Préparation des substrats pour la croissance VLS de nanofils

Sébastien Plissard

Summary of the presentation

- The Vapor Liquid Solid mechanism (VLS)
- The physical modeling of the system
- The possible catalyst particles
- The self-catalyzed Nanowires
  - The Vapor Solid mechanism
  - The droplet assisted growth of nanowires
- The homosubstrates
- The silicon integration

The VLS mechanism

VAPOR-LIQUID-SOLID MECHANISM OF SINGLE CRYSTAL GROWTH

R. S. Wagner and W. C. Ellis
Bell Telephone Laboratories, Inc.
Murray Hill, New Jersey
(Received 4 February 1964)

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

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

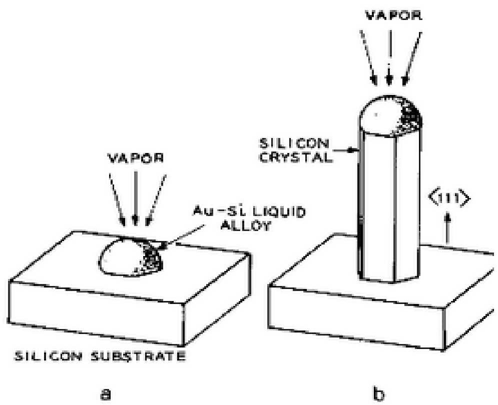


Fig. 1. Schematic illustration: Growth of a silicon crystal by VLS. *a*. Initial condition with liquid droplet on substrate. *b*. Growing crystal with liquid droplet at the tip.

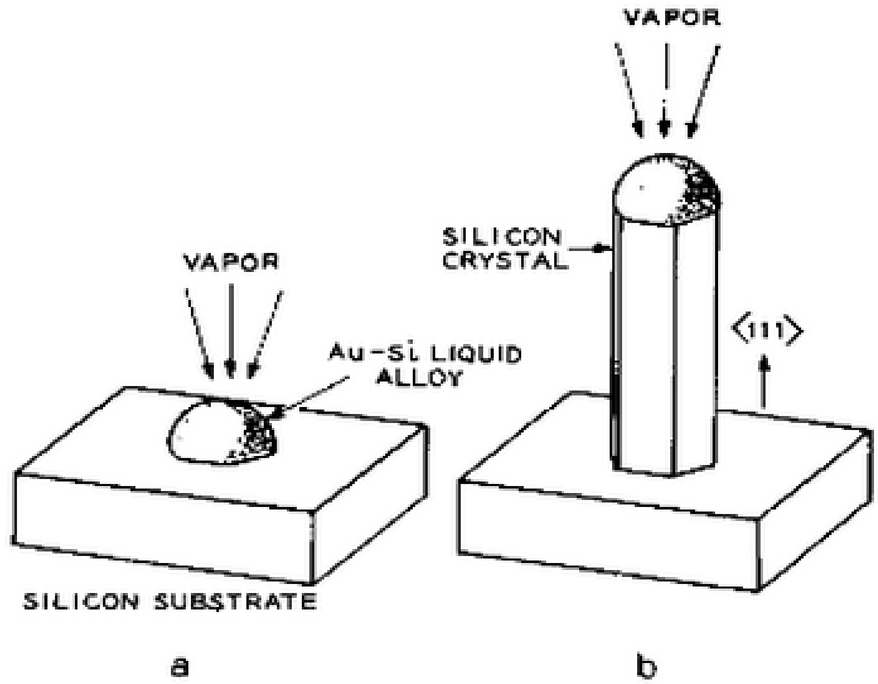
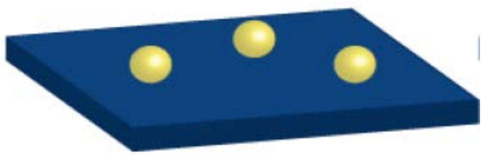


Fig. 1. Schematic illustration: Growth of a silicon crystal by VLS. *a*. Initial condition with liquid droplet on substrate. *b*. Growing crystal with liquid droplet at the tip.

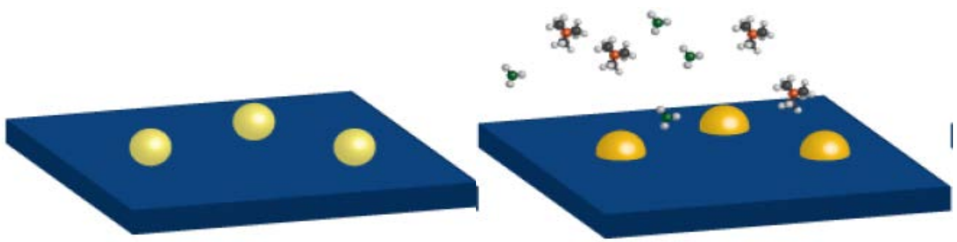
THE « BOTTOM-UP » INTEGRATION

THE VAPOUR-LIQUID-SOLID (VLS) MECHANISM



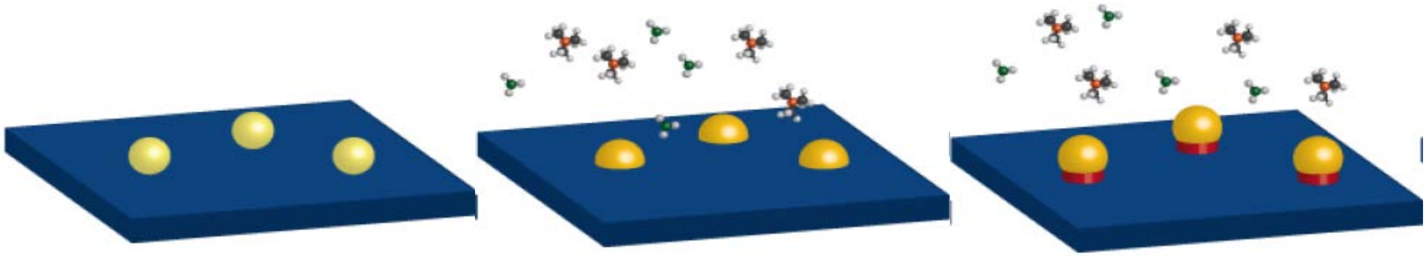
THE « BOTTOM-UP » INTEGRATION

THE VAPOUR-LIQUID-SOLID (VLS) MECHANISM



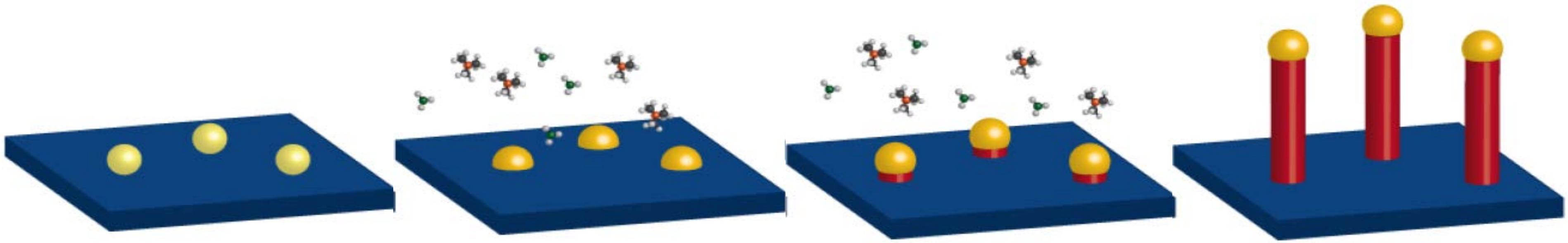
THE « BOTTOM-UP » INTEGRATION

THE VAPOUR-LIQUID-SOLID (VLS) MECHANISM



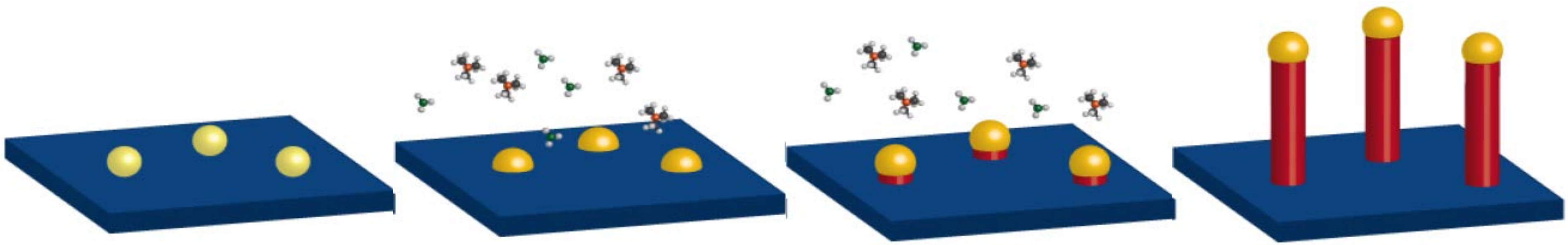
THE « BOTTOM-UP » INTEGRATION

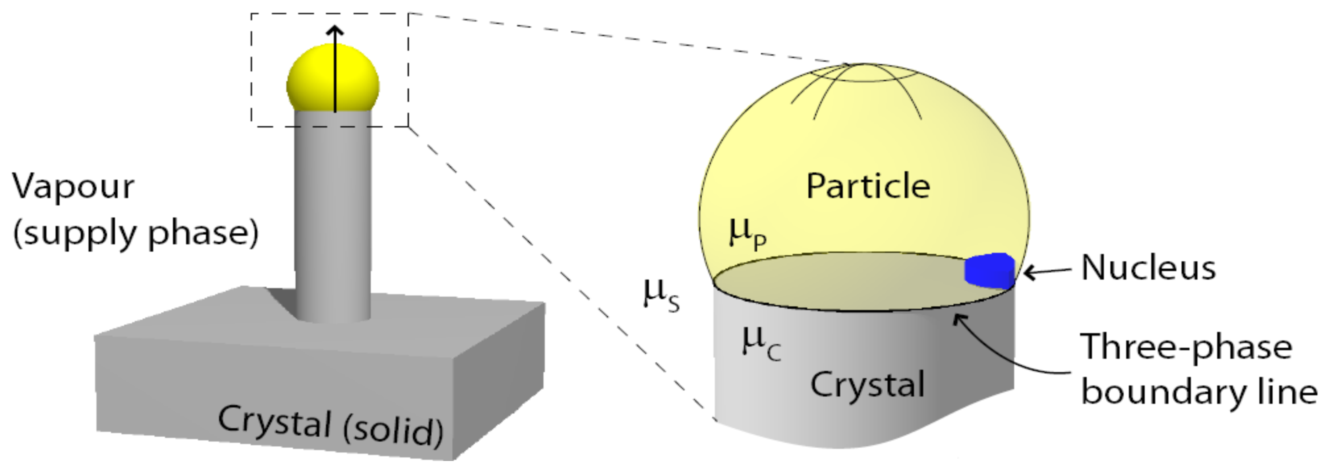
THE VAPOUR-LIQUID-SOLID (VLS) MECHANISM



THE « BOTTOM-UP » INTEGRATION

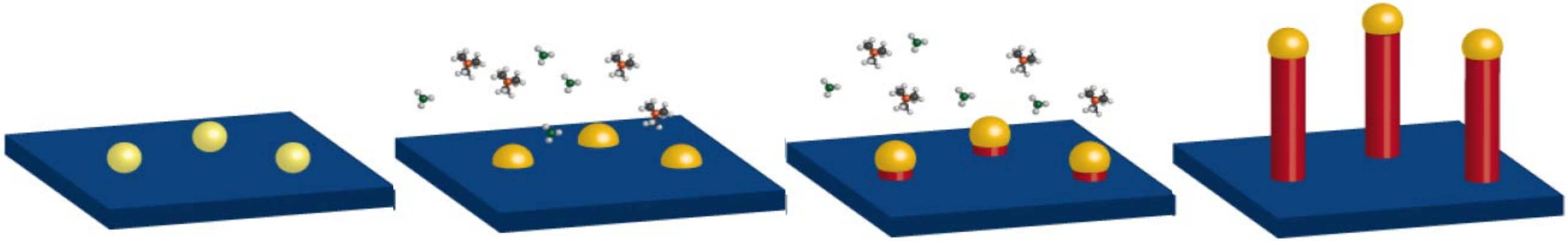
THE VAPOUR-LIQUID-SOLID (VLS) MECHANISM

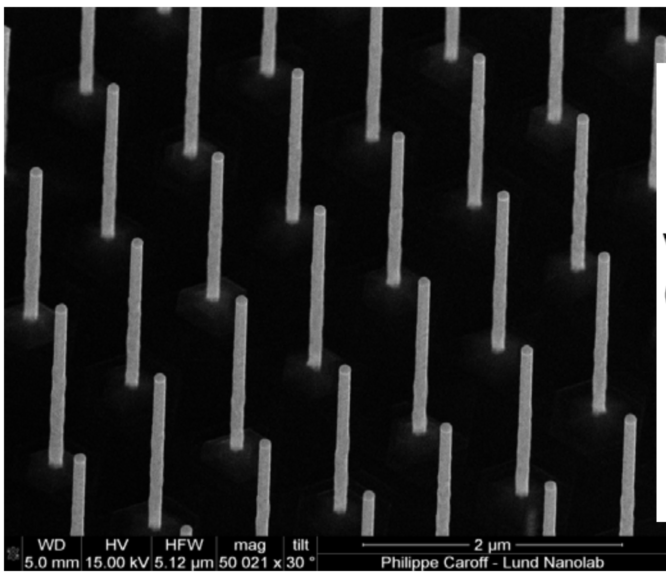


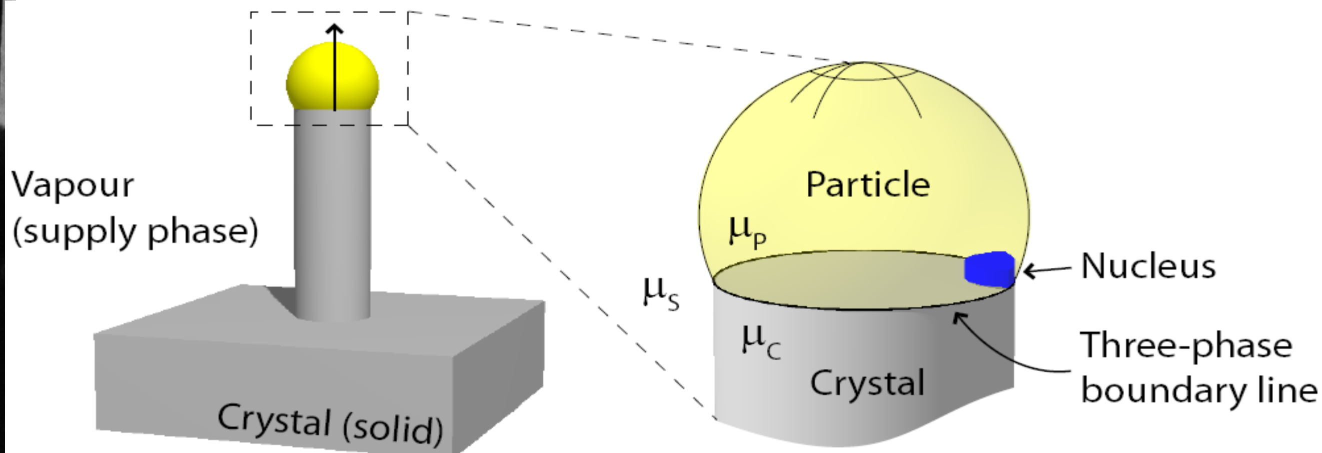


THE « BOTTOM-UP » INTEGRATION

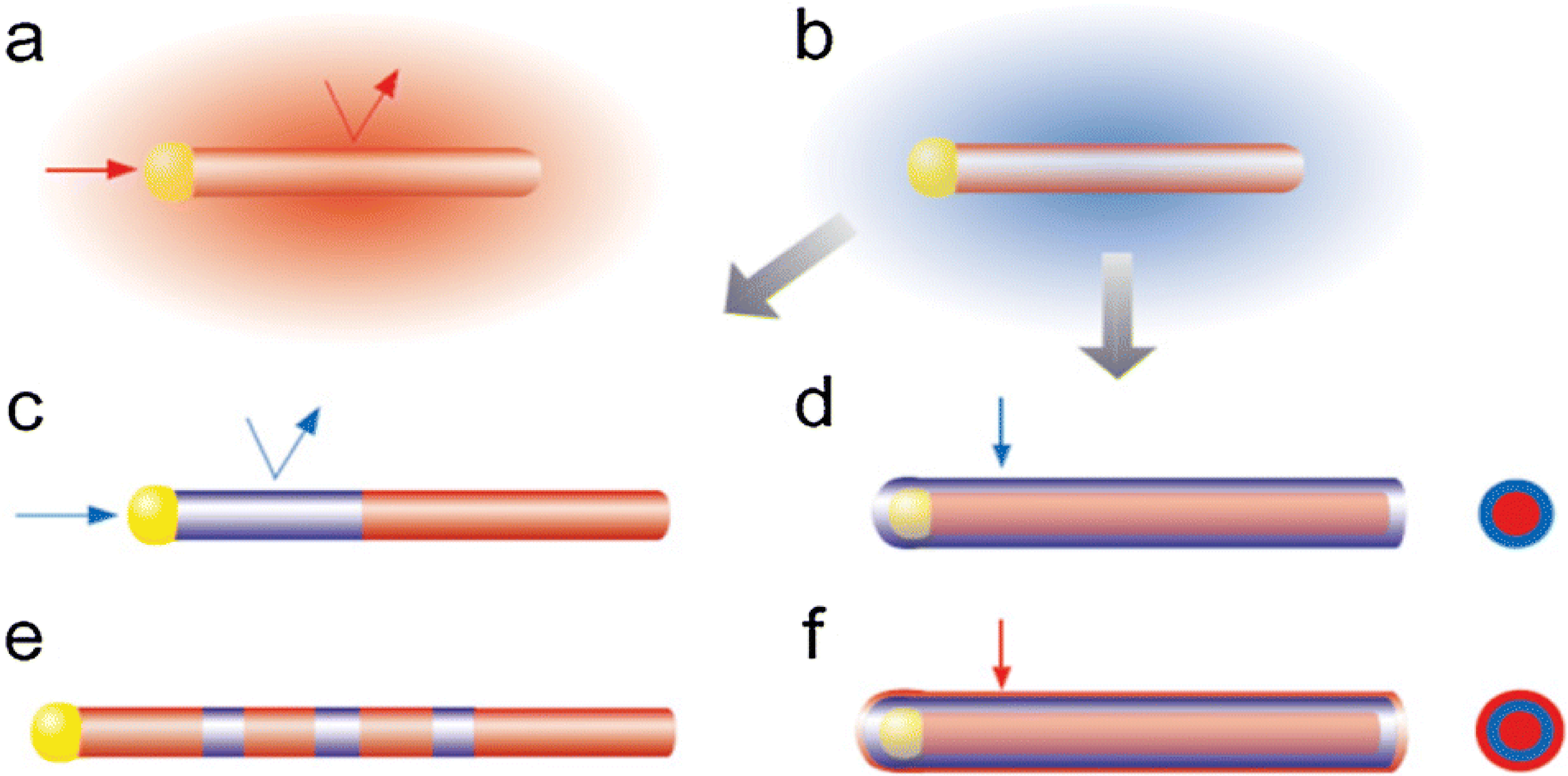
THE VAPOUR-LIQUID-SOLID (VLS) MECHANISM





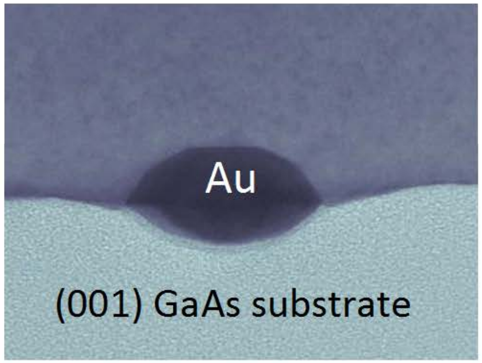


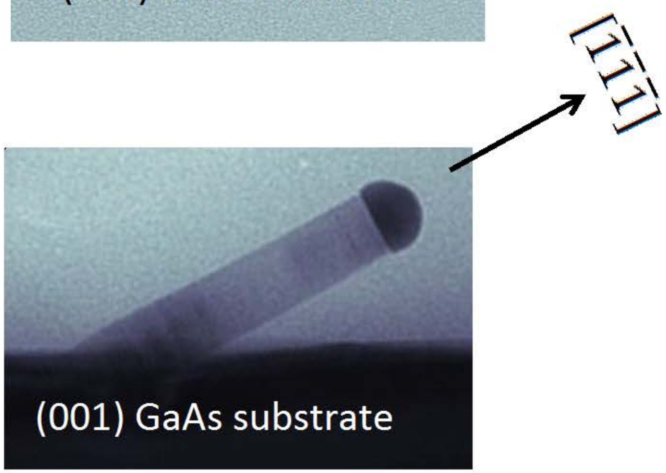
ENABLE NEW MATERIAL COMBINATIONS

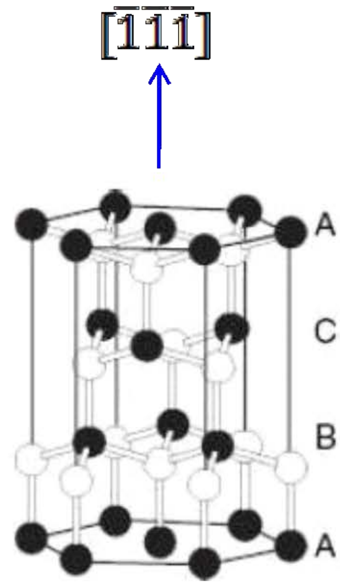


Preferential growth axis

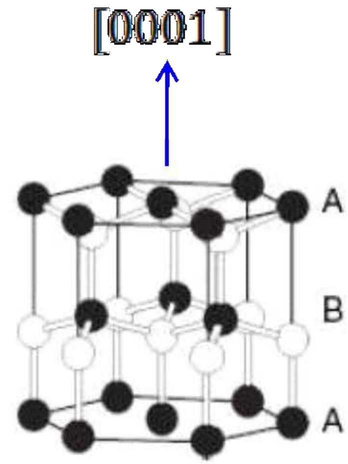
Au-catalyzed semiconductor nanowires







Cubic (Zinc Blende)

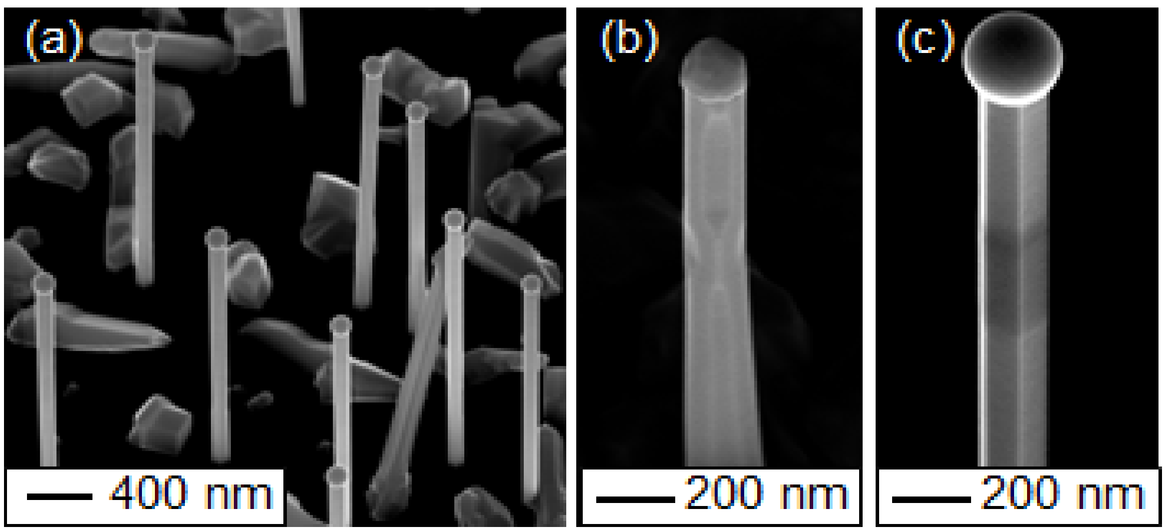


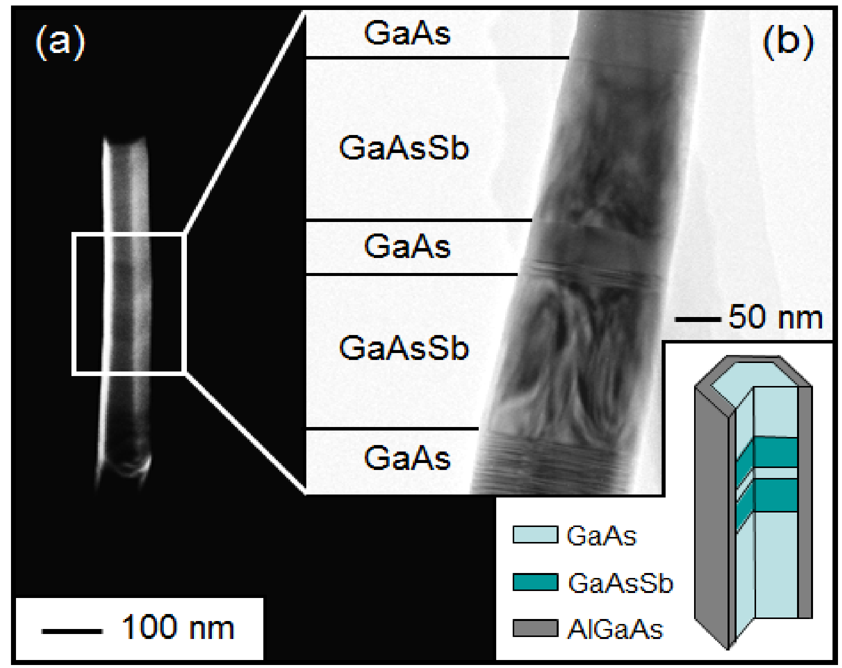
Hexagonal (Wurtzite)

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

AN EXAMPLE OF INTEGRATION ON SILICON

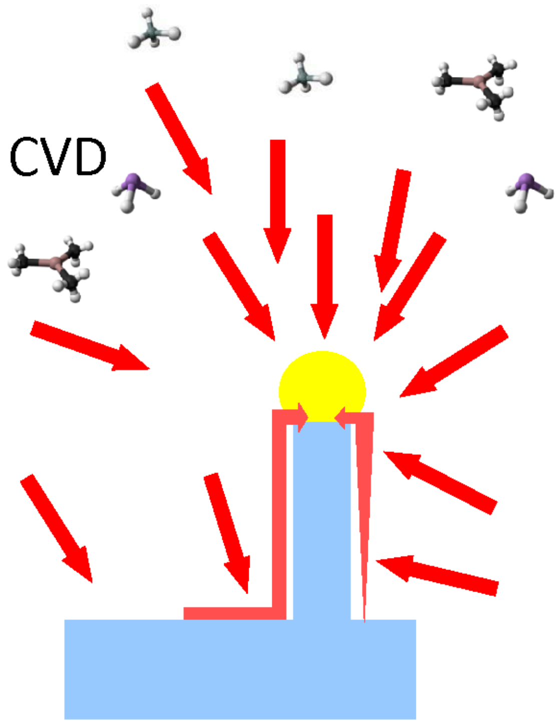
Growth of GaAs and GaAsSb nanowires on Si(111)

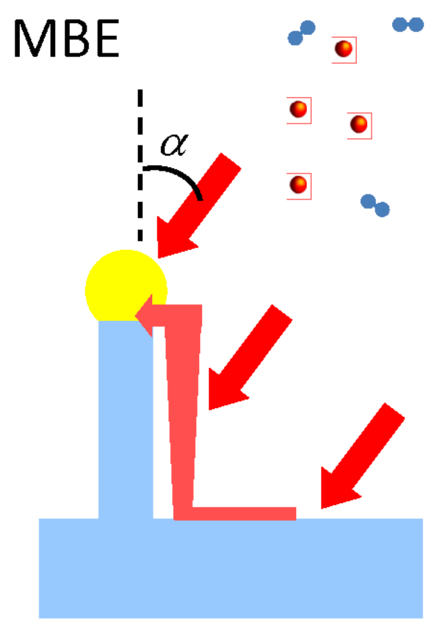


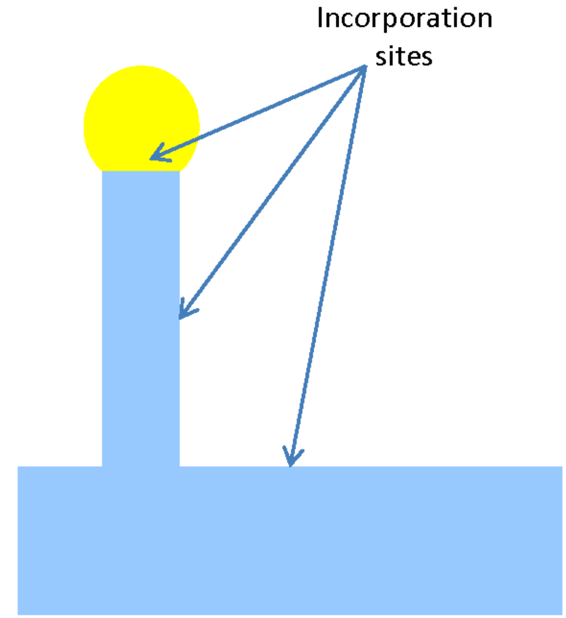


The physical modeling of the system

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 »

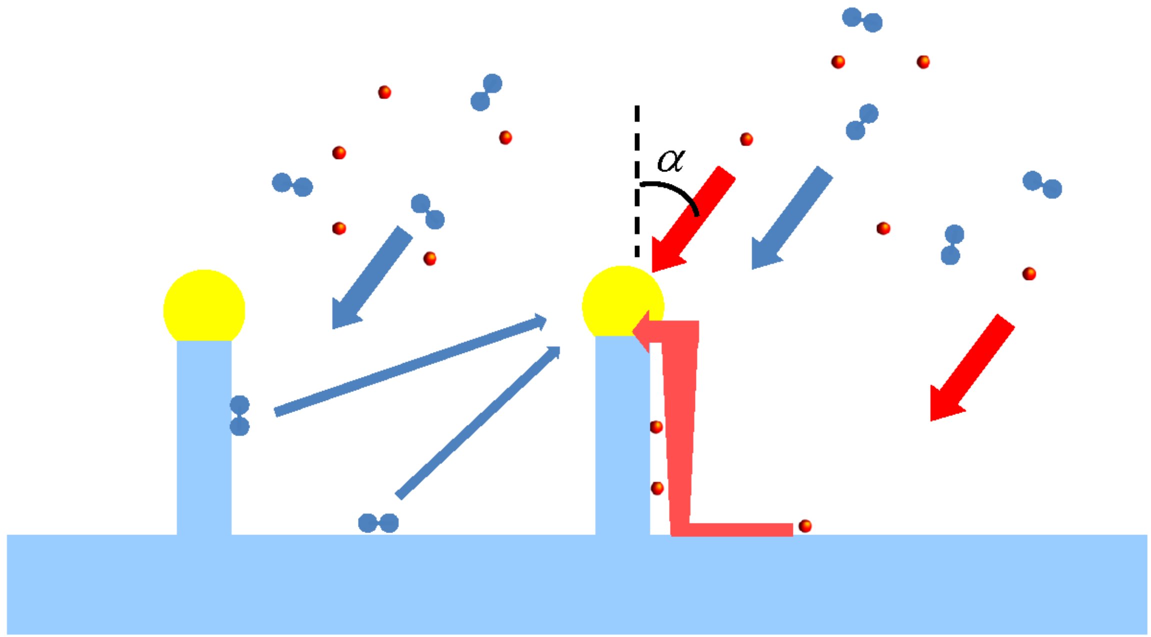
The liquid drop is a dense phase:

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



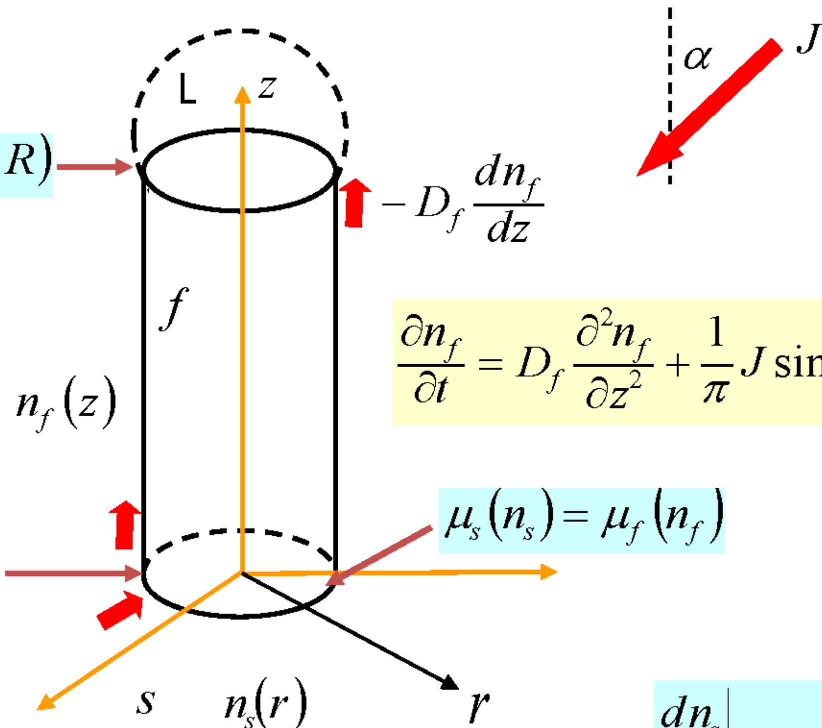
Group V : sticking coefficient <<1
Surface adsorption + reemission in the vapor phase

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



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

$$n_f(z)$$

$$n_s(r)$$

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

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

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

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

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

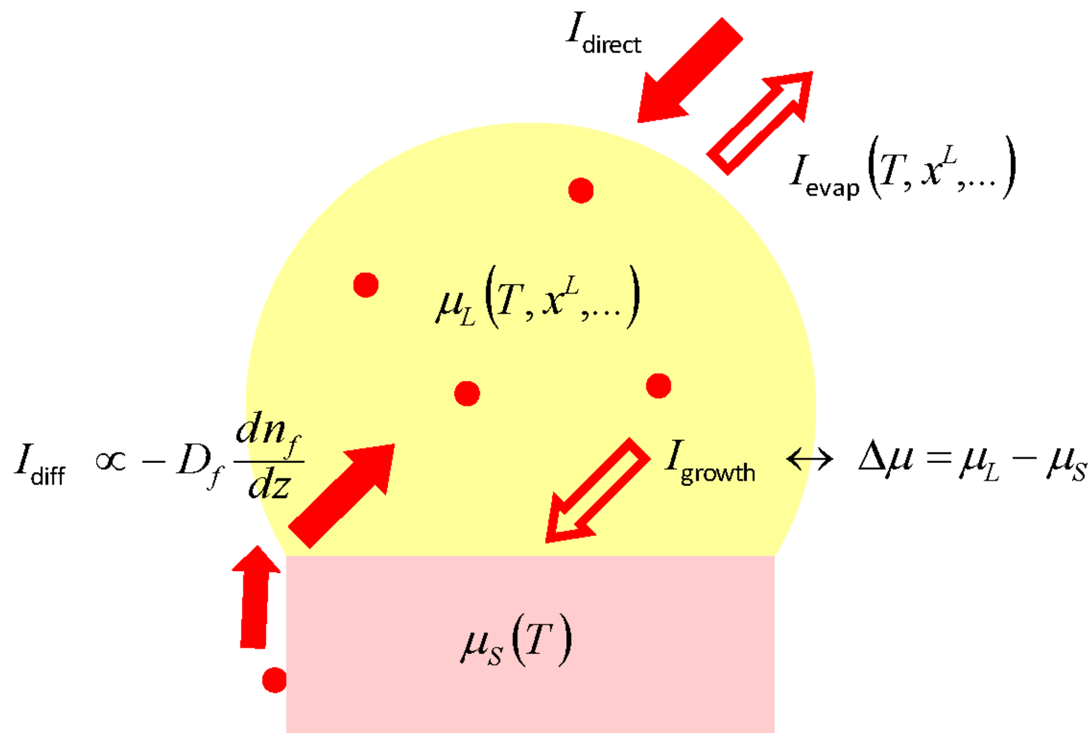
$$\left.\frac{dn_s}{dr}\right|_{r\to\infty} = 0$$

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

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

$\rightarrow$ Diffusion flux into the drop

Coupling between diffusion and incorporation

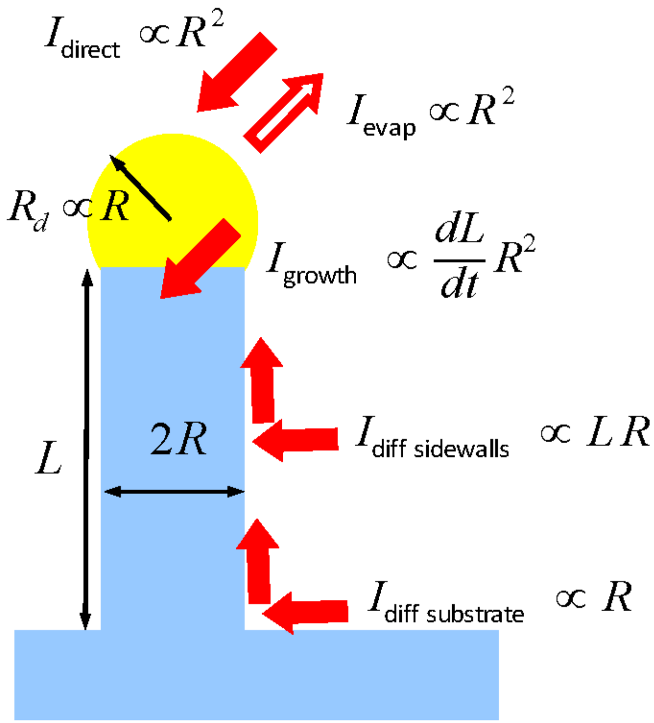


- Material balance $I_{\text{direct}} + I_{\text{diff}} = I_{\text{growth}} + I_{\text{evap}}$ ⟶

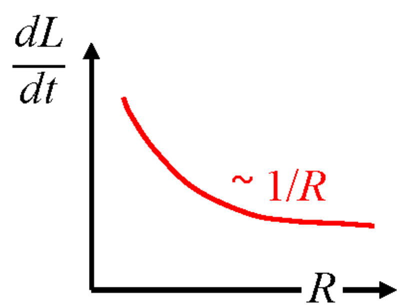
  self-consistent determination of x^L and growth rate possible in principle in simple sytems

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

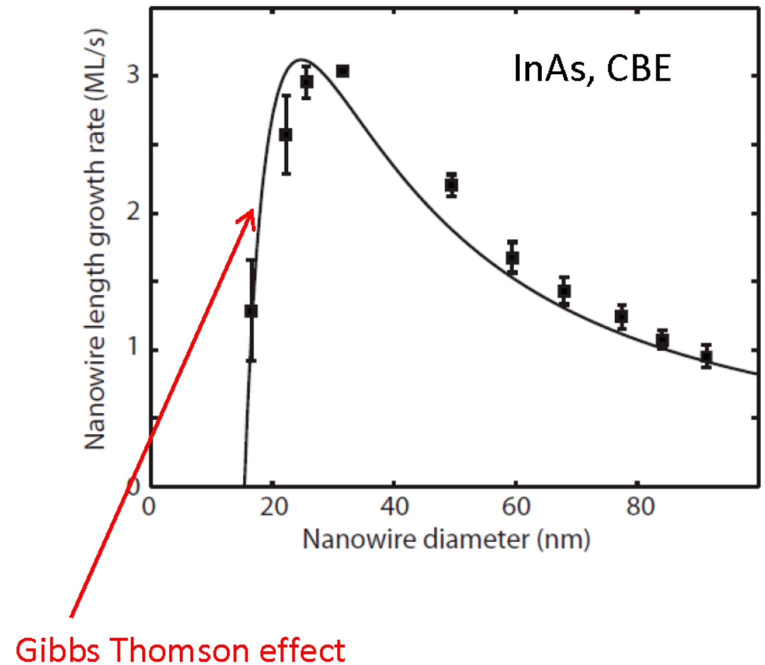
Length / radius dependence



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



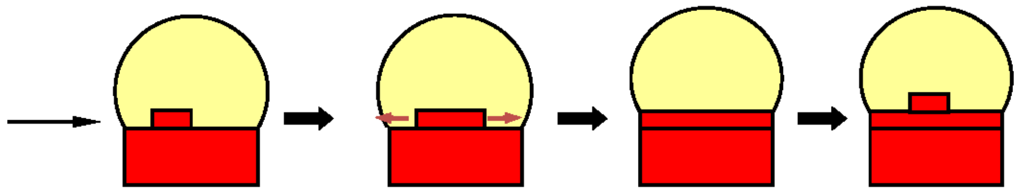
μ^L treated as a fitting parameter

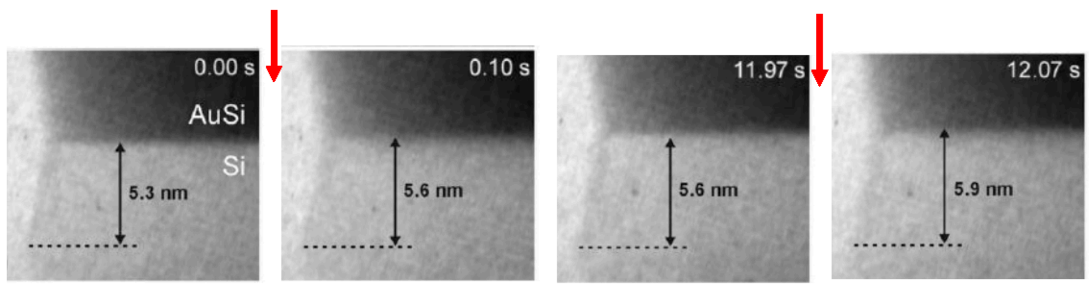


Fröberg et al., Phys. Rev. B 76, 153401 (2007)

How does VLS growth proceed

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

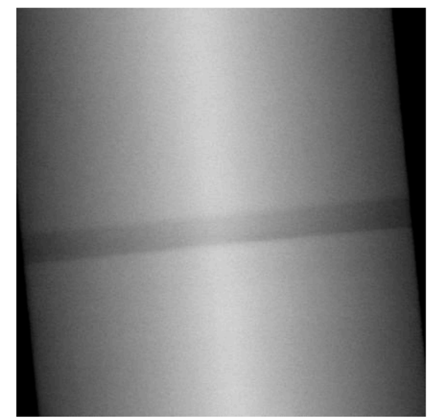




Si NW growth in a TEM

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

Flat heterointerfaces



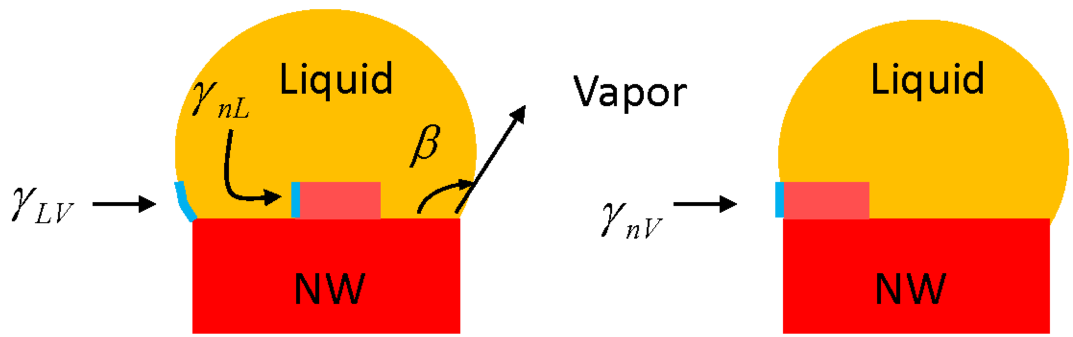
AlGaAs insertion in GaAs NW

- At least one new 2D nucleus is needed for each ML

- If top facet is narrow enough, mononuclear regime

  1 ML ↔ 1 nucleation event

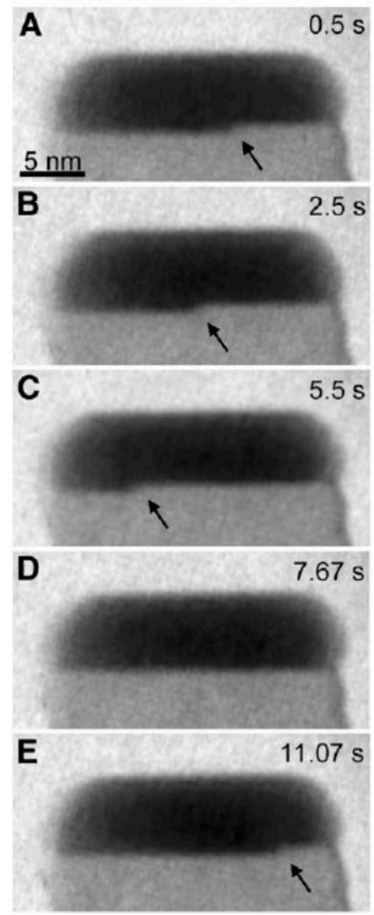
Where ?



Nucleus entirely surrounded by liquid

Nucleus at the periphery

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

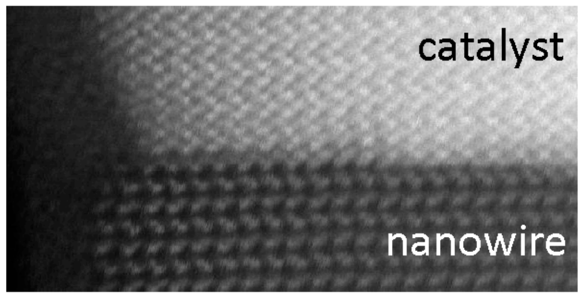


Nucleation at the triple phase line if $\gamma_{nV} < \gamma_{nL} + \gamma_{LV} \sin\beta$

Easily satisfied for β ~90°

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

Some experimental indications of nucleation at TPL



The possible catalyst particles

The list of the possible catalysts:

- Gold (Au): Mostly used catalyst

- Silver (Ag)

- Platinum (Pt)

- Copper (Cu)

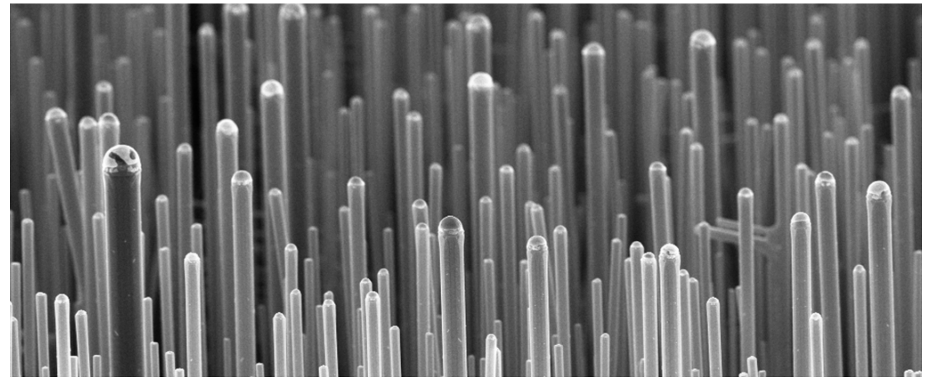
- Tin (Sn)

- Element III (III-V nanowires)

- …

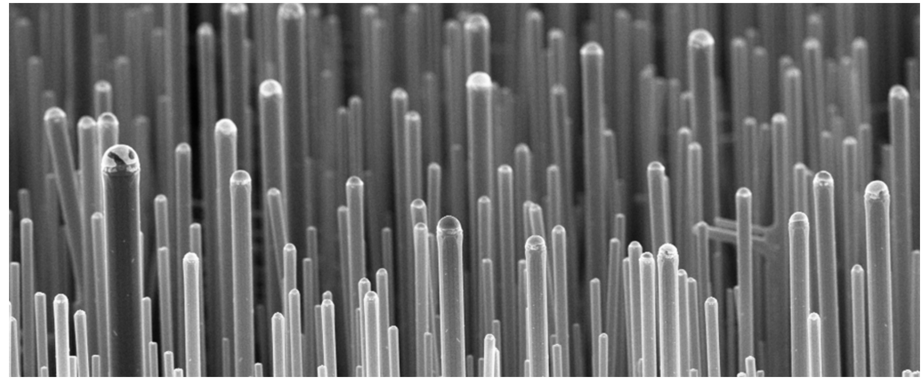
The deposition methods

- Colloids + spinner

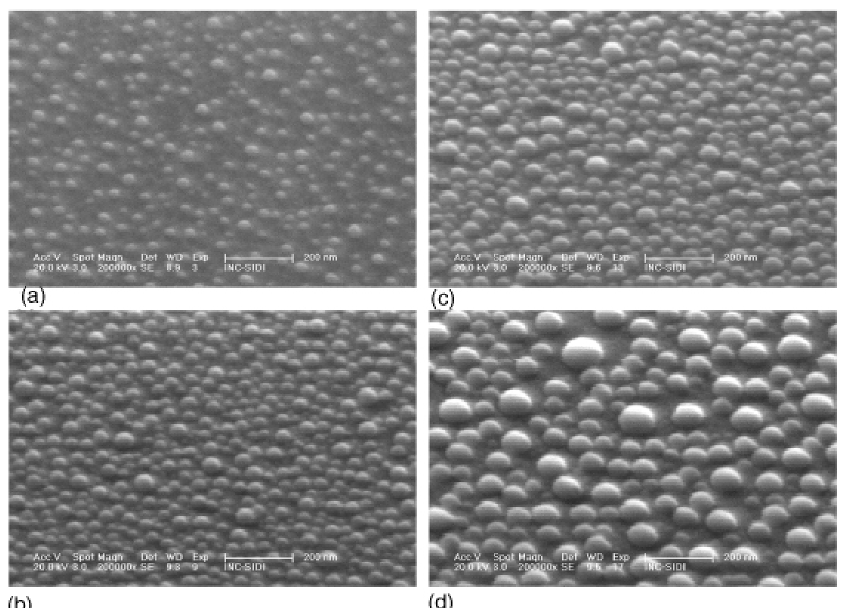


The deposition methods

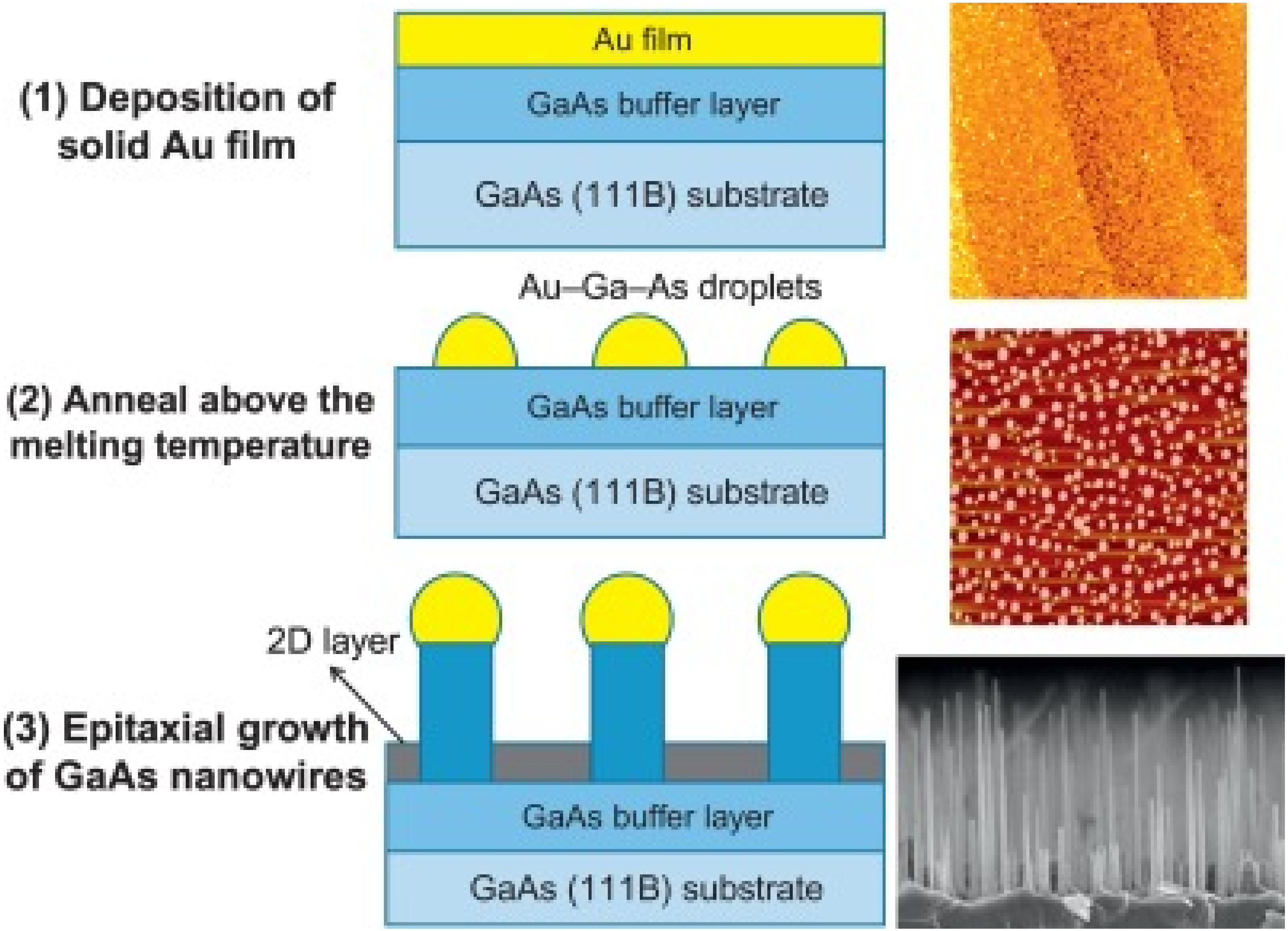
- Colloids + spinner



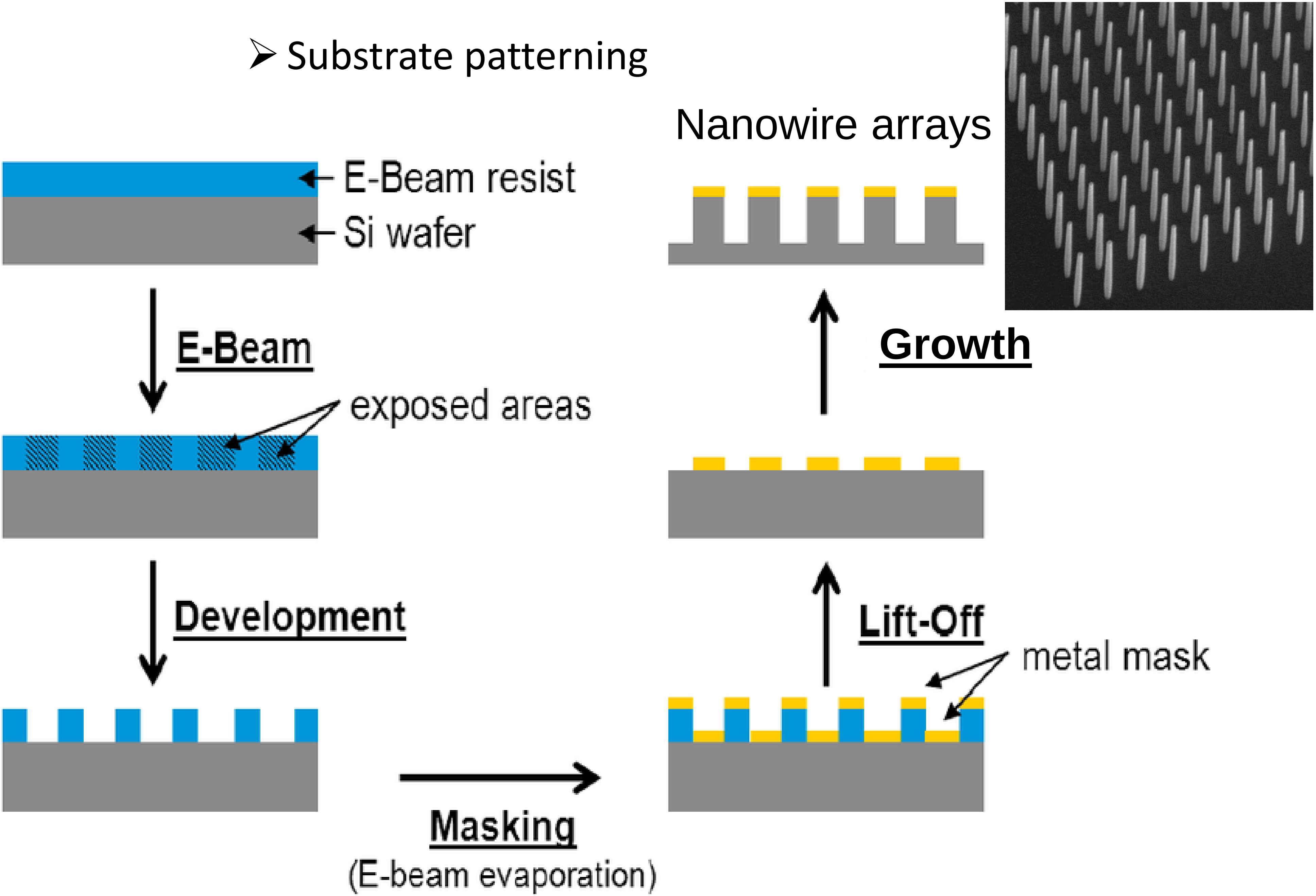
- In-situ deposition (gold or element III)



➢ Layer dewetting



➢ Substrate patterning



Why is Au such a successful catalyst?

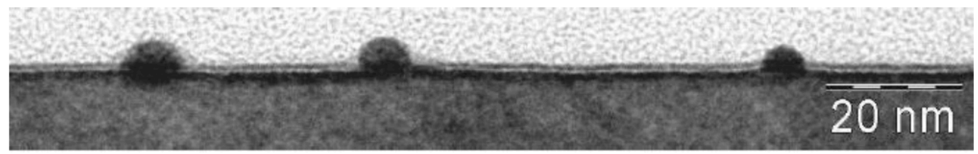
✓No oxidation in air

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

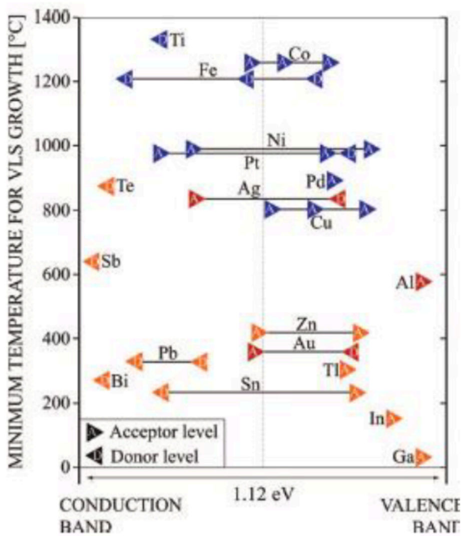
→VLS growth is possible

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

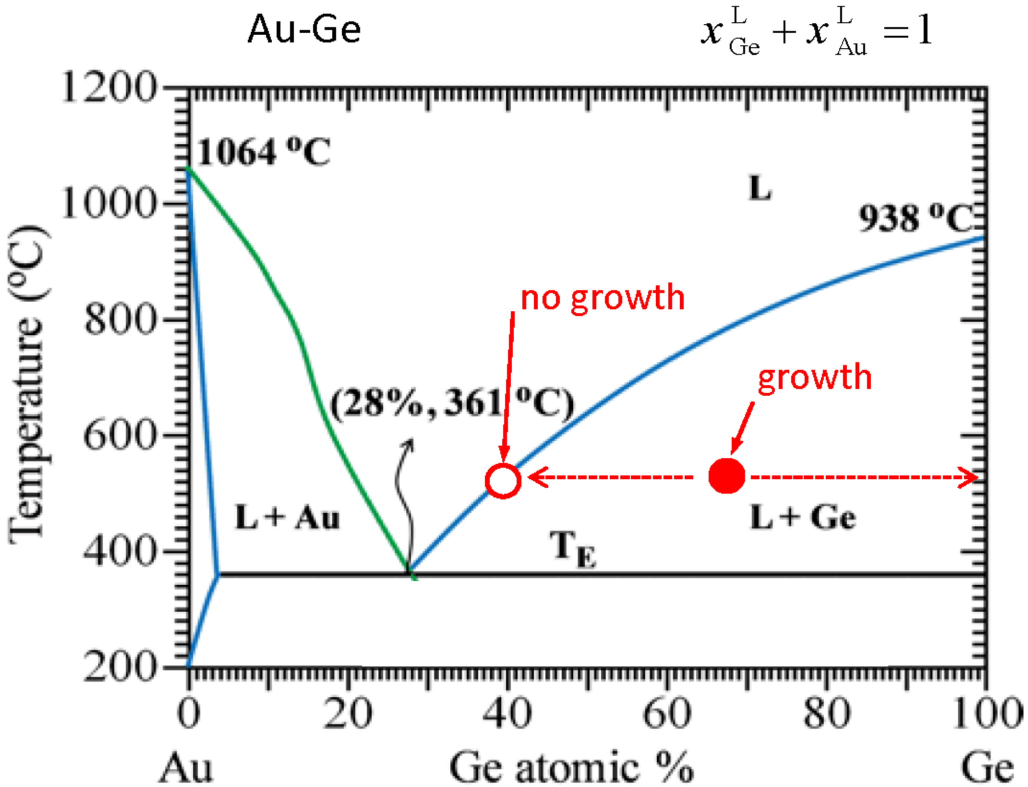


Metal catalysts for Si NW growth

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

The catalyst is a reservoir of NW constituents

$$x_{Ge}^{L} + x_{Au}^{L} = 1$$

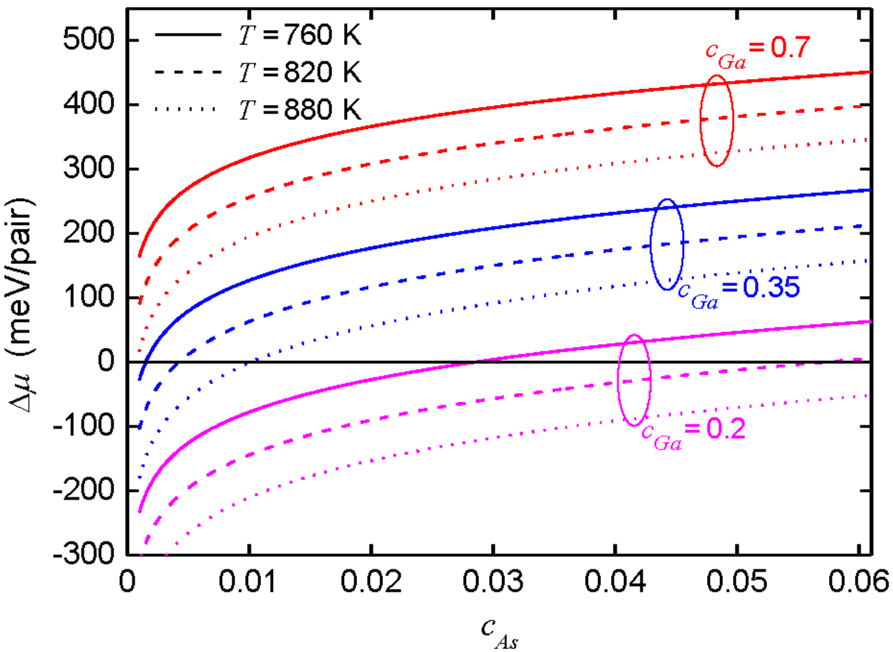


x_{Ge}^{L} must be higher than the equilibrium concentration to start growing

Case of III-V compounds

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

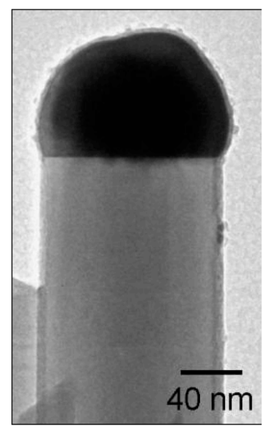
AuGaAs liquid catalyst $x^L_{Ga} + x^L_{As} + x^L_{Au} = 1$



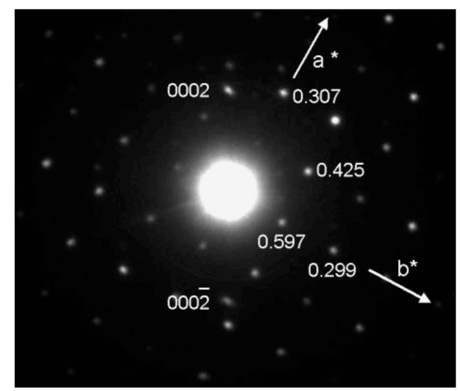
$$\Delta\mu(x^L_{Ga}, x^L_{As}, T)$$

Group III atoms are much more soluble than group V atoms

Catalyst composition after GaAs NW growth



$Au_{0.5}Ga_{0.5}$ phase



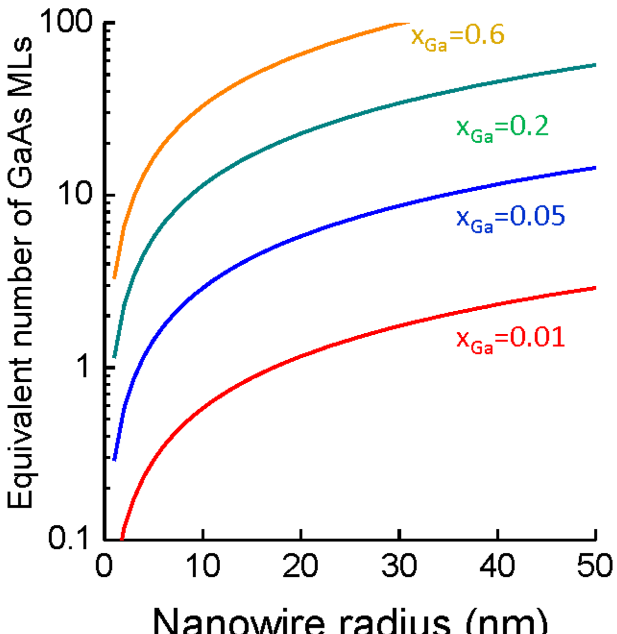
Glas, J. Appl. Phys. 108, 073506 (2010)

How much of each constituent in the reservoir?

During growth

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

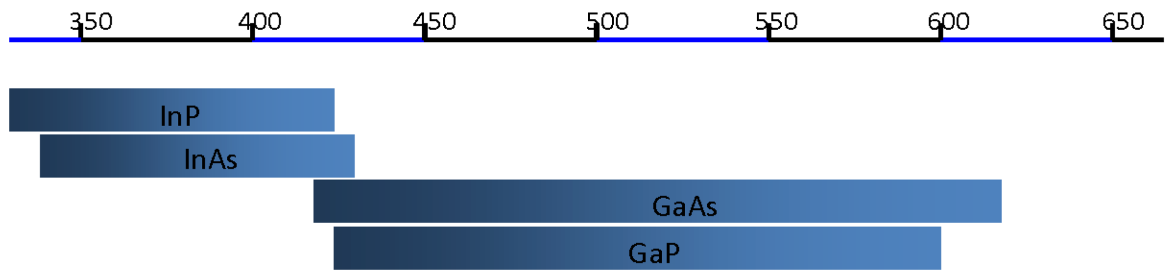
As composition: not more than a few % ≡ a few monolayers of solid NW (can be less than 1ML)



Drop contact angle 90°

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

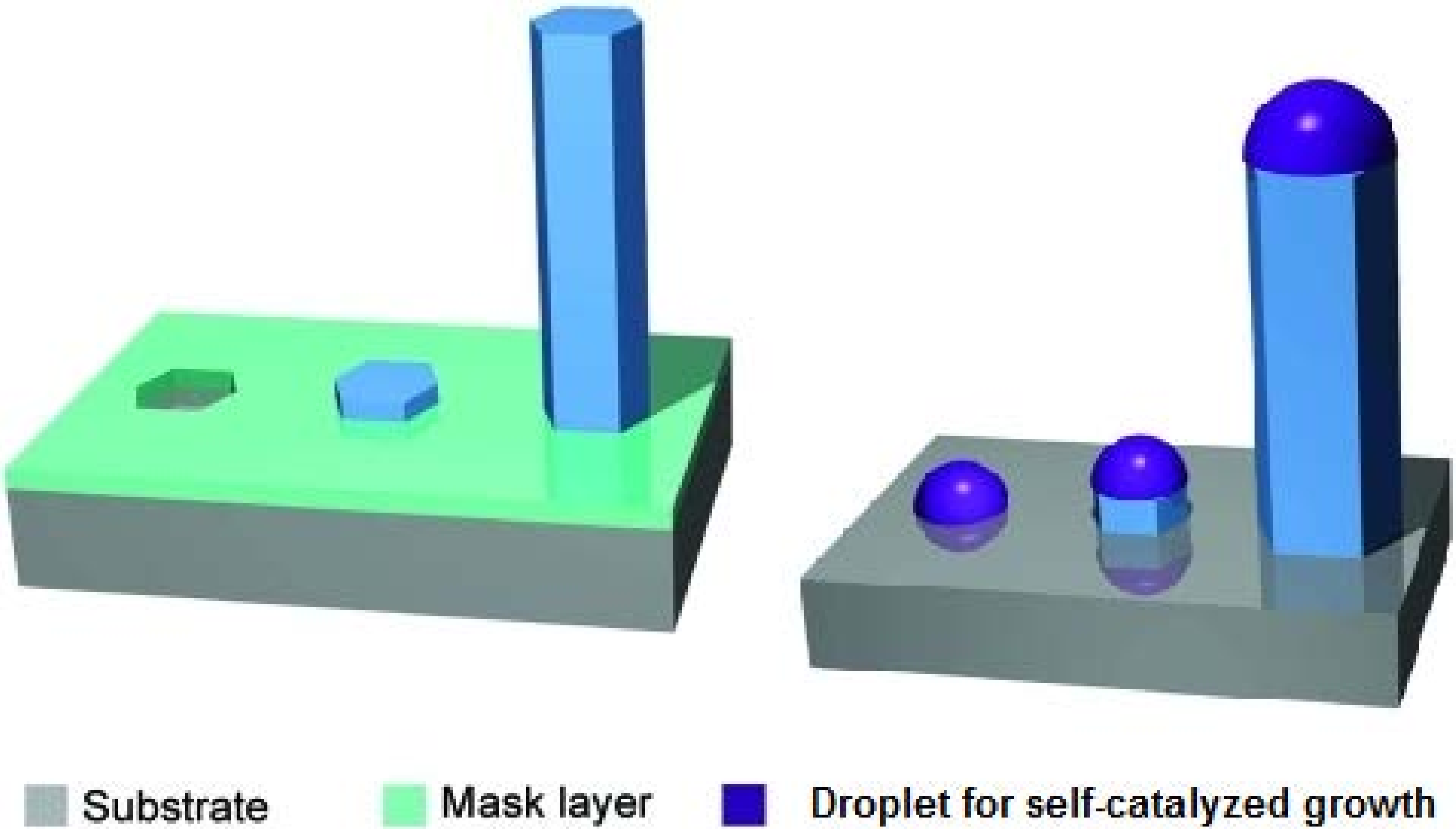


Temperature range for NW growth by MBE of different III-V compounds

The self-catalyzed Nanowires

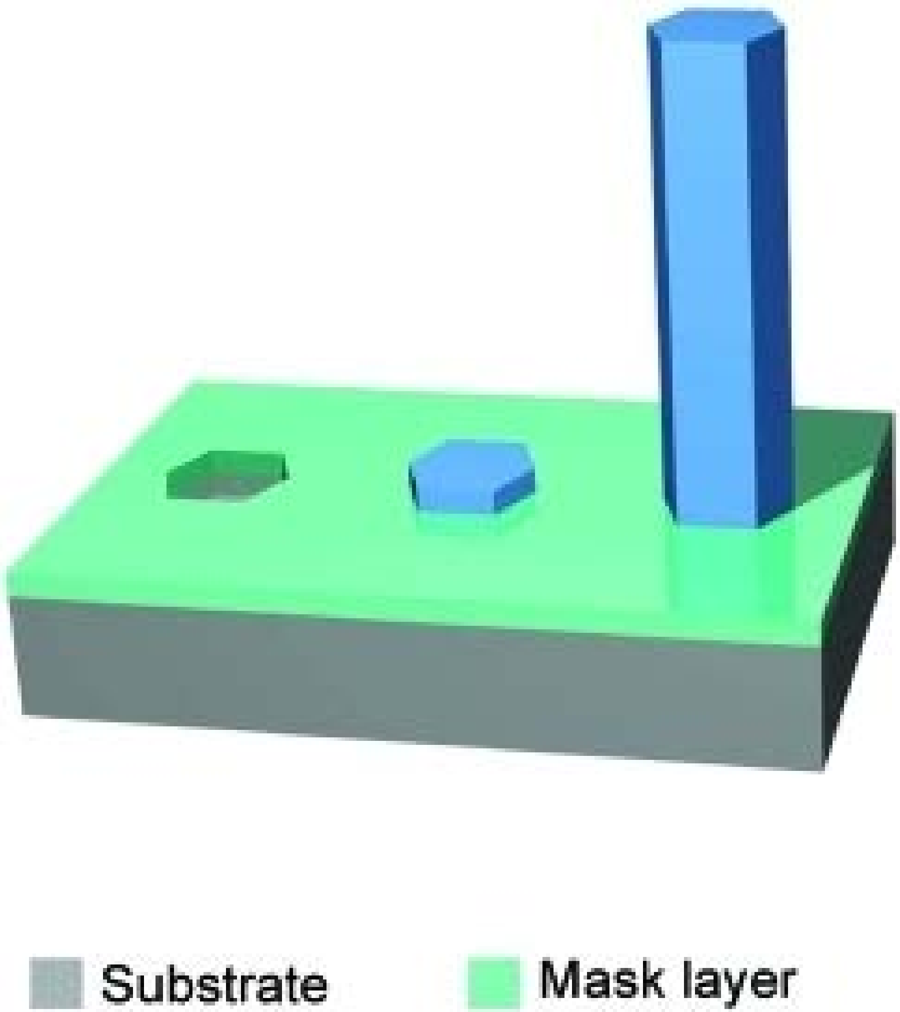
Selective-Area Growth vs Self-Catalyzed Growth

- The Vapor Solid mechanism (VS)
- The droplet assisted growth of nanowires (VLS)



Selective-Area Growth

- The Vapor Solid mechanism (VS)



Same issues than for 2D growth on Si

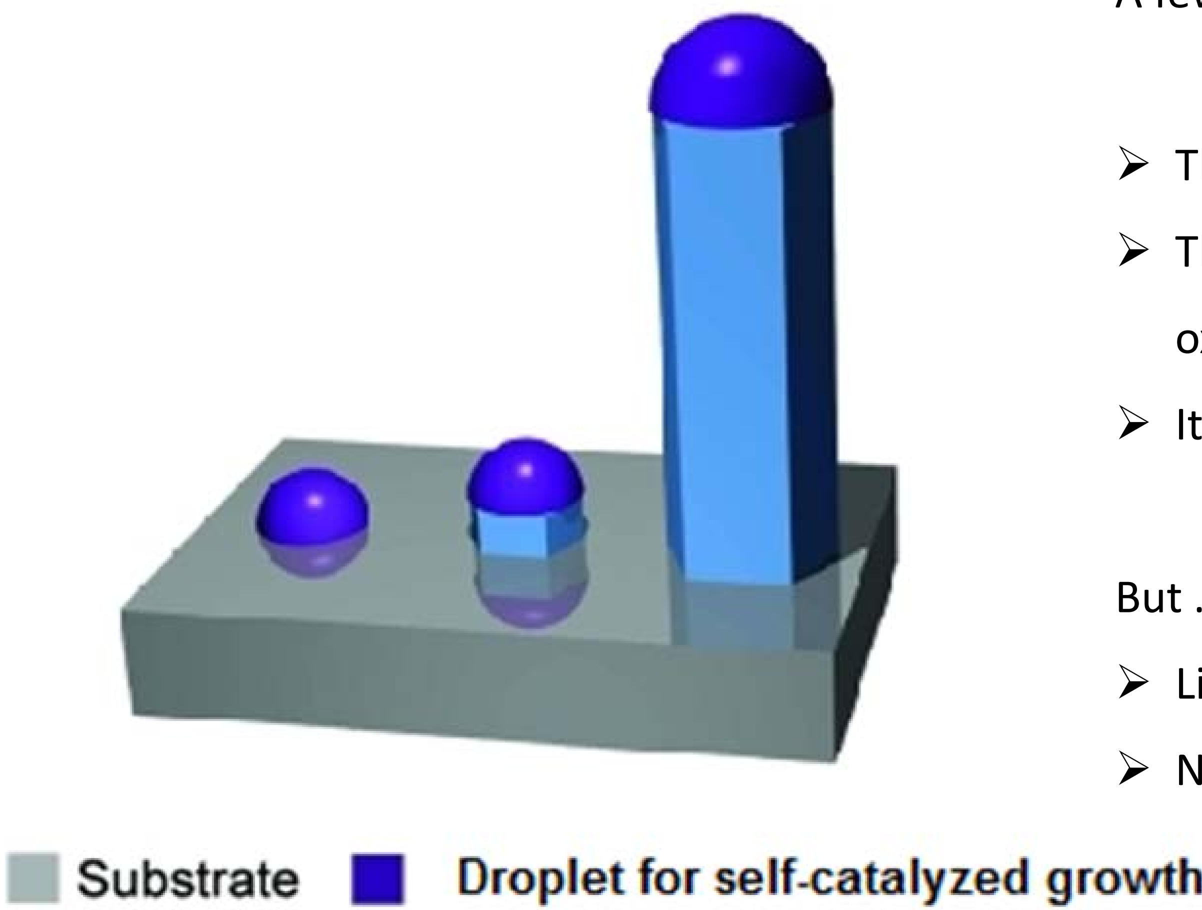
- Pollution
- Oxide removal
- APD

One advantage:

- The diffusion length on the oxide mask
- No “parasitic” growth

Self-Catalyzed Growth

- The droplet assisted growth of nanowires (VLS)



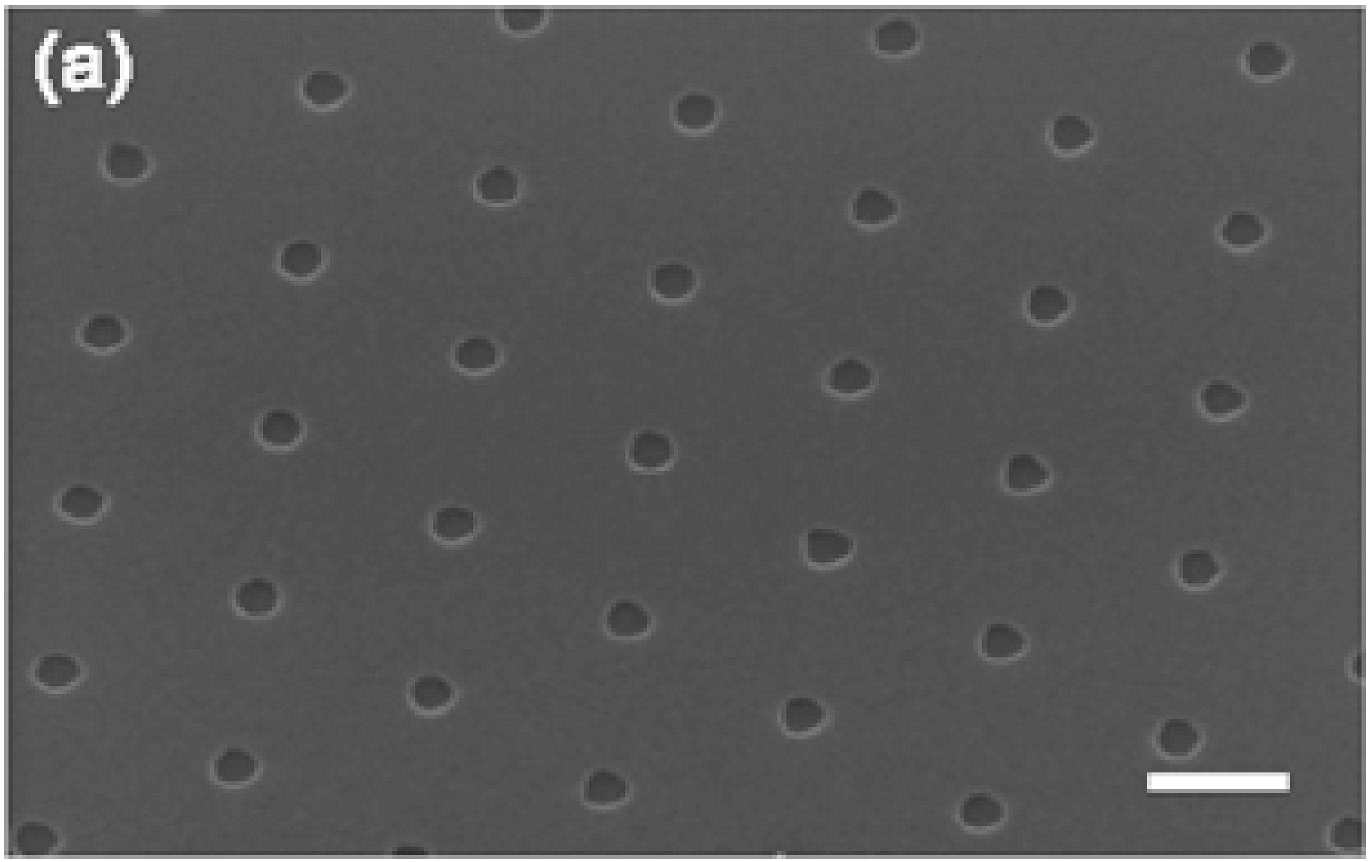
A few advantages compared to VS growth:

- The NW diameter depends of the droplet
- The droplet can remove the last traces of oxide (example of Au or Ga)
- It is possible to switch from VLS to VS

But …

- Limited by the pollution
- Not always possible

THE SUBSTRATE PREPARATION



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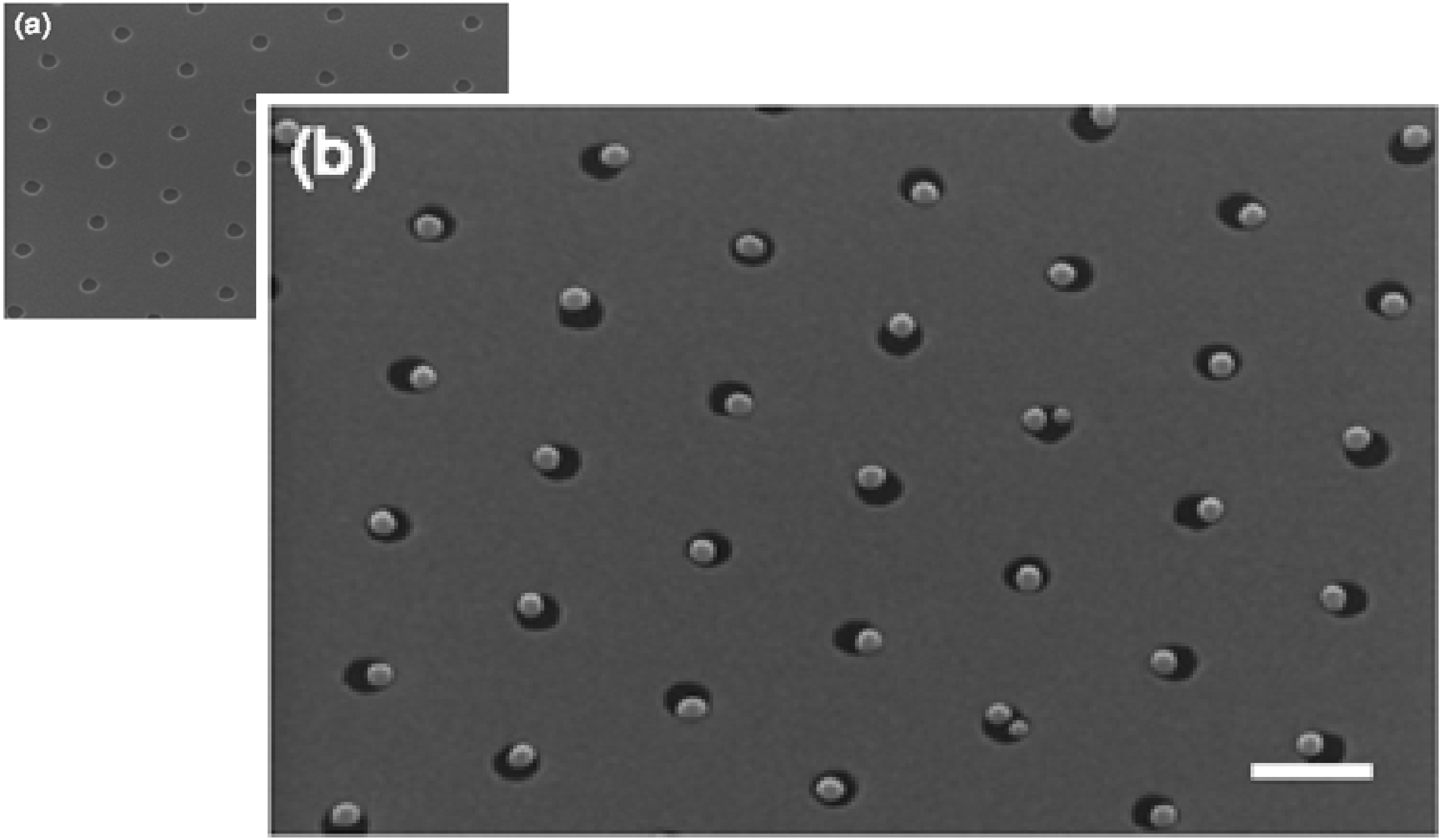

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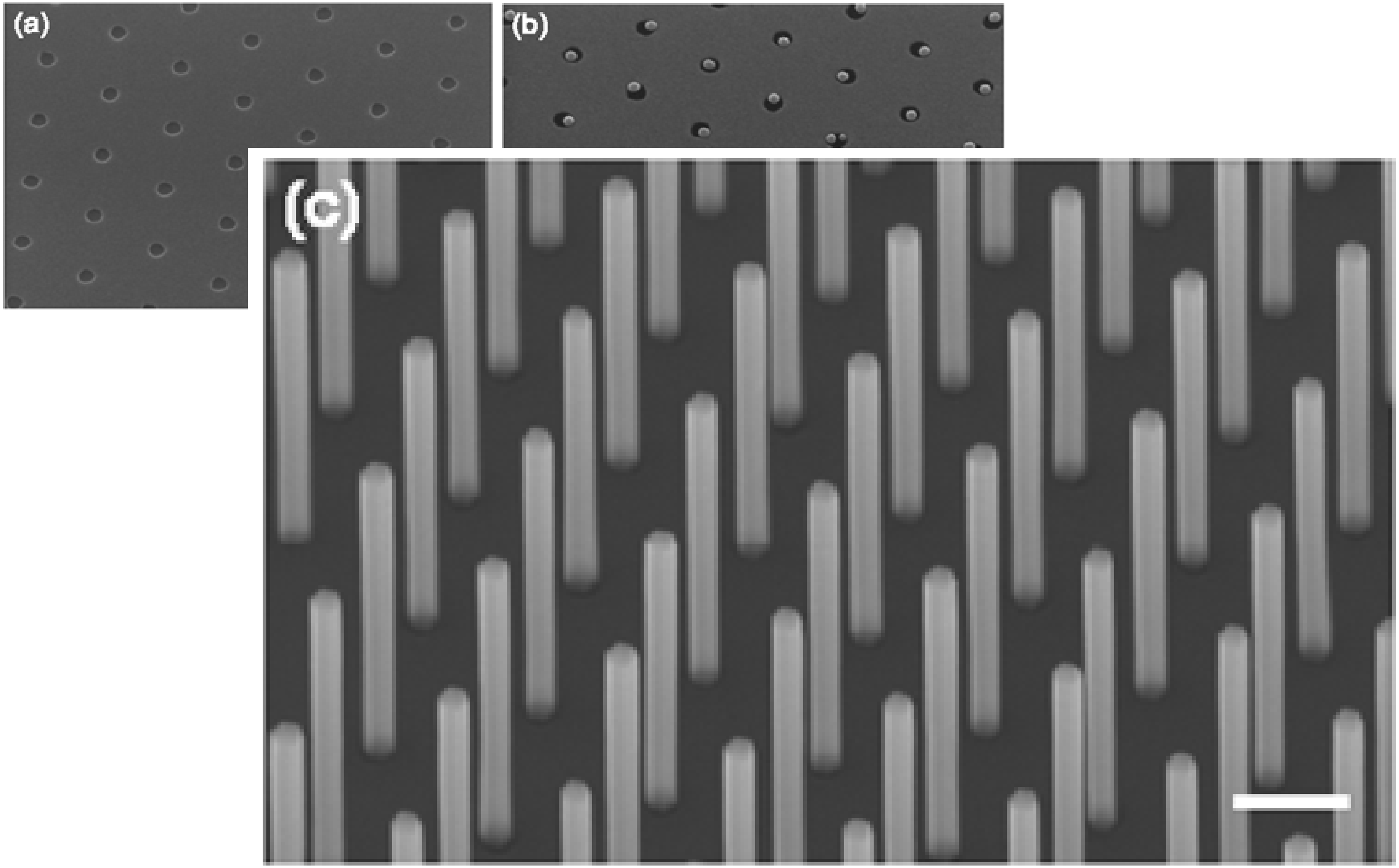
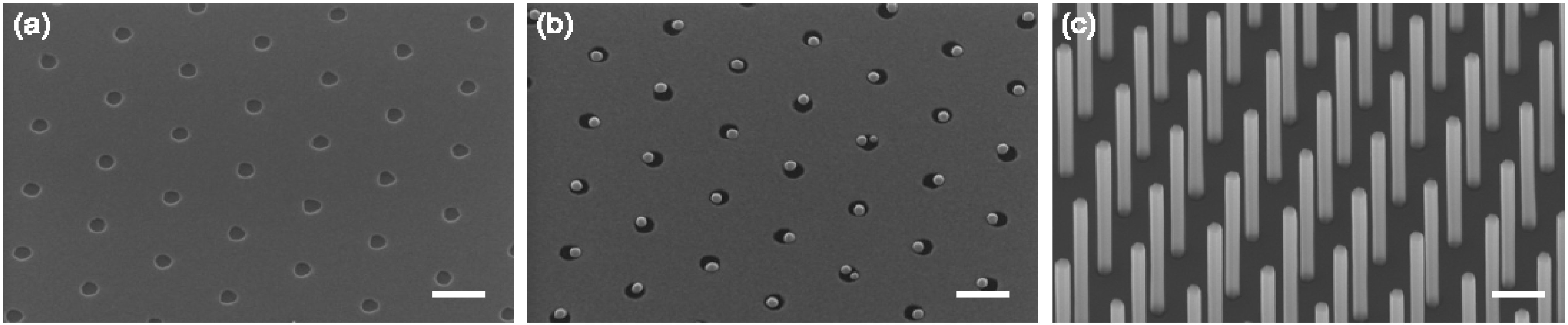


THE SUBSTRATE PREPARATION

Self-catalyzed GaAs nanowires on Si(111) with e-beam lithography



THE SUBSTRATE PREPARATION

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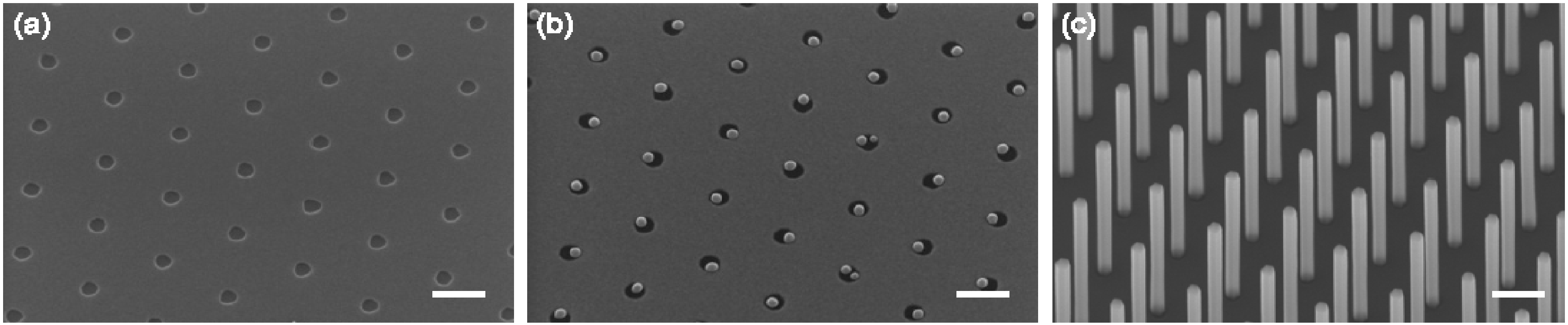
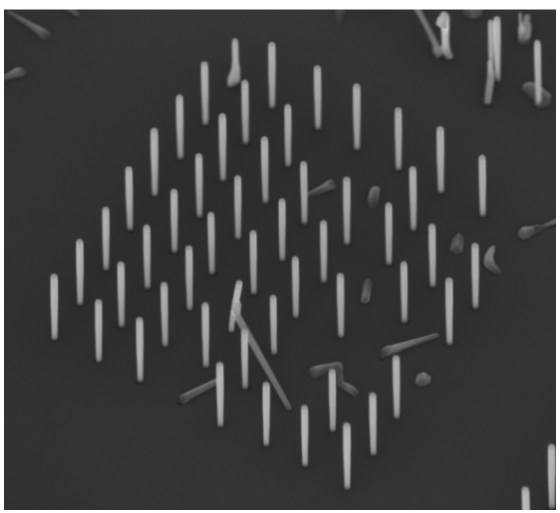
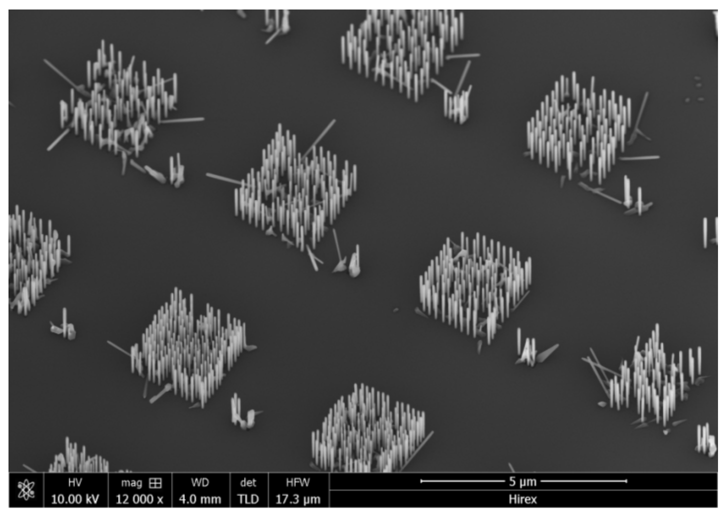
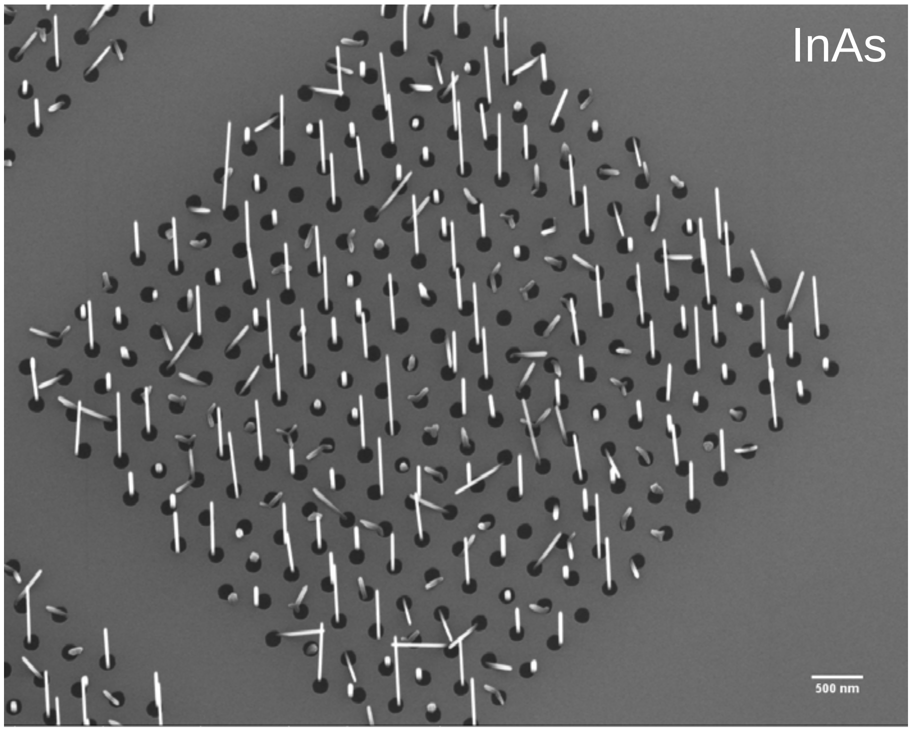


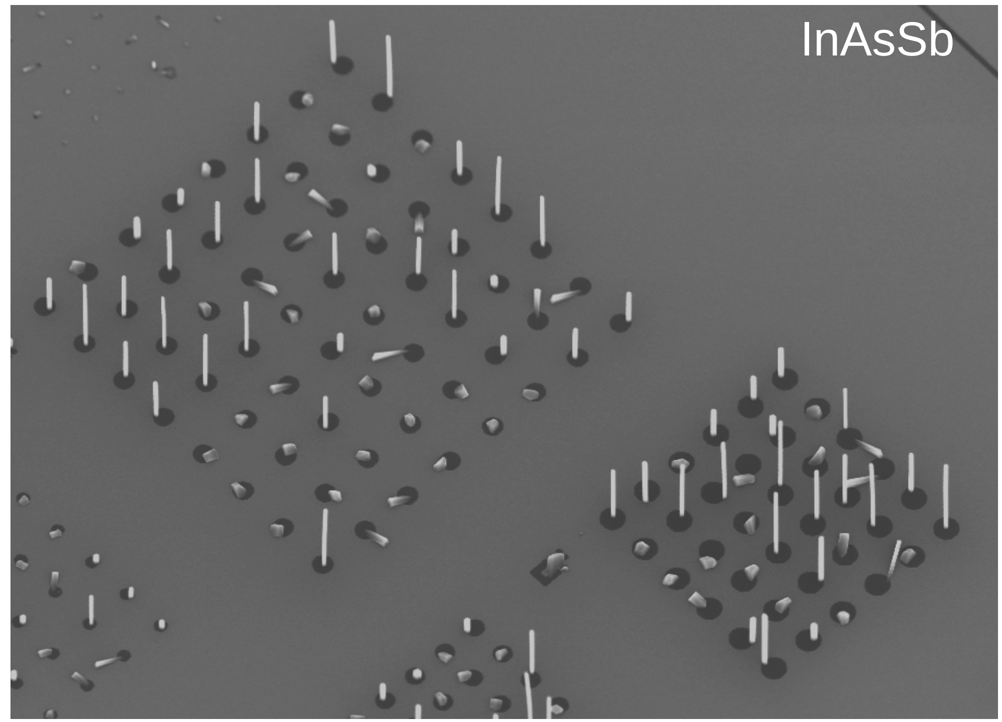
… also possible with Nano-Imprint lithography





More complicated with Indium based materials (no droplet - VS growth)



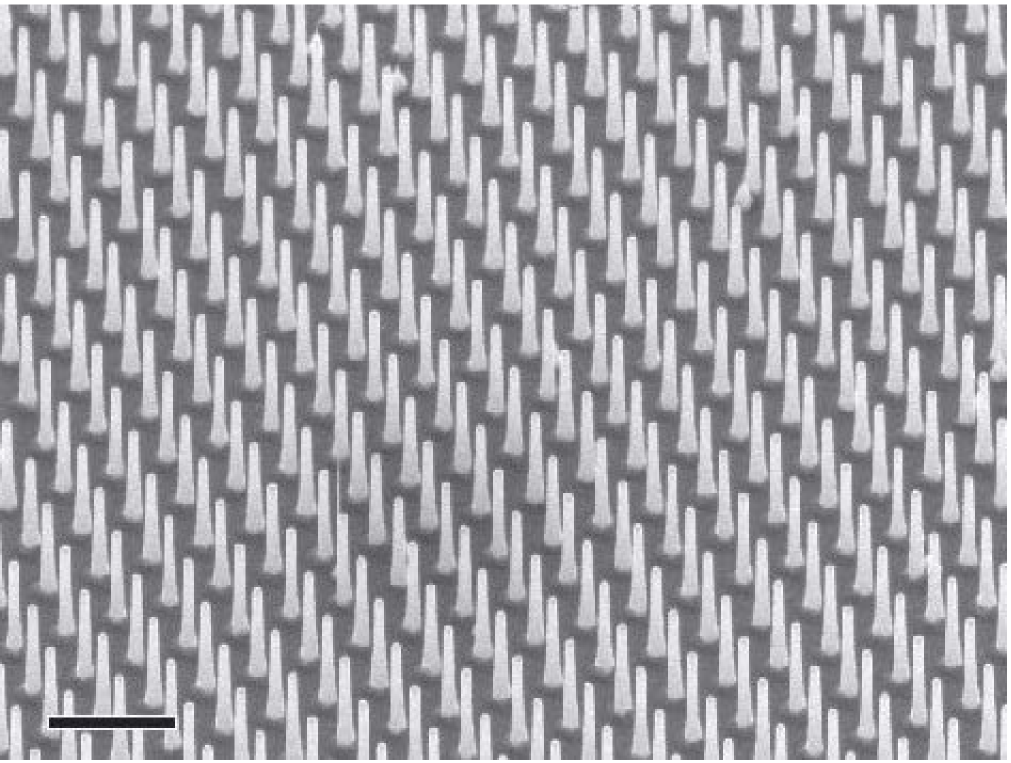


In_2O_3 more stable than Ga_2O_3

The homosubstrates

A large variety of materials: II-VI, III-V and IV-IV

InP nanowires



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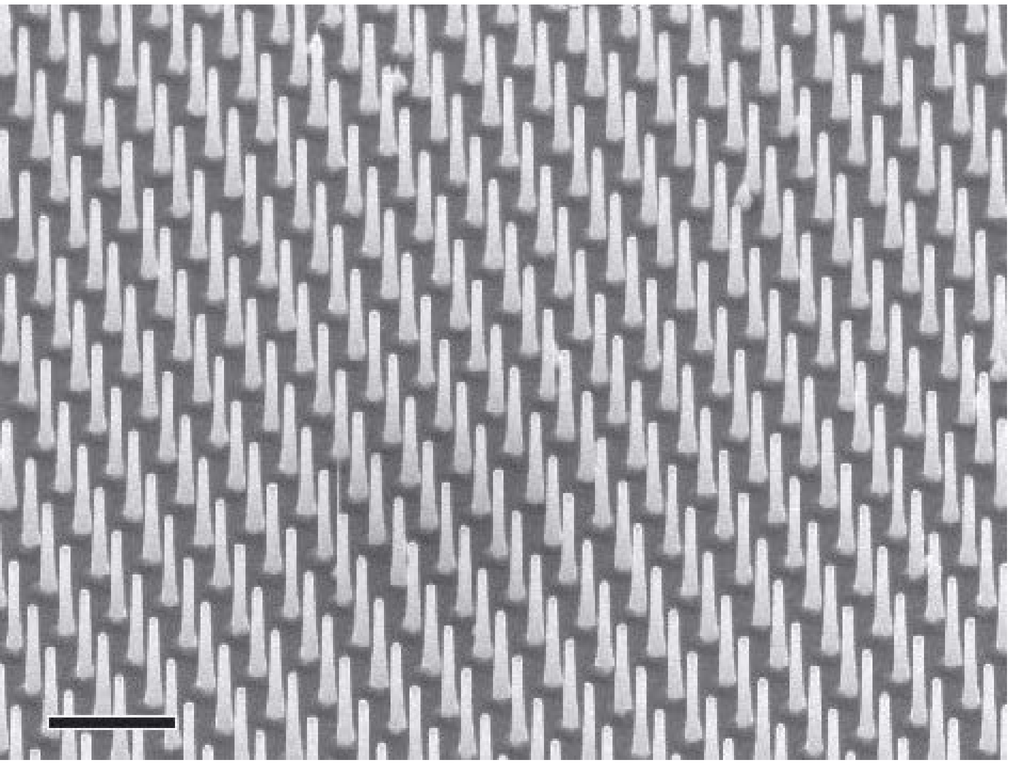
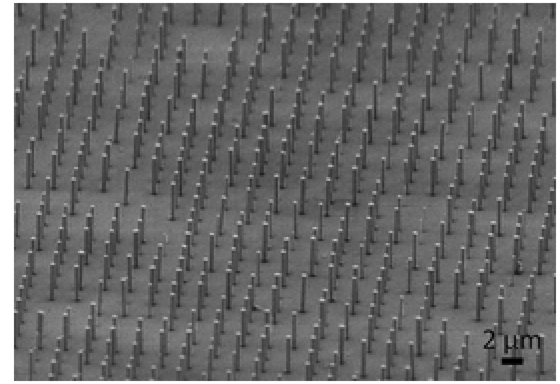
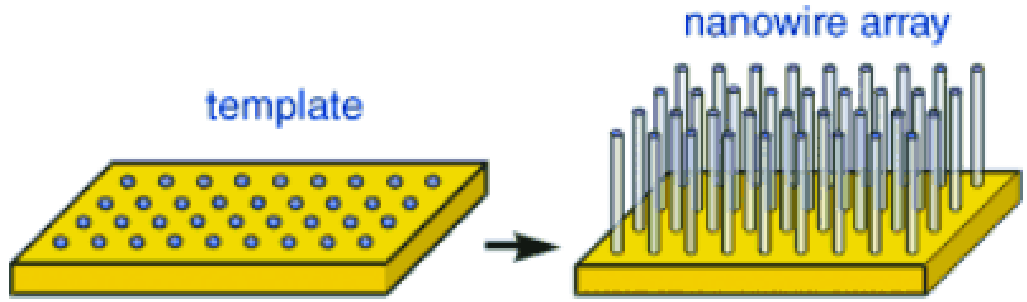
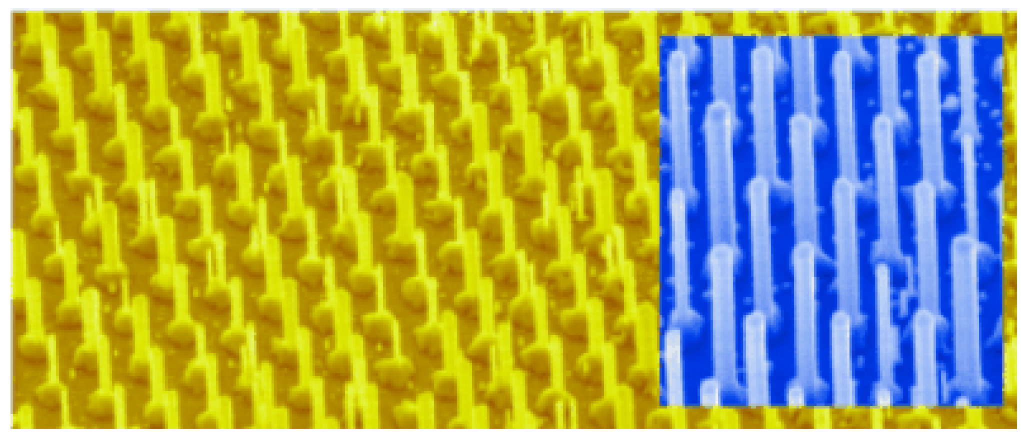


ZnO nanowires

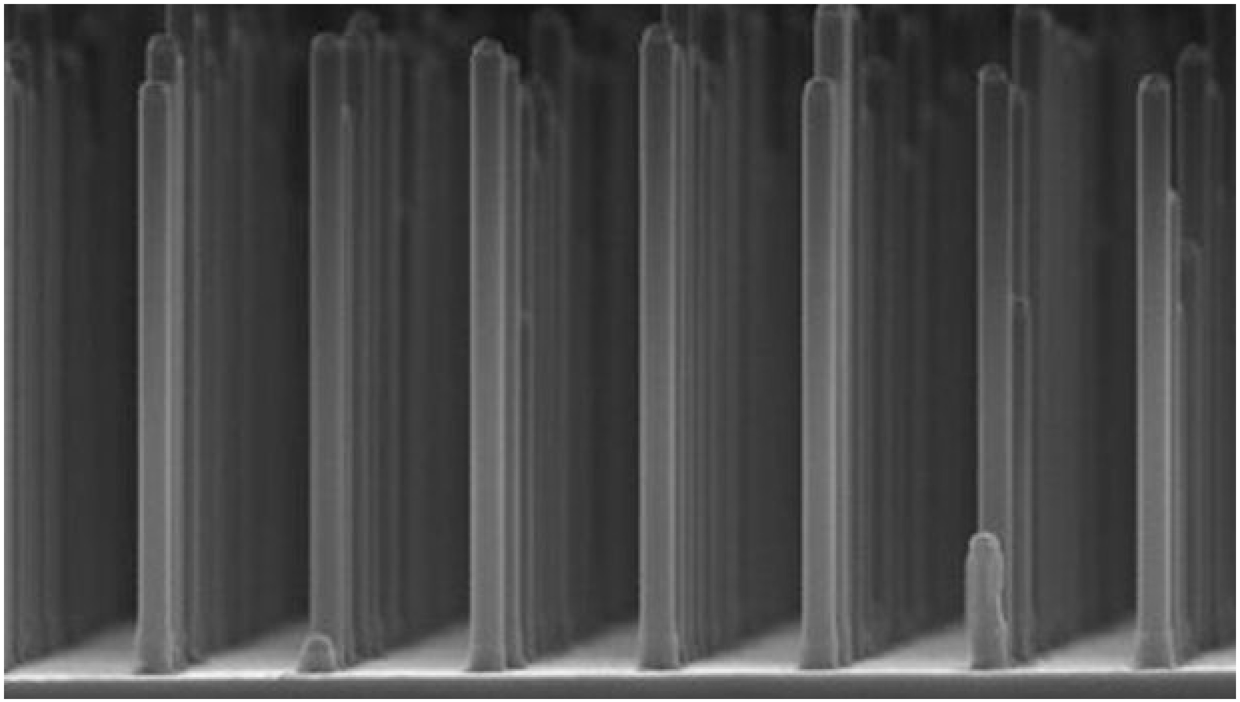






A large variety of materials: II-VI, III-V and IV-IV

GaP nanowires



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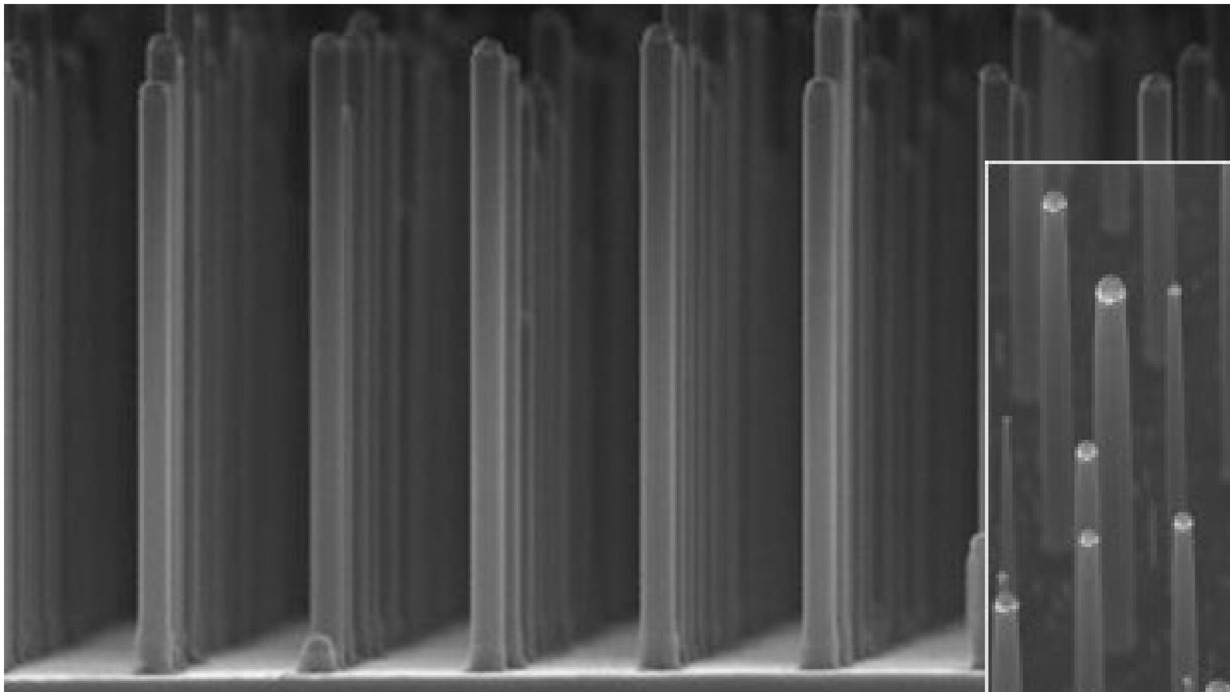
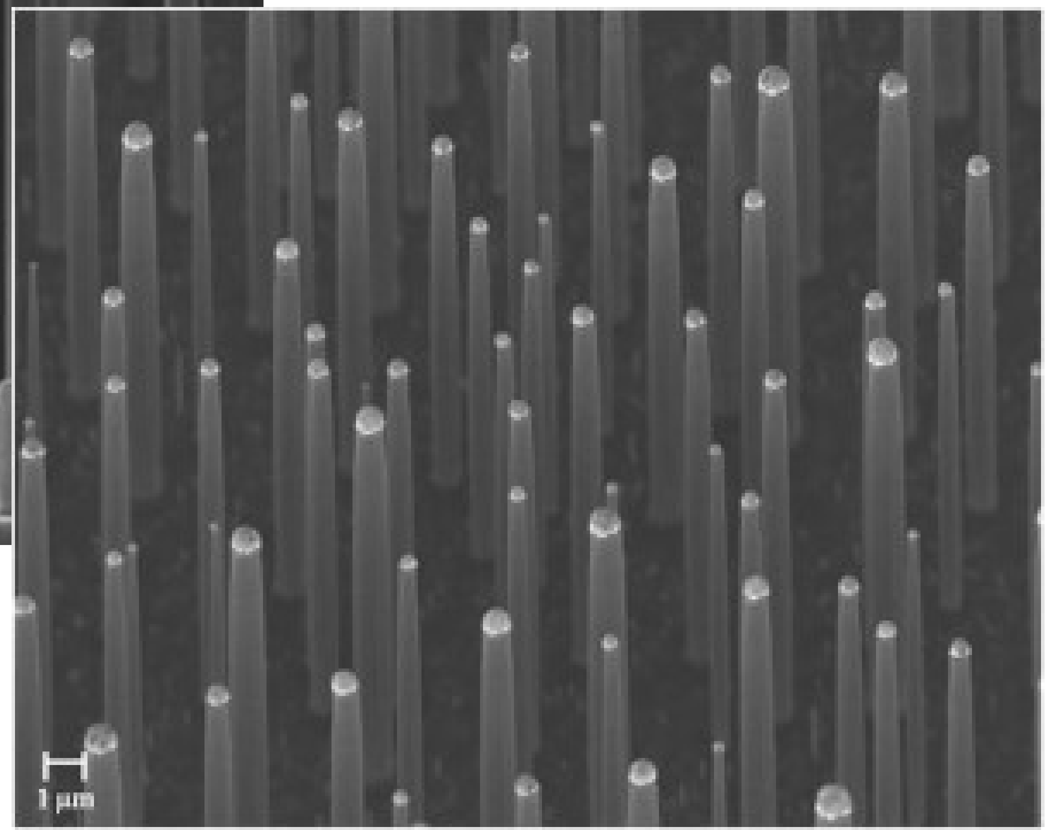
GaP nanowires

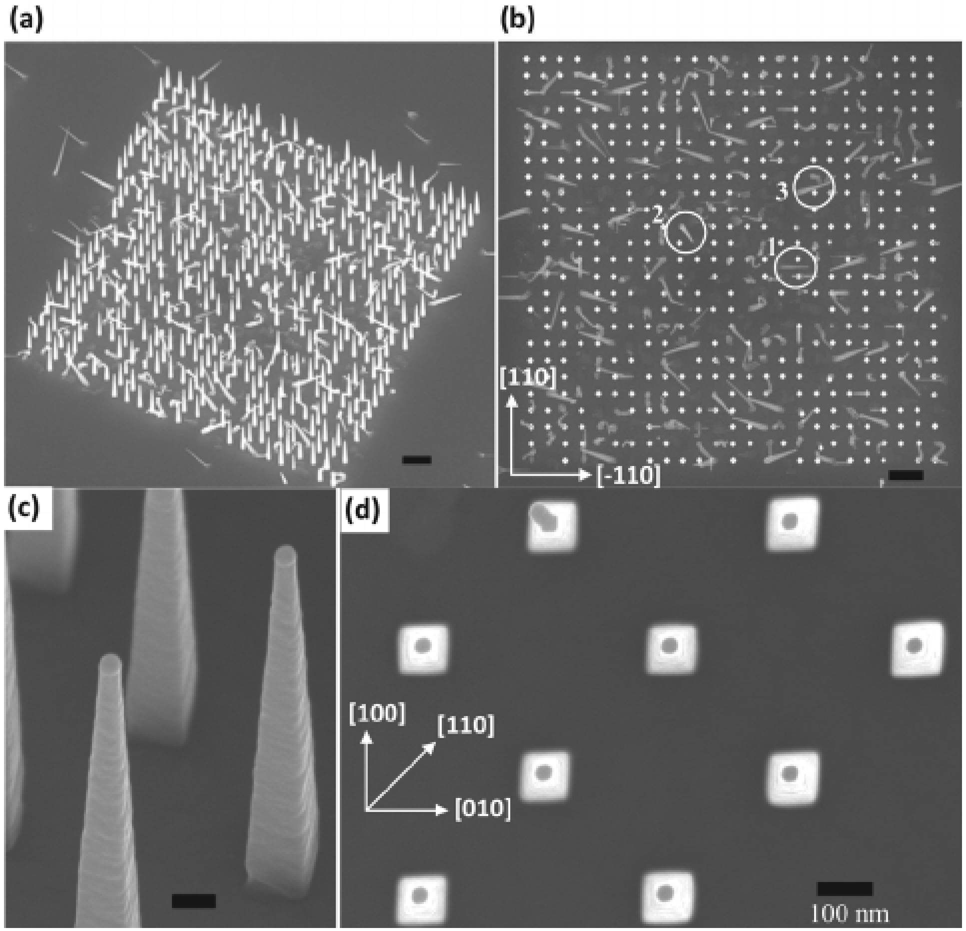


Si nanowires



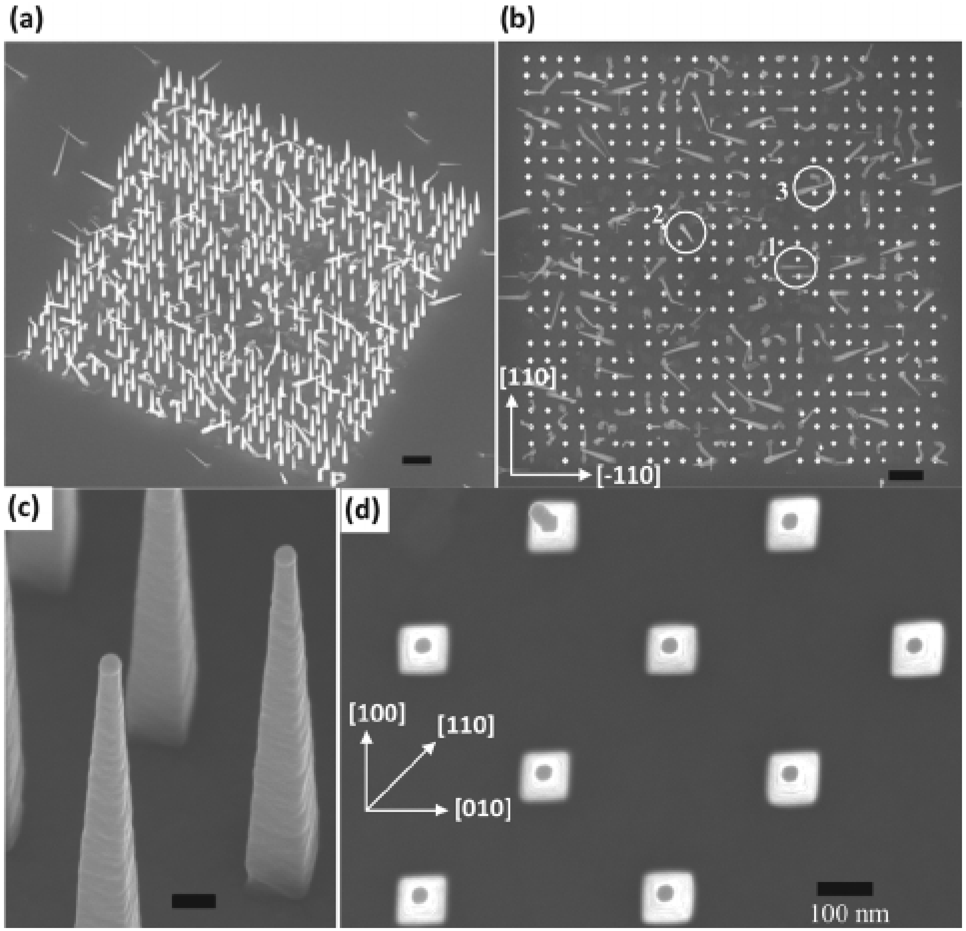
Other substrates

InP (001)

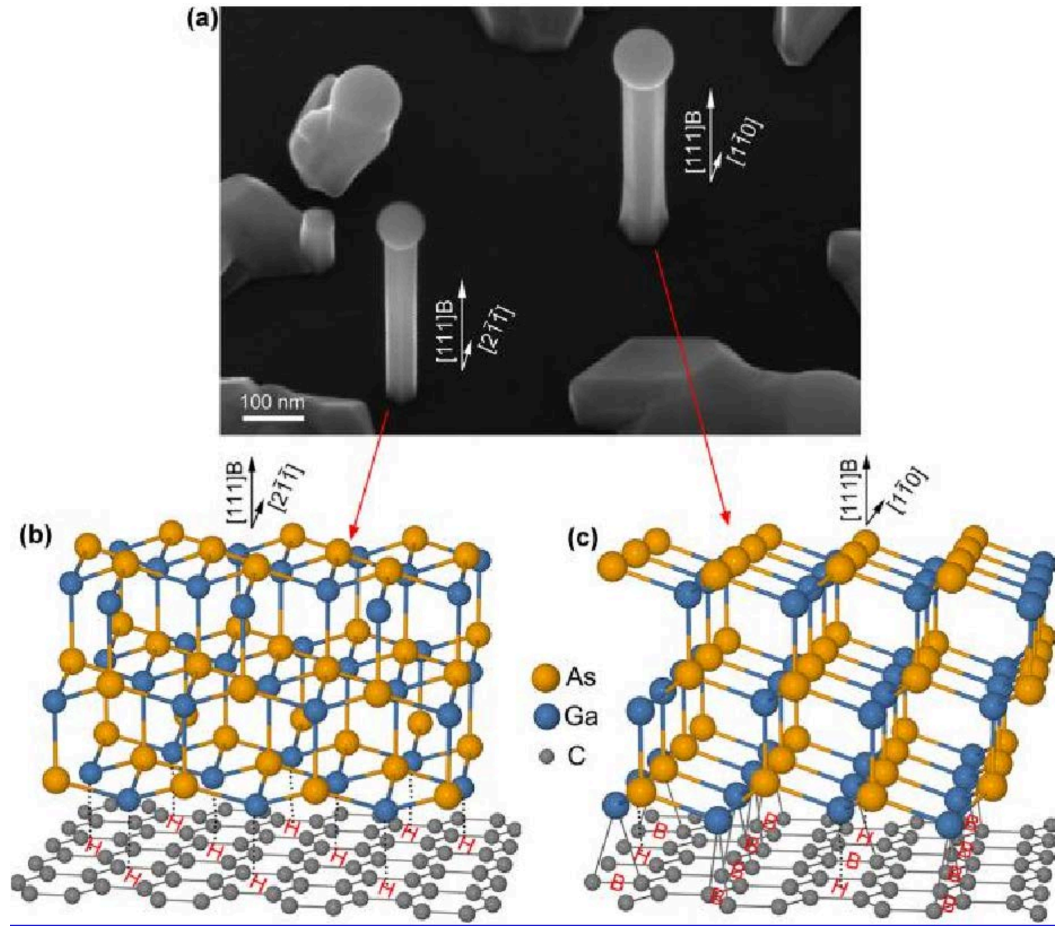


Other substrates

InP (001)



GaAs on graphene



The silicon integration

Requirements for the Silicon integration

- Substrates: Si(001) vs Si(110) vs Si(111)
- Vertical or Horizontal nanowires (surface preparation)
- No “parasitic” growth (patterns)
- No Cu or Au catalyst (create mid-gap levels)
- Thermal budget < 450°C

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MOVPE:

- Better homogeneity
- Large scale

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MOVPE:

- Better homogeneity
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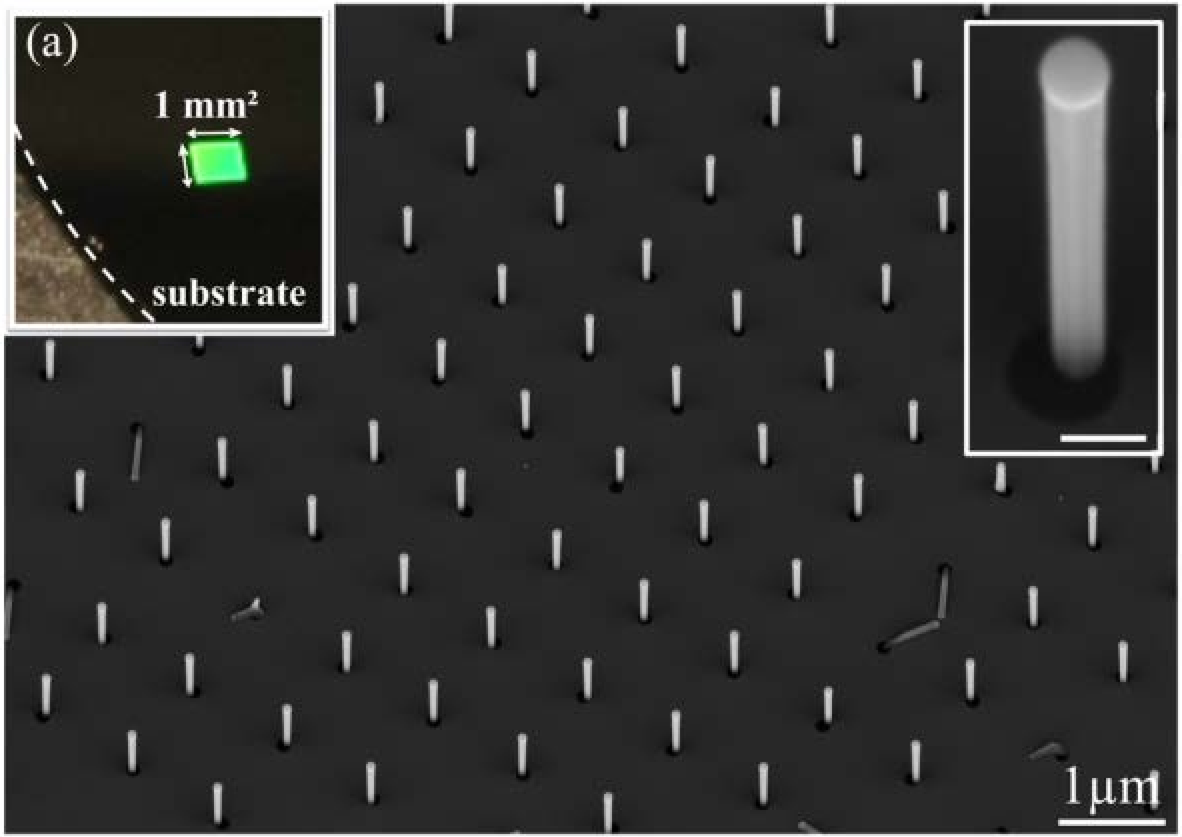
MBE:

- Smaller diameters
- Better interfaces

Ga-based materials (GaP, GaAs, GaSb) by MBE



GaAs(Sb) nanowires on Si(111)

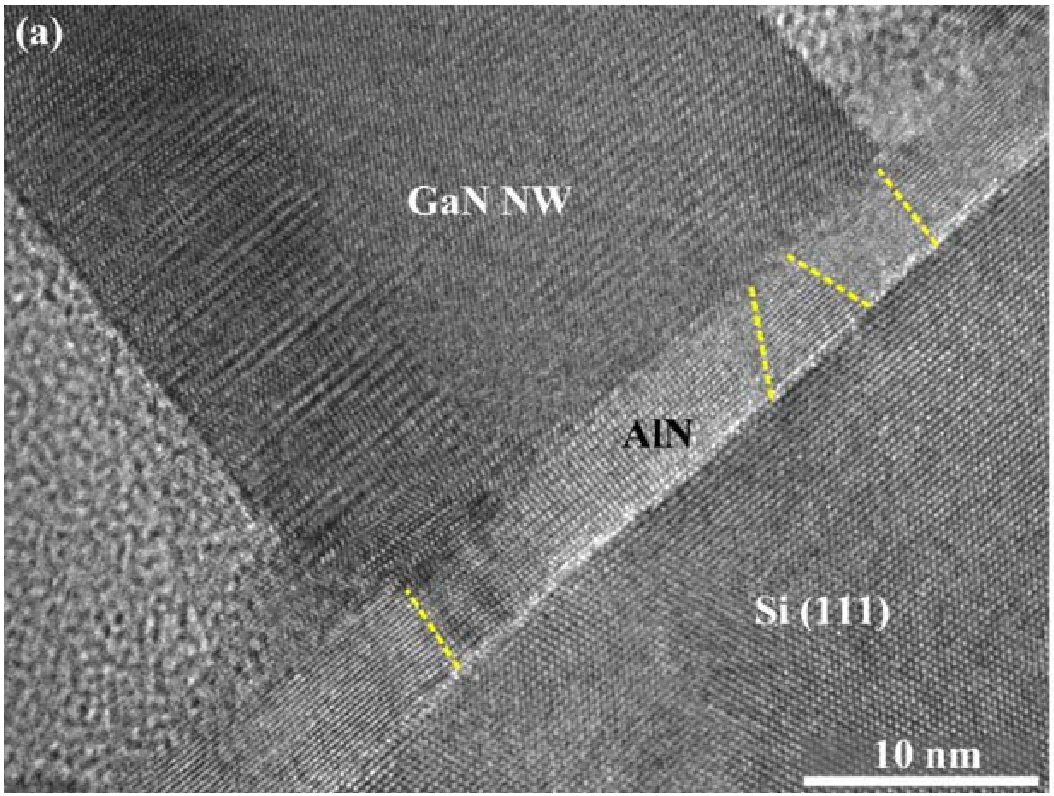
Standard HF de-oxidation

The Ga droplet can "clean" the substrate (easy to remove the Ga_2O_3)

The oxide help to increase the dewetting of the Ga droplets

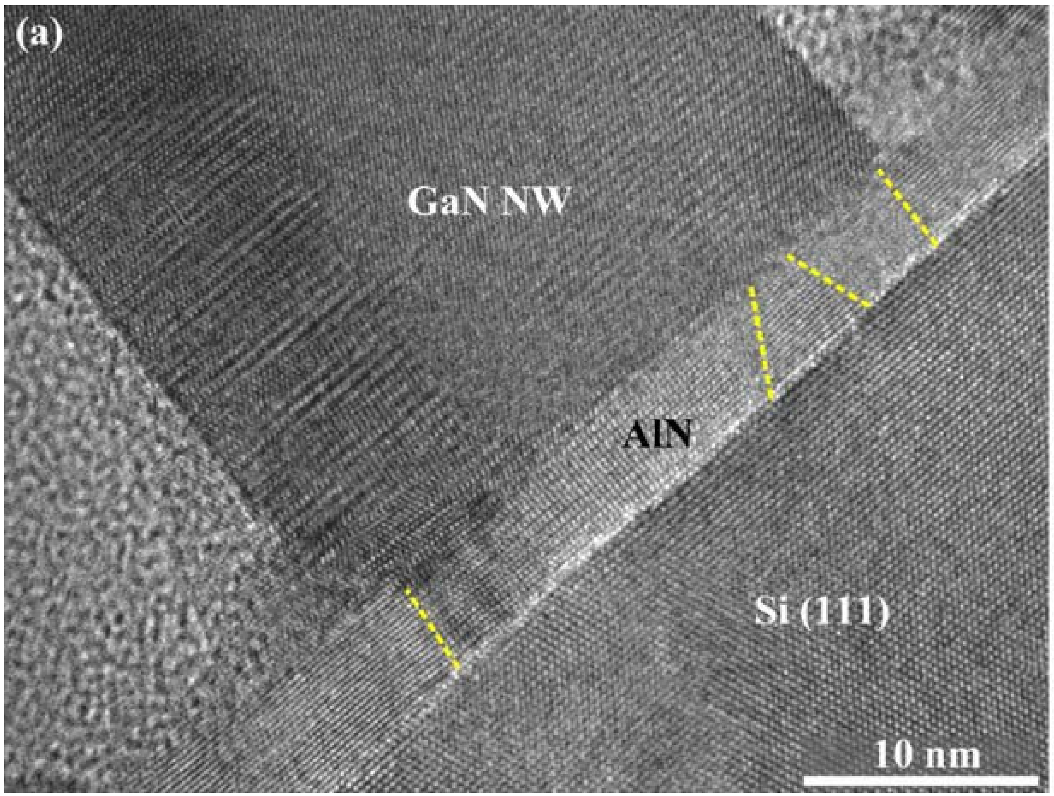
A particular case GaN nanowires

GaN nanowires

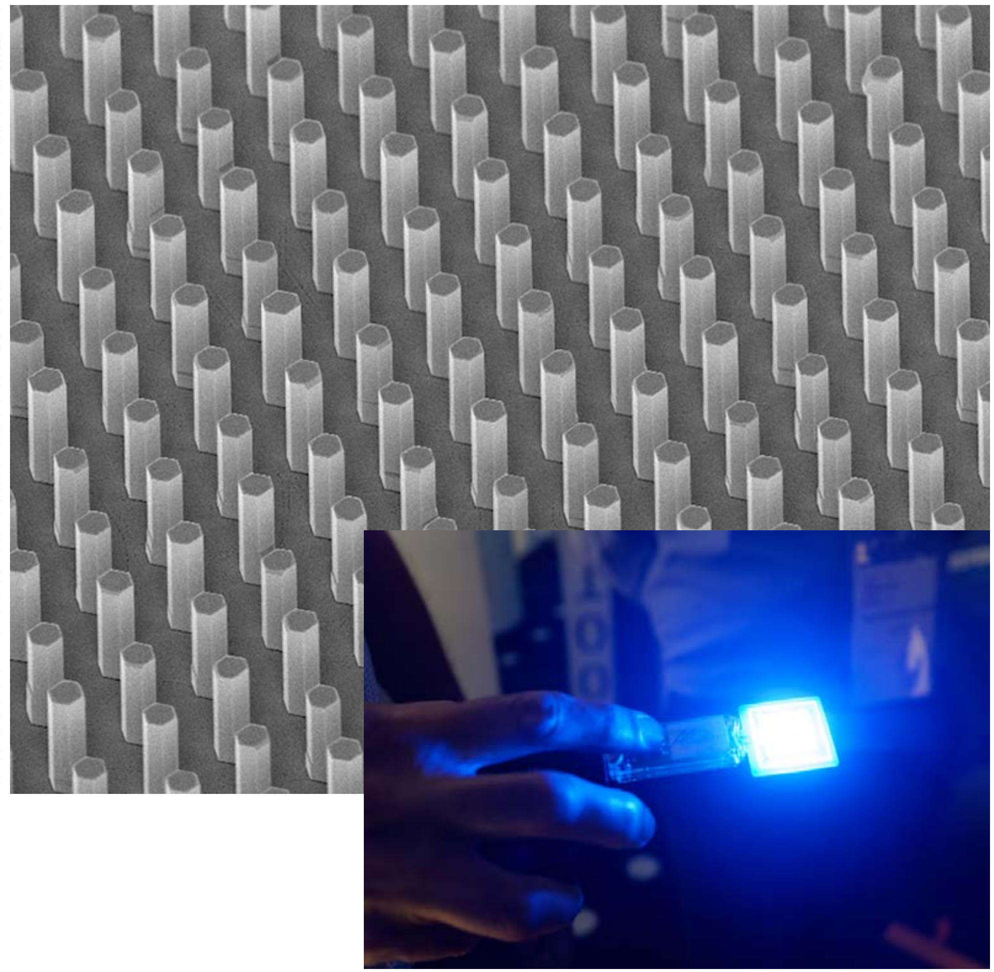


A particular case GaN nanowires

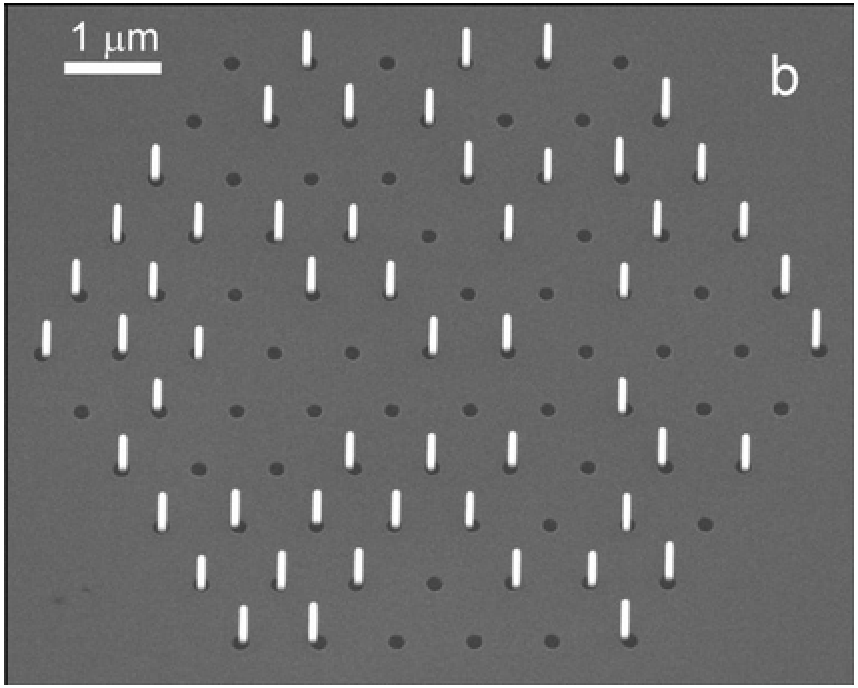
GaN nanowires



Aledia



In-based materials (InP, InAs, InSb) by MBE

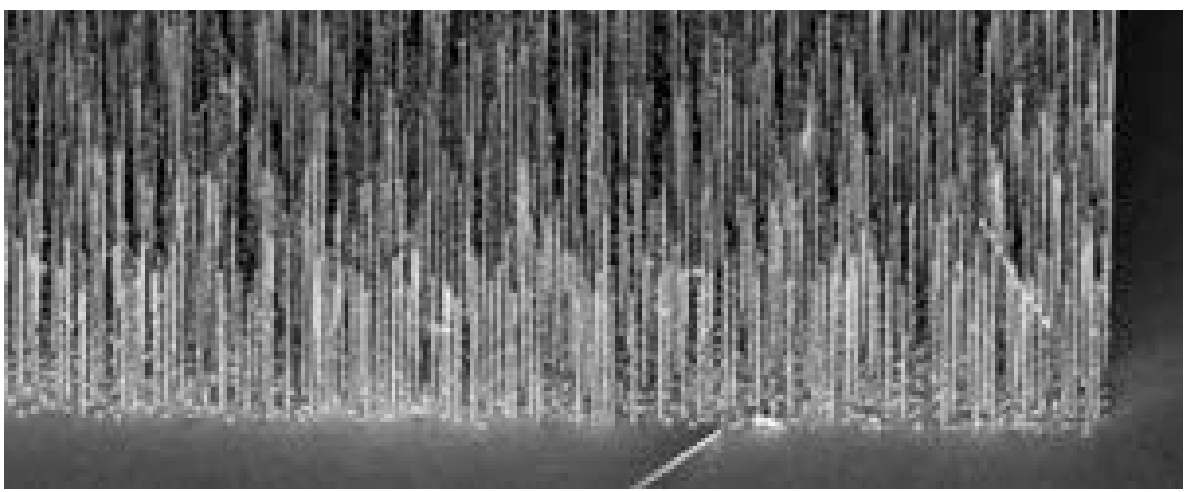


InAs nanowires on Si(111) by MBE

Standard HF de-oxidation

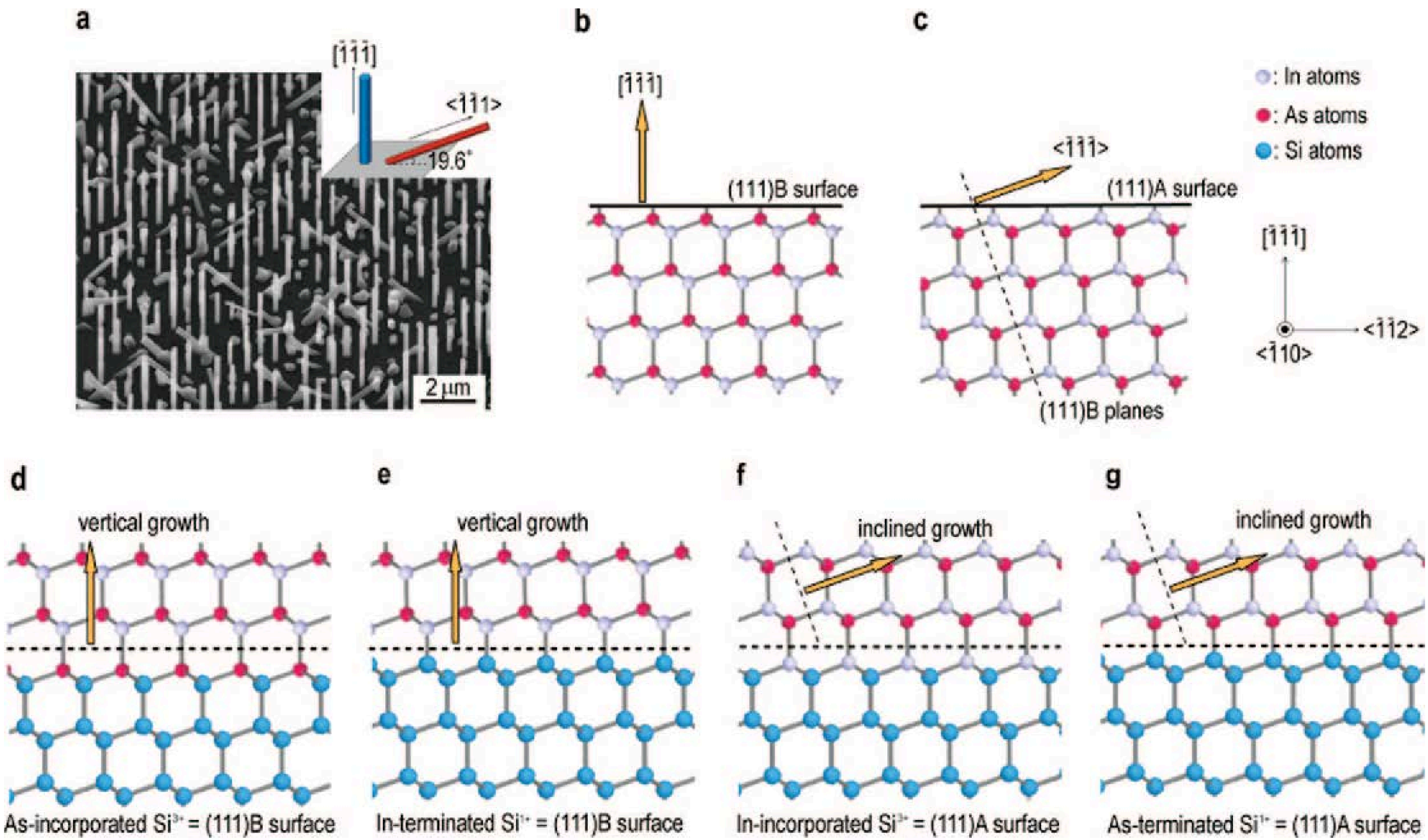
The growth can be either VS or VLS

If VLS then often missing wires
If VS then T_0 is not well defined

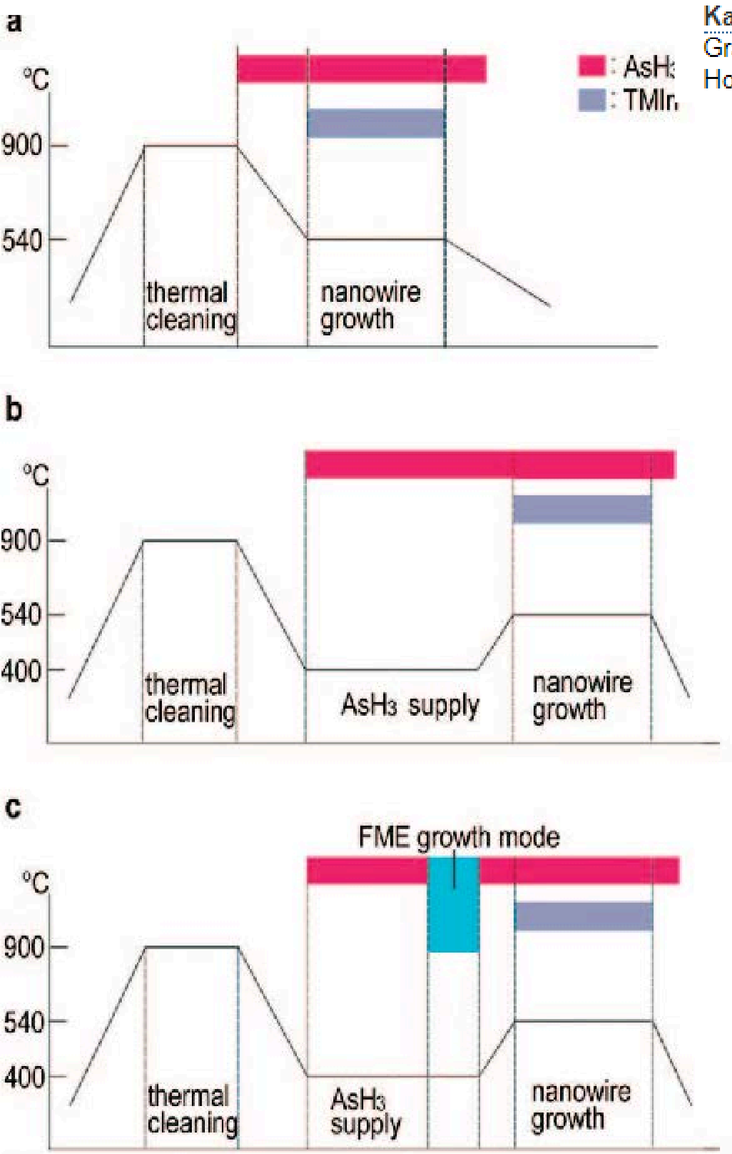


In addition:
- In do not "clean" the substrate
- Difficult to remove the In_2O_3

Creating a B-type Si(111) surface



State of the art of InAs integration on Si(111) by MOVPE



Control of InAs Nanowire Growth Directions on Si

Katsuhiro Tomioka*‡, Junichi Motohisa‡, Shinjiroh Hara† and Takashi Fukui‡†
Graduate School of Information Science and Technology, Research Center for Integrated Quantum Electronics (RCIQE), Hokkaido University, North14 West9, 060-0814, Sapporo, Japan

Nano Lett., **2008**, *8* (10), pp 3475–3480
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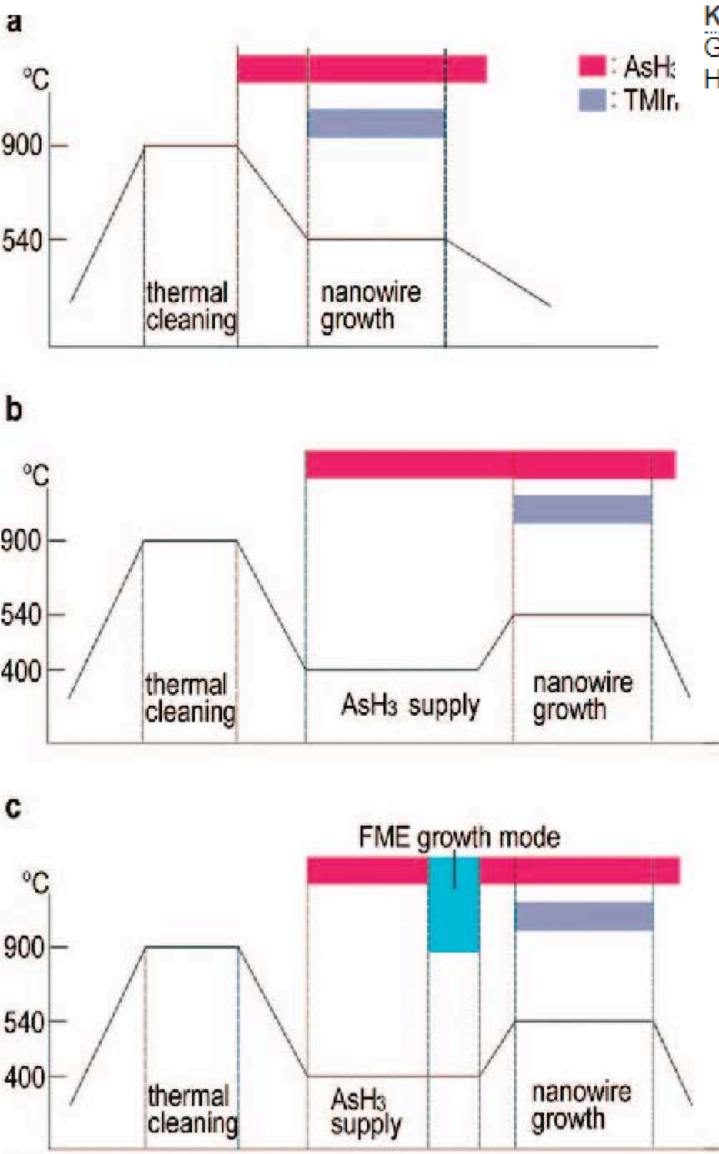

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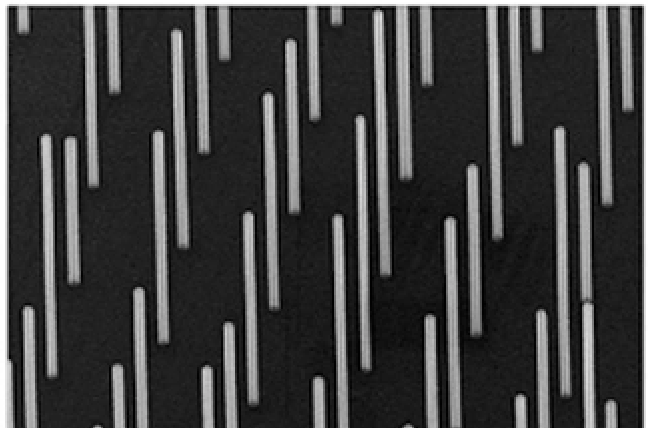

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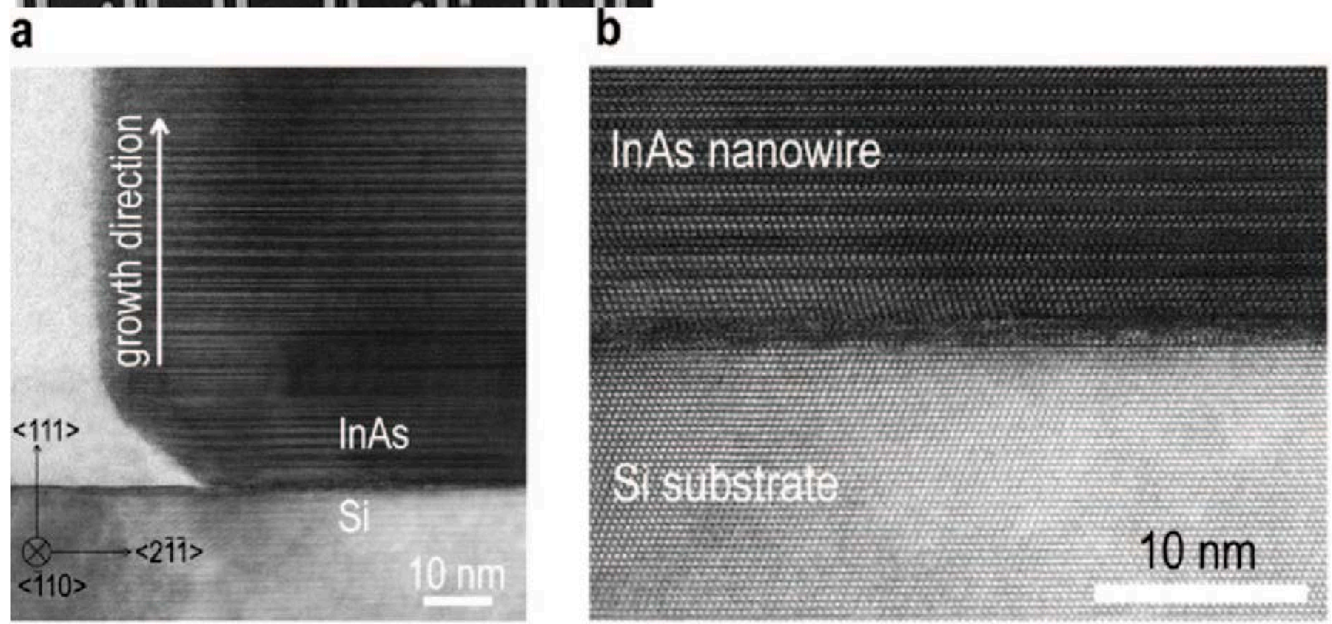

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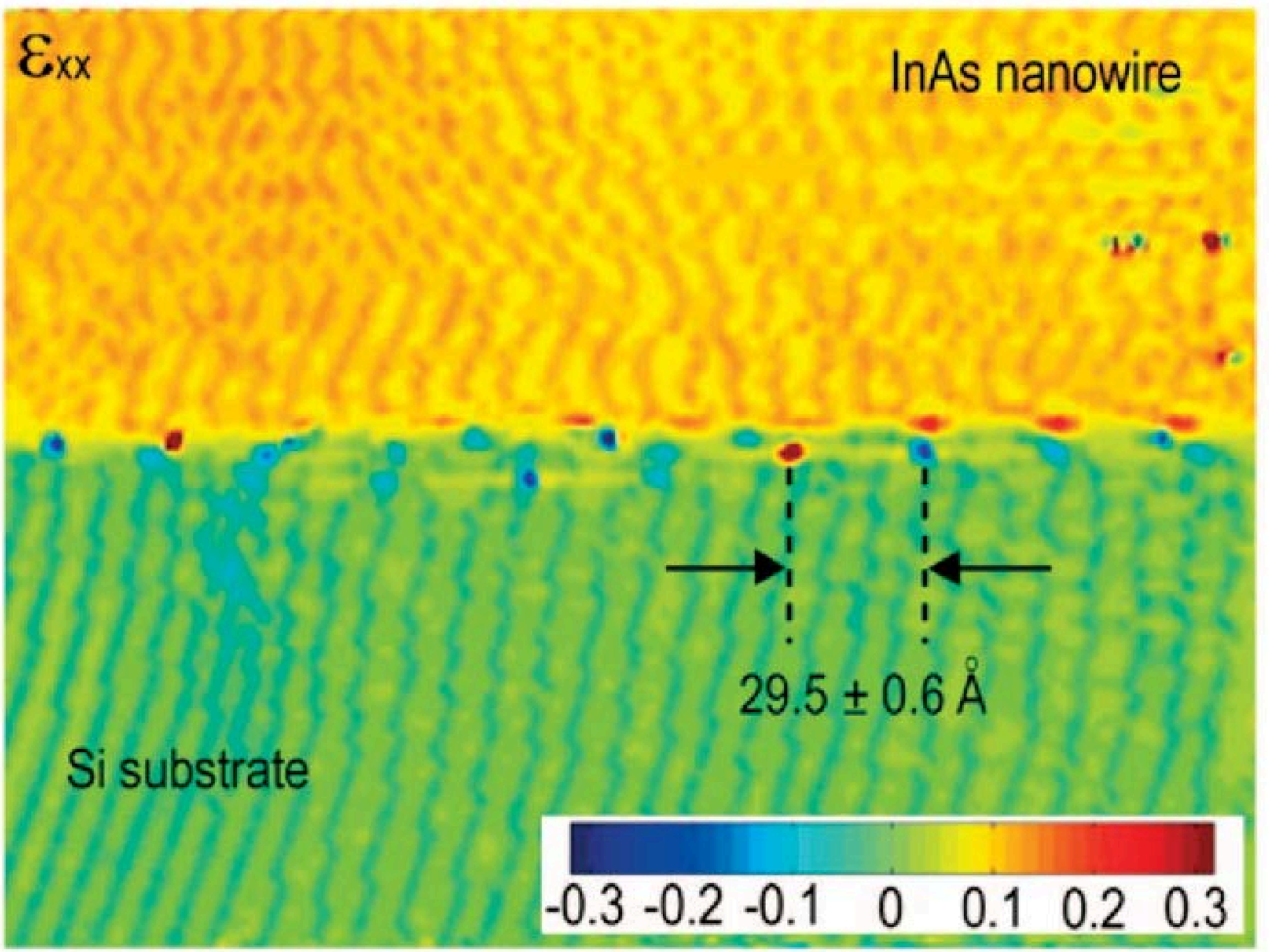

The dislocation are locked at the interface

The InAs nanowires can be defect-free and fully relaxed

… but not achieved at this yield for MBE

An example of CMOS compatible InAs growth

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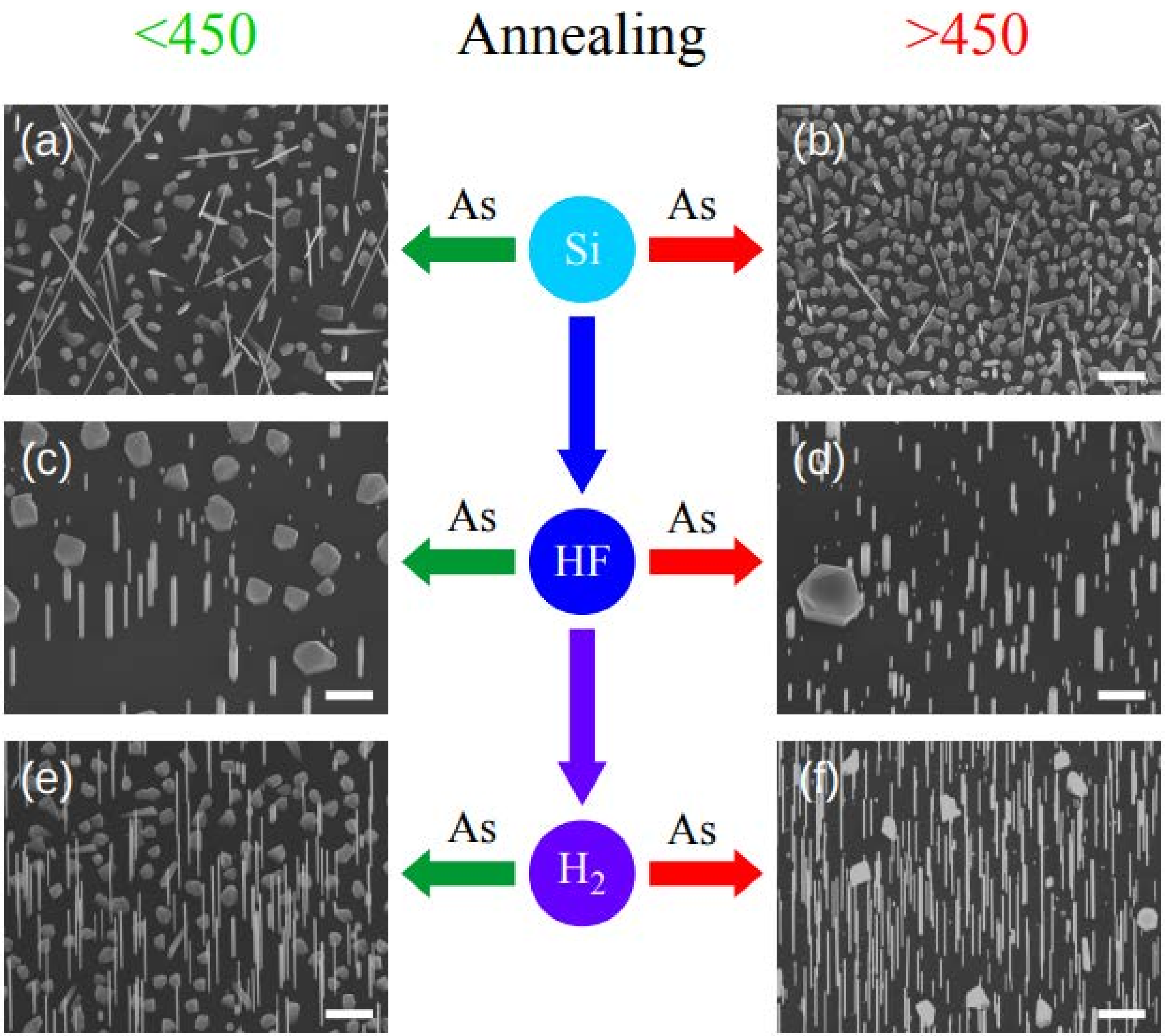

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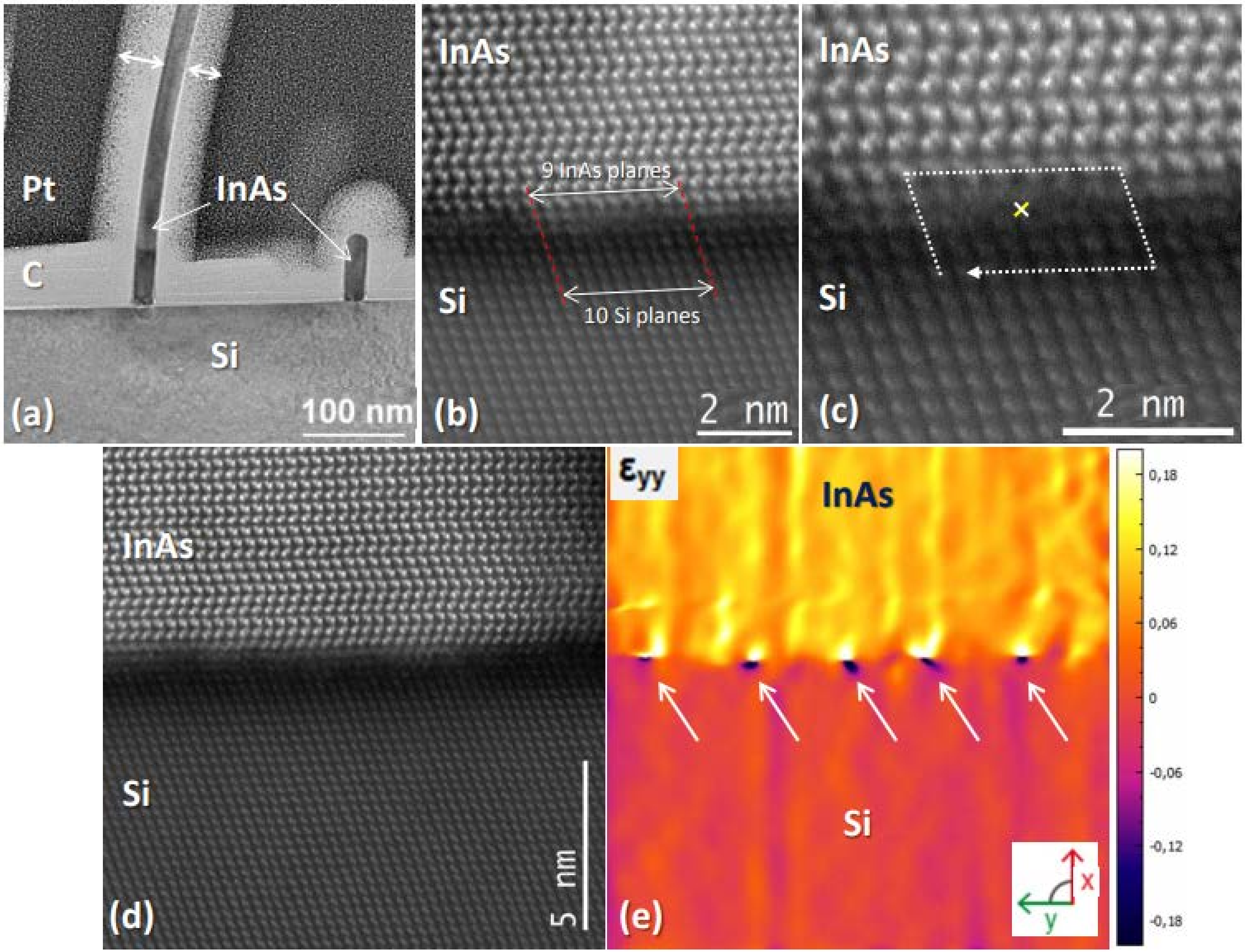

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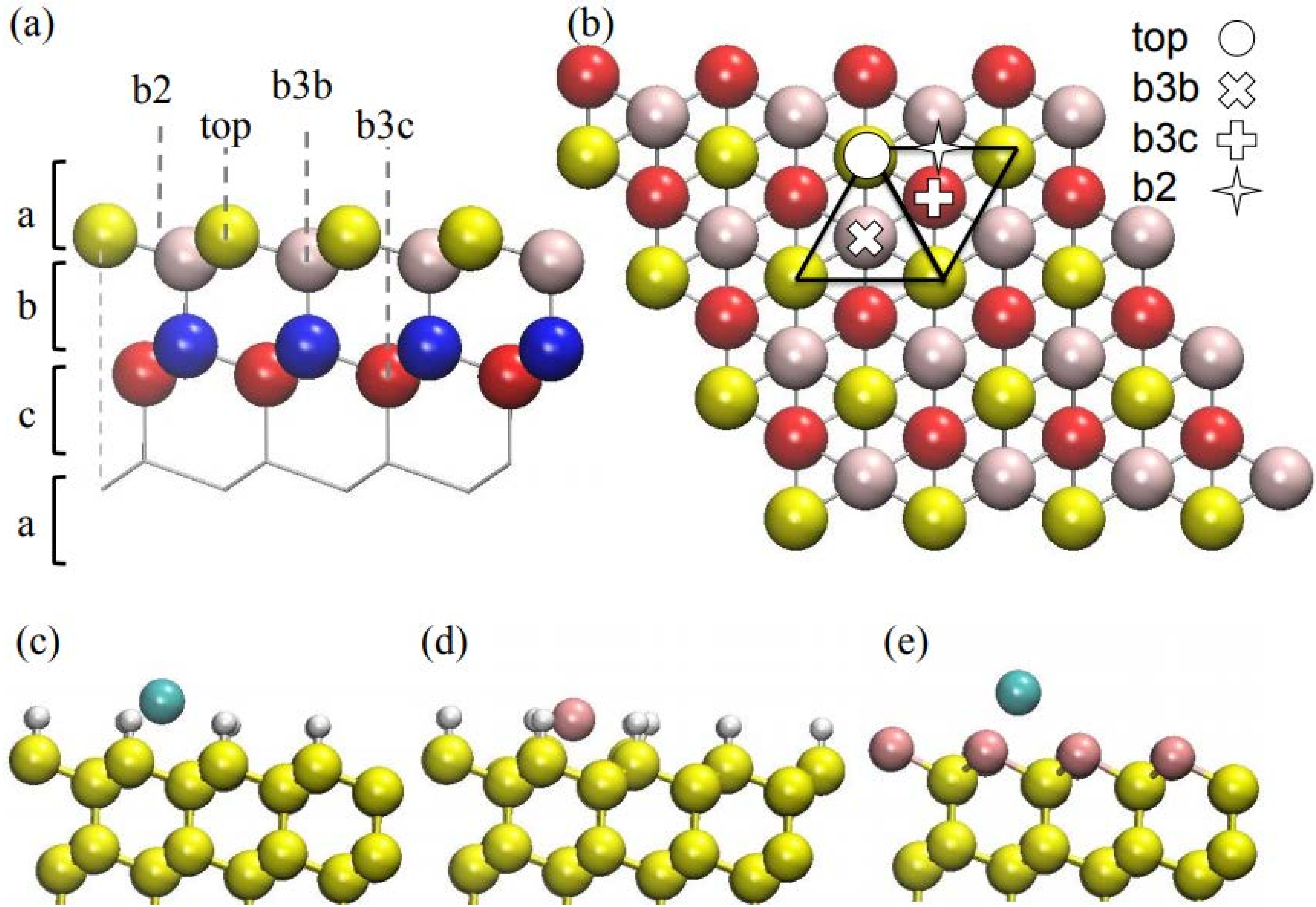

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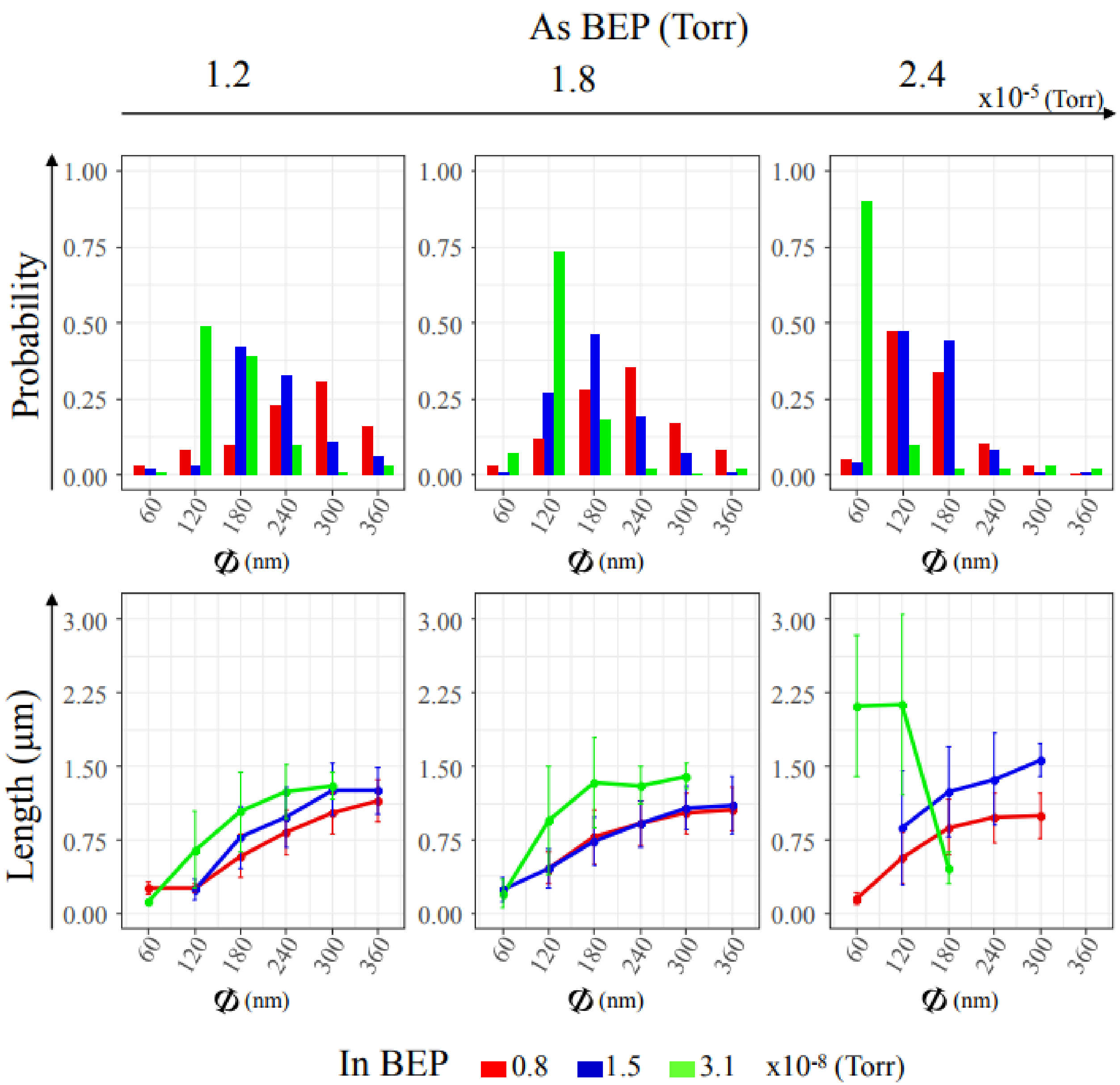

The saturation of the surface with H atoms allows to switch from VS to VLS due to an improved diffusion length on the surface

Merci pour votre attention