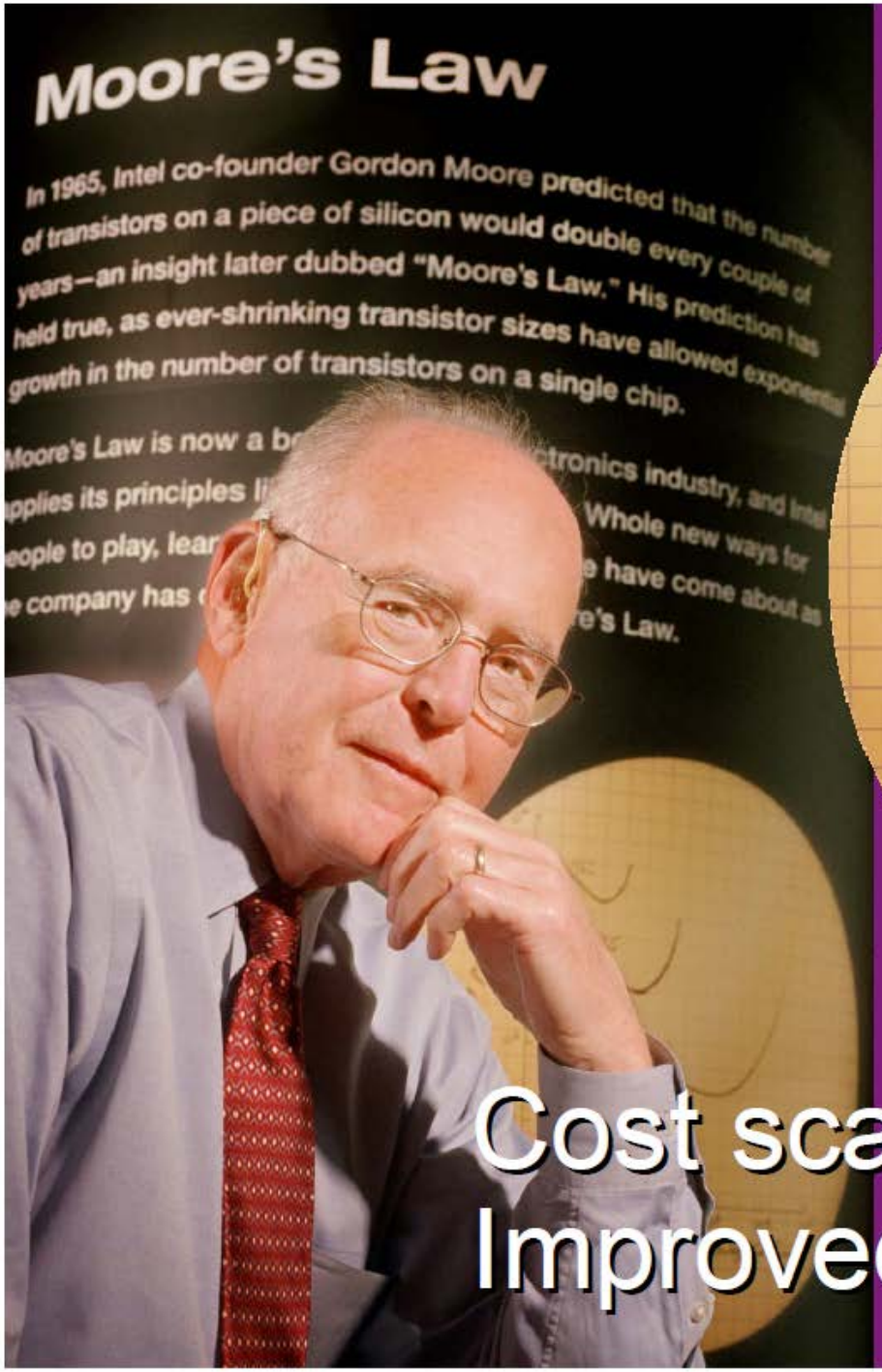
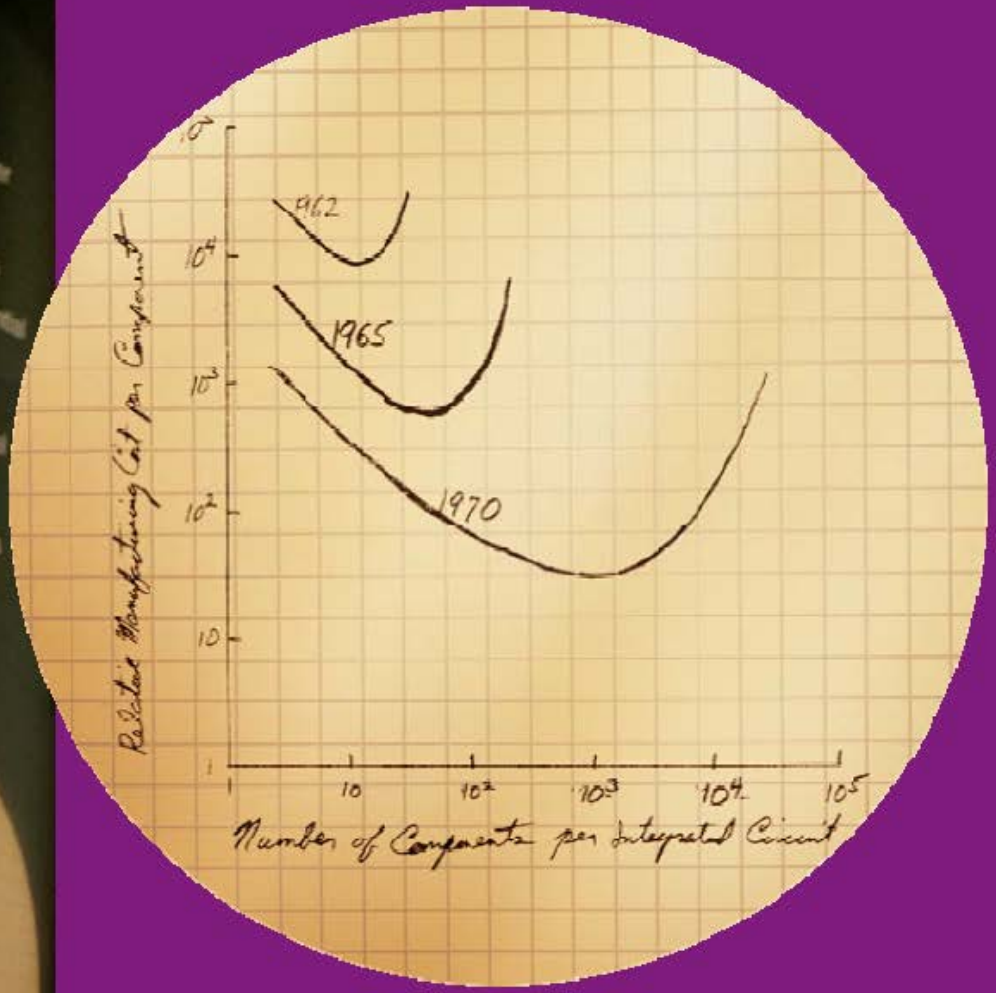
Croissance de matériaux 1D, 2D, 3D pour l'optoélectronique et la nanoélectronique

Sébastien Plissard

Croissance de matériaux 1D: les nanofils: Le Contexte





Cost scaling
Improved performance

Nanoscale dimensions by lithography

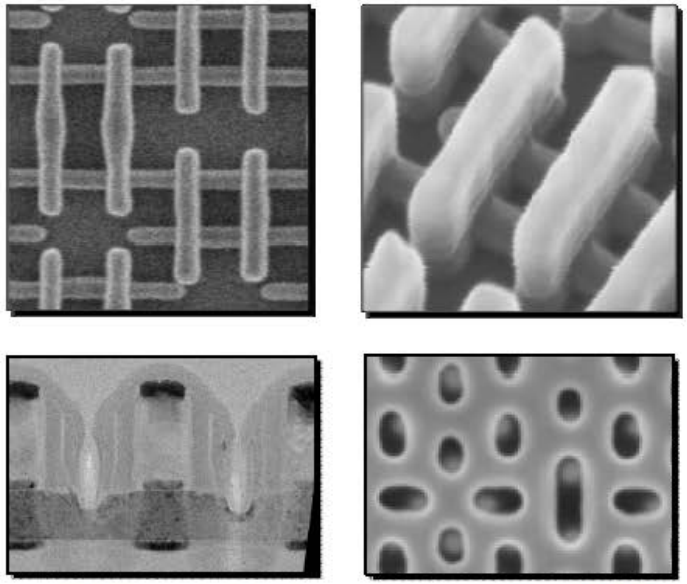
Exposure wavelength (λ)

- 436nm : g-line
- 365nm : i-line
- 248nm : Deep-UV (KrF)
- **193nm : Deep-UV (ArF)**
- 157nm : Vacuum UV (F2)
- **13.5nm: Extreme UV (EUV)**

Lord Rayleigh

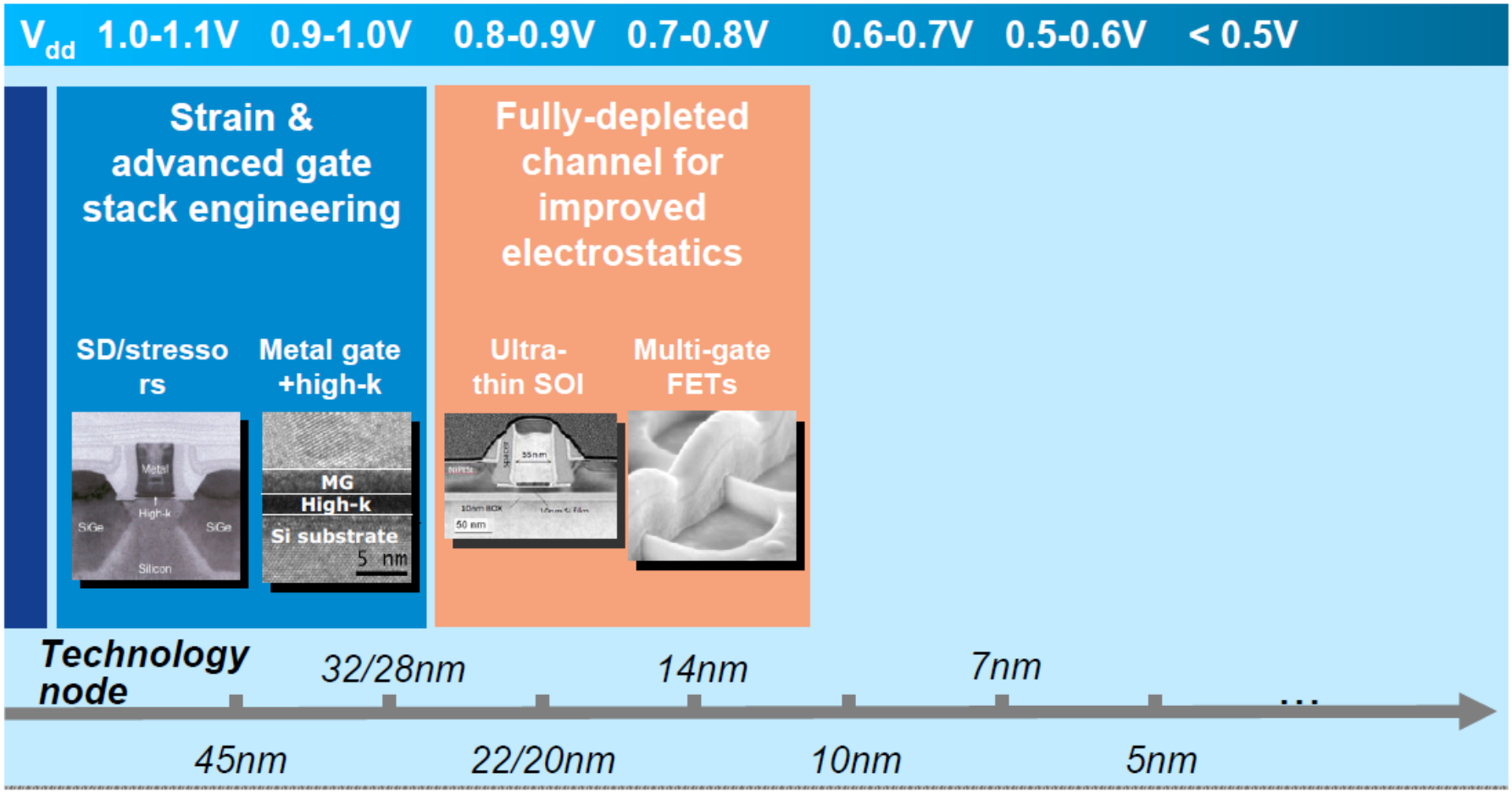
Rayleigh equation defines litho roadmap

$$resolution = k_1 . \frac{\lambda}{NA}$$



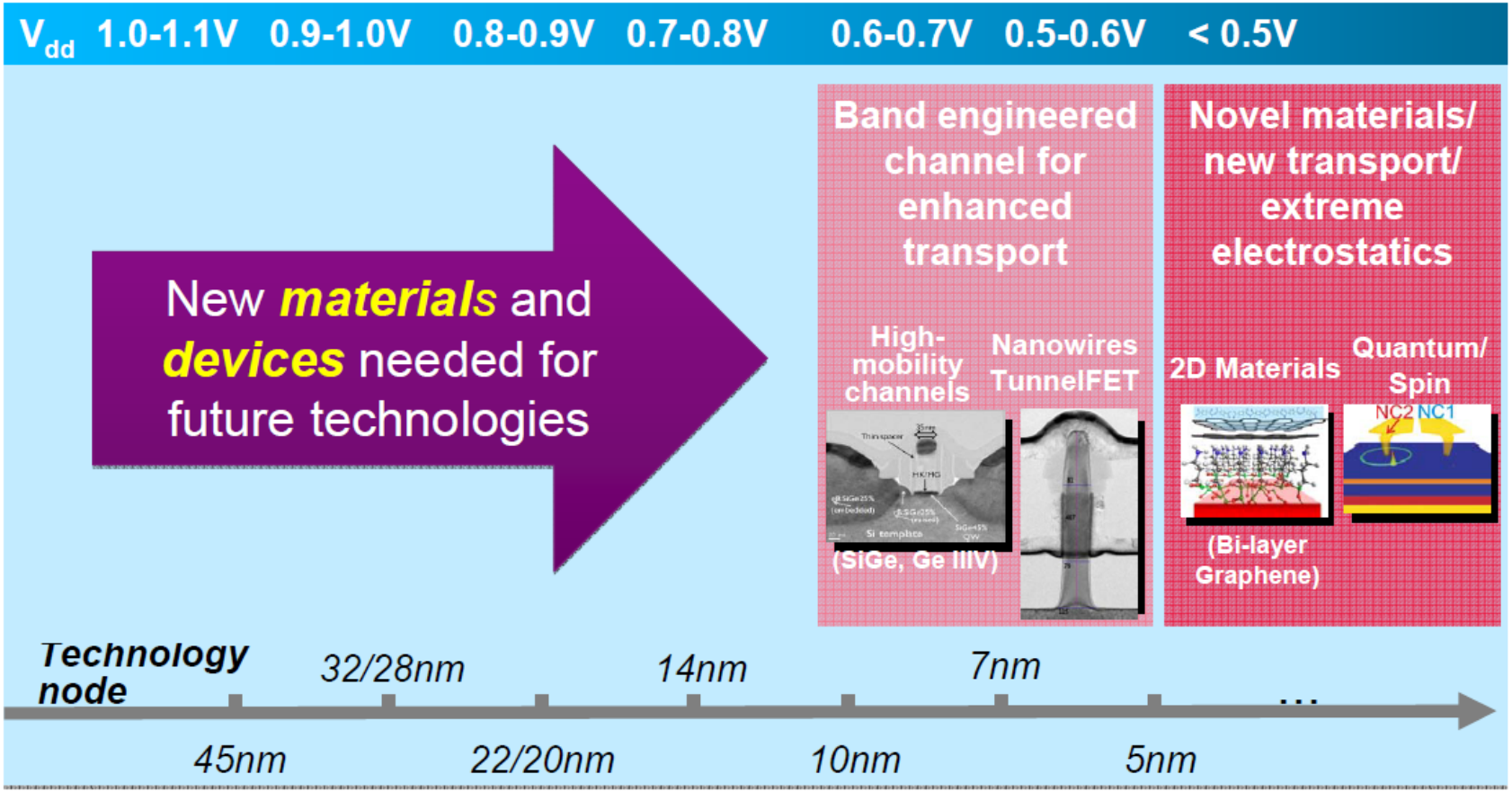
22-16nm SRAM fabricated with EUV

Logic scaling trend and roadmap



- Feature dimension & voltage scaling are concurrent drivers

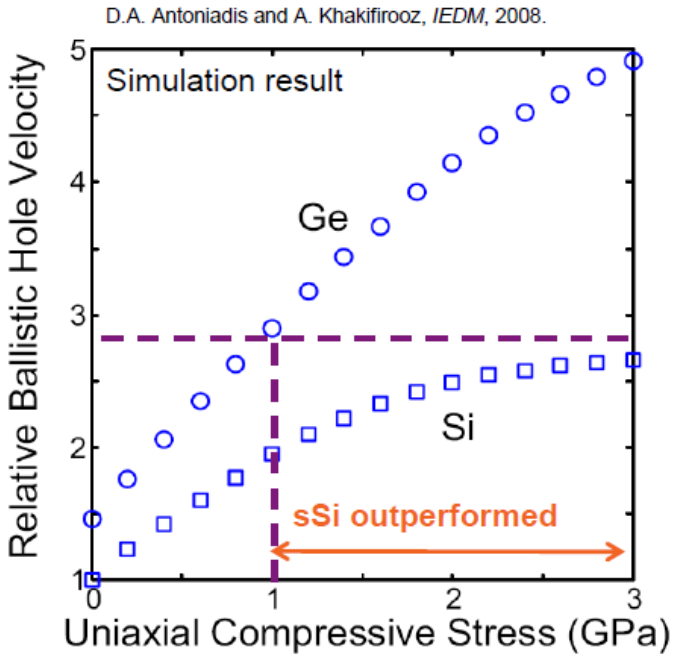
Logic scaling trend and roadmap



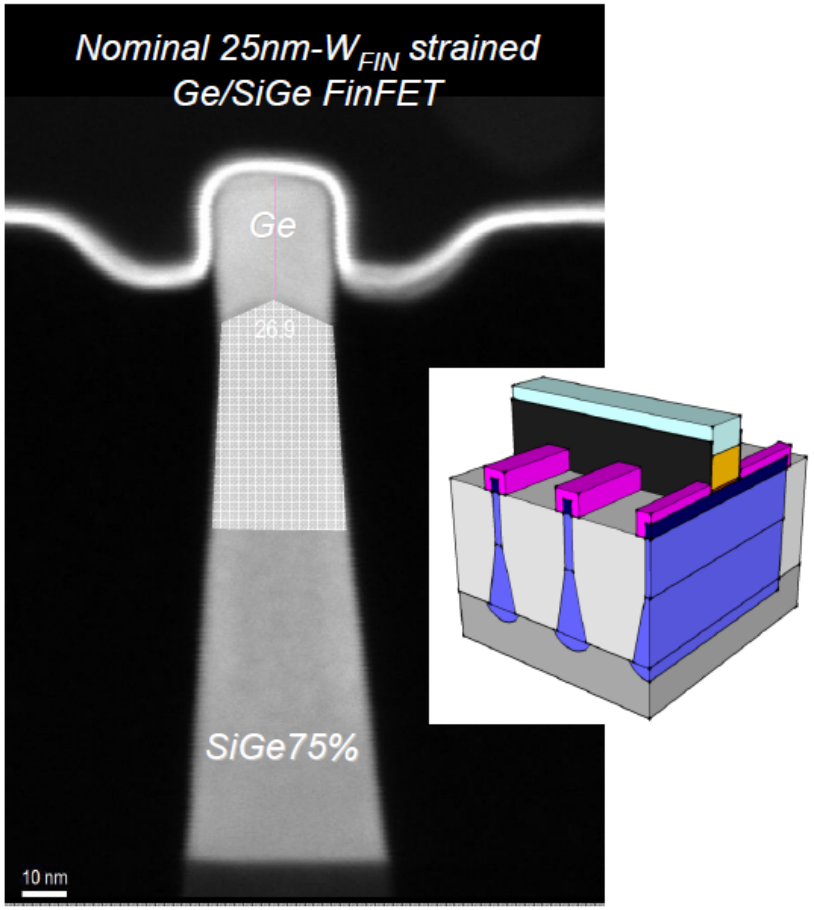
- Feature dimension & voltage scaling are concurrent drivers
- Material & device architecture innovations enablers of continual scaling

Strained Ge pMOS devices

- Compressively strained Ge can outperform sSi pMOS



- Demonstration of strained Ge/SiGe FinFETs shows promising electrical results



Strained Ge pMOS devices

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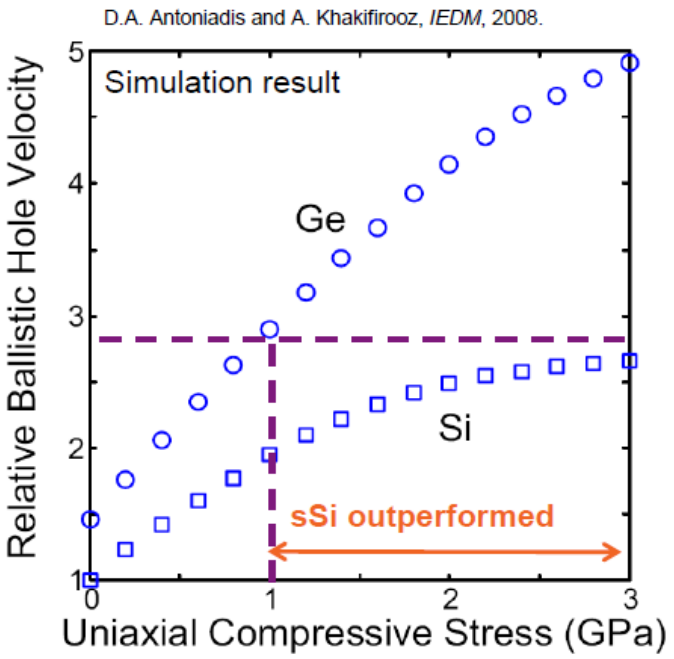
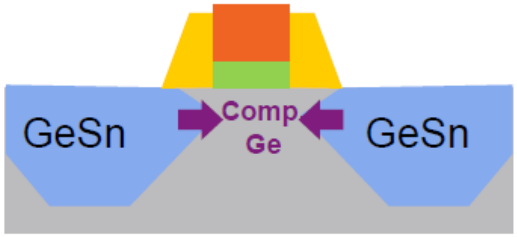
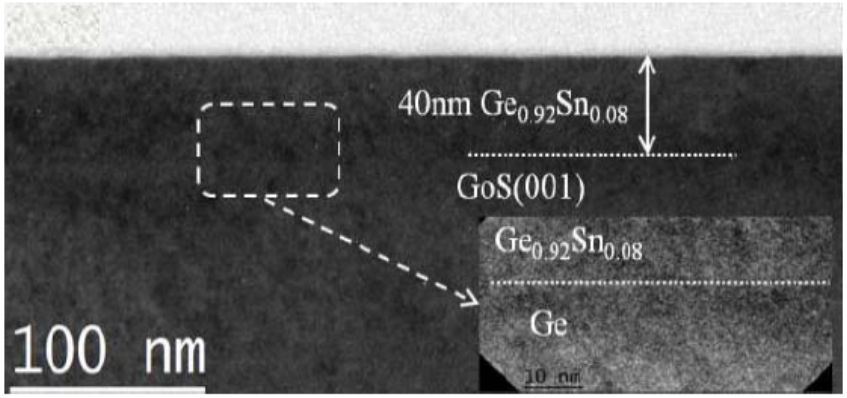




Compressive stress in Ge by GeSn S/D



- Compressively strained Ge channels using GeSn requires strained GeSn with Sn content higher than Sn solubility in Ge (<1%)
- Defect free, fully strained GeSn grown on Ge with 8% Sn demonstrated by Atmospheric Pressure –CVD of GeSn at 320ºC

Alternative materials for CMOS

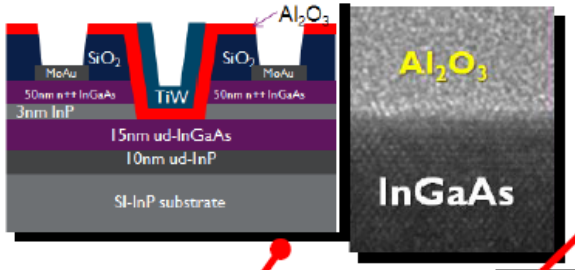
Material / Property	IV – IV		III - V					
	Si	Ge	InP	GaAs	$In_{0.5}Ga_{0.5}As$	GaSb	InAs	InSb
Elec. mobility (cm^2 / V·sec)	1 400	3 900	5400	8 500	12 000	3000	40 000	77 000
Electron effective mass ($/m_0$)	m_t: 0.19 m_l: 0.98	m_t: 0.082 m_l: 1.6	0.082	0.067	0.041	0.041	0.023	0.014
Hole mobility (cm^2 / V·sec)	450	1 900	200	400	450	1000	500	850
Hole effective mass ($/m_0$)	m_{HH}: 0.49 m_{LH}: 0.16	m_{HH}: 0.33 m_{LH}: 0.043	m_{HH}: 0.6 m_{LH}: 0.089	m_{HH}: 0.51 m_{LH}: 0.082	m_{HH}: 0.45 m_{LH}: 0.052	m_{HH}: 0.4 m_{LH}: 0.05	m_{HH}: 0.41 m_{LH}: 0.026	m_{HH}: 0.43 m_{LH}: 0.015
Bandgap (eV)	1.11	0.67	1.34	1.42	0.74	0.72	0.36	0.17
Lattice parameter (A)	5.431	5.658	5.868	5.653	5.868	6.095	6.058	6.479

- Low effective mass ➔ high source injection velocity and drive currents.
- Smaller bandgap materials ➔ low V_t possible with 'reasonable' work-function metals, allowing to reduce V_{dd}

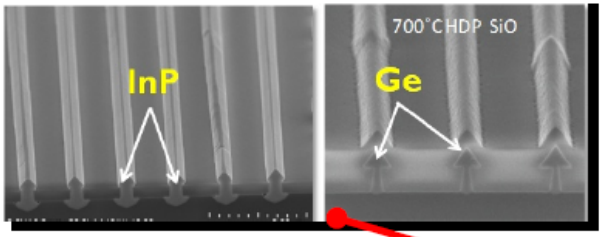
Heterogeneous CMOS integration

- Heterogeneous integration of high-mobility channel materials (Ge and III/V) in FinFETs for next-generation CMOS technology

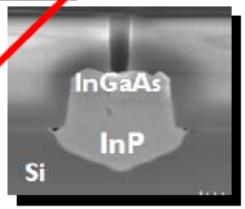
III/V & Ge gate stack & channel passivation

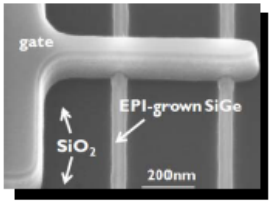


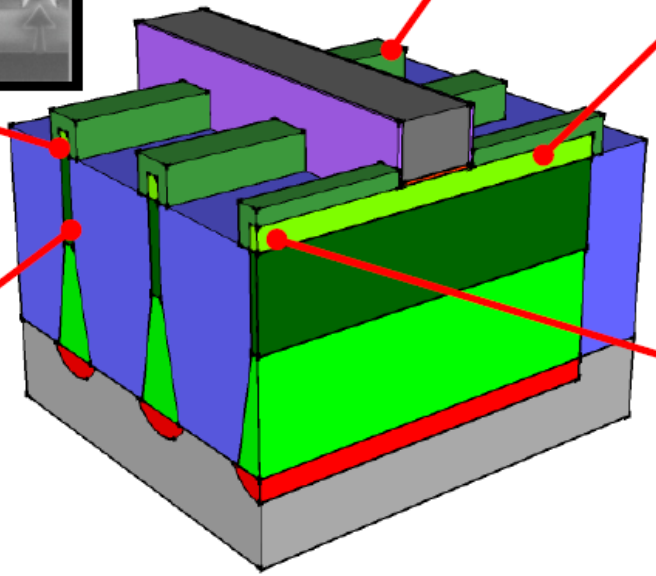
III/V-IV heterogeneous material integration



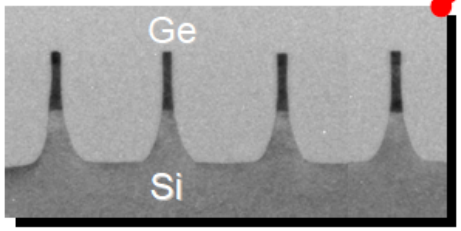
Device integration (RMG, SD Epi, Contact)



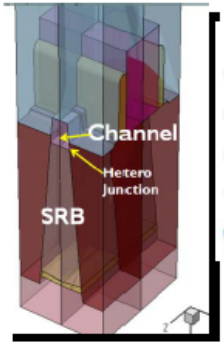


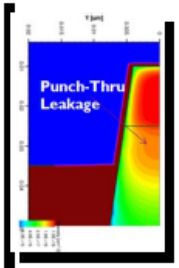


Epitaxial defect trapping & replacement Fin process

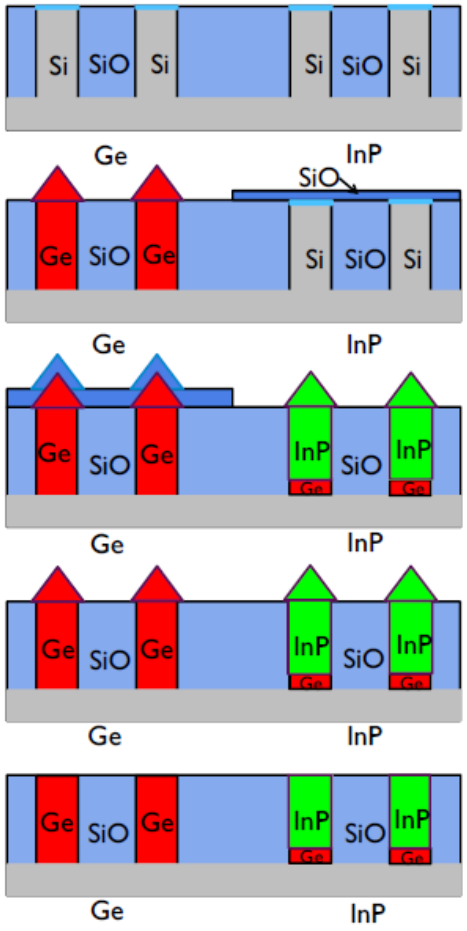


III-V/Ge FinFET Design





CMOS Ge and III/V virtual substrate



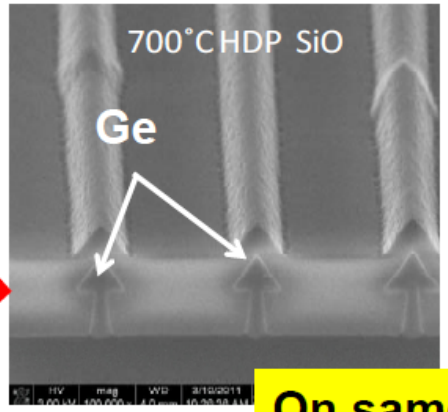
Start with STI template

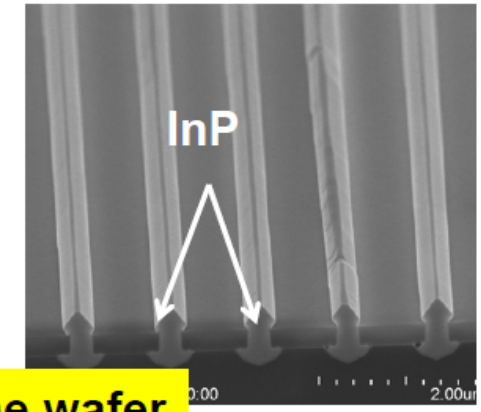
Cover InP areas and grow Ge

Cover Ge areas and grow InP

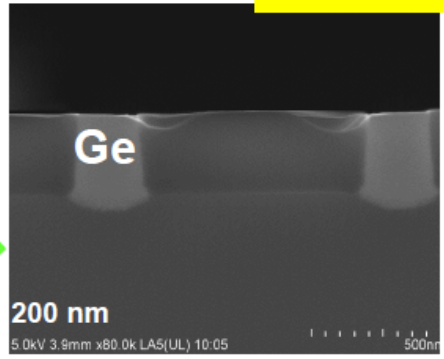
Remove oxide from Ge areas

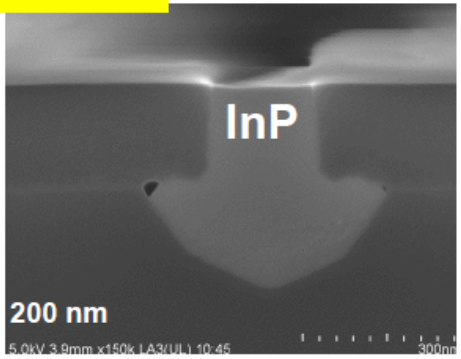
CMP to planarize surface





On same wafer

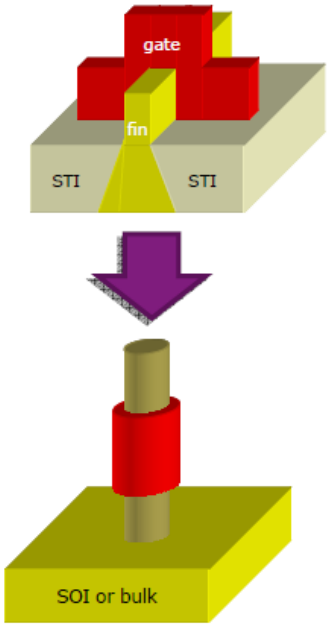


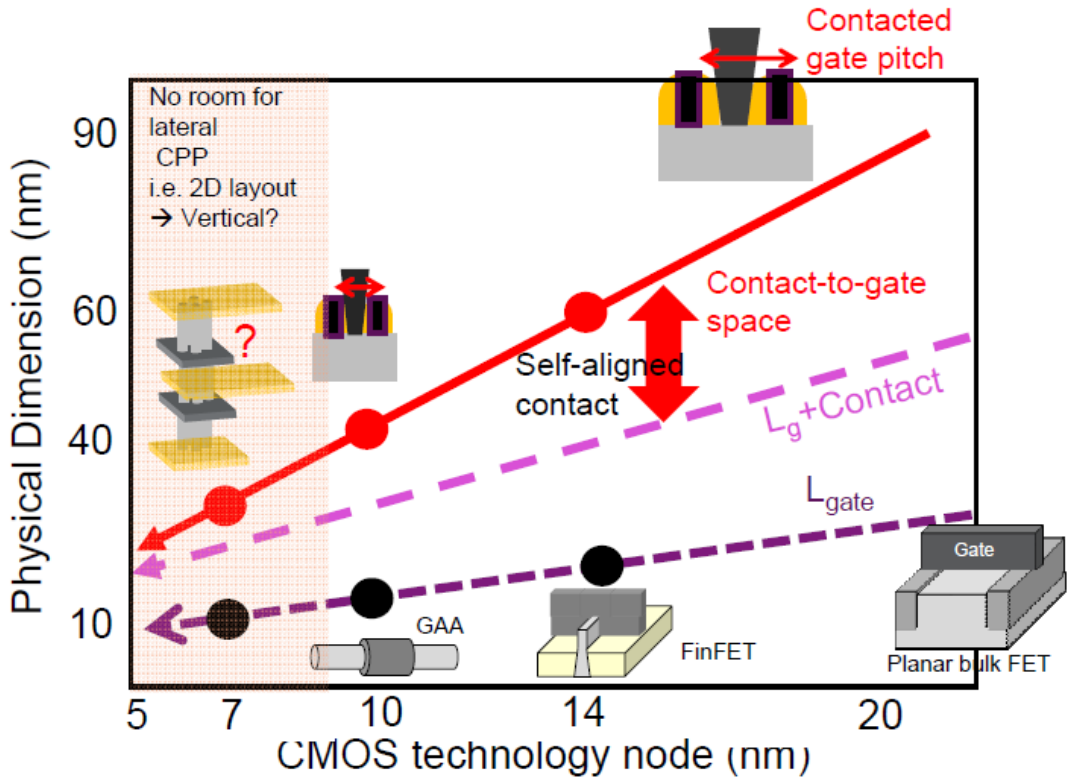


- Demonstration of CMOS Ge/InP virtual substrate by ART (Aspect Ratio Trapping)

Density scaling for sub 7nm CMOS

- Vertical nanowires will be needed to maintain the density scaling below 7nm.



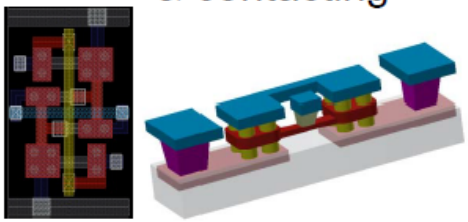


- Contacted gate pitch reduction necessary for continual density scaling
- L_{gate} scaling limited by device electrostatics - out of space for contact and gate

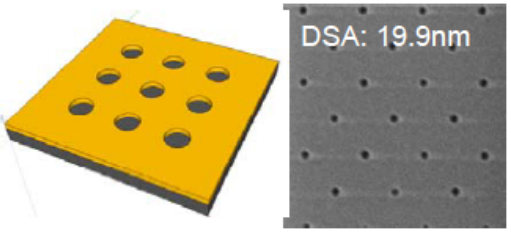
III-V nanowires

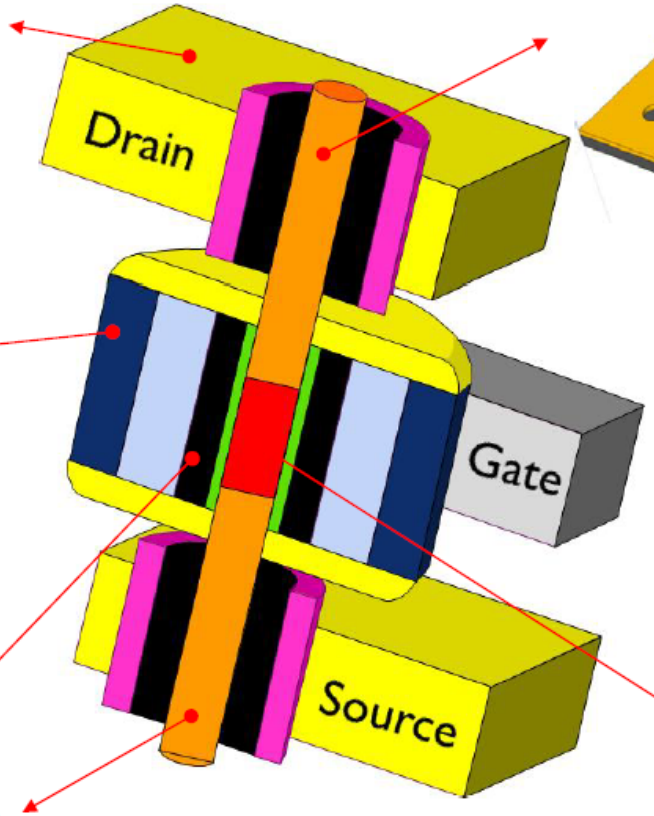
- Vertical nanowires will be needed to maintain the density scaling below 7nm.

Layout efficiency & contacting

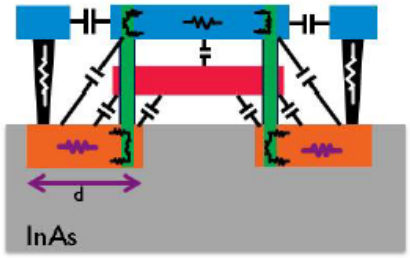


Nanowire diameter control

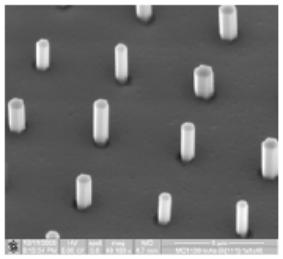




Parasitics



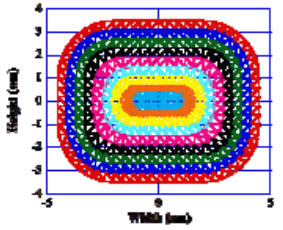
III-V nanowire growth



Gate length control

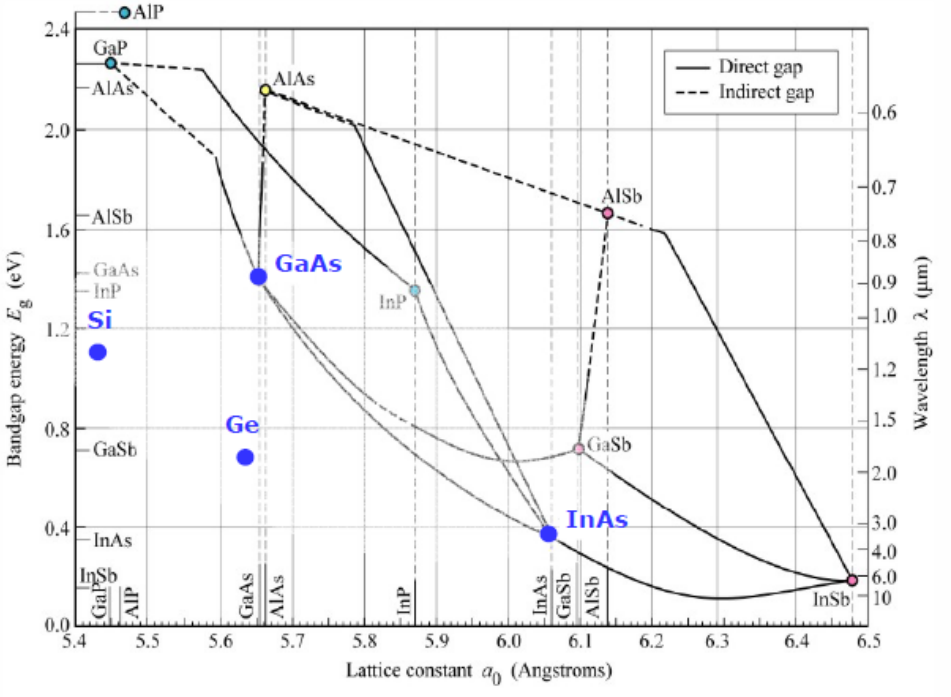
Junction formation

Nanowire device design



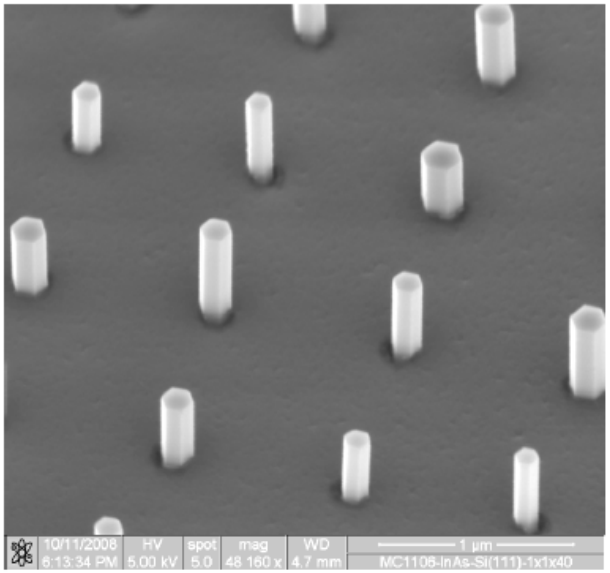
III-V nanowires

- Large lattice mismatch (eg InAs on Si) can be covered by nanowires
- Very interesting technique to introduce various III/V materials on Si



Mismatch w/Si	Ge	InAs	$In_{0.6}Ga_{0.4}As$
Lattice	4.2%	11.6%	8.6%
Thermal	127%	74%	120%

InAs NW growth on patterned Si(111)



- (111) nanowire growth direction
- High growth selectivity
- Desired crystallisation/faceting
- ~0.5 nm/s growth rate
- ~100-200 nm diameter

Croissance de matériaux 1D: les nanofils: La Croissance des Nanofils

VAPOR-LIQUID-SOLID MECHANISM OF SINGLE CRYSTAL GROWTH

(new method: growth "catalysis" from impurity; whiskers, epitaxial, and large crystals; Si; E)

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Bell Telephone Laboratories, Inc.
Murray Hill, New Jersey
(Received 4 February 1964)

Detailed studies of the morphology and growth of silicon whiskers[1] have led to a new concept of crystal growth from the vapor, which we call here the vapor-liquid-solid (VLS) mechanism. From these and subsequent studies, in which Si whiskers were grown by the disproportionation of SiI_2 or by the hydrogen reduction of $SiCl_4$, three important facts emerged: (a) silicon whiskers do not contain an axial screw dislocation;[2] (b) an impurity is essential for whisker growth;[3] (c) a small globule is present at the tip of the whisker during growth.

From fact (a) and related evidence, it became clear that growth from the vapor did not occur by the Frank[4] screw dislocation mechanism. From facts (b) and (c), and much additional evidence, the VLS mechanism emerged. In this mechanism, the role of the impurity is to form a liquid alloy droplet of relatively low freezing temperature. The liquid droplet is a preferred site for deposition from the vapor, which causes the liquid to become supersaturated with Si. The whisker grows by precipitation of Si from the droplet. Since the whisker grows from the liquid, a screw dislocation is unnecessary.

Growth of seeded whiskers of Si using gold as an impurity occurs as follows: A small particle of Au is placed on a {111} surface of a Si wafer and heated to 950°C, forming a small droplet of Au–Si alloy as shown in Fig. 1*a*. A mixture of hydrogen and $SiCl_4$ is introduced as described by H. C. Theuerer.[5] The liquid alloy acts as a preferred sink for arriving Si atoms or, perhaps more likely, as a catalyst for the chemical process involved. The Si enters the liquid and freezes out, with a very small concentration of Au in solid solution, at the interface between solid Si and the liquid alloy. By a continuation of this process the alloy droplet becomes displaced from the substrate crystal and "rides" atop the growing whisker, as shown in Fig. 1*b*. The growth direction is <111>, and the side faces of the whisker are usually {211} but sometimes {211} and {110}. The whisker grows in length by this mechanism until the Au is consumed or until the growth conditions are changed.

VLS growth of Si whiskers can occur over a wide range of cross-sectional dimensions, as shown by the 1000-Å whisker and the 0.2-mm needle in Fig 2*a* and 2*b*. In these examples, VLS growth wa interrupted before the Au was consumed. Simila results were obtained with Pt, Ag, Pd, Cu, or N either by placing a particle on the Si substrate o by co-deposition. VLS growth of twinned Si ribbon having a <211> or a <110> growth direction an {111} main faces[6] has been observed.

The selection of a proper impurity for VLS growt depends on a number of factors such as, formatio of a liquid alloy at the deposition temperature vapor-liquid-solid interfacial energies, distributio coefficient and inertness to the reaction products The term impurity is used in a broad sense. Fo VLS growth of compound crystals, for exampl GaAs, an excess of one of the component material can act as a liquid-forming impurity. In some case a combination of two or more impurities can be used

The VLS growth mechanism explains many observa tions of the effect of impurities in crystal growt from the vapor. Crystals of α-Al_2O_3 (ref 7) an

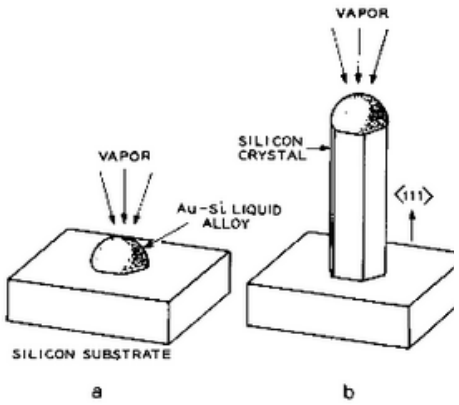
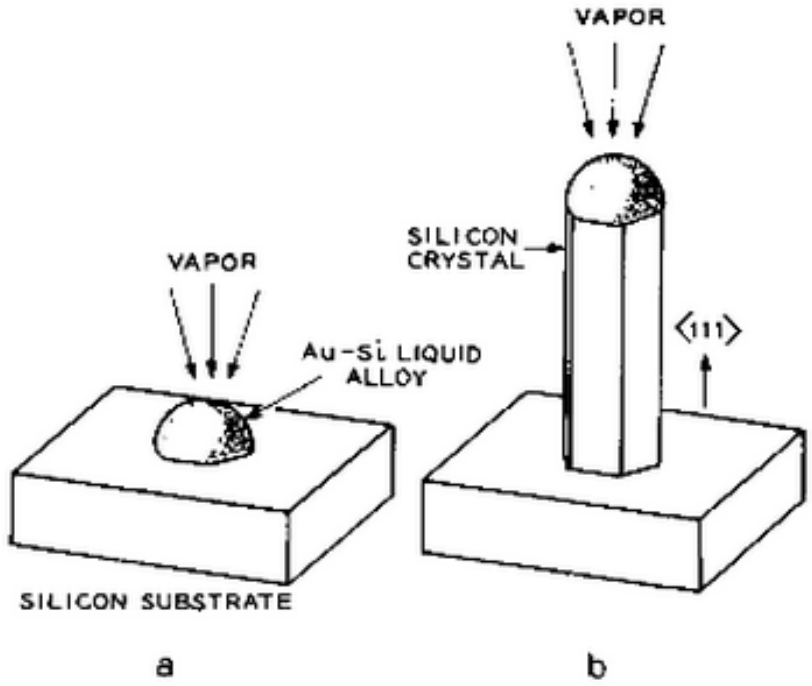


Fig. 1. Schematic illustration: Growth of a silicon crystal by VLS. *a*. Initial condition with liquid droplet on substrate. *b*. Growing crystal with liquid droplet at the tip.



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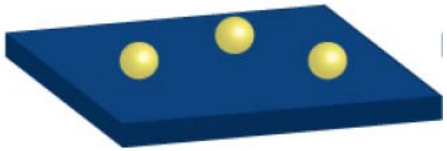
L’INTÉRGATION « BOTTOM-UP »

LE MÉCANISME DE CROISSANCE VAPEUR-LIQUIDE-SOLIDE (VLS)



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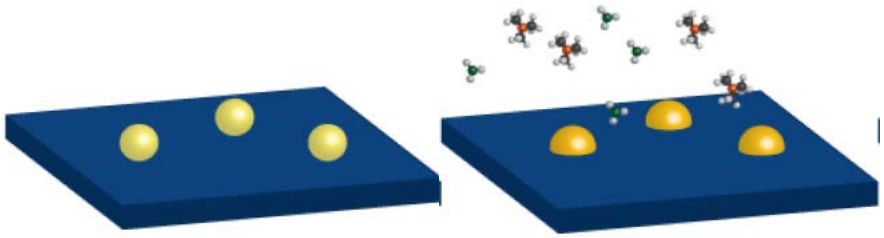

L'INTÉRGATION « BOTTOM-UP »

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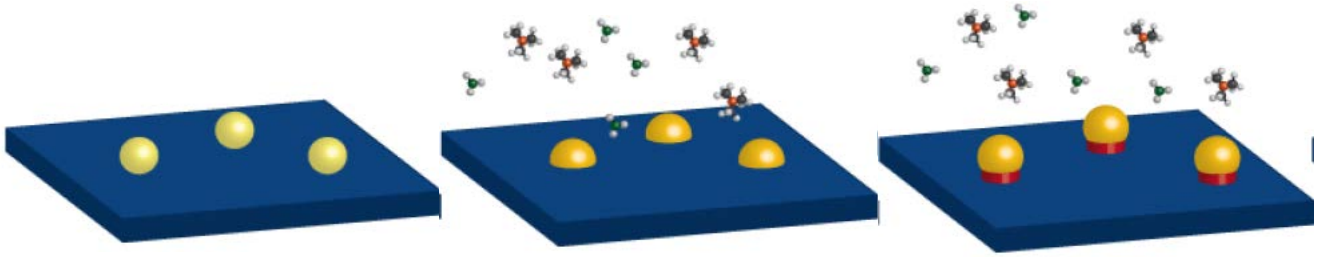

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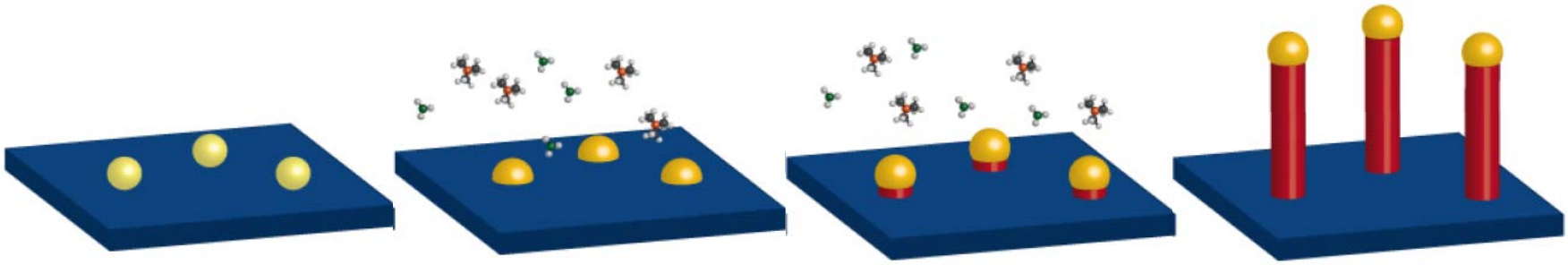
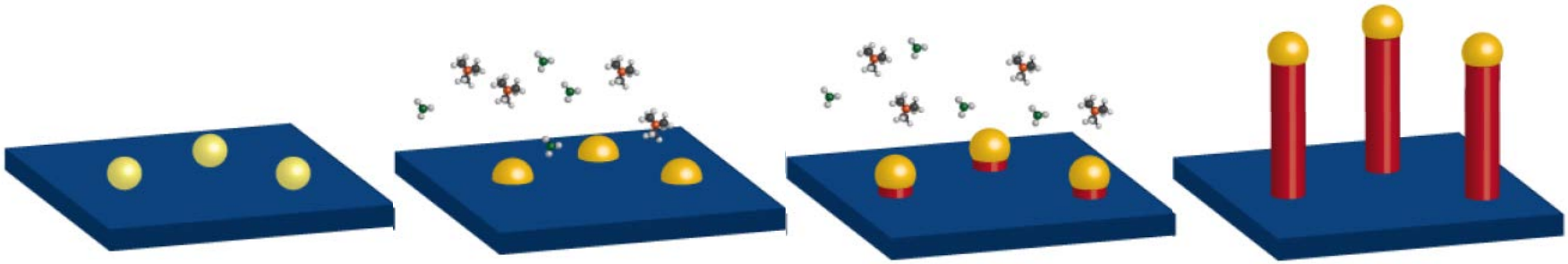
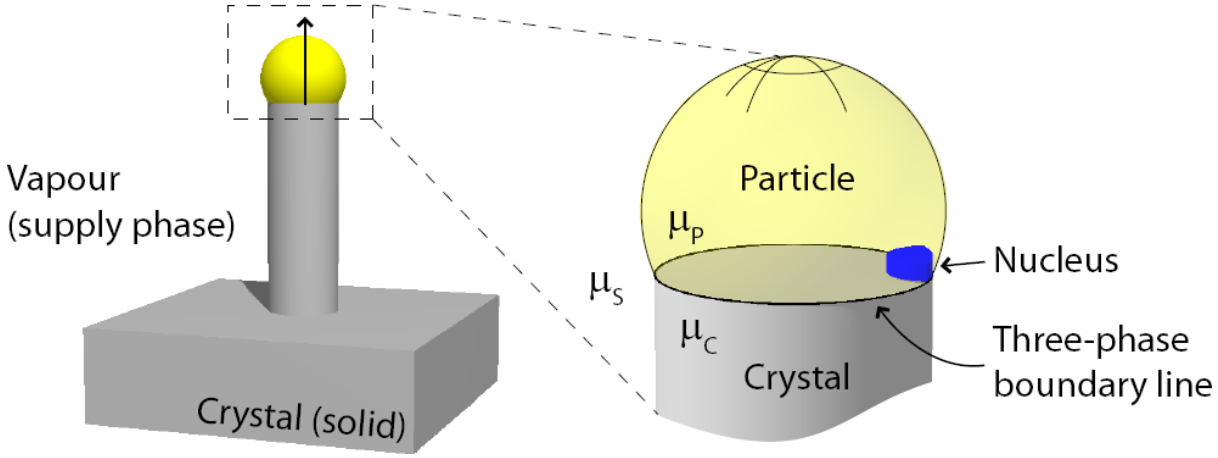


L'INTÉRGATION « BOTTOM-UP »

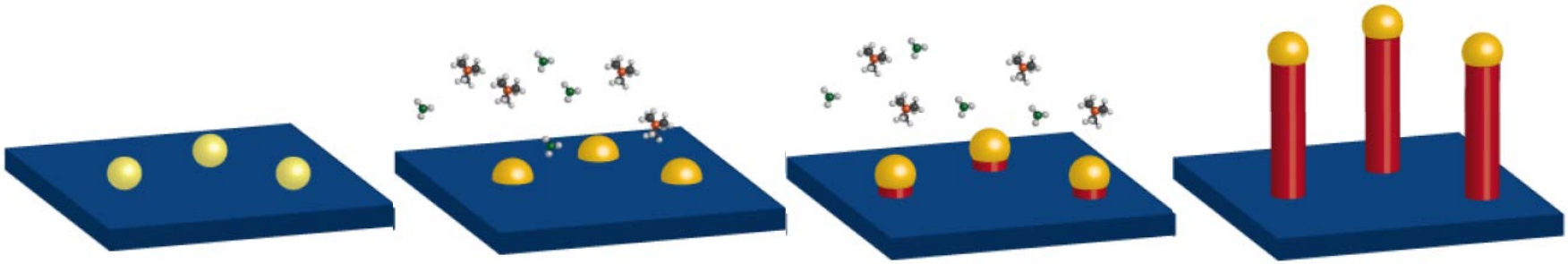
LE MÉCANISME DE CROISSANCE VAPEUR-LIQUIDE-SOLIDE (VLS)

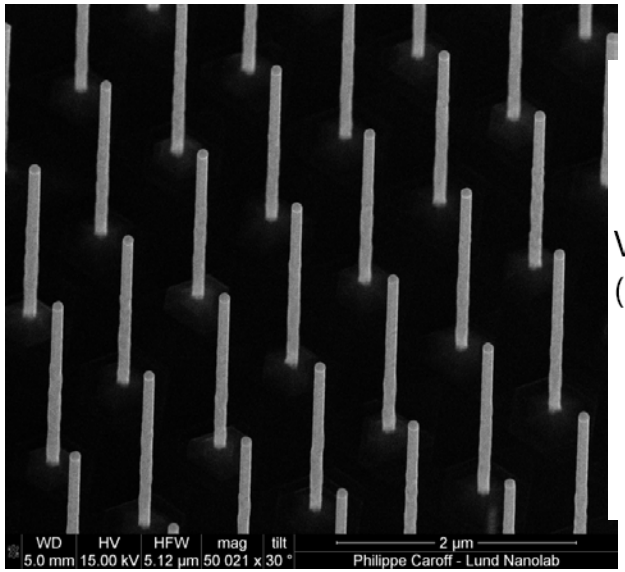


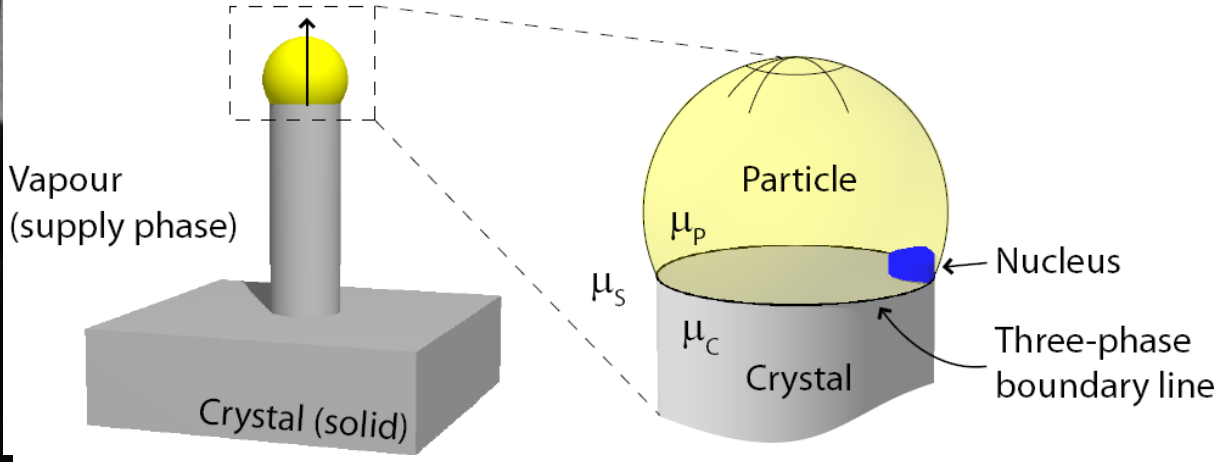


L'INTÉRGATION « BOTTOM-UP »

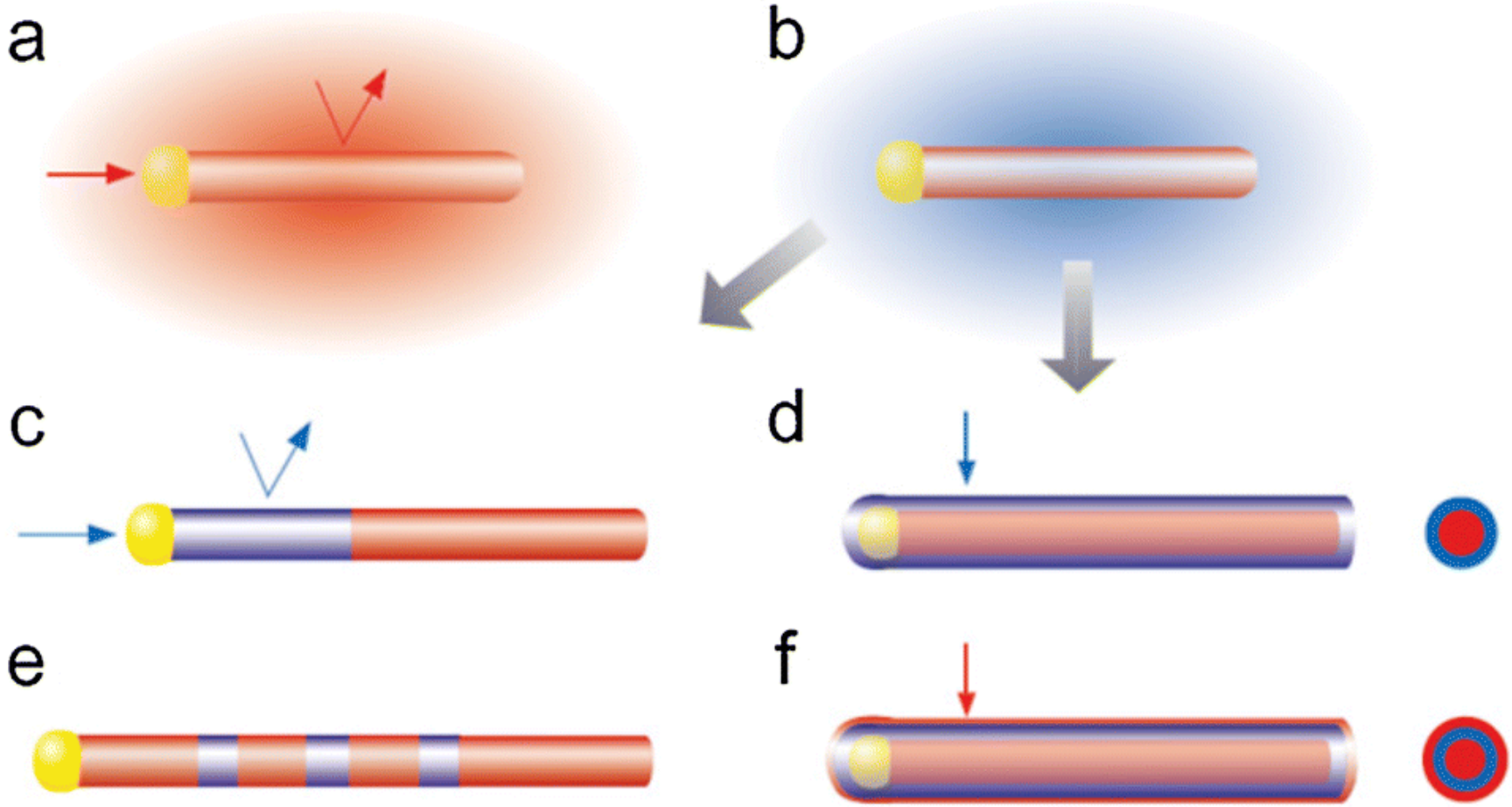
LE MÉCANISME DE CROISSANCE VAPEUR-LIQUIDE-SOLIDE (VLS)





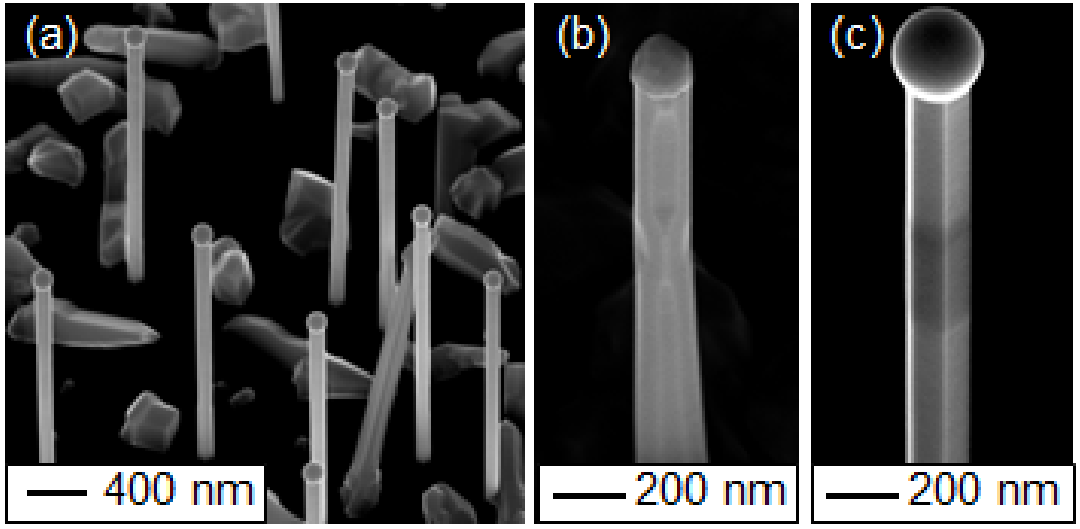


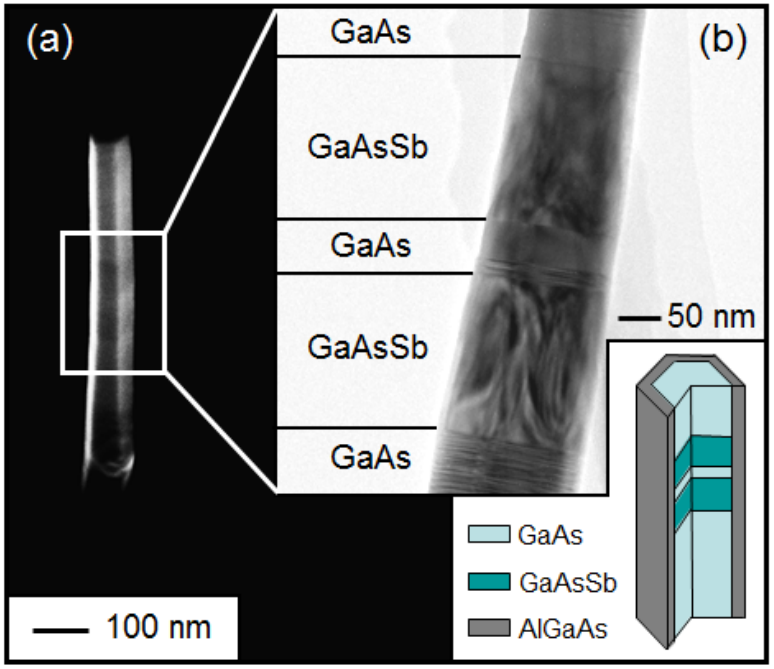
COMBINER DIFFÉRENTS MATÉRIAUX



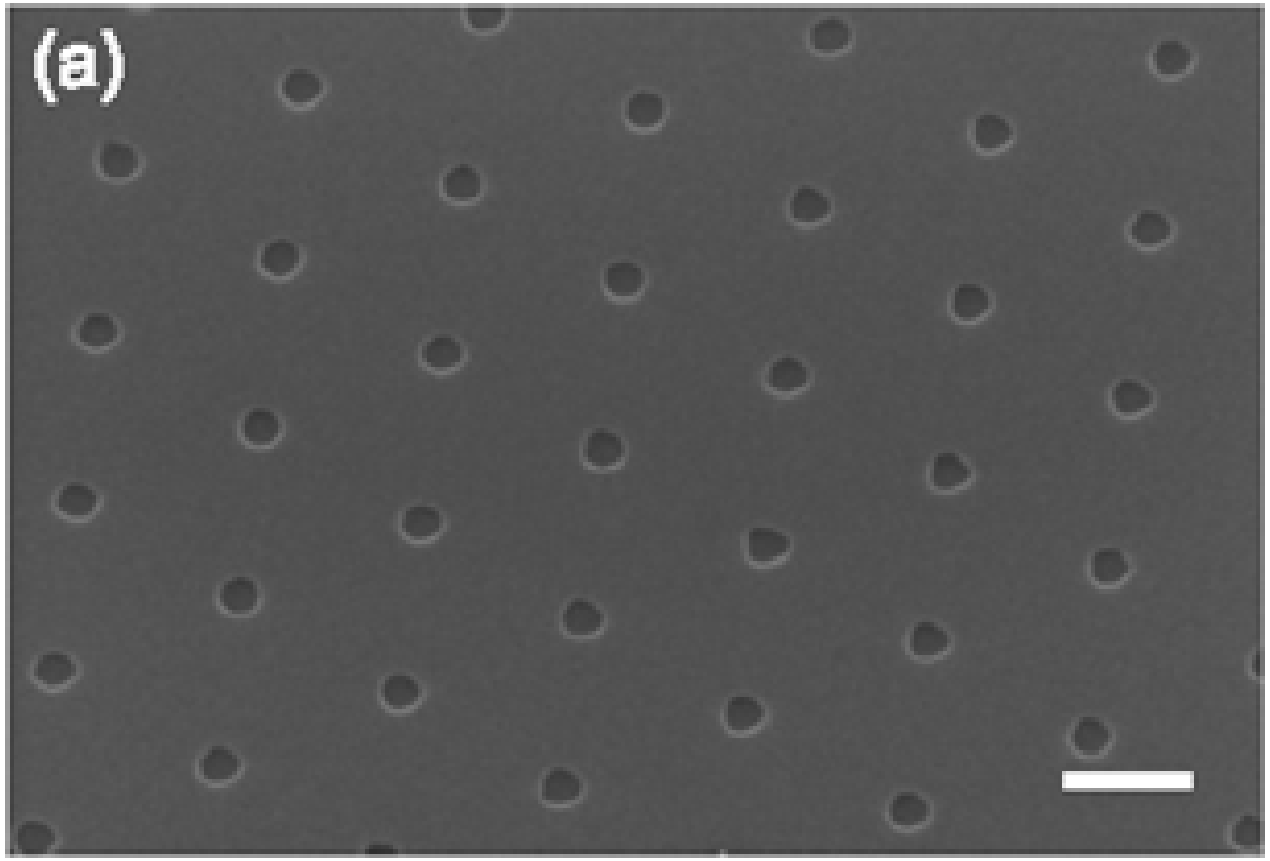
UN EXEMPLE DE NANOFILS SUR SILICIUM

Exemple de croissance de nanofils GaAs et GaAsSb intégrés sur Silicium

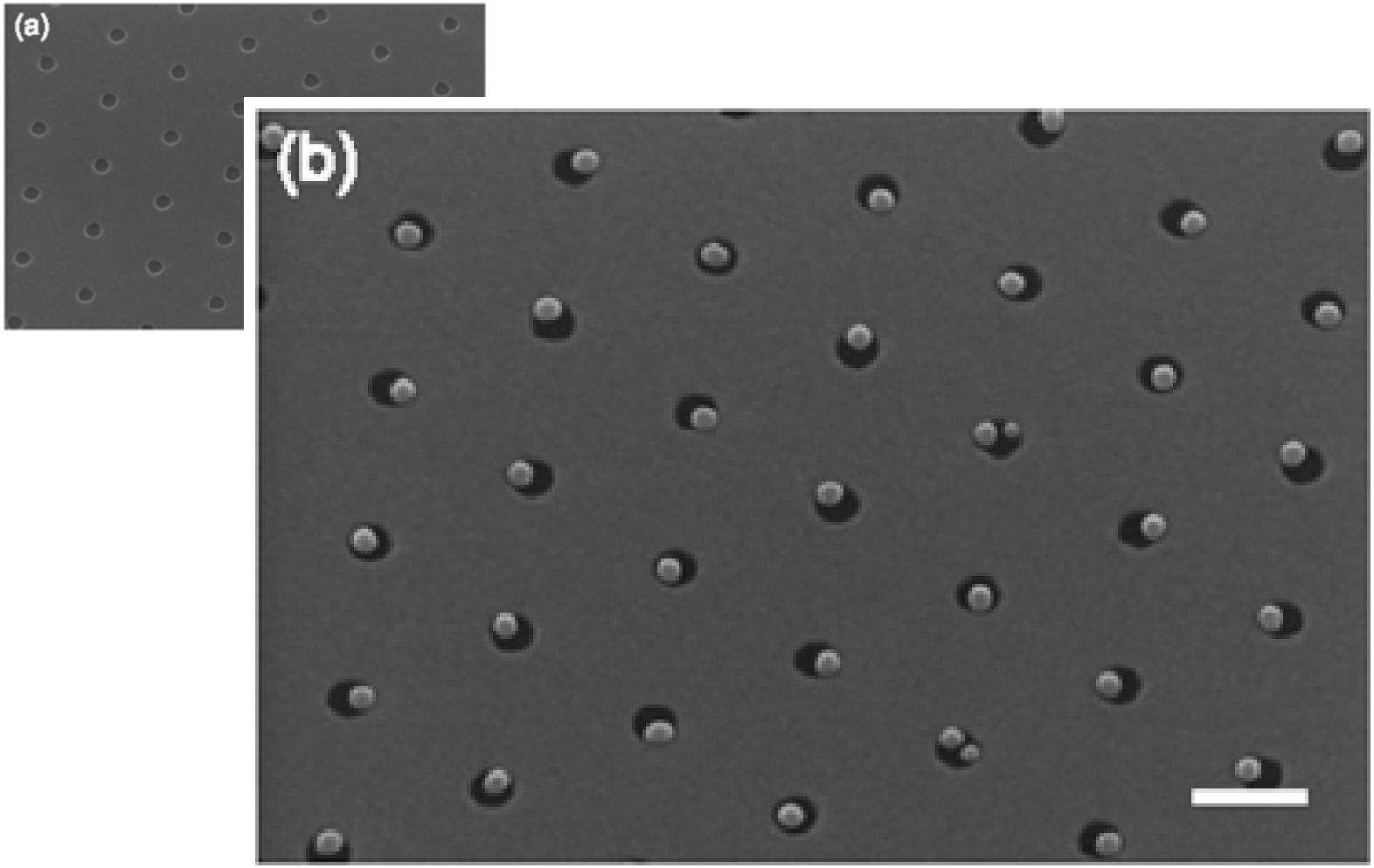




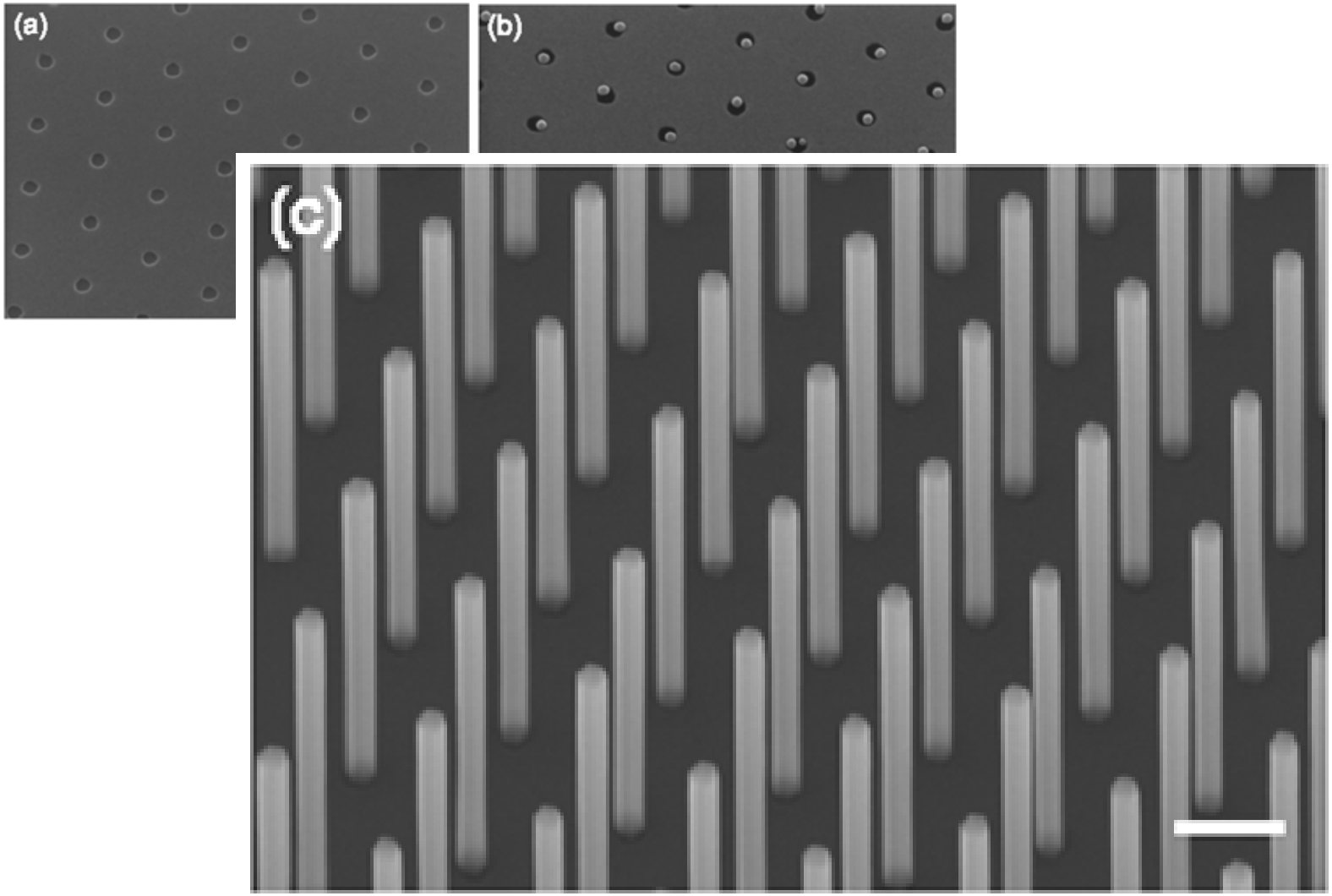
LA PRÉPARATION DES SUBSTRATS



LA PRÉPARATION DES SUBSTRATS

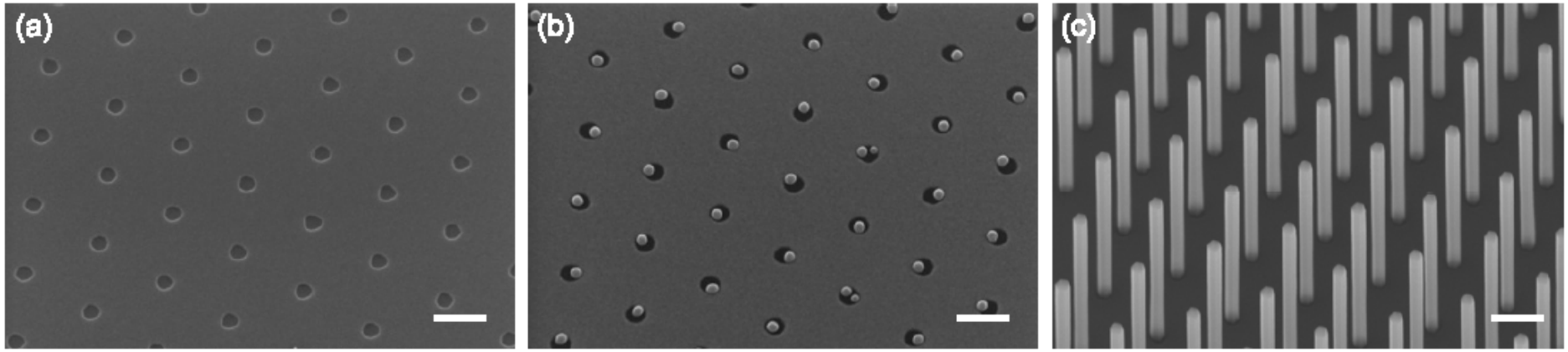


LA PRÉPARATION DES SUBSTRATS



LA PRÉPARATION DES SUBSTRATS

Exemple d’un réseau de fils GaAs(111) autocatalysés sur Si(111) via e-beam



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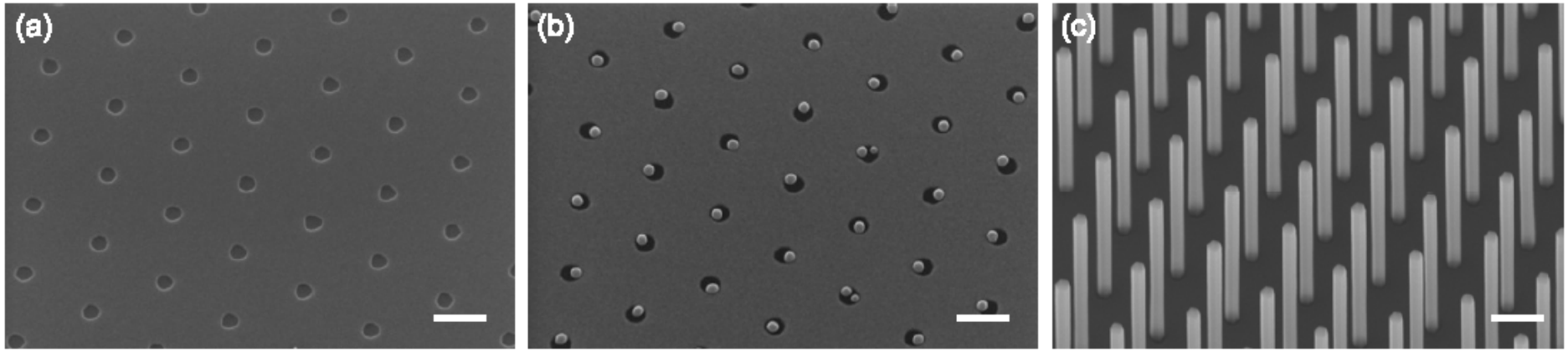
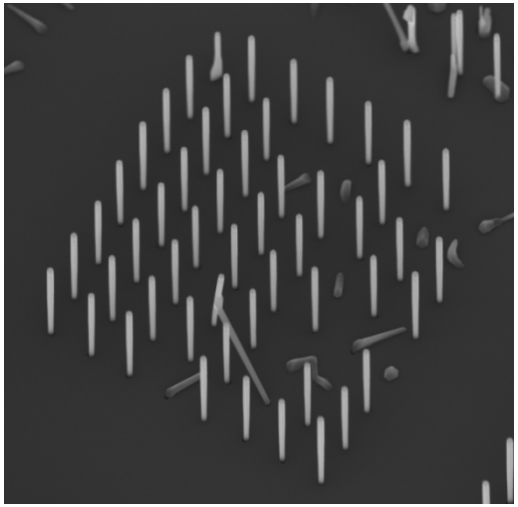
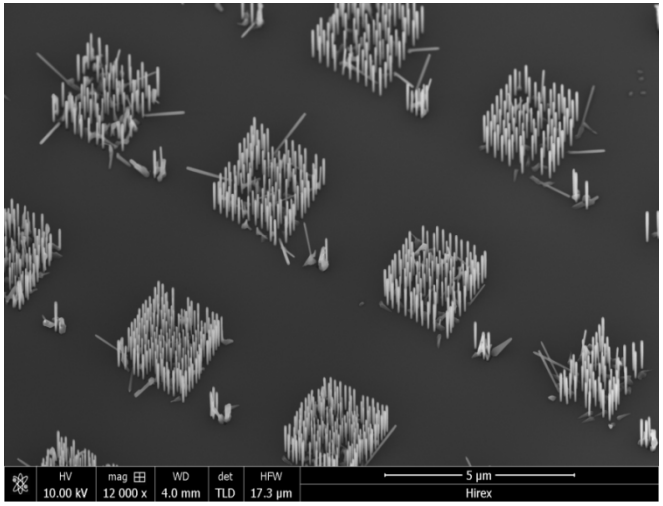


Egalement possible via Nano. Imprint





Why is Au such a successful catalyst?

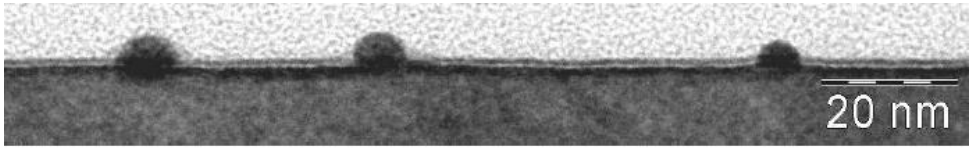
✓No oxidation in air

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

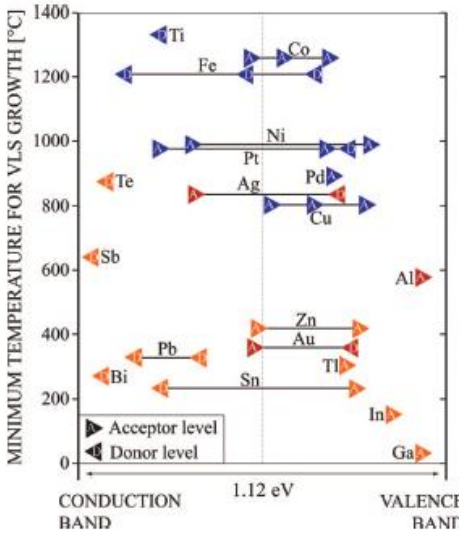
→VLS growth is possible

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



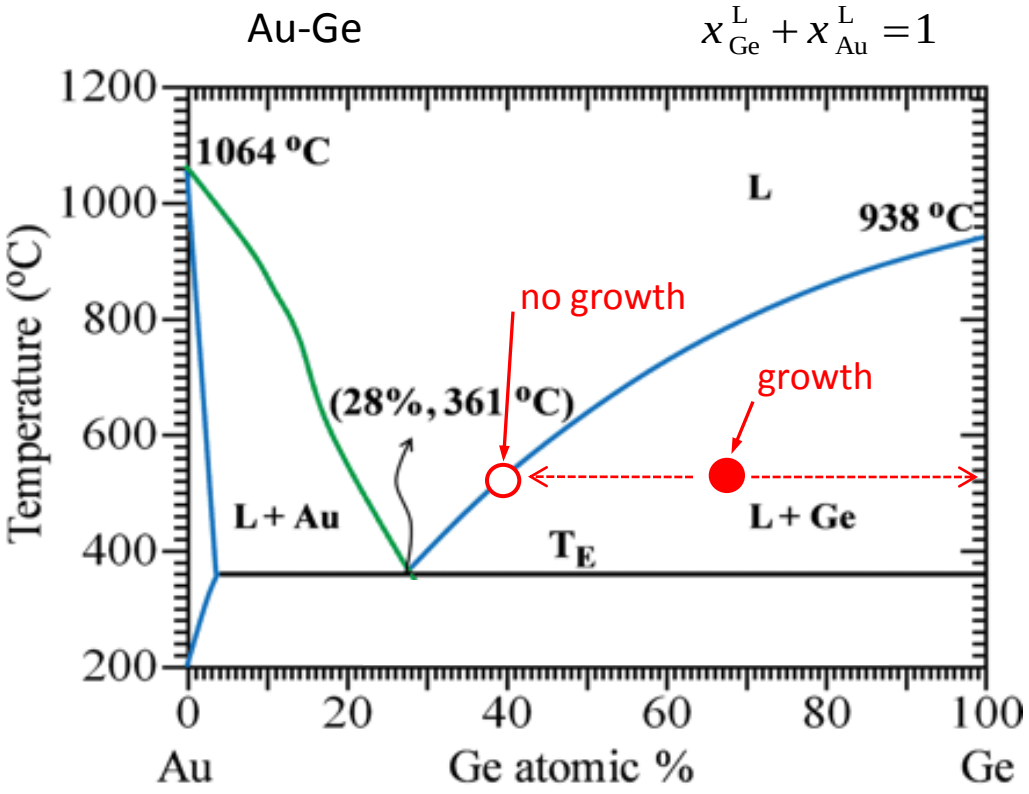
Au ≡ Deep level



Metal catalysts for Si NW growth

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

The catalyst is a reservoir of NW constituents

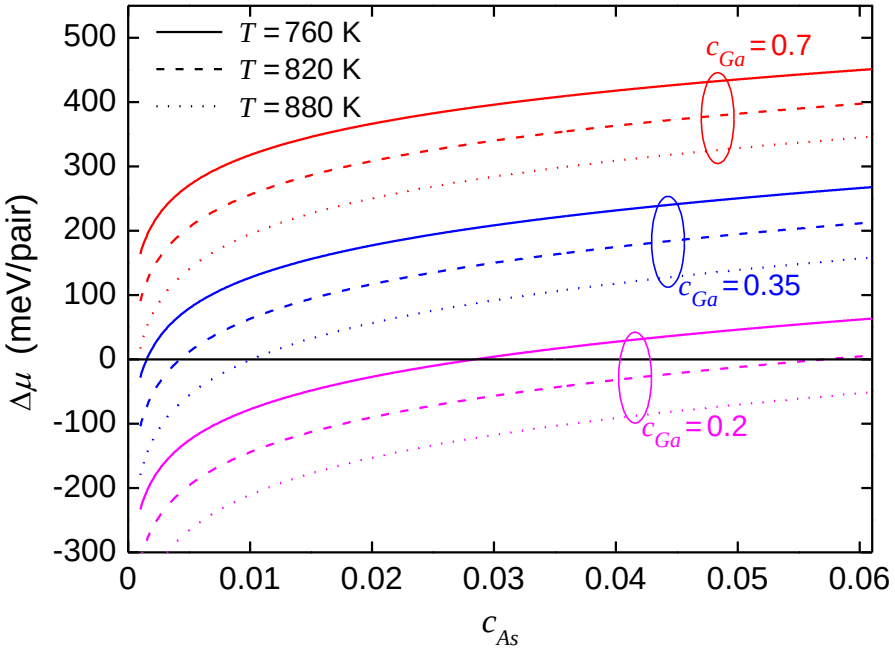


x^{L}_{Ge} must be higher than the equilibrium concentration to start growing

Case of III-V compounds

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

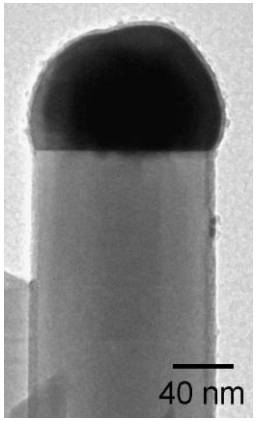
AuGaAs liquid catalyst $x_{Ga}^{L} + x_{As}^{L} + x_{Au}^{L} = 1$



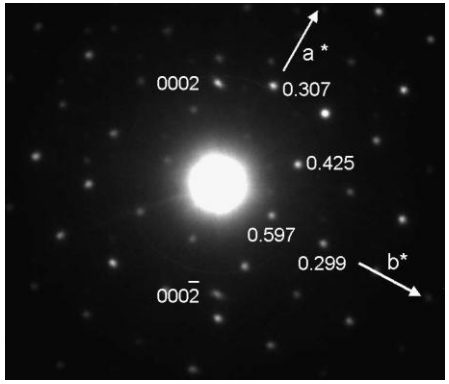
$$\Delta\mu(x_{Ga}^{L}, x_{As}^{L}, T)$$

Group III atoms are much more soluble than group V atoms

Catalyst composition after GaAs NW growth



$Au_{0.5}Ga_{0.5}$ phase



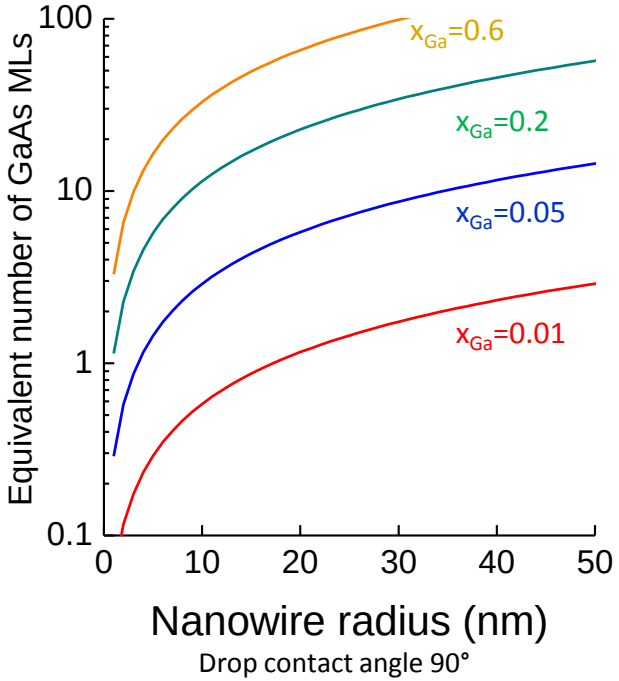
Glas, J. Appl. Phys. 108, 073506 (2010)

How much of each constituent in the reservoir?

During growth

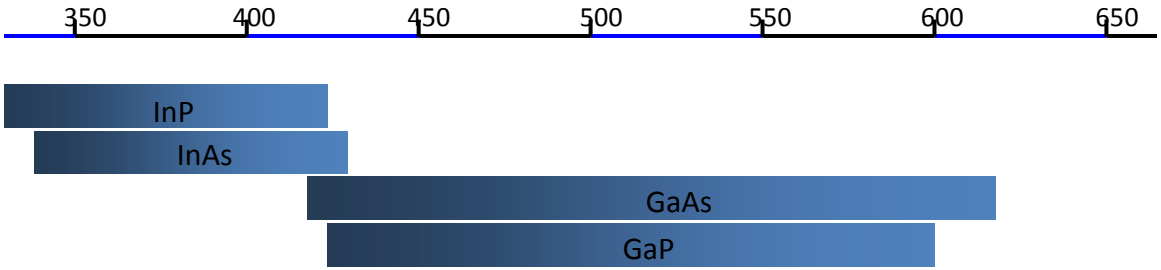
Ga composition: several 10% ≡ tens to hundreds of monolayers of solid NW

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)

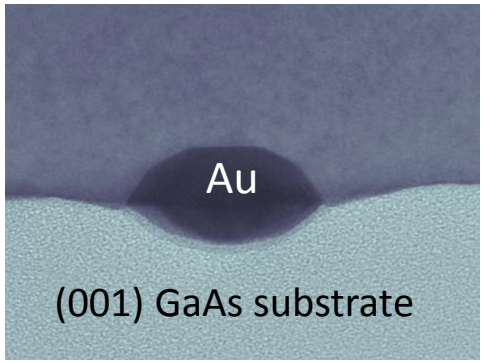
Compounds with same group III atoms have comparable ranges of growth temperature

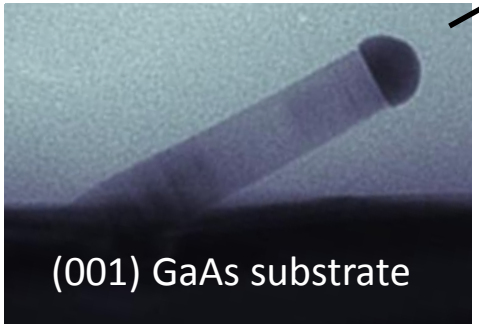


Temperature range for NW growth by MBE of different III-V compounds

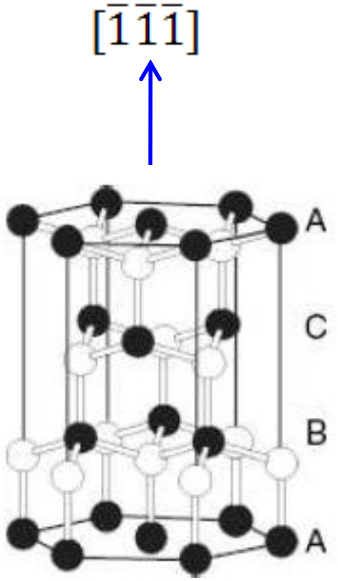
Preferential growth axis

Au-catalyzed semiconductor nanowires

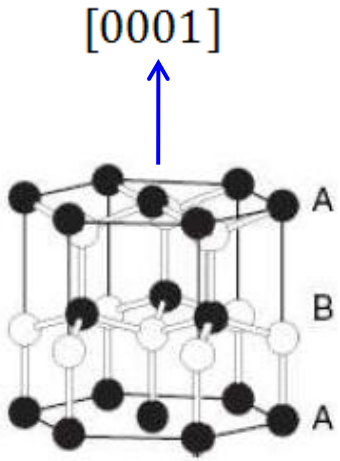




$[\bar{1}\bar{1}\bar{1}]$



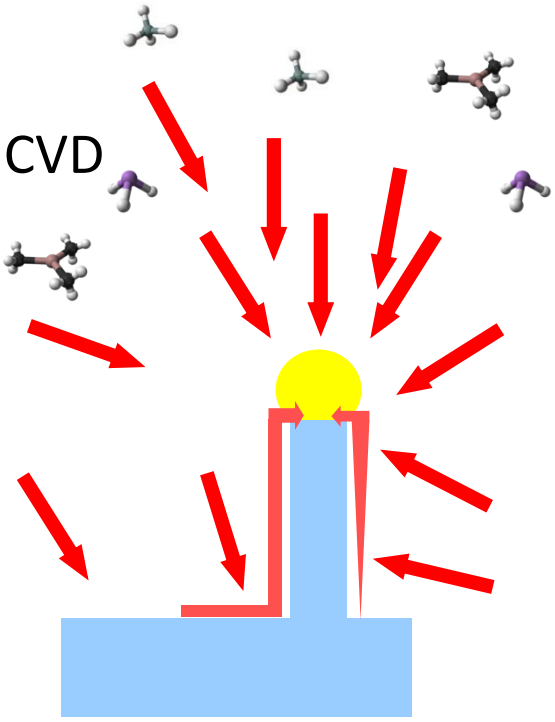
Cubic
(Zinc Blende)



Hexagonal
(Wurtzite)

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

Why is growth faster under the metal drops ?

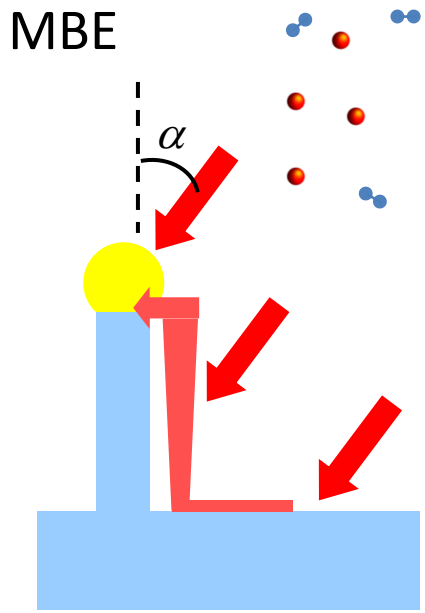


Precursors are gas molecules ($TMGa$, AsH_3, SiH_4…)

The metal droplet can promote their decomposition

« Chemical catalyst »

Precursor flow from the vapor to the droplet

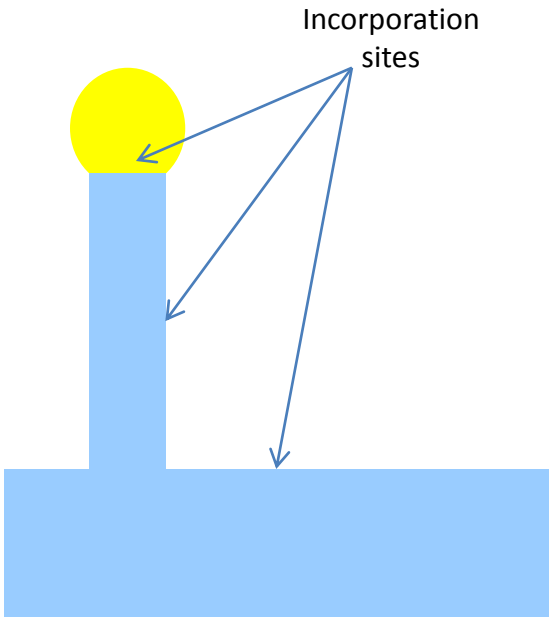


Constituents are brought as directional beams of atoms or simple molecules (Si , Ge, Ga, In, P_2, As_4…)

no chemical reaction needed

The metal droplet promotes incorporation of atoms in the solid phase

« Physical catalyst »



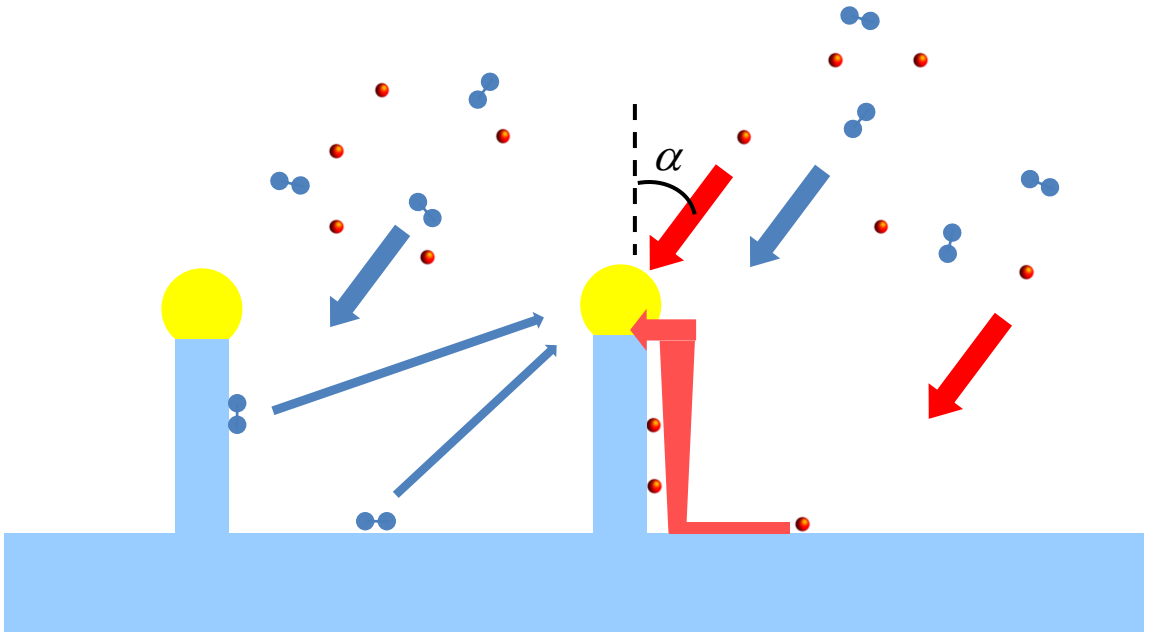
The liquid drop is a dense phase:

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



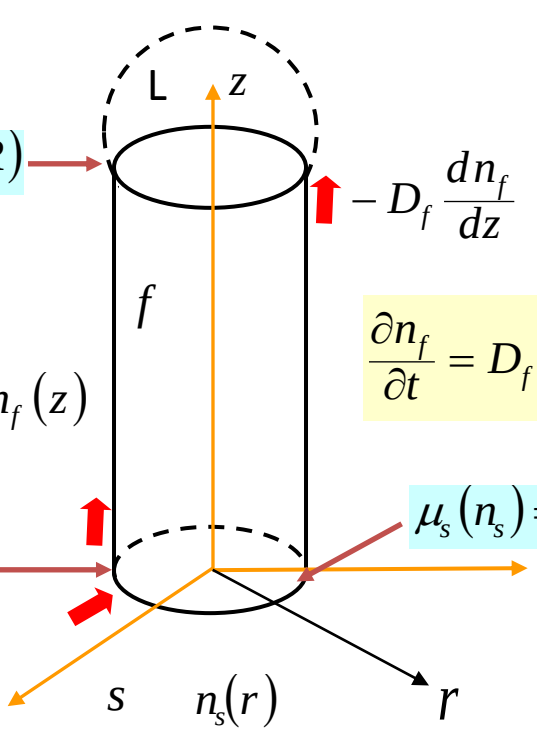
Group V : sticking coefficient <<1
Surface adsorption + reemission in the vapor phase

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



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

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

$$\alpha \qquad J$$

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

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

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

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

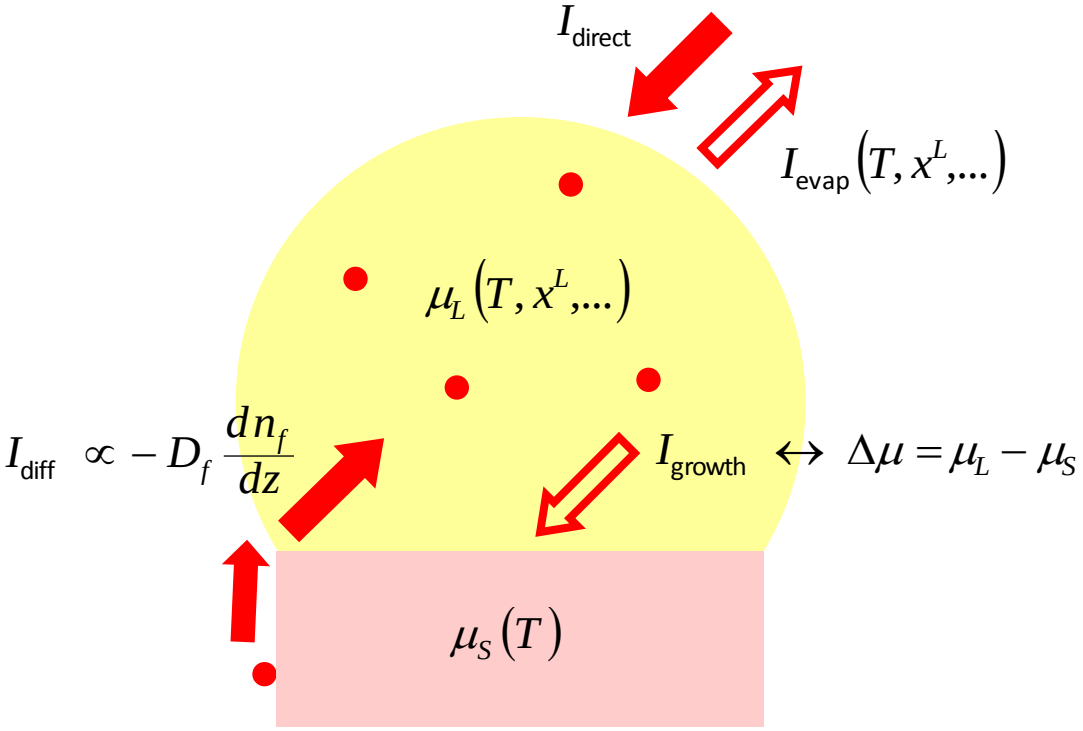
$$\left.\frac{dn_s}{dr}\right|_{r\to\infty} = 0$$

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

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

$\rightarrow$ Diffusion flux into the drop

Coupling between diffusion and incorporation

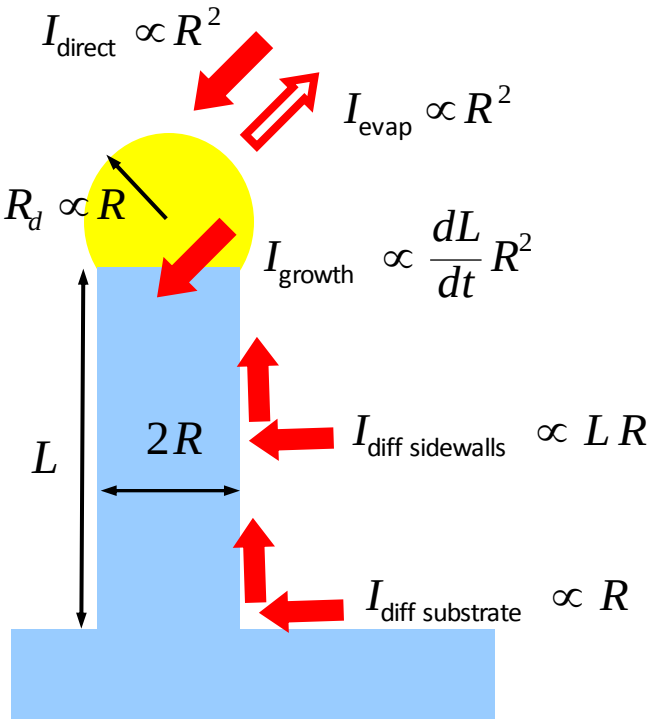


- Material balance $I_{\text{direct}} + I_{\text{diff}} = I_{\text{growth}} + I_{\text{evap}}$ ⟶

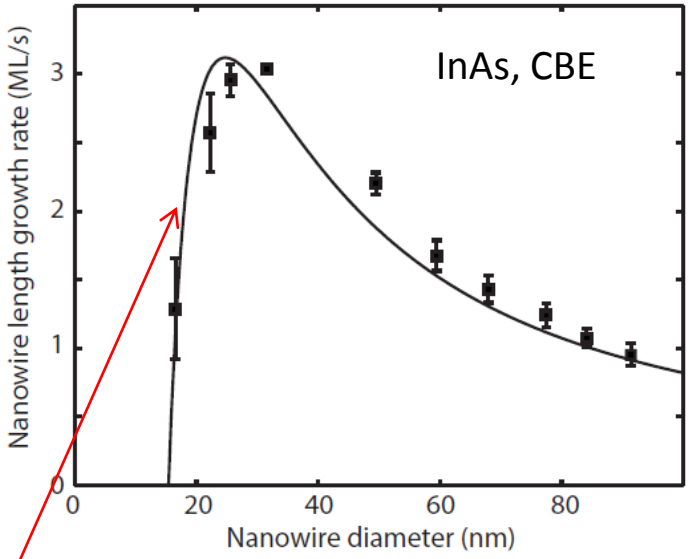
  self-consistent determination of x^L and growth rate possible in principle in simple sytems

- 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

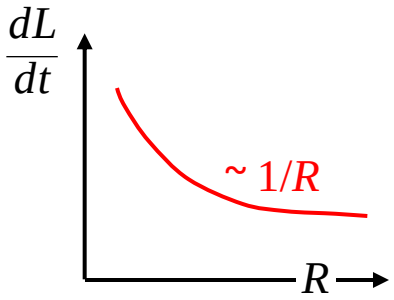


μ^L treated as a fitting parameter



Gibbs Thomson effect

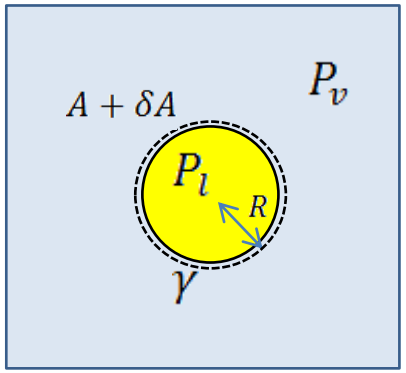
$$\frac{dL}{dt} = A + \frac{B}{R}$$



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

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

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

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

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

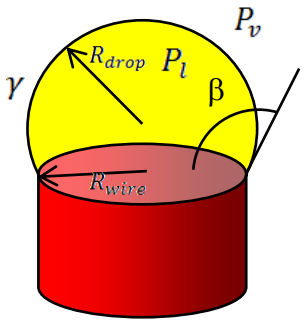
$$for\ a\ \ 10\ nm\ radius\ Au\ droplet\ (\gamma_{Au} = 0.91\ J.m^{-2})$$

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

Nanodroplets are under very high pressures

GT effect in the catalyst droplet of a nanowire

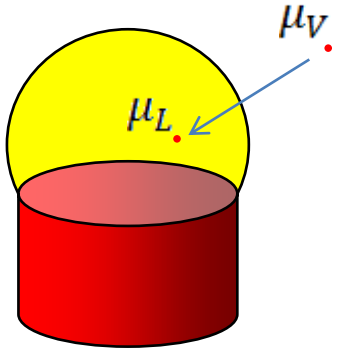
Generally, the shape of the catalyst is a truncated sphere on top of the nanowire of radius R_{wire}



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)

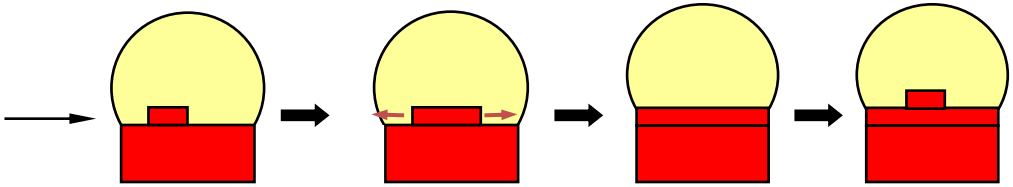
$$P = P^{\infty} \exp \frac{2\gamma\Omega_L}{R k_B T}$$

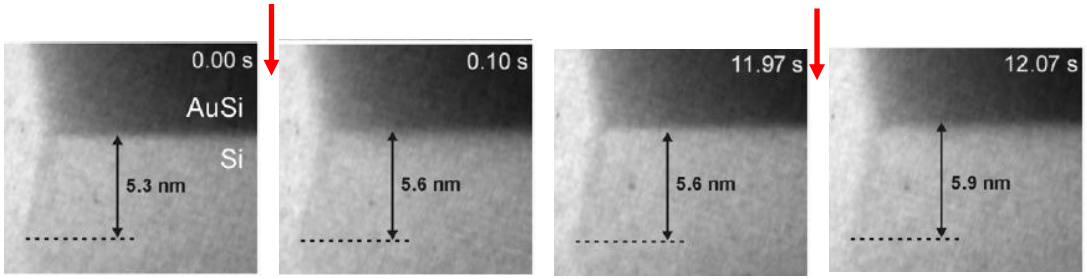
for a NW of 10 nm radius

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

How does VLS growth proceed

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

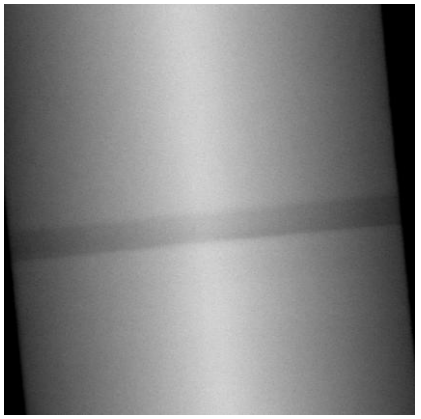




Si NW growth in a TEM

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

Flat heterointerfaces



AlGaAs insertion in GaAs NW

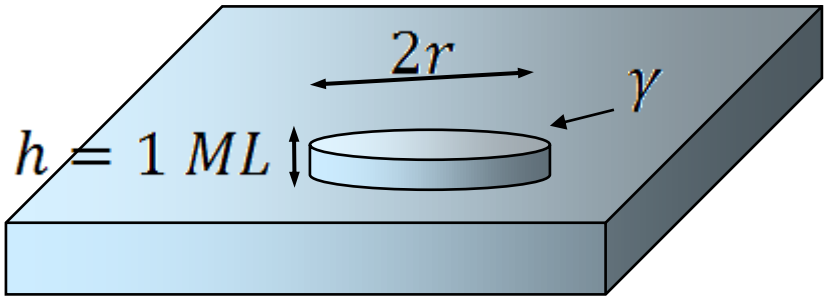
- At least one new 2D nucleus is needed for each ML
- If top facet is narrow enough, mononuclear regime

1 ML ↔ 1 nucleation event

Classical 2D nucleation theory

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

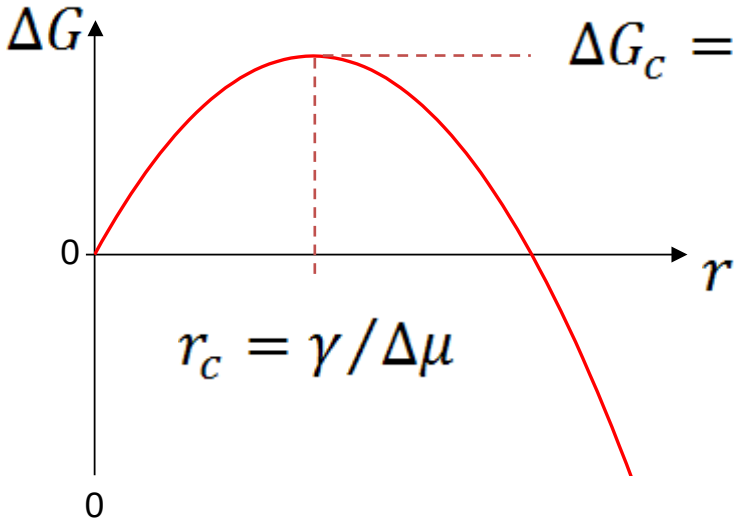
Venables et al, Rep. Prog. Phys. 47, 399 (1984)



Gibbs free energy of nucleus formation

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

Nucleation barrier



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

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

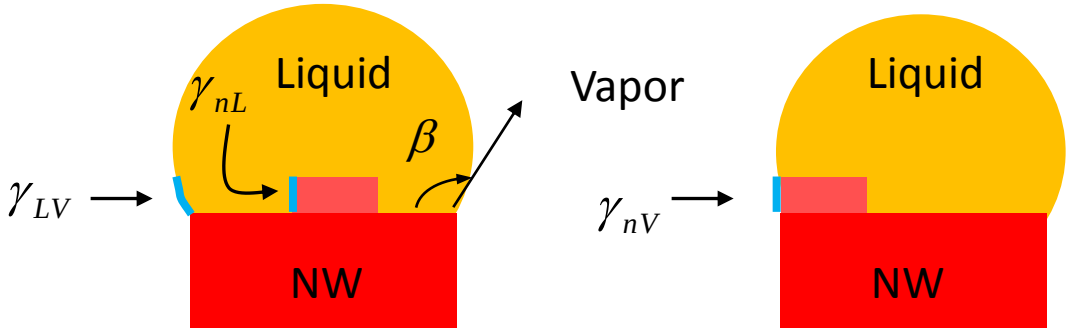
Nucleation rate:
Probability of forming a 2D nucleus
/(unit time x unit area)

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

$r<r_c$ nuclei decompose easily

$r>r_c$ nuclei can extend by step flow

Where ?



Nucleus entirely surrounded by liquid

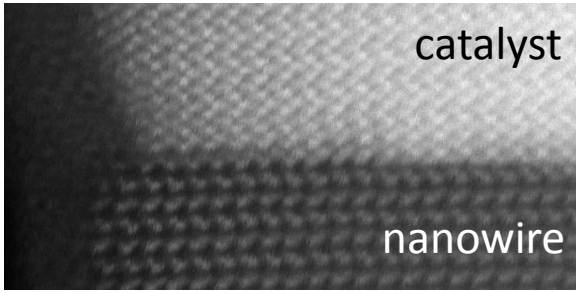
Nucleus at the periphery

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