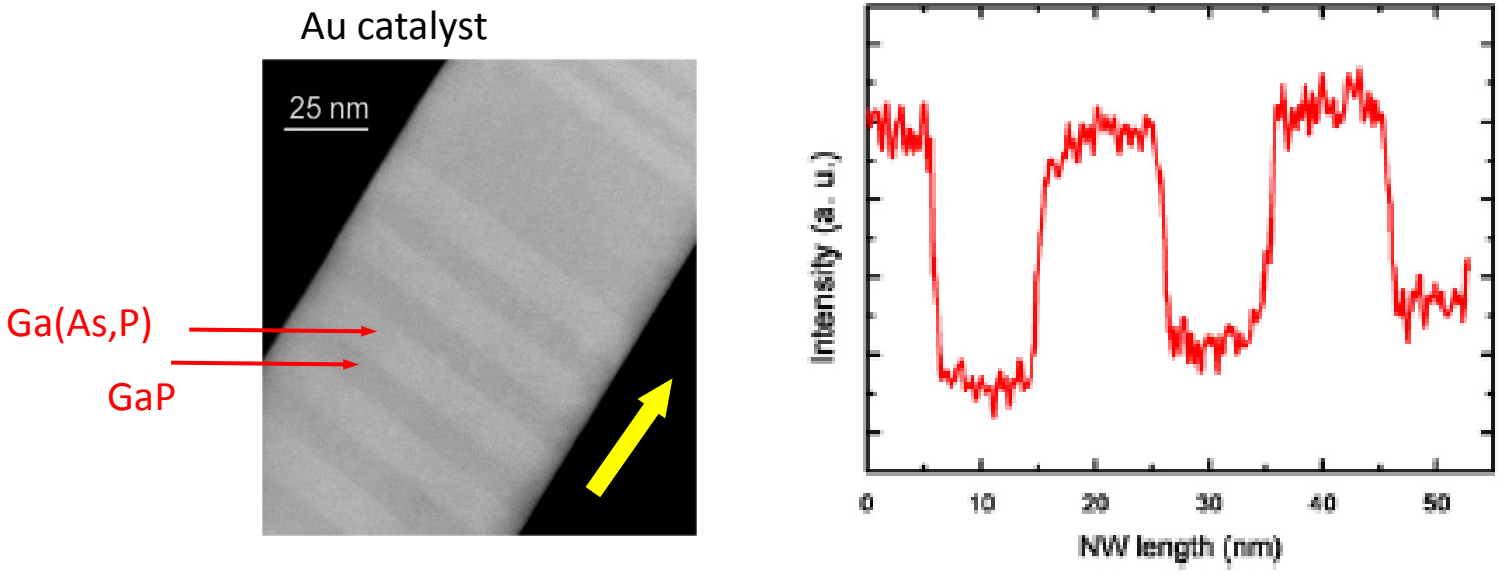
$Au_{0.66}Ga_{0.34}$ catalyst

Perea et al., Nano Lett. 11, 3117 (2011)

Getting around the reservoir effect

Commute elements of low solubility

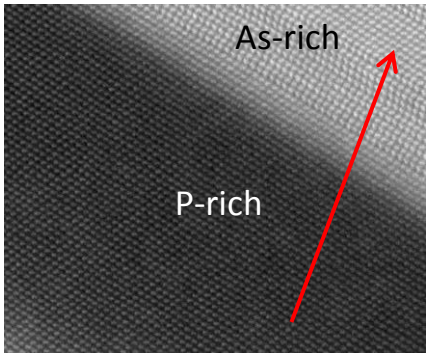
GaAs/GaP heterostructures



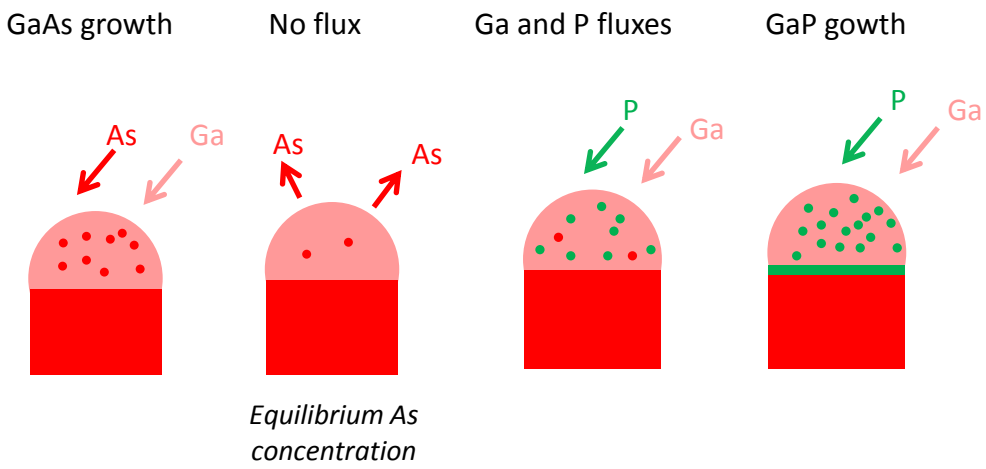
Jabeen, Patriarche, Glas, Harmand, J. Cryst. Growth 323, 293 (2011)
LPN Marcoussis

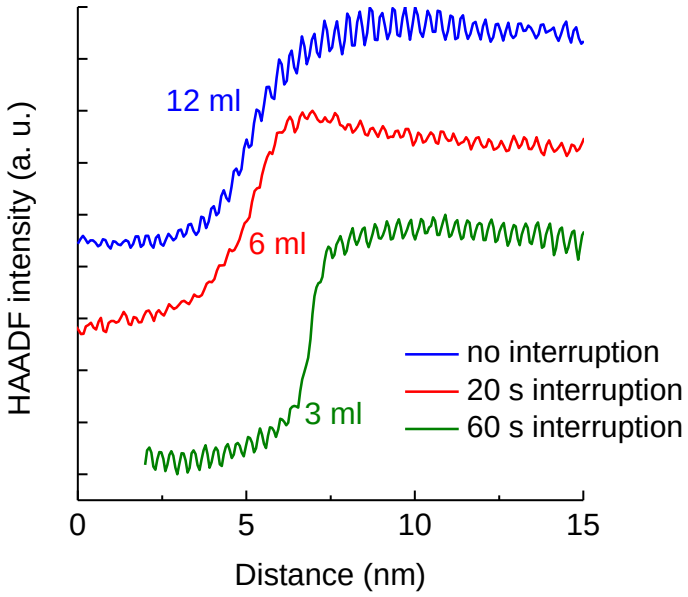
Getting around the reservoir effect

Purge the droplet at the heterointerface



GaAs/GaP heterostructures / self-catalyzed growth





Priante, Patriarche, Oehler, Glas, Harmand, Nano Lett. 15, 6036, 2015

Conclusions

Catalyst-assisted nanowire growth is governed by specific mechanisms which differ from those at play in standard 2D growth

- Catalyst particle ≡ dense reservoir of constituents
- Faster growth at the catalyst/nanowire interface
- Diffusion of adatoms to the drop
- Non-constant growth rate
- Stochastic formation of monolayers, but can be regulated by dilute constituents in the droplet
- Nucleation at the triple phase line is favorable and metastable crystal phase can form
- Formation of abrupt interfaces is challenging

Acknowledgements

Co-workers at LPN
Frank Glas
Gilles Patriarche
Ludovic Largeau
Fabrice Oehler
Noëlle Gogneau
Laurent Travers, Olivia Mauguin, Elisabeth Galopin

Post-docs at LPN
Maria Tchernycheva, Corinne Sartel, Linsheng Liu, Damien Lucot, Fauzia Jabeen, Reda Ramdani

PhDs at LPN
Yann Cohin, Giacomo Priante, Theo Jegorel, Vishnuvarthan Kumaresan

Vladimir Dubrovskii, George Cirlin *St Petersburg Academic University of the RAS and Ioffe Institute*