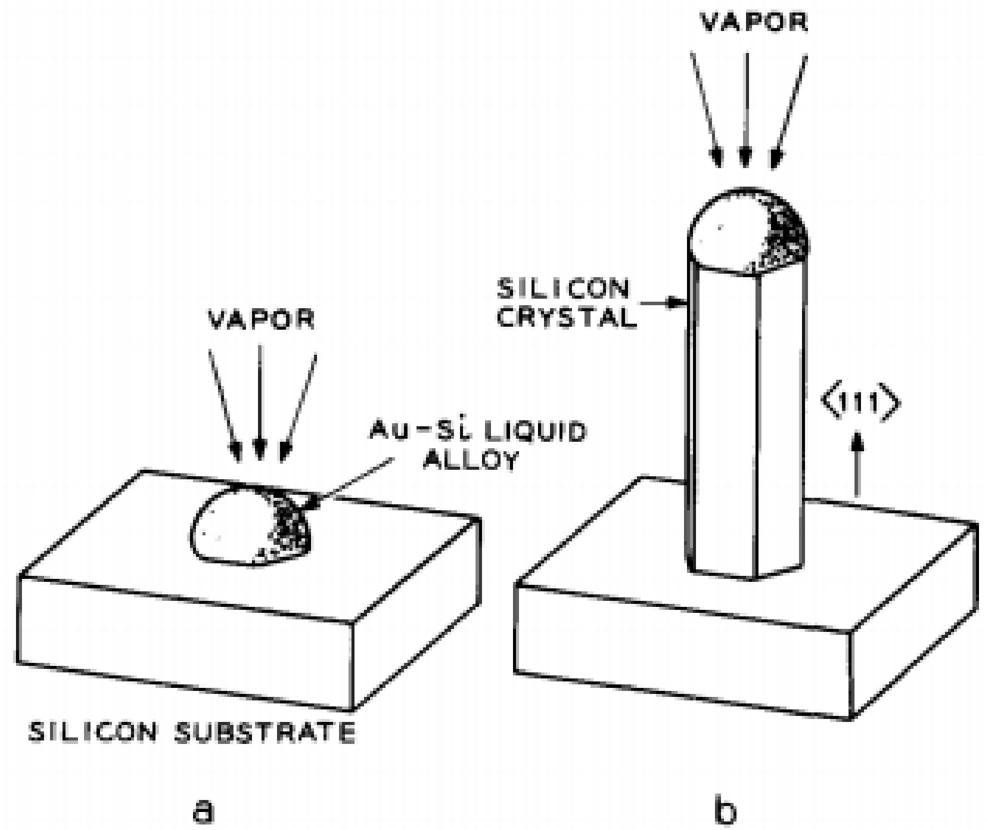
Growth of nanostructures (mostly nanowires)

EPFL

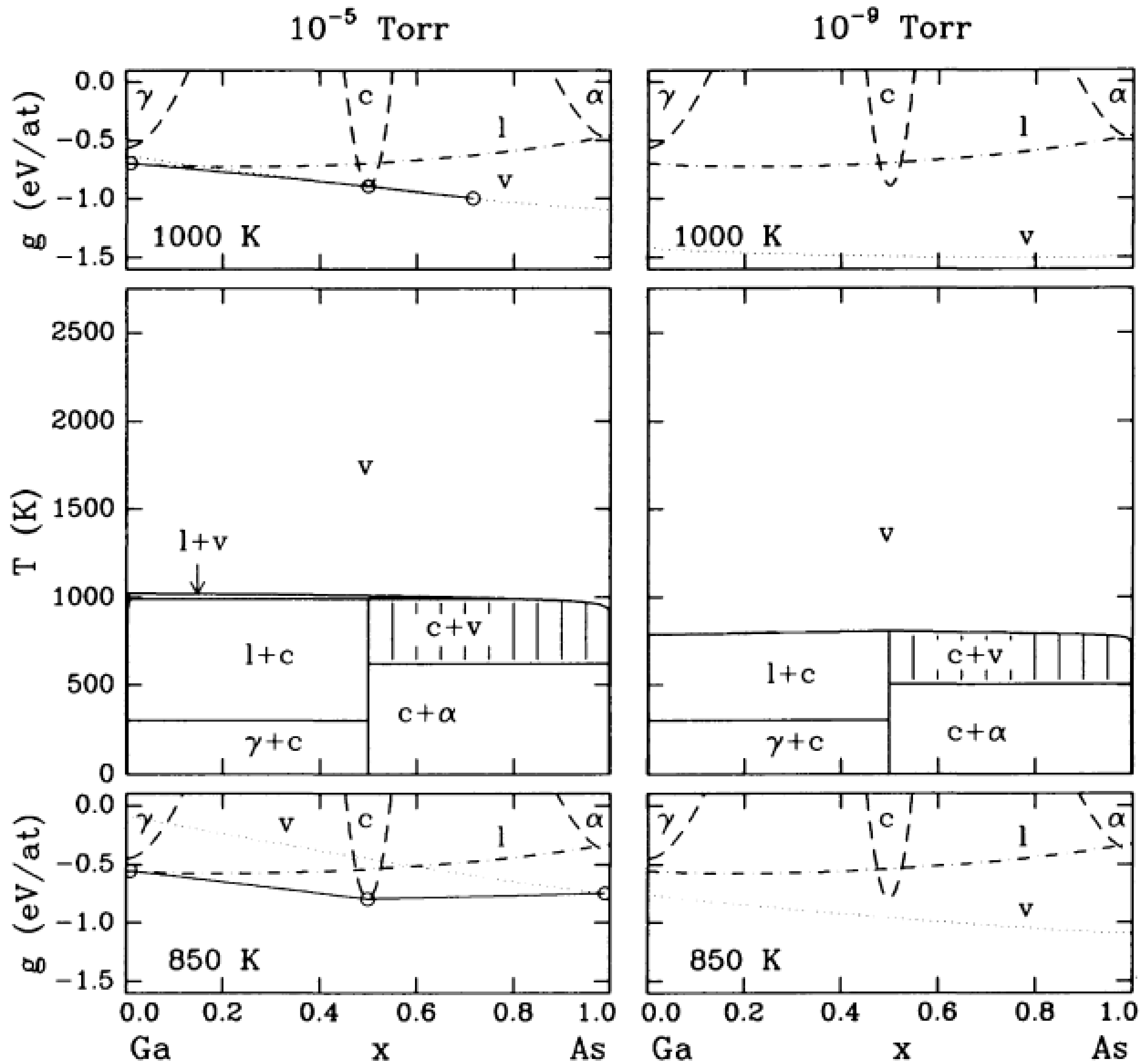
LABORATOIRE DES MATERIAUX SEMICONDUCTEURS

Vapor-Liquid-Solid method (VLS)

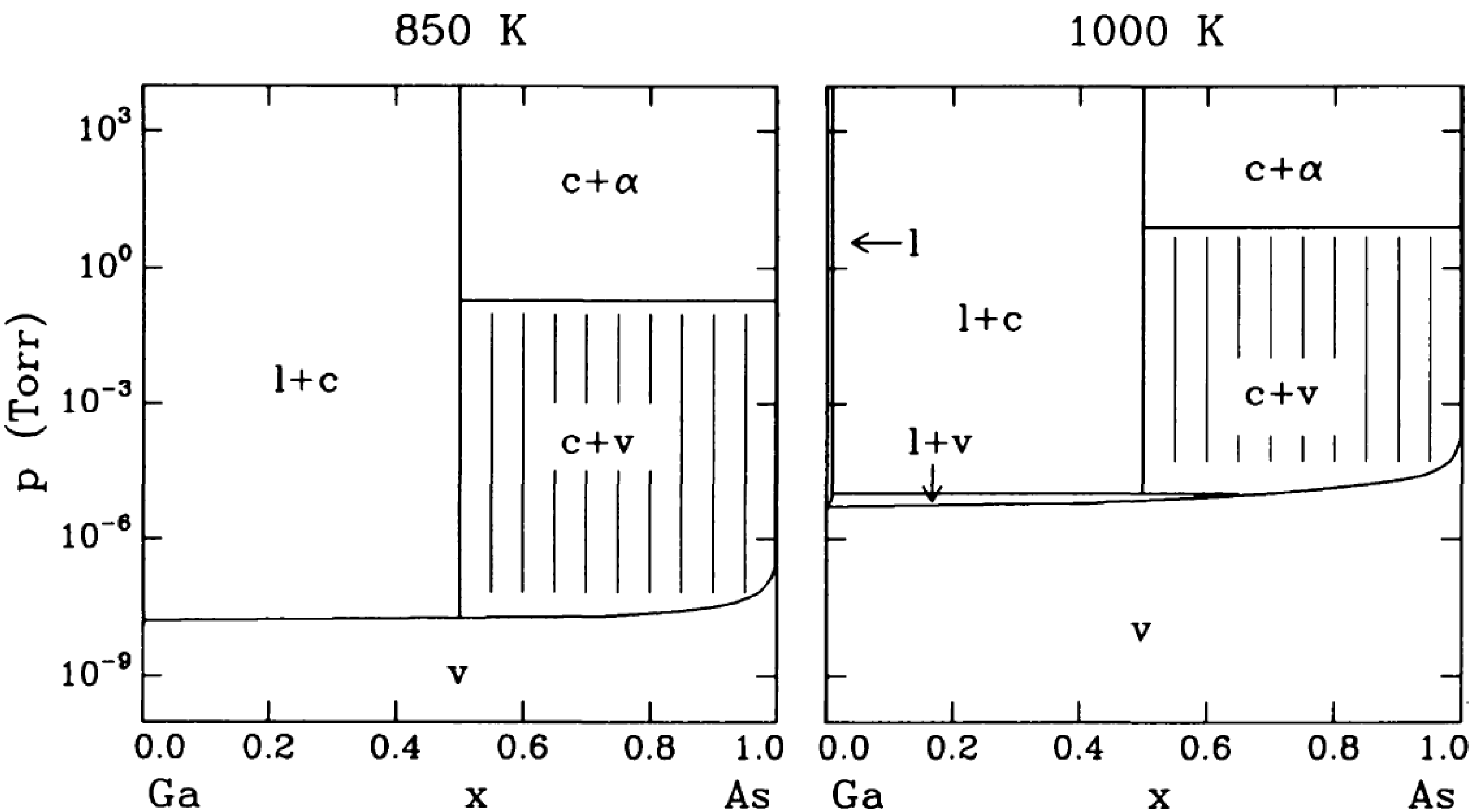


Wagner & Ellis, Appl. Phys. Lett. (1964)

GaAs

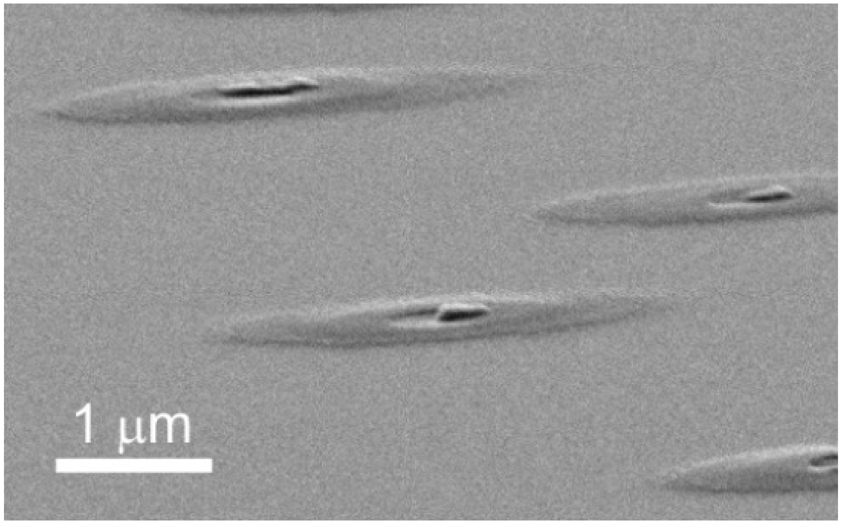

10⁻⁵ Torr
10⁻⁹ Torr
g (eV/at)
T (K)
1000 K
850 K
γ
c
α
l
v
l+v
l+c
c+v
γ+c
c+α
0.0
−0.5
−1.0
−1.5
2500
2000
1500
1000
500
0
0.2
0.4
0.6
0.8
1.0
Ga
x
As

GaAs



850 K
1000 K
p (Torr)
10^3
10^0
10^{-3}
10^{-6}
10^{-9}
c+α
l+c
c+v
v
←l
l+v
0.0
0.2
0.4
0.6
0.8
1.0
Ga
x
As

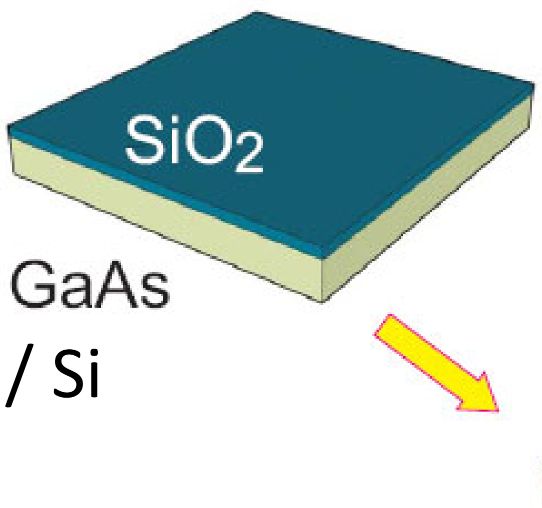
Using GaAs substrate?



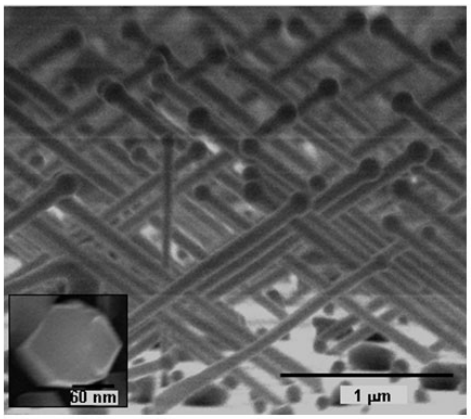
Need to use a surface that gallium does not wet!

What then?

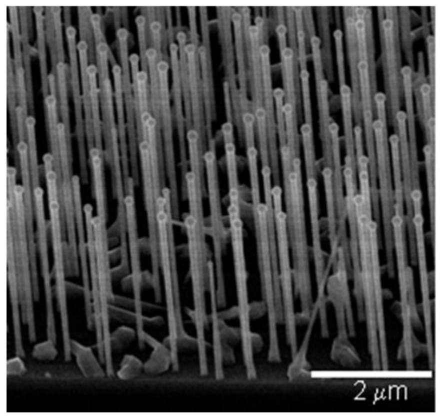
1. Use a substrate that does not wet
2. Coat the substrate with a layer that does not wet



What then?



(001) GaAs substrate

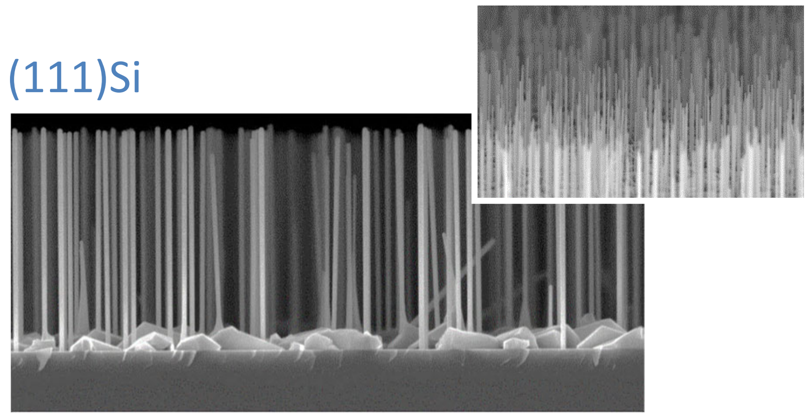


(111) GaAs substrate

Physical Review B 77, 155326 (2008);

Appl. Phys. Lett. 92, 063112 (2008)

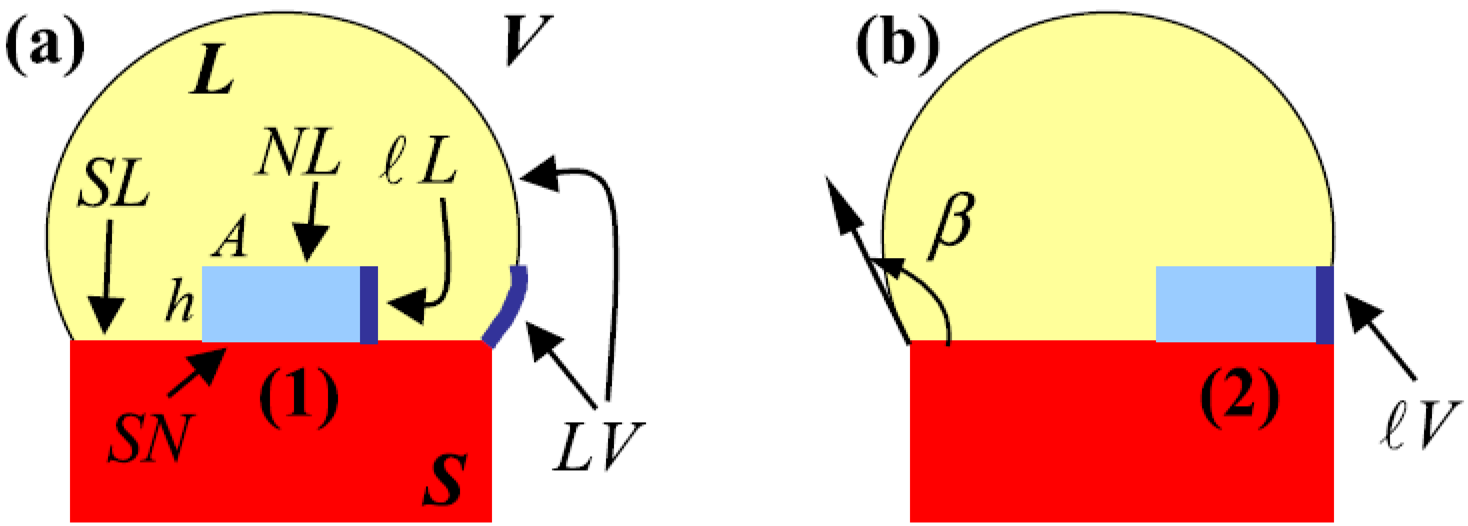
(111)Si



Nanoscale 4 1486 (2012)

Nano Lett. 11, 3827 (2011)

Does it work?

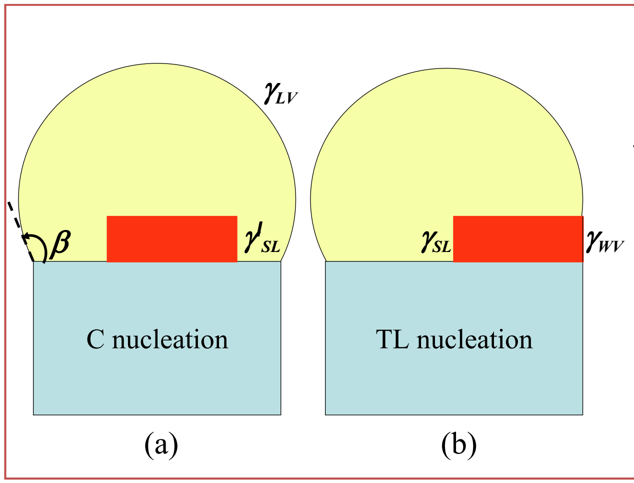


F. Glas et al PRL 99, 146101 (2007)

Role of nucleation in polytypism of III-V nanowires

F.Glas *et al*., Phys. Rev. Lett. 2007, Dubrovskii *et a*l., PRB 2008, Johansson *et al*, Cryst. Growth & design 2009, Dubrovskii *et al*. Nano Letters 2011, Dubrovskii APL 2014 …

- **At low surface energy of WS NW sidewalls, WZ phase can form only via TPL nucleation**
- **In a mononuclear mode, the structure is dictated by the island orientation**

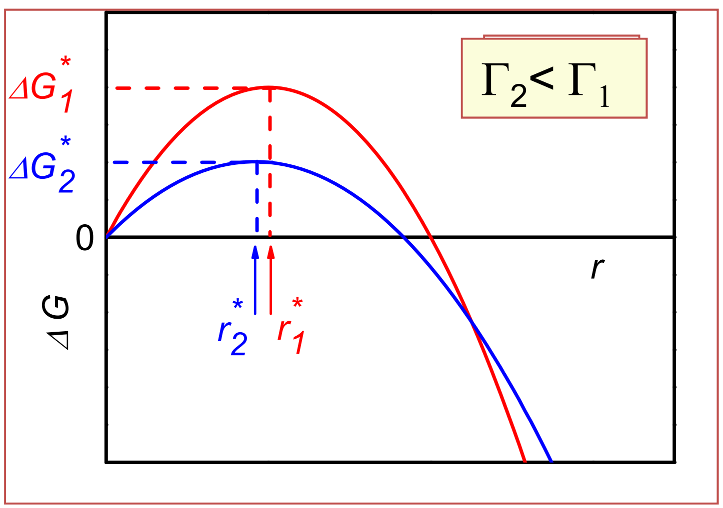


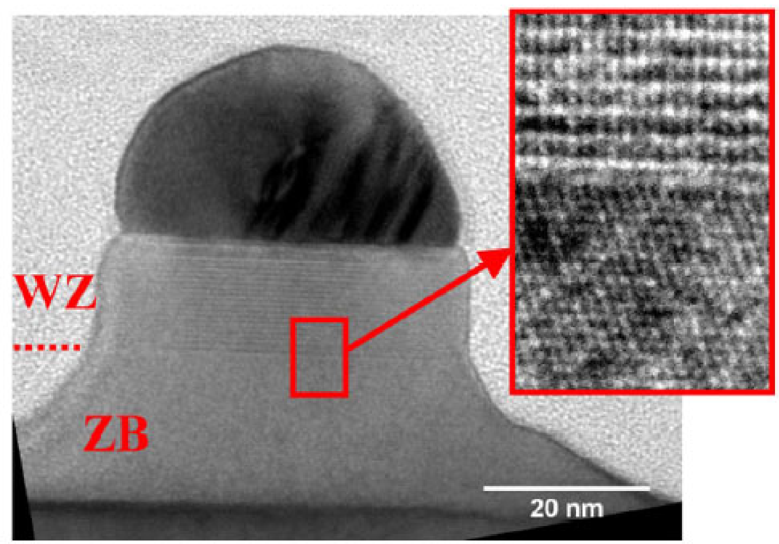
❖ Condition for TL nucleation:

$$\gamma_{WV} - \gamma_{LV} \sin\beta < \gamma^{l}_{SL}$$

❖ High supersaturation to create a stacking fault

$$\Delta\mu > \Delta\mu_c = \frac{\psi_{WZ}}{1-(\Gamma_{WZ}/\Gamma_{ZB})^2}$$





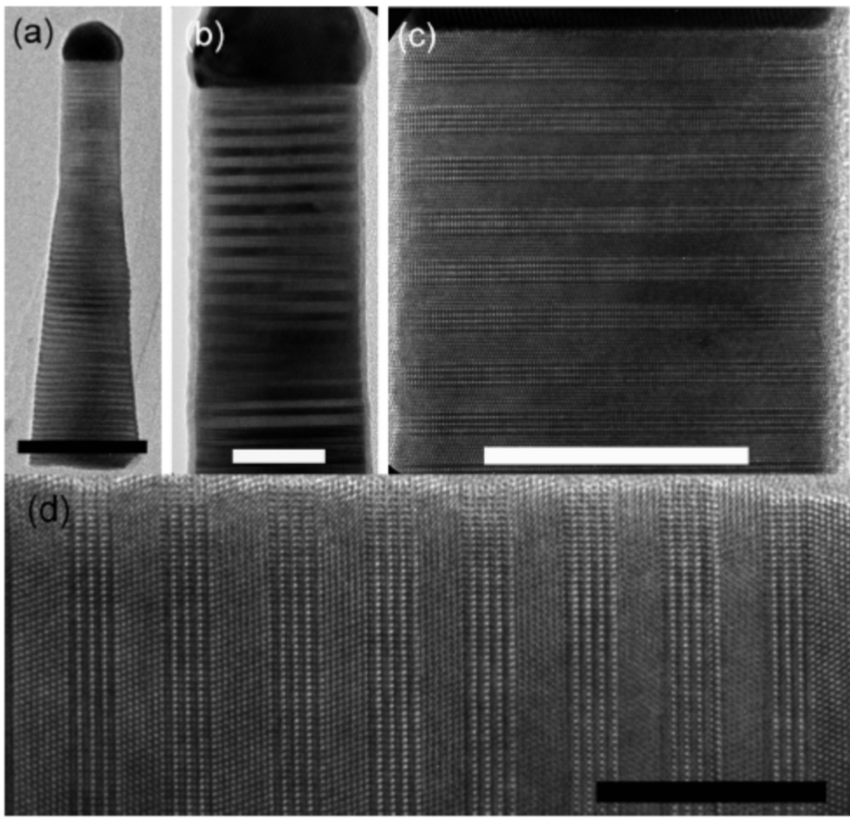
Controlled crystal phase heterostructures

NANO LETTERS
pubs.acs.org/NanoLett

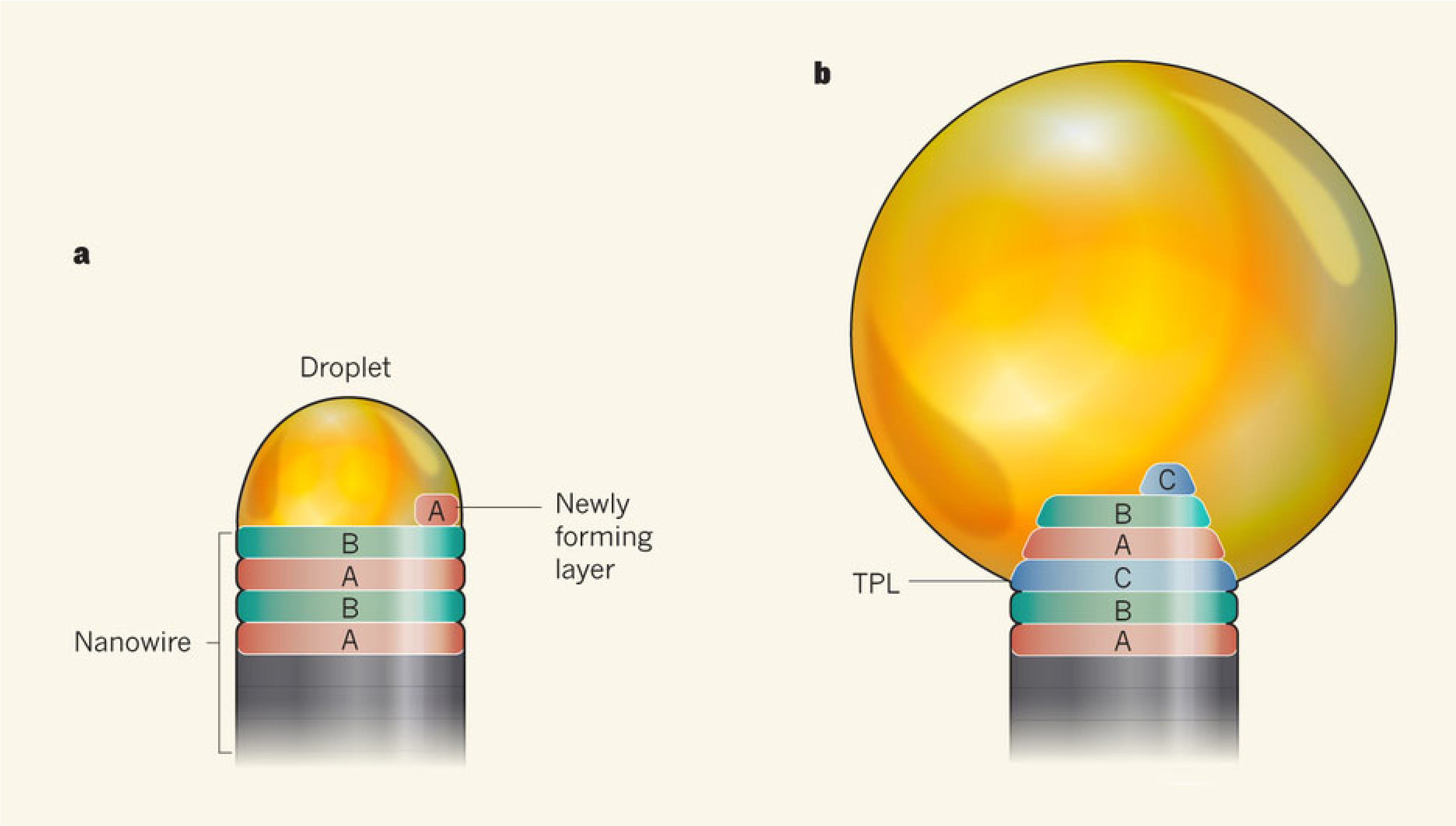
Crystal Phase Engineering in Single InAs Nanowires

Kimberly A. Dick,*[†,‡] Claes Thelander,[†] Lars Samuelson,[†] and Philippe Caroff*[§]

[†]Solid State Physics, Lund University, Box 118, S-221 00 Lund, Sweden, [‡]Polymer & Materials Chemistry, Lund University, Box 124, S-221 00 Lund, Sweden, and [§]Institut d'Electronique, de Microélectronique et de Nanotechnologie, UMR CNRS 8520, Avenue Poincaré, B.P. 60069, 59652 Villeneuve d'Ascq, France



TEM images of InAs nanowire superlattices, defined by 60 periods of alternating ZB and WZ structure Nanowires are grown at 380 °C with WZ segments being formed during growth interrupts under group V flow. (a) Full-length nanowire. (b) Higher-magnification image showing the regular length of the striped segments; the scale bar is 20 nm. (c) High-resolution image, with different crystal structure visible in different regions; the scale bar is 20 nm. (d) High-resolution image with different positions of atom columns in ZB and WZ structure apparent; the scale bar is 10 nm



Materials science: How crystals get an edge

Anna Fontcuberta i Morral

Nature **531**, 308–309 (17 March 2016) | doi:10.1038/531308a

ARTICLE

doi:10.1038/nature17148

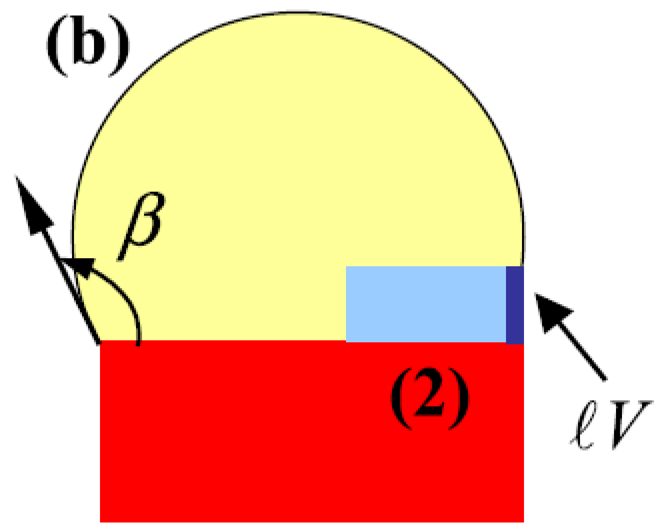
Interface dynamics and crystal phase switching in GaAs nanowires

Daniel Jacobsson[1,2], Federico Panciera[3,4], Jerry Tersoff[4], Mark C. Reuter[4], Sebastian Lehmann[1], Stephan Hofmann[3], Kimberly A. Dick[1,2] & Frances M. Ross[4]

Controlled formation of non-equilibrium crystal structures is one of the most important challenges in crystal growth. Catalytically grown nanowires are ideal systems for studying the fundamental physics of phase selection, and could lead to new electronic applications based on the engineering of crystal phases. Here we image gallium arsenide (GaAs) nanowires during growth as they switch between phases as a result of varying growth conditions. We find clear differences between the growth dynamics of the phases, including differences in interface morphology, step flow and catalyst geometry. We explain these differences, and the phase selection, using a model that relates the catalyst volume, the contact angle at the trijunction (the point at which solid, liquid and vapour meet) and the nucleation site of each new layer of GaAs. This model allows us to predict the conditions under which each phase should be observed, and use these predictions to design GaAs heterostructures. These results could apply to phase selection in other nanowire systems.

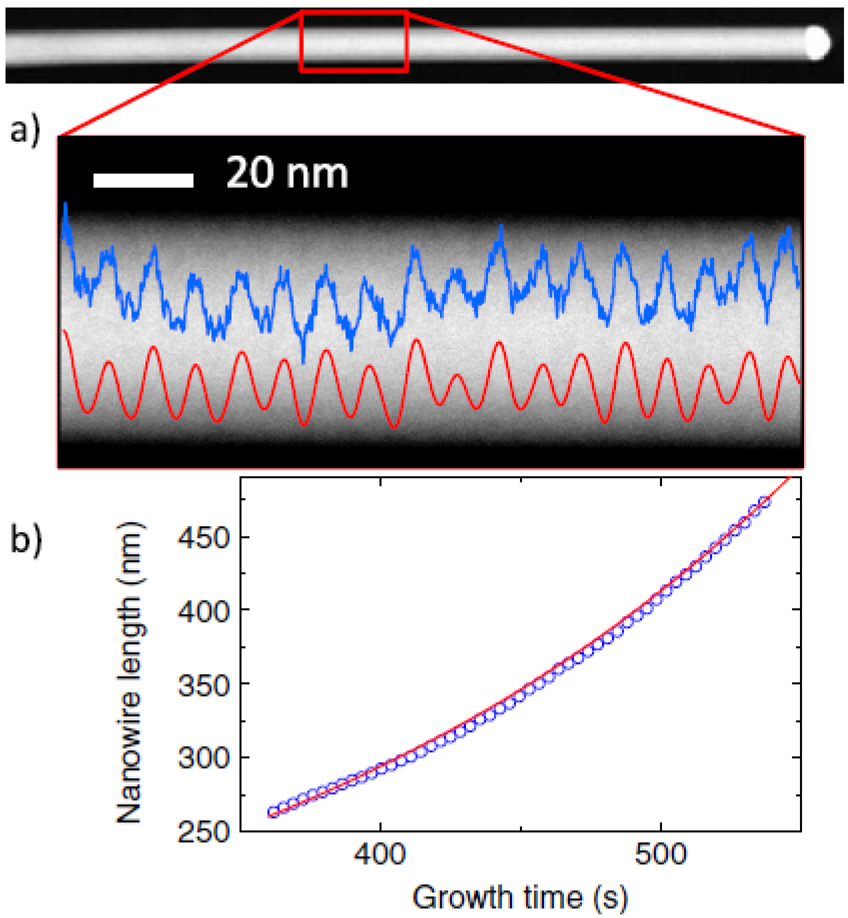
(movies)

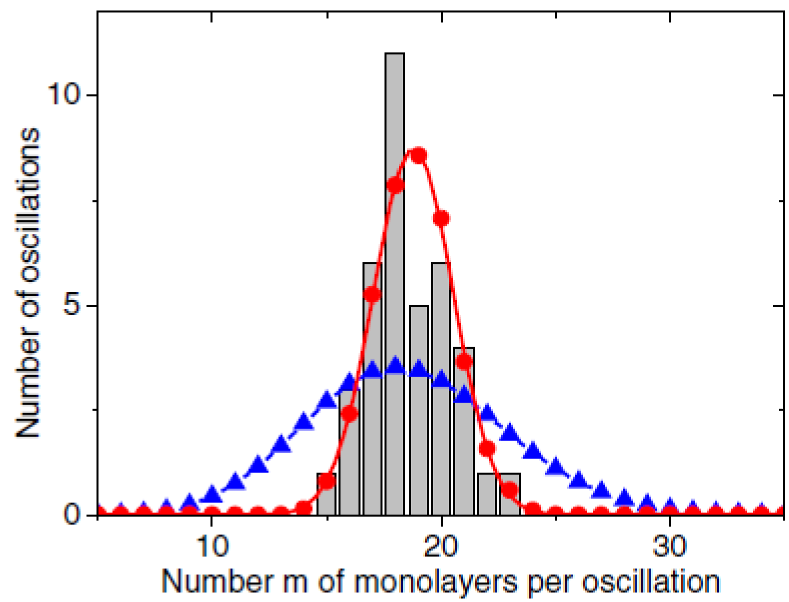
Statistics of nucleation?



F. Glas et al PRL 99, 146101 (2007)

Does it work?

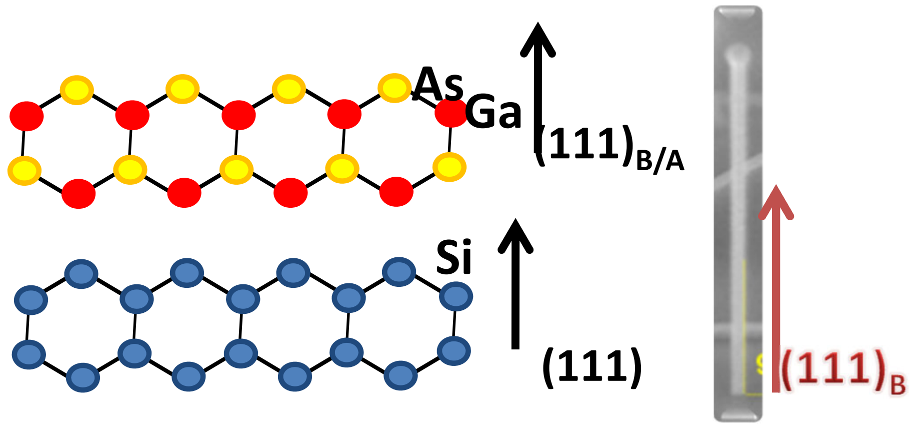




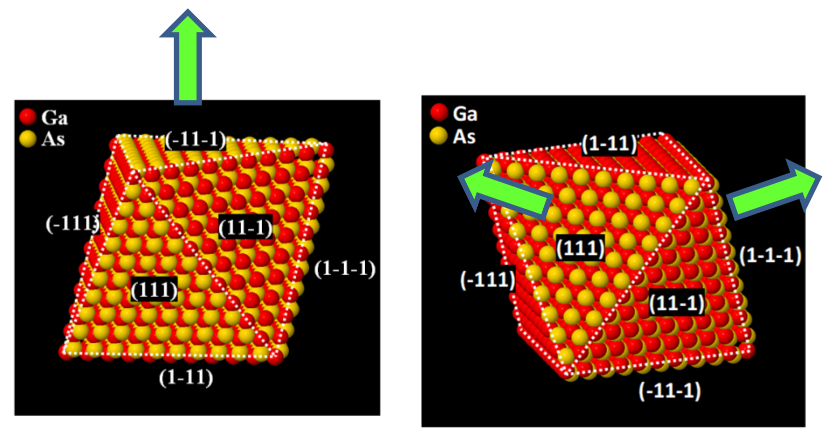
F. Glas et al PRL 104, 135501 (2010)

Growth on Si(111): what about polarity and lattice mismatch in nanostructures?

Growth on Si(111): what about polarity?



GaAs seed



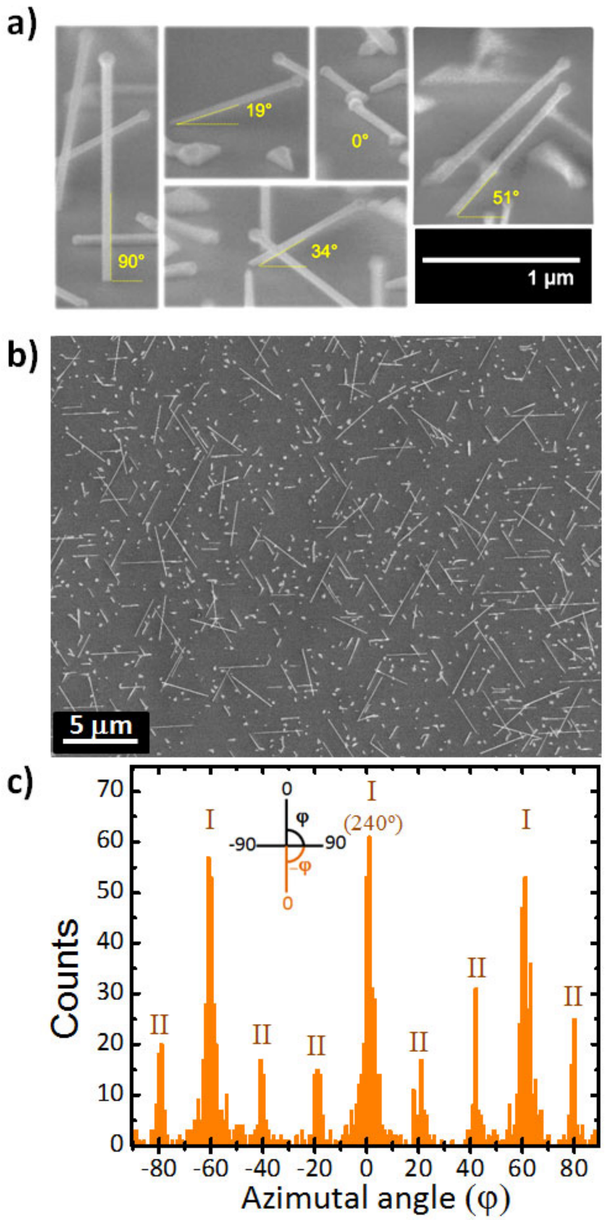
Polarity B
(As terminated)

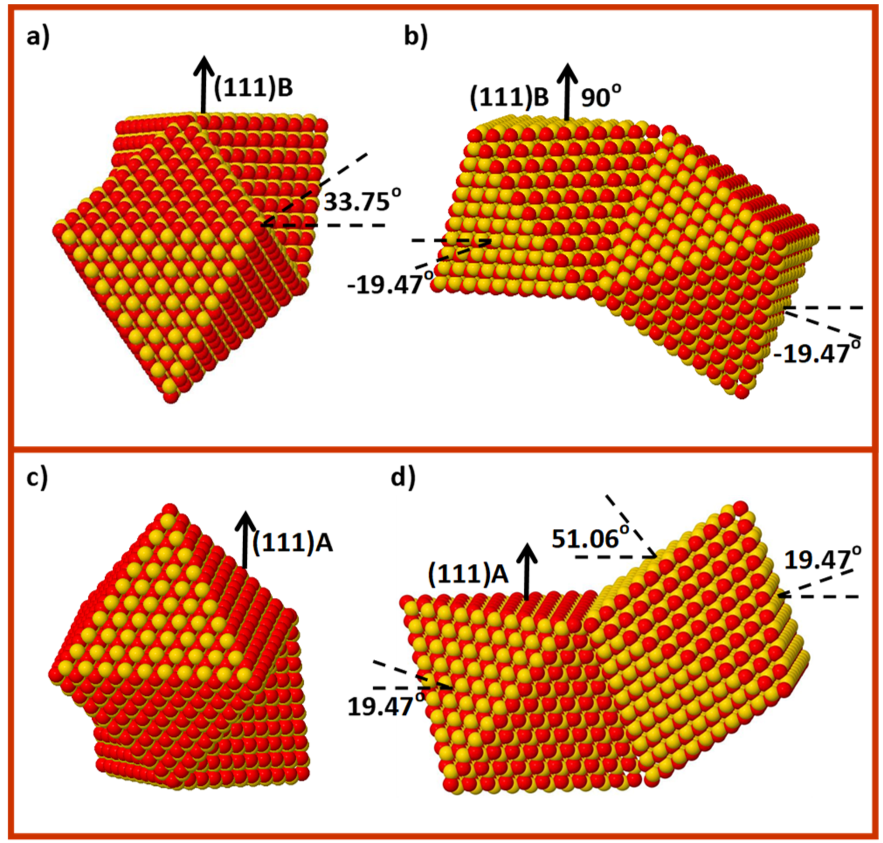
Polarity A
(Ga terminated)

Assuming that growth occurs in the (111)B direction,
it is often assumed that:

1. **If the first layer nucleates with B polarity, then we have growth perpendicular to the substrate**
2. **Otherwise, growth proceeds in a 19^{o}**

3D twinning



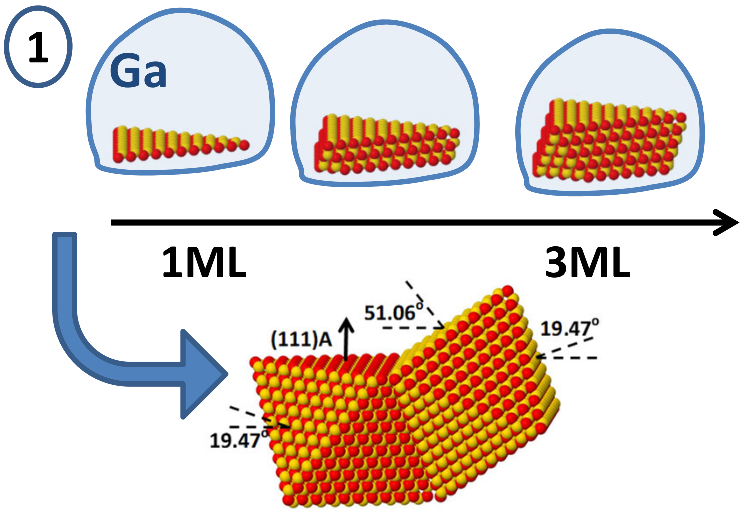


Sequential seed formation and 3D twinning at the initial stages of growth.

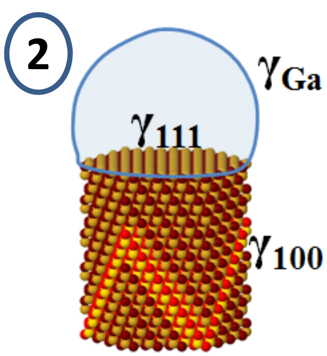
Nano Lett. 11, 3827 (2011)

3D twinning

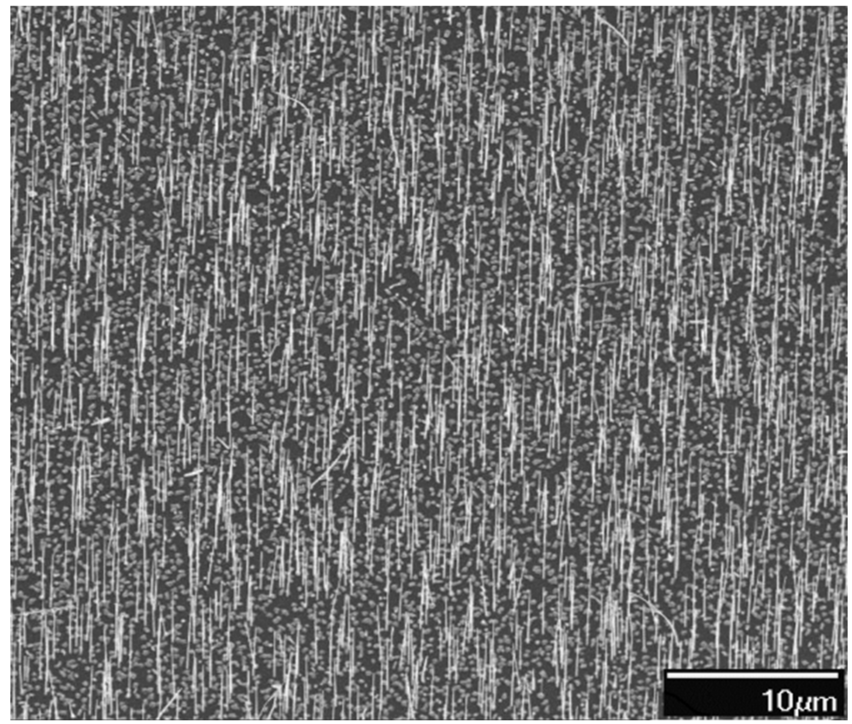
Importance of initial stages



Multiple seed + 3D twinning: Non-vertical growth



Vertical growth

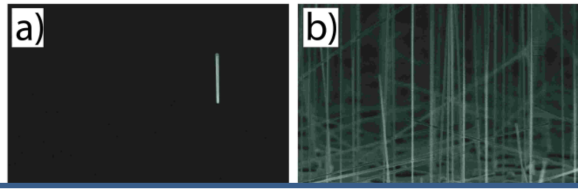


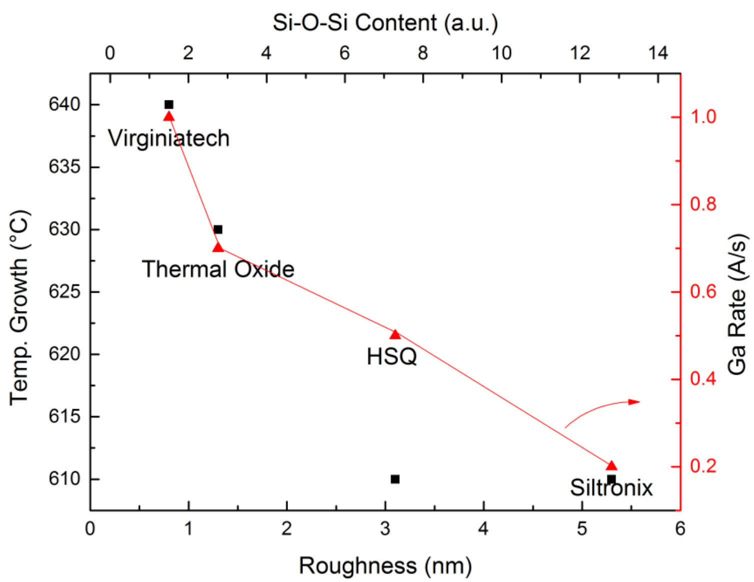
100% yield of vertical wires

Nanoscale 4 1486 (2012)
Nano Lett. 11, 3827 (2011)

Surface preparation

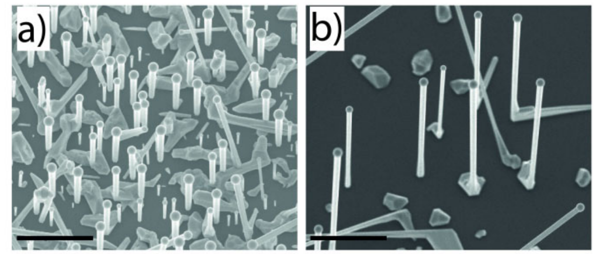
Si Virginiatech Si Siltronix





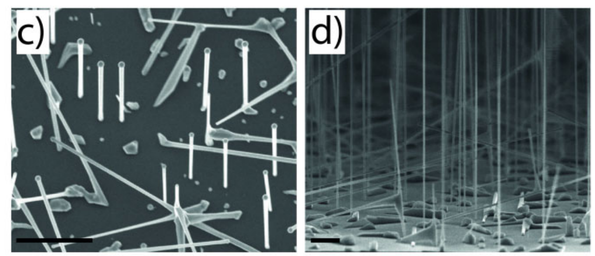
Surface roughness and Si-O-Si content determine the diffusion coefficient of Ga adatoms and thereby the formation of Ga droplets

Virginiatech
Ga: 1 Å/s
T=640°C

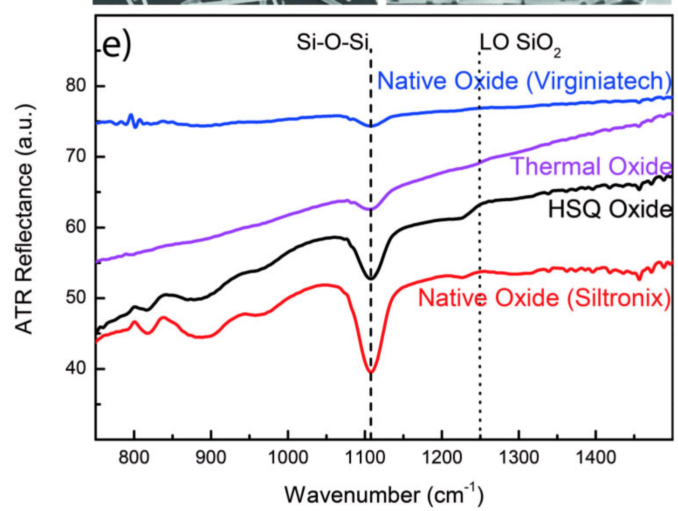


Thermal ox
Ga: 0.7 Å/s
T=630°C

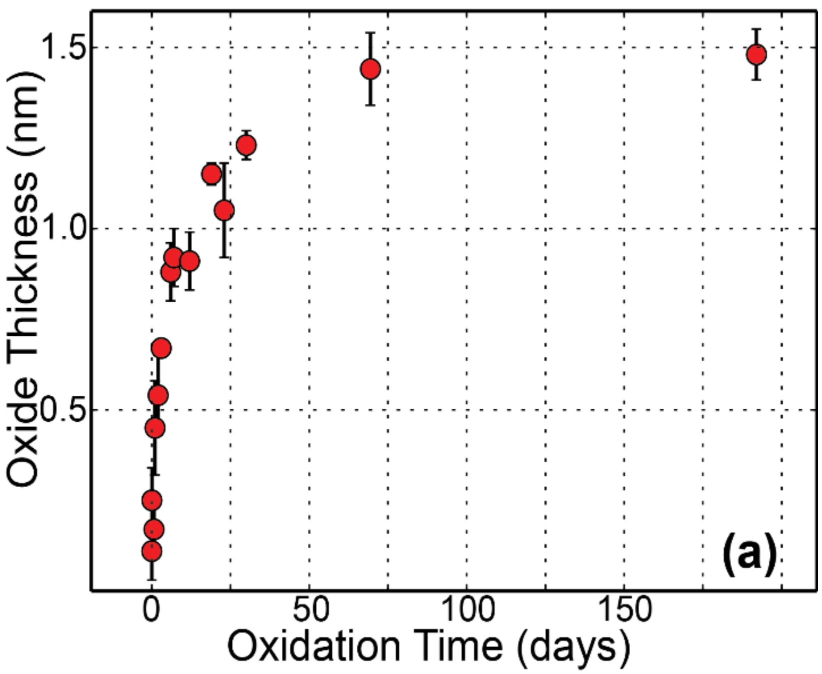
HSQ
Ga: 0.5 Å/s
T=630°C

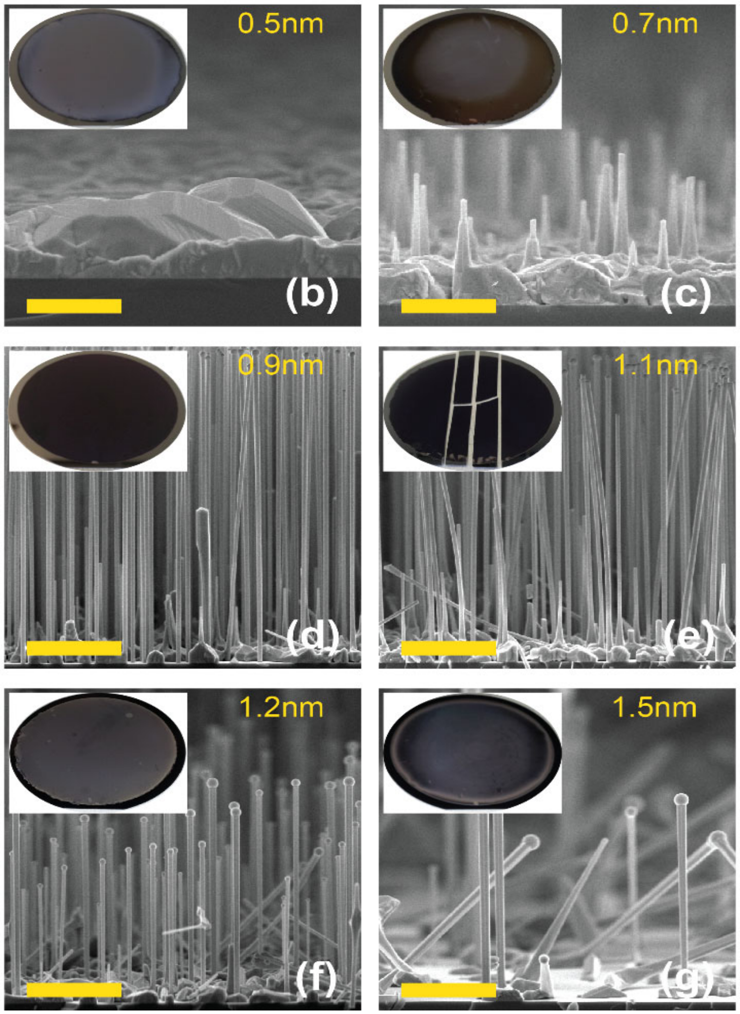


Siltronix
Ga: 0.2 Å/s
T=610°C

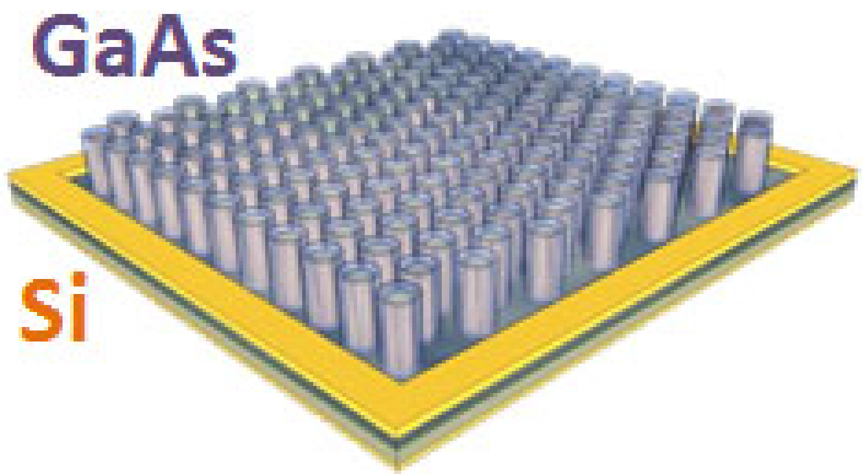


Surface preparation

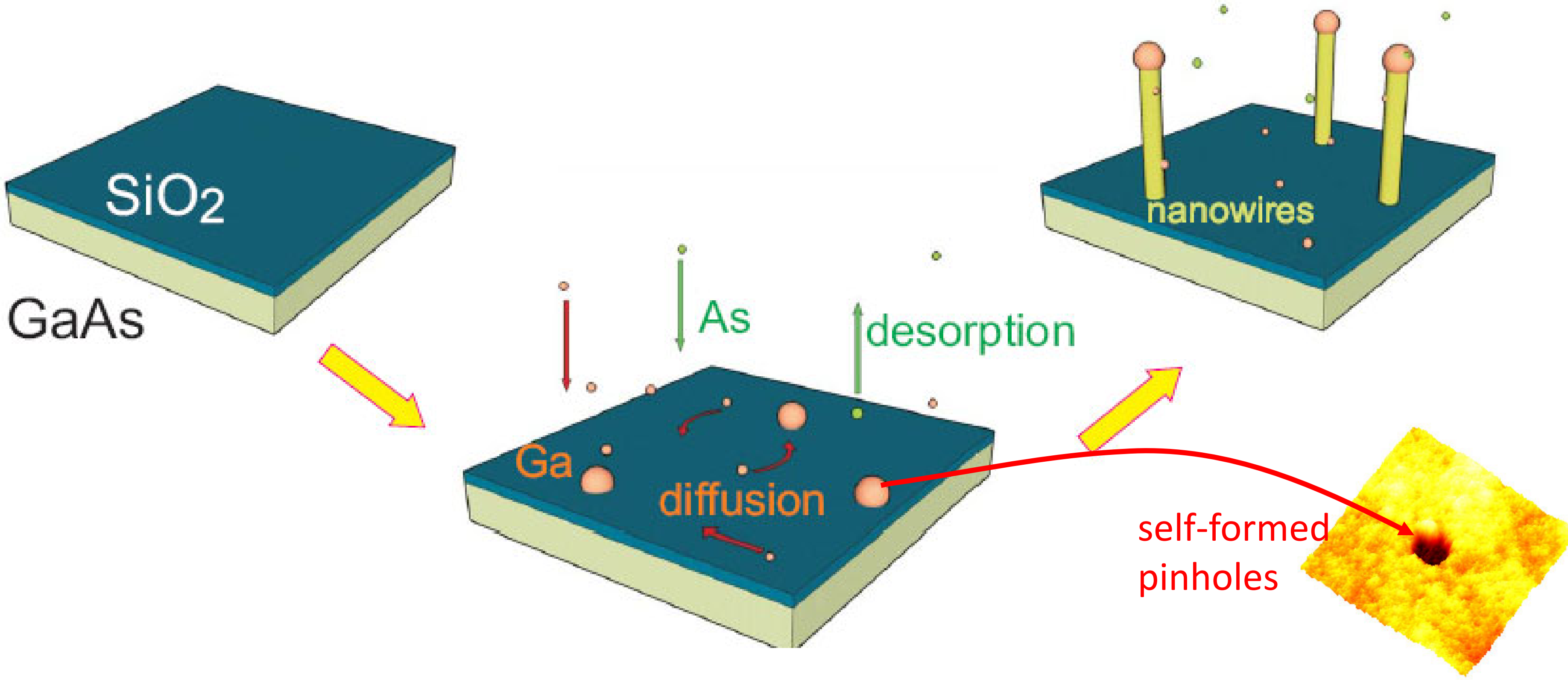




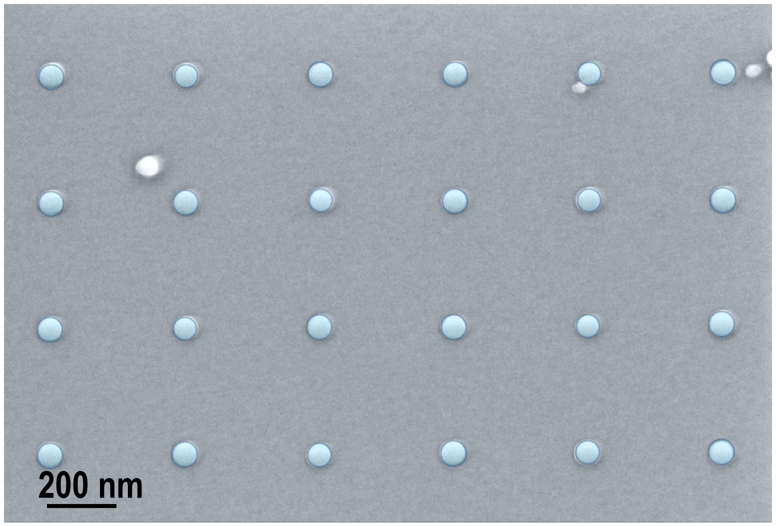
How about ordered growth?

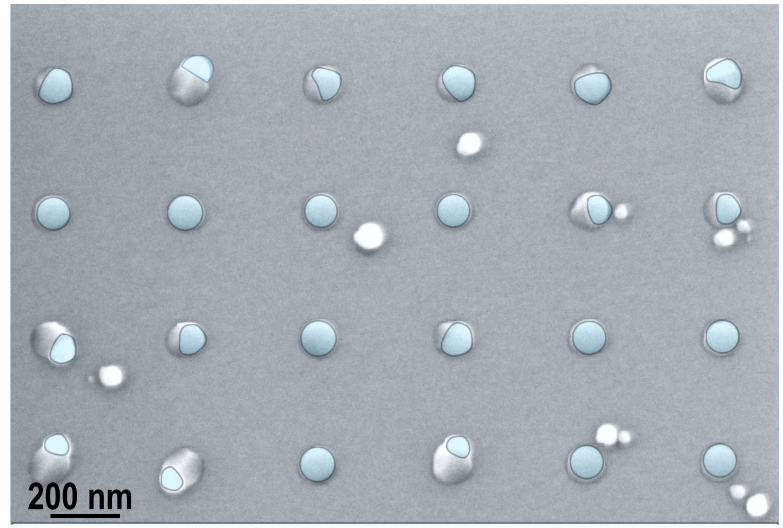


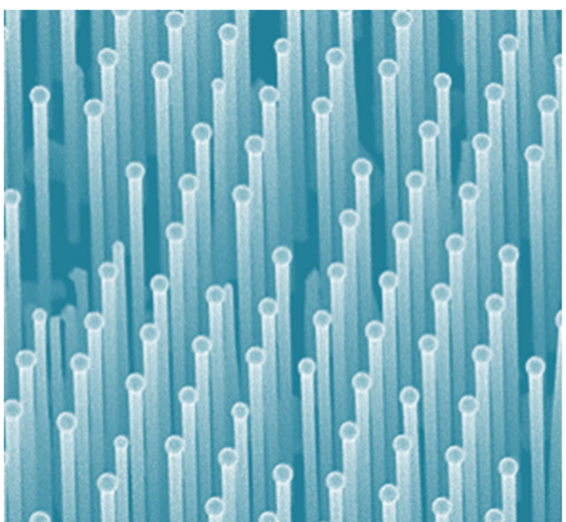
How about ordered growth?



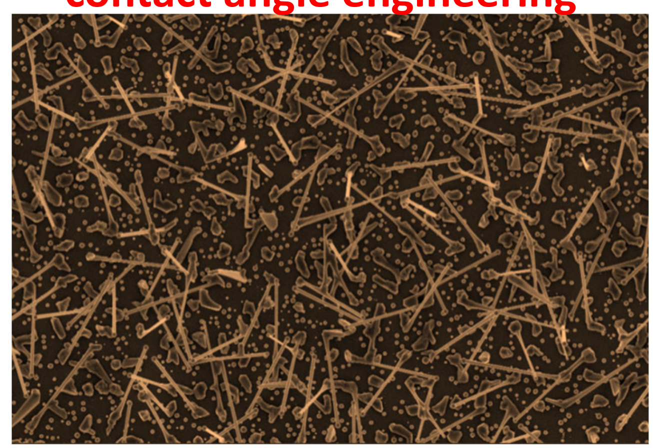
Growth on patterned substrates





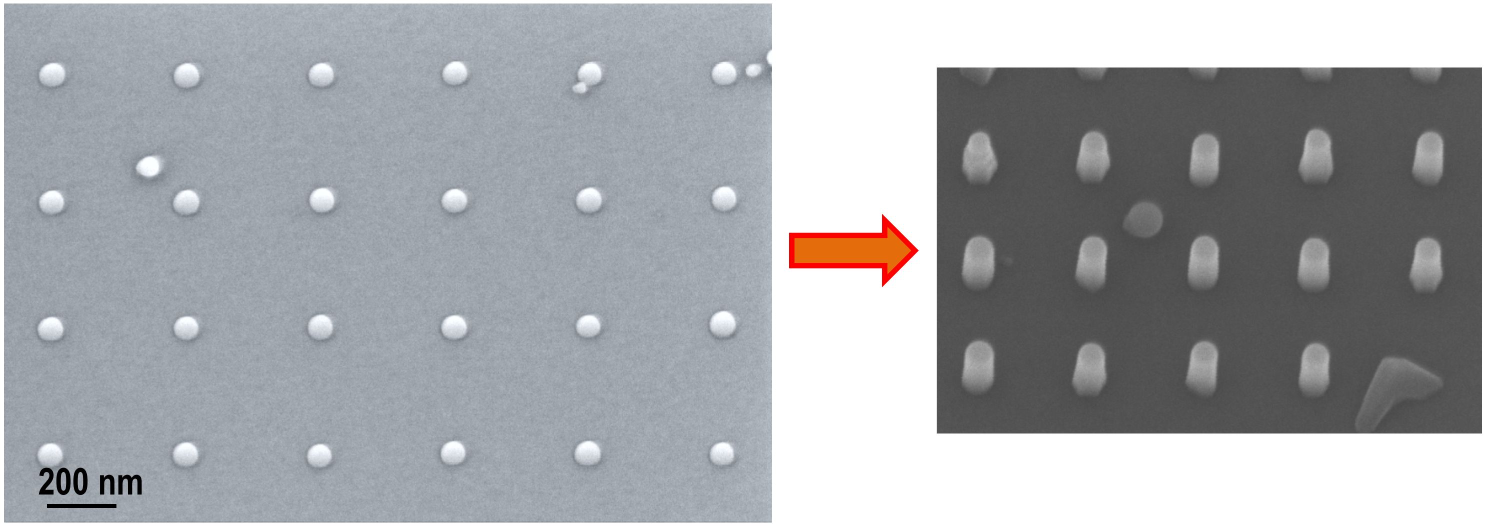


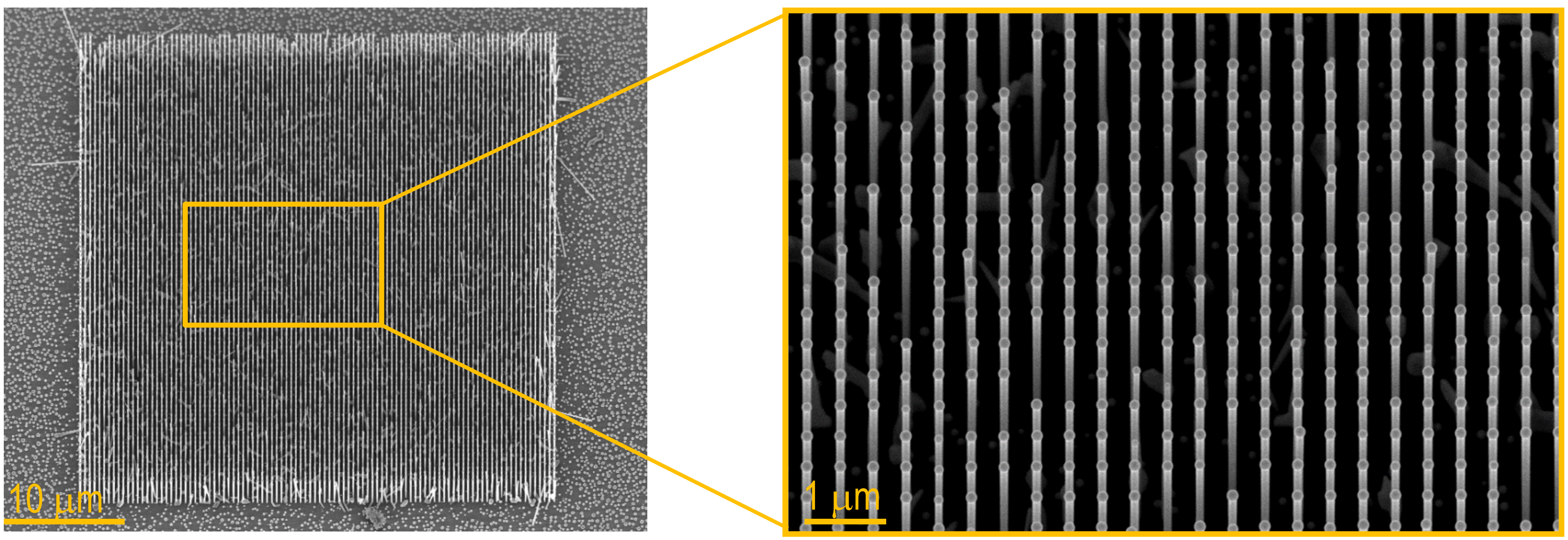
Without
contact angle engineering



J. Vukajlovic-Plestina et al, Nano Lett..17, 4101 (2017)

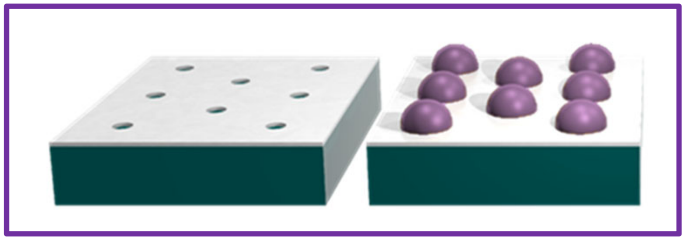
High yield



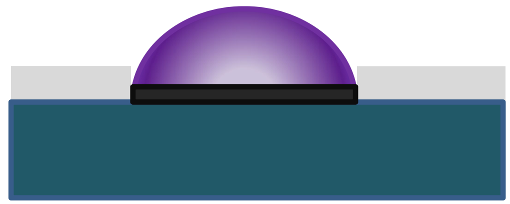


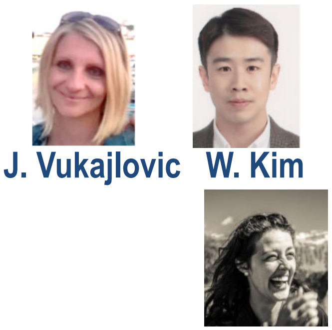
J. Vukajlovic-Plestina et al, Nano Lett..17, 4101 (2017)

Ordered nanowires on silicon



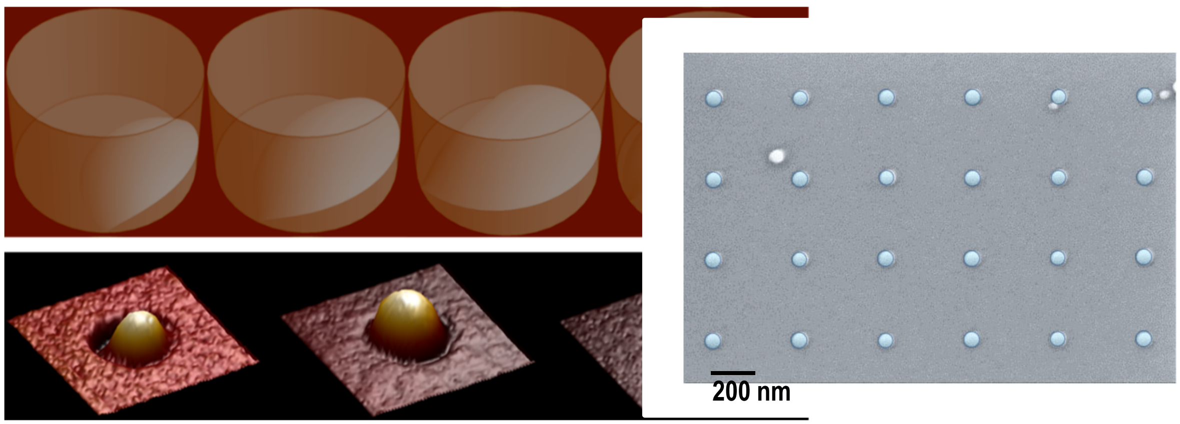
Ideal case:

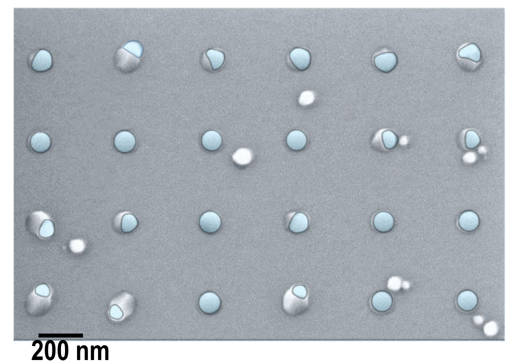




J. Vukajlovic W. Kim

L. Ghisalberti





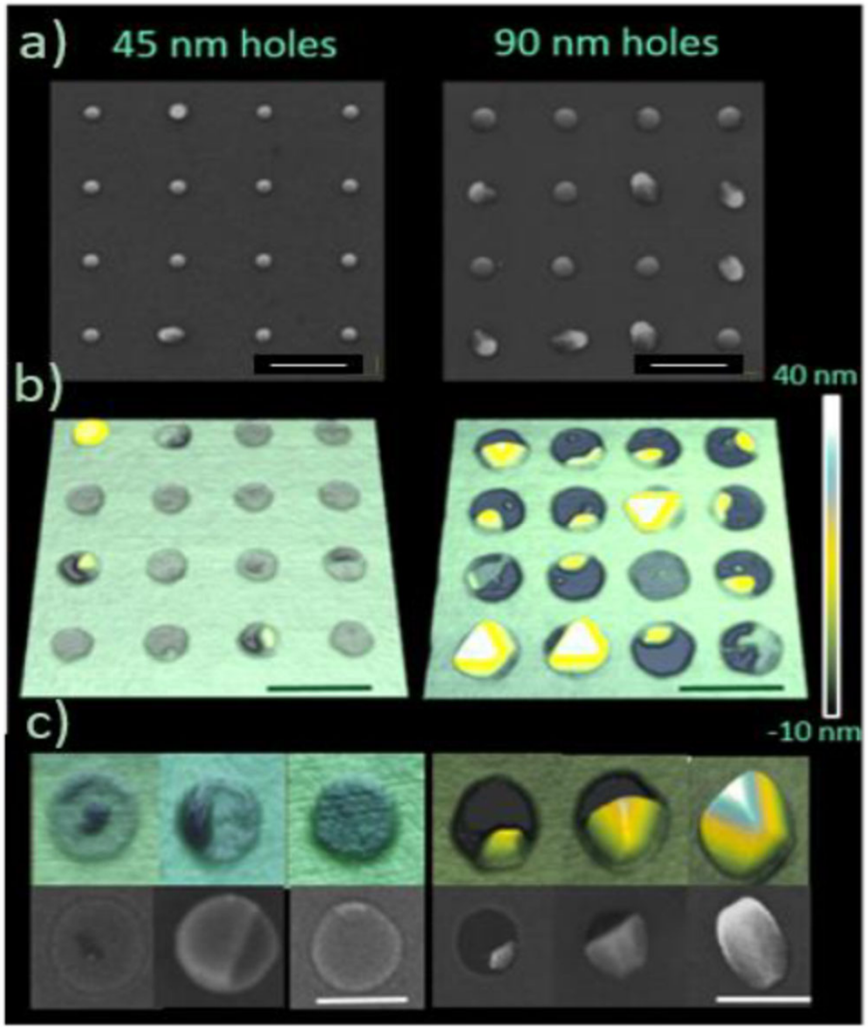
J. Vukajlovic-Plestina et al, Nano Lett.17, 4101 (2017)
J. Vukajlovic-Plestina, , Nature Comm. 10, 869 (2019)

EPFL

LMSC LABORATOIRE DES MATERIAUX SEMICONDUCTEURS

Fundamental mechanism: initial stages

high yield low yield



J. Vukajlovic

W. Kim

L. Ghisalberti

EPFL

J. Vukajlovic-Plestina, , Nature Comm. 10, 869 (2019)

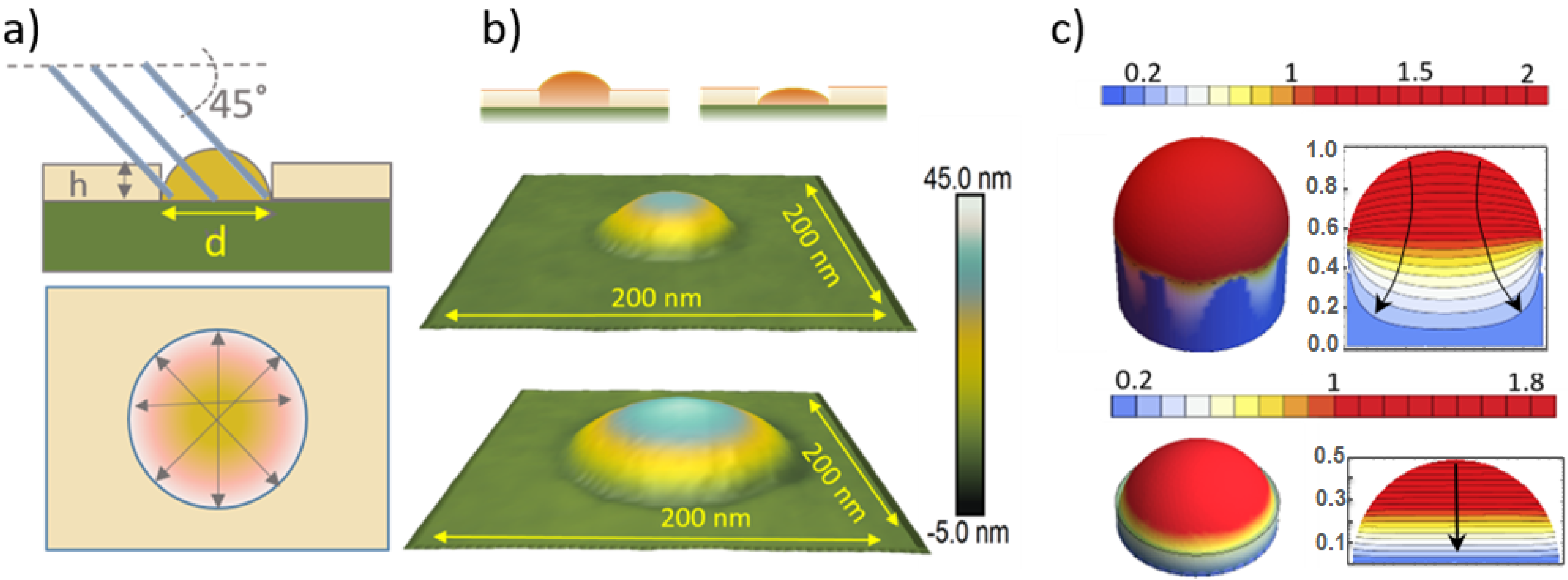
LABORATOIRE DES MATERIAUX SEMICONDUCTEURS

Initial stages determine the yield


J. Vukajlovic W. Kim

L. Ghisalberti

The gradient field in the Ga droplet has a strong influence on the initial stages



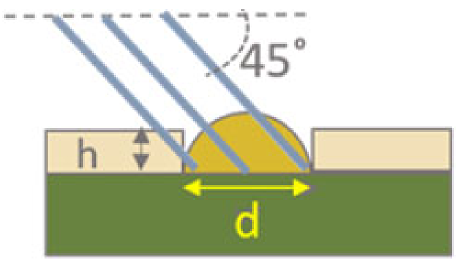
J. Vukajlovic-Plestina, , Nature Comm. 10, 869 (2019)

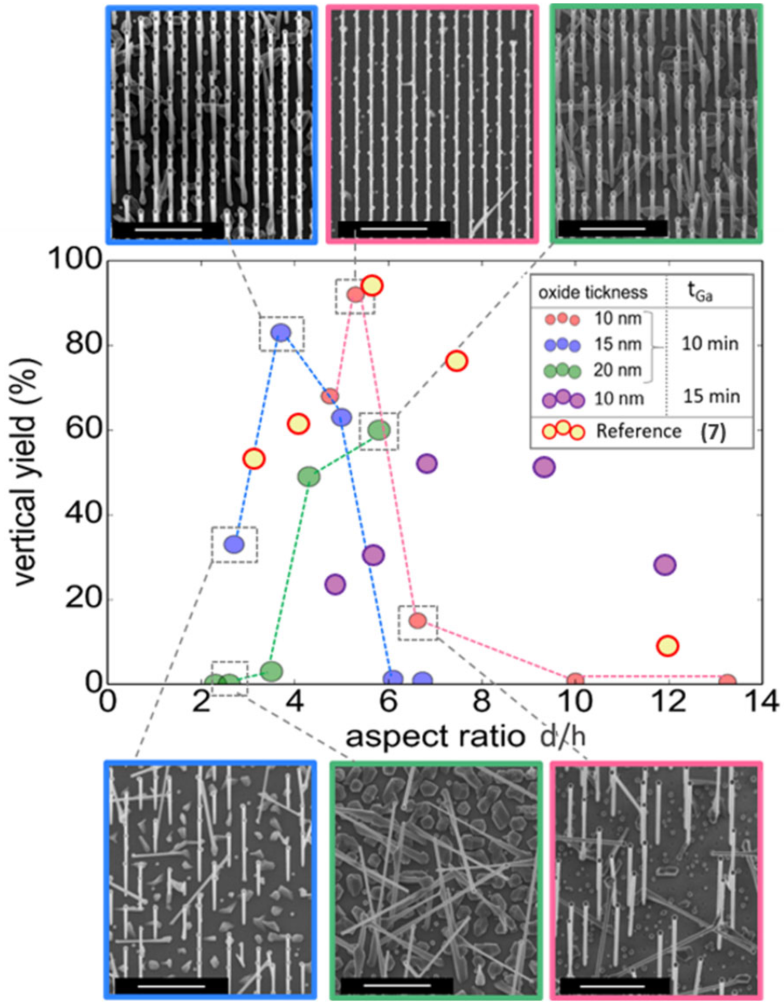
In cooperation with W.C. Carter (DMSE, MIT)

EPFL

LABORATOIRE DES MATERIAUX SEMICONDUCTEURS

Ideal aspect ratio of the hole






J. Vukajlovic


W. Kim

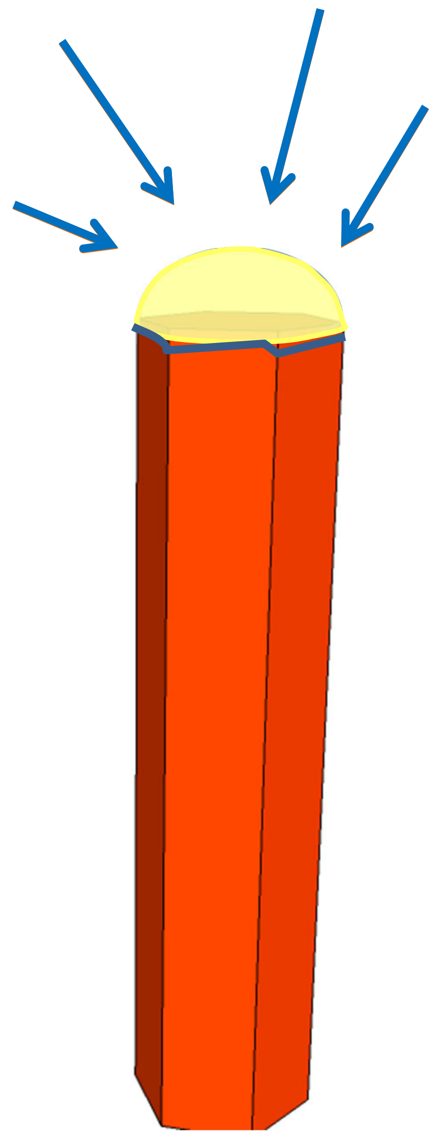

L. Ghisalberti

EPFL

J. Vukajlovic-Plestina, , Nature Comm. 10, 869 (2019)

LMSC LABORATOIRE DES MATERIAUX SEMICONDUCTEURS

Changing the material composition along the nanowire axis



How to obtain abrupt axial interfaces?

NANO LETTERS

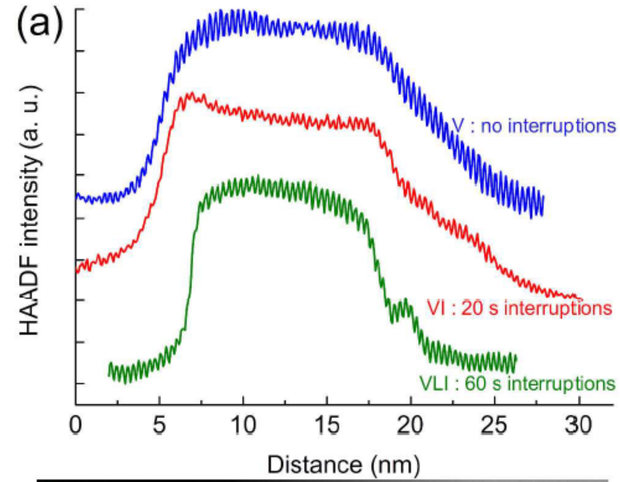
Communication

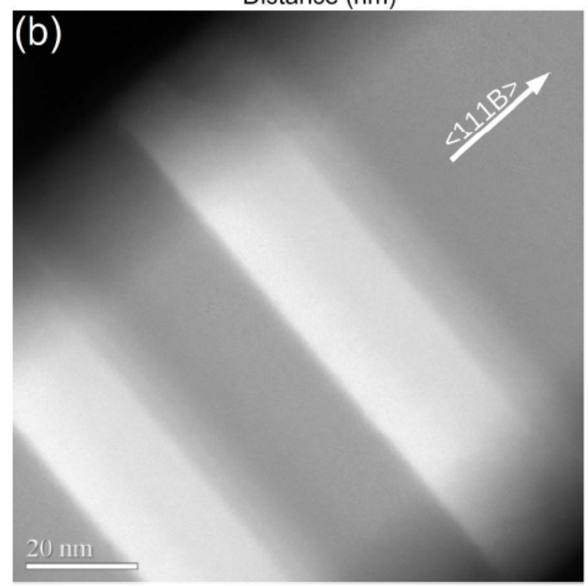
Abrupt GaP/GaAs interfaces in self-catalyzed nanowires

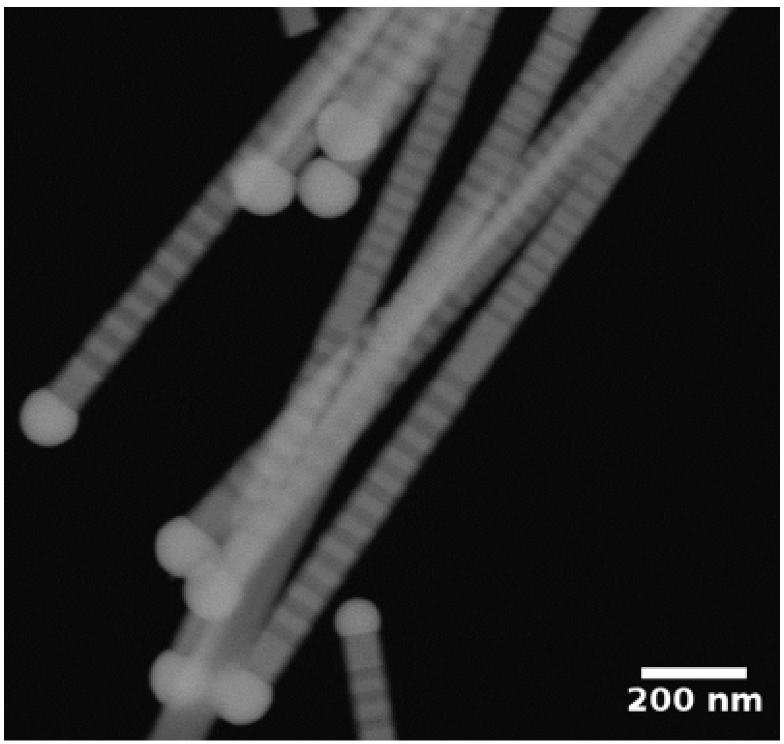
Giacomo Priante, Gilles Patriarche, Fabrice Oehler, Frank Glas, and Jean-Christophe Harmand

Nano Lett., **Just Accepted Manuscript** • DOI: 10.1021/acs.nanolett.5b02224 • Publication Date (Web): 28 Jul 2015

- Ga-catalyzed growth of GaP/GaAs NWs by MBE
- Test different flux switching procedures
- Measure interfacial profiles by HAADF STEM
- Interfacial abruptness is drastically improved by switching off all fluxes at the group V commutation

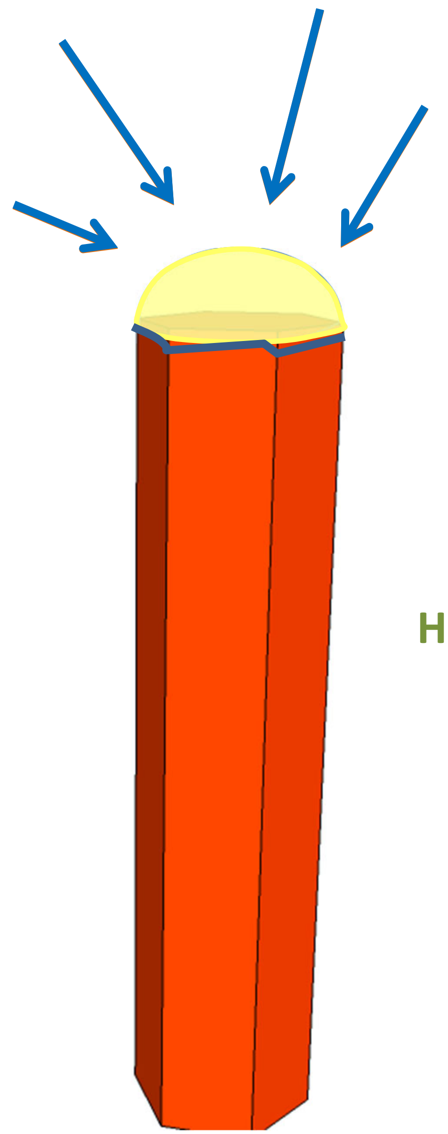






(a) HAADF intensities with 0, 20 and 60 s interruptions for GaAs insertions grown for 10 s
(b) Details of interfaces

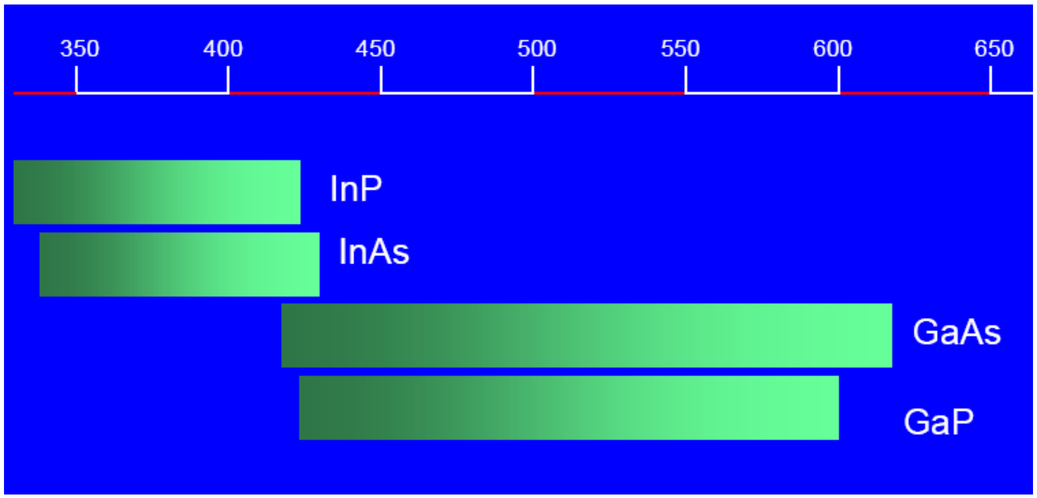
Changing the material composition along the nanowire axis



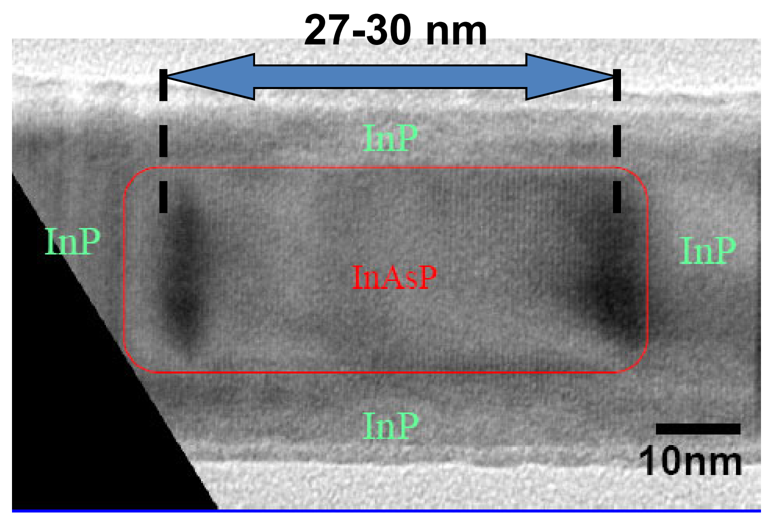
How to grow then around the nanowire?

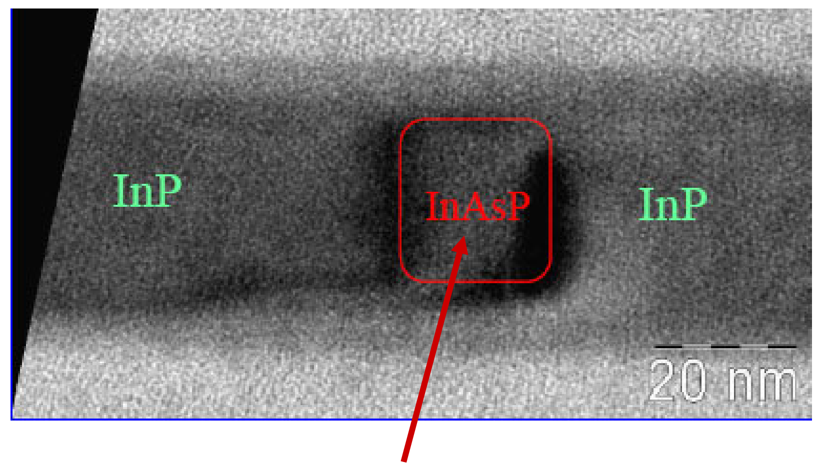
Formation of InAsP/InAs NW heterostructures

Temperature domains for Au-assisted MBE:



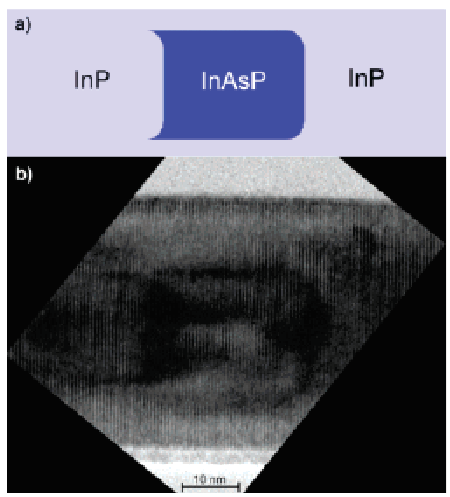
InAsP QD in InP NW:





$InAs_{0.35}P_{0.65}$

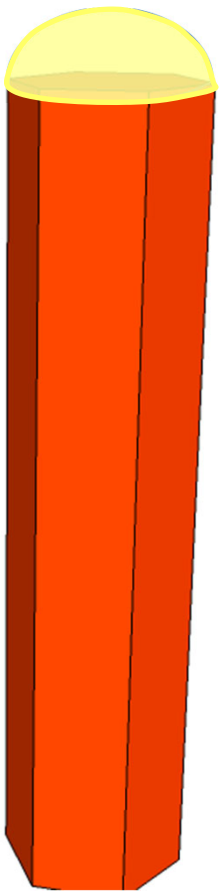
InAsP formed at 390^0C and overgrown by InAs at 420^0C



Pure WZ structure

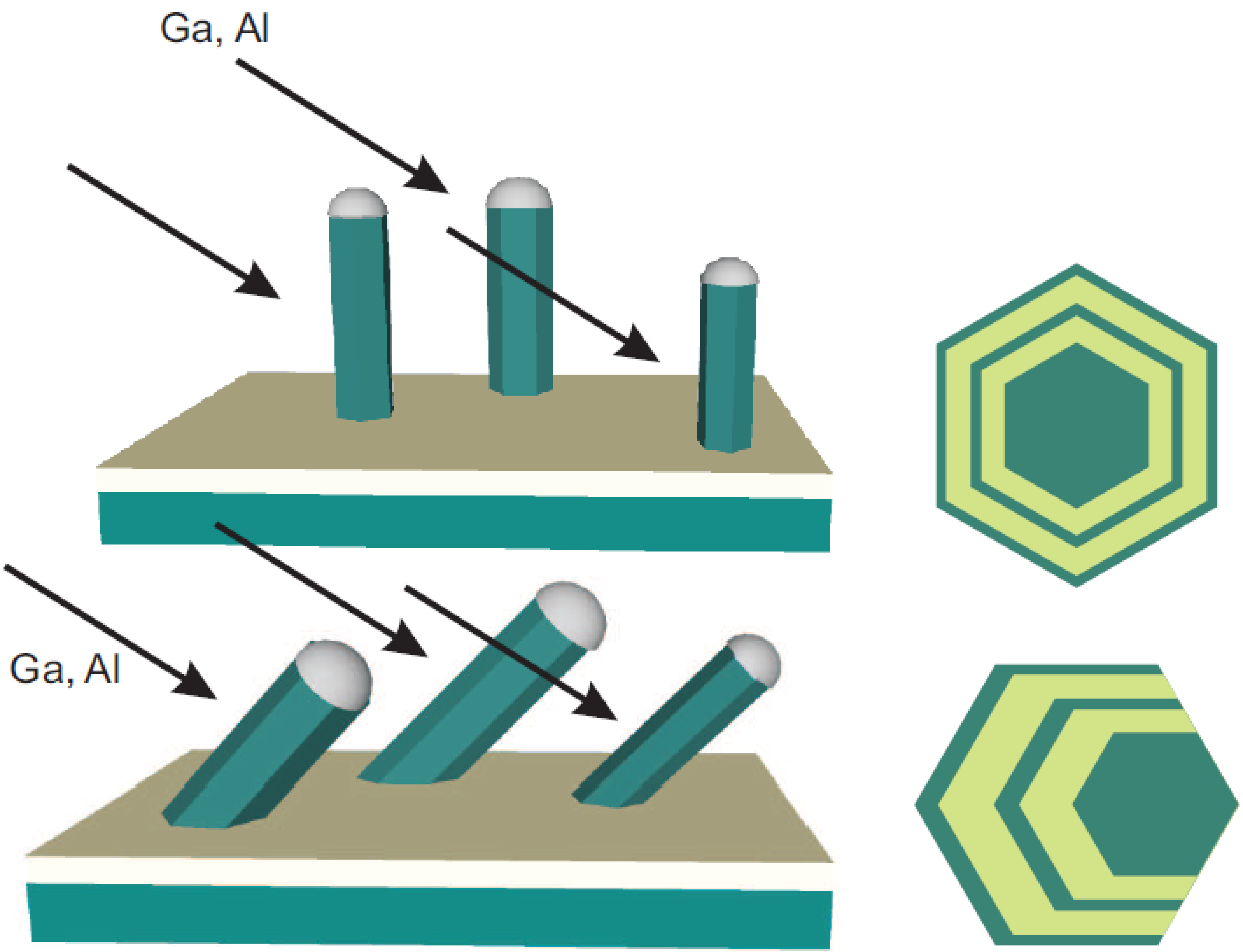
M. Tchernycheva *et al.* NanoLetters 2007

Can we still grow 2D-like?

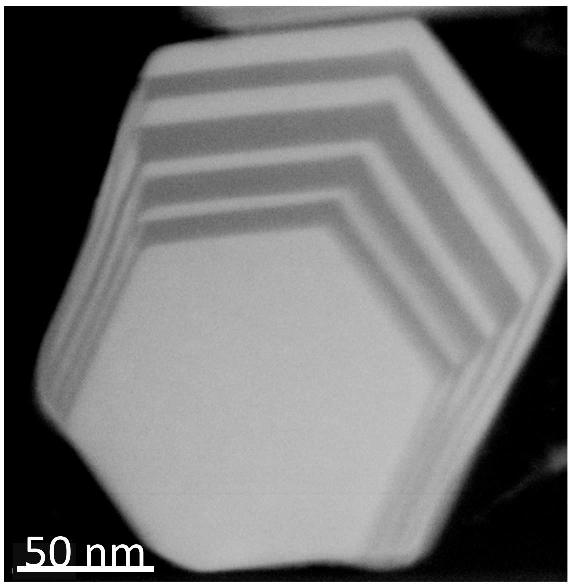


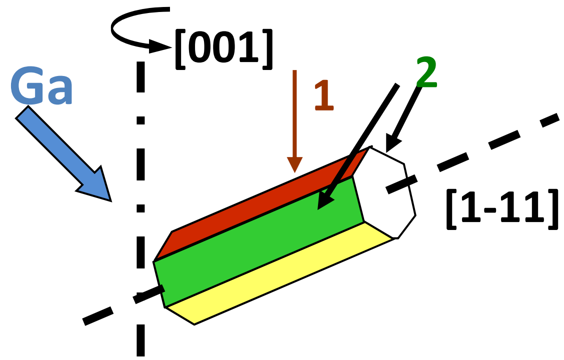
Stopping the Ga flux +
Increase of Arsenic flux → consumption of the Ga droplet
Radial growth can proceed by normal 2D MBE growth

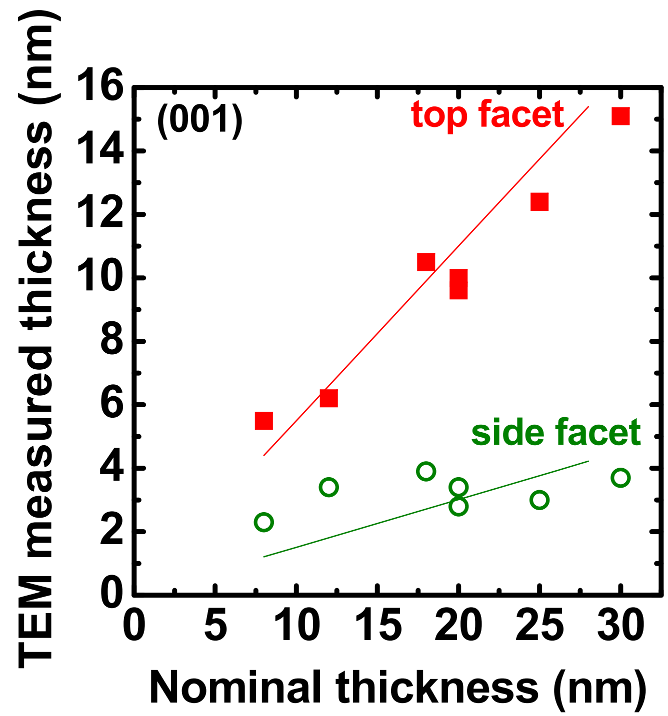
‘Nano’-epitaxy on the facets



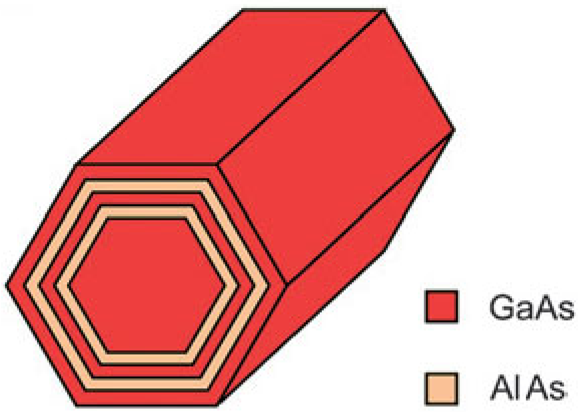
Radial heterostructures

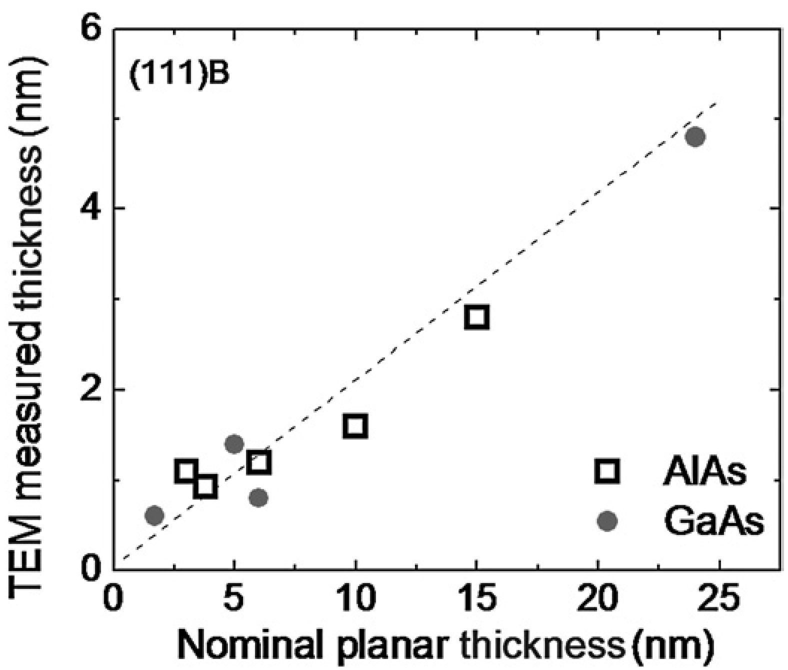


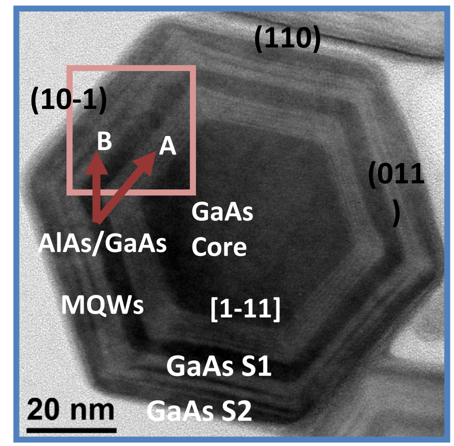


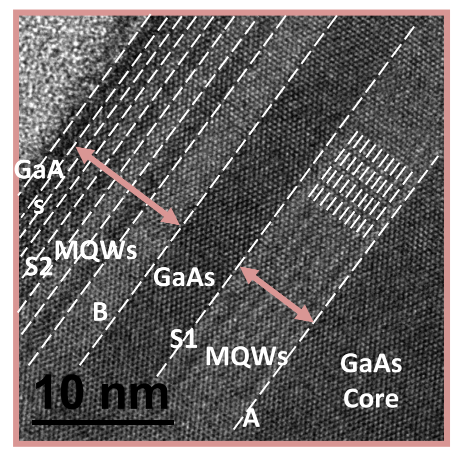


Radial heterostructures



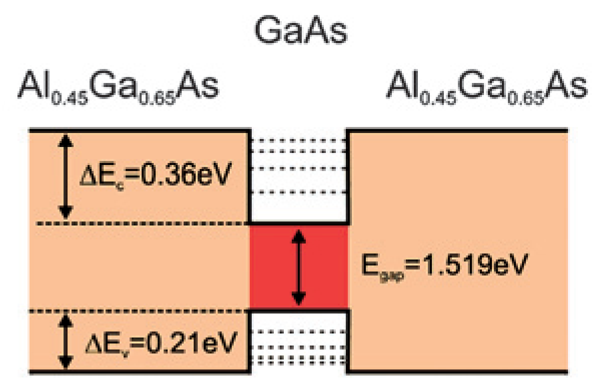


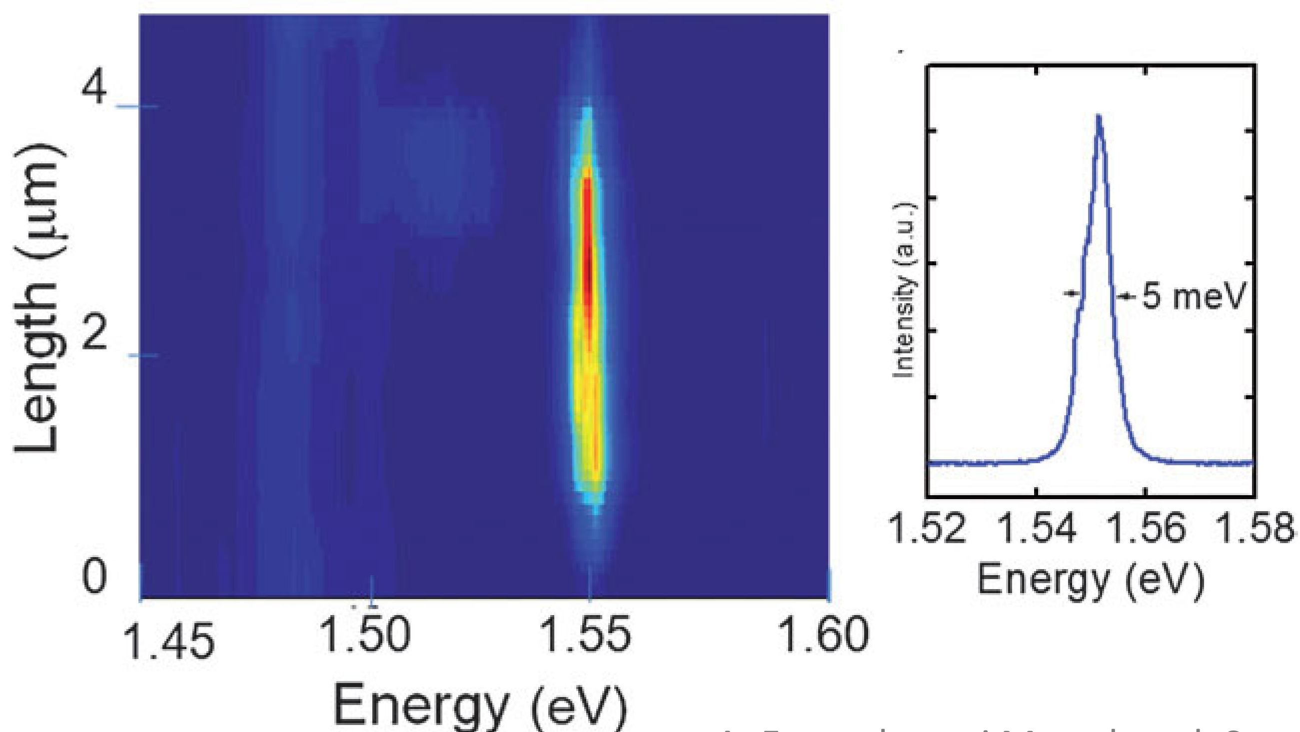




A. Fontcuberta i Morral et al, Small **4** 899-903 (2008)
M. Heigoldt et al, J. Mater. Chem. (2009)

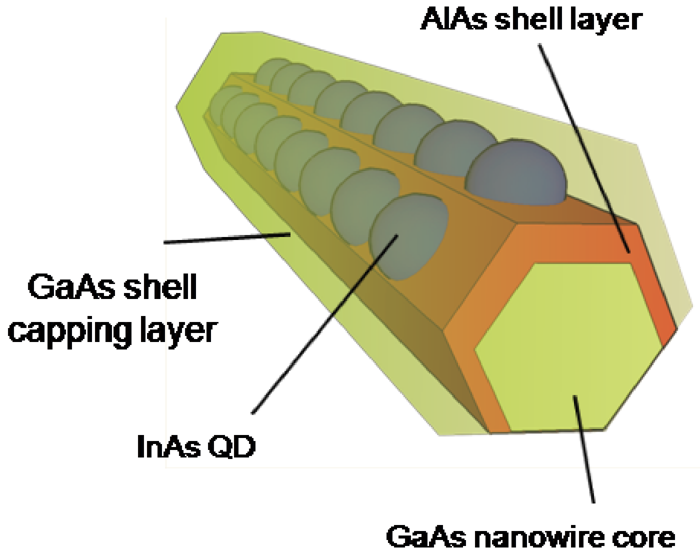
Interfaces and homogeneity

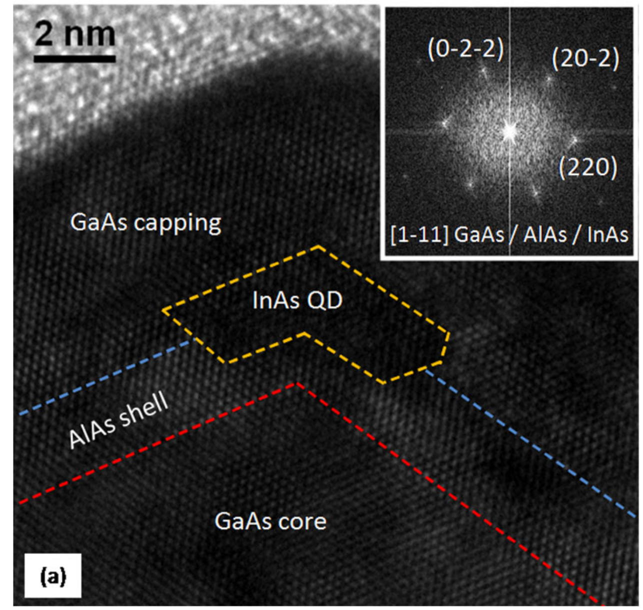


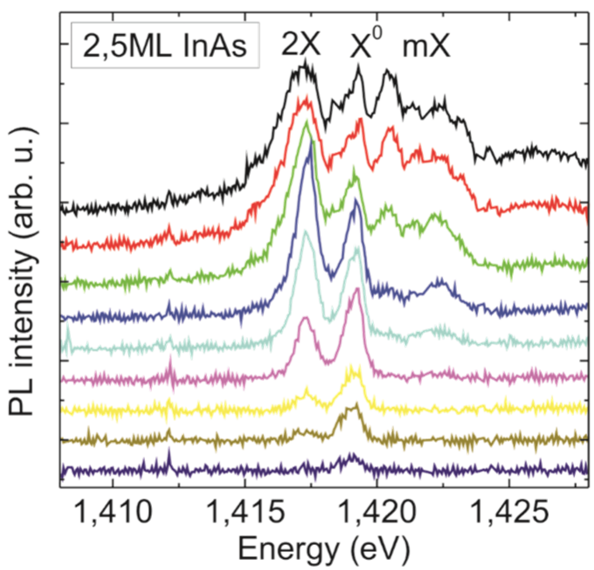


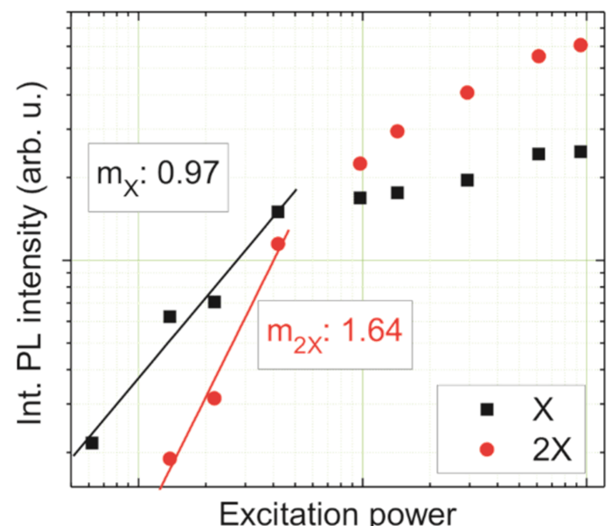
A. Fontcuberta i Morral et al, Small **4** 899-903 (2008)
M. Heigoldt et al, J. Mater. Chem. (2009)

Stranski-Krastanov quantum dots





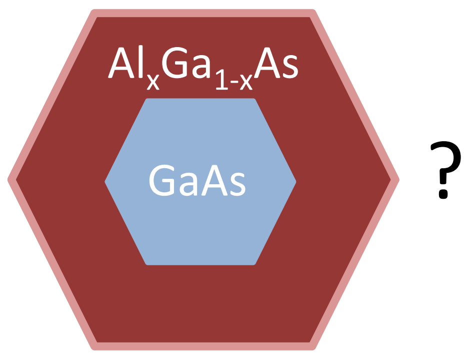




E. Ucelli et al, ACS Nano(2010)

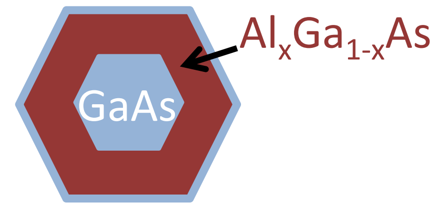
Everything so nice and smooth?

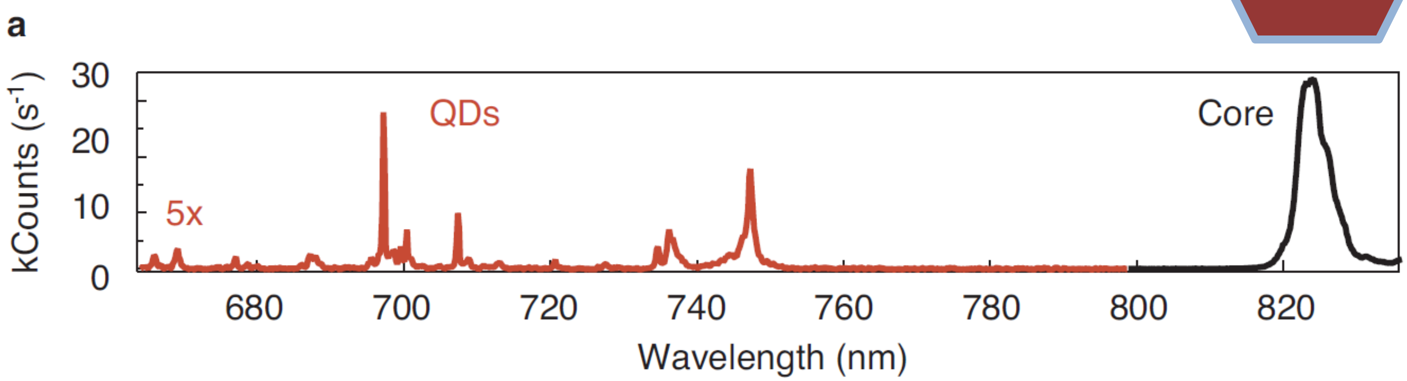
What about just having an AlGaAs shell?

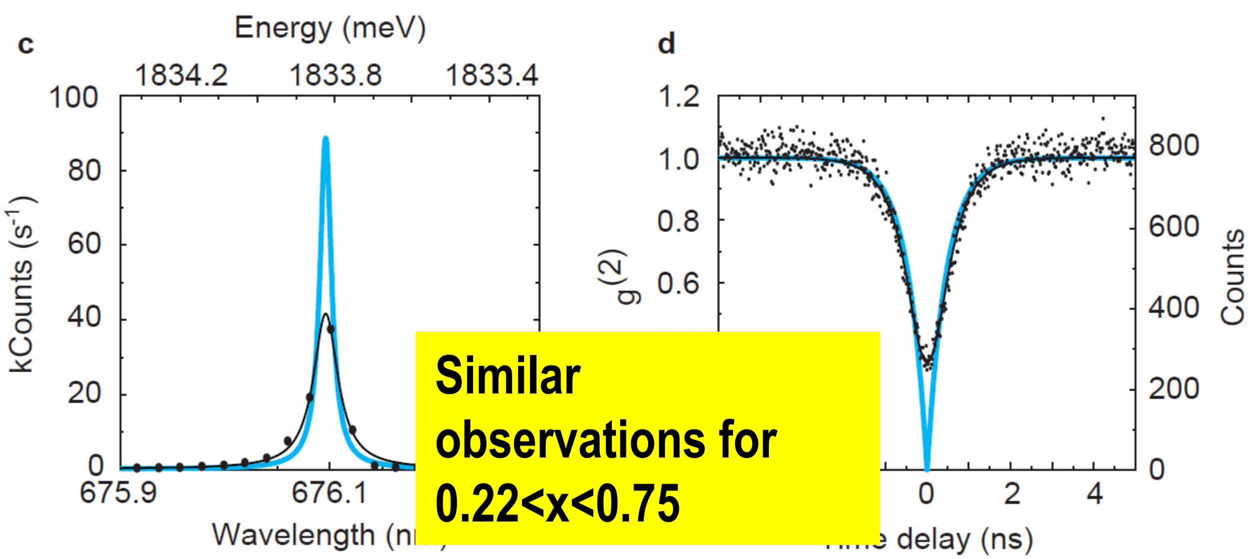


Can we still grow 2D-like?

GaAs nanowires with a single $Al_xGa_{1-x}As$ shell





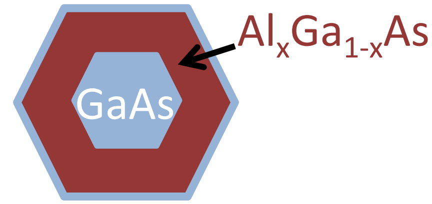


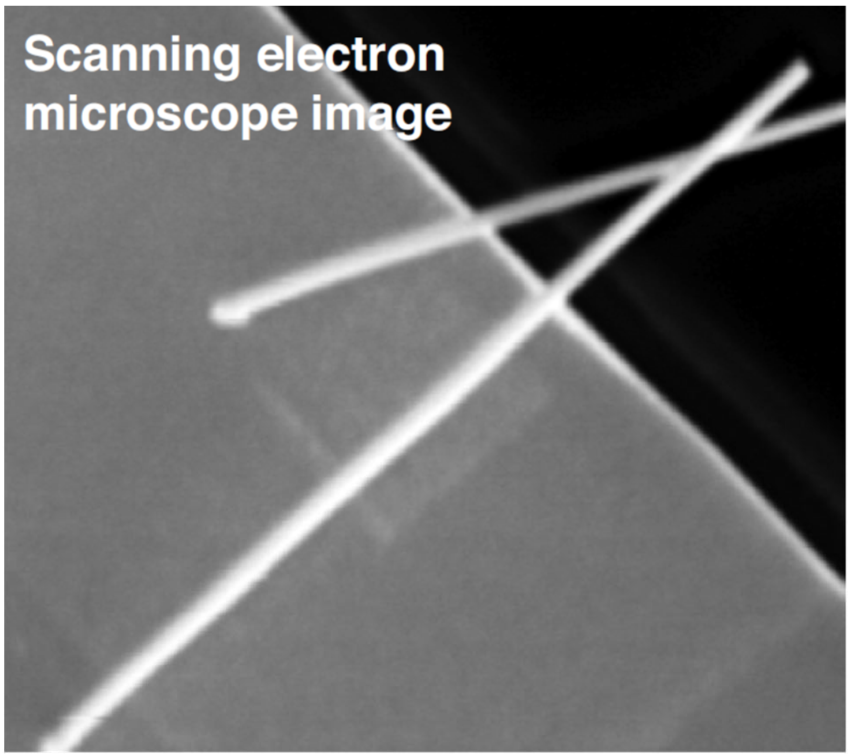
Similar observations for 0.22<x<0.75

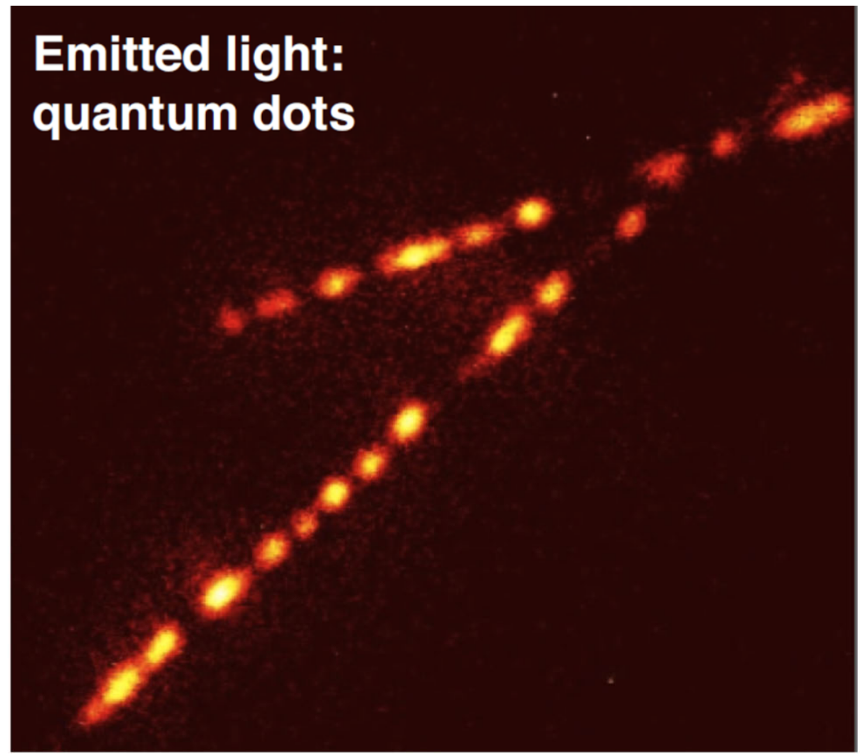
M. Heiss et al, Nature Mater 12, 439 (2013)

Optical properties at the nanoscale

GaAs nanowires with a single $Al_xGa_{1-x}As$ shell



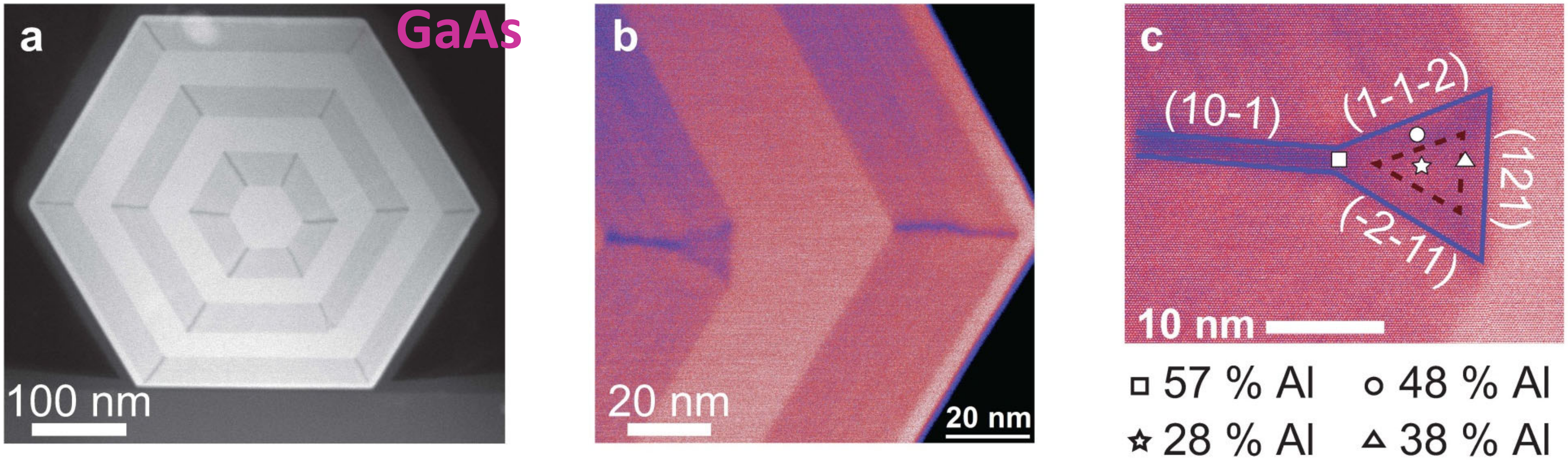




Cathodoluminescence:
A. Gustafsson (Lund)

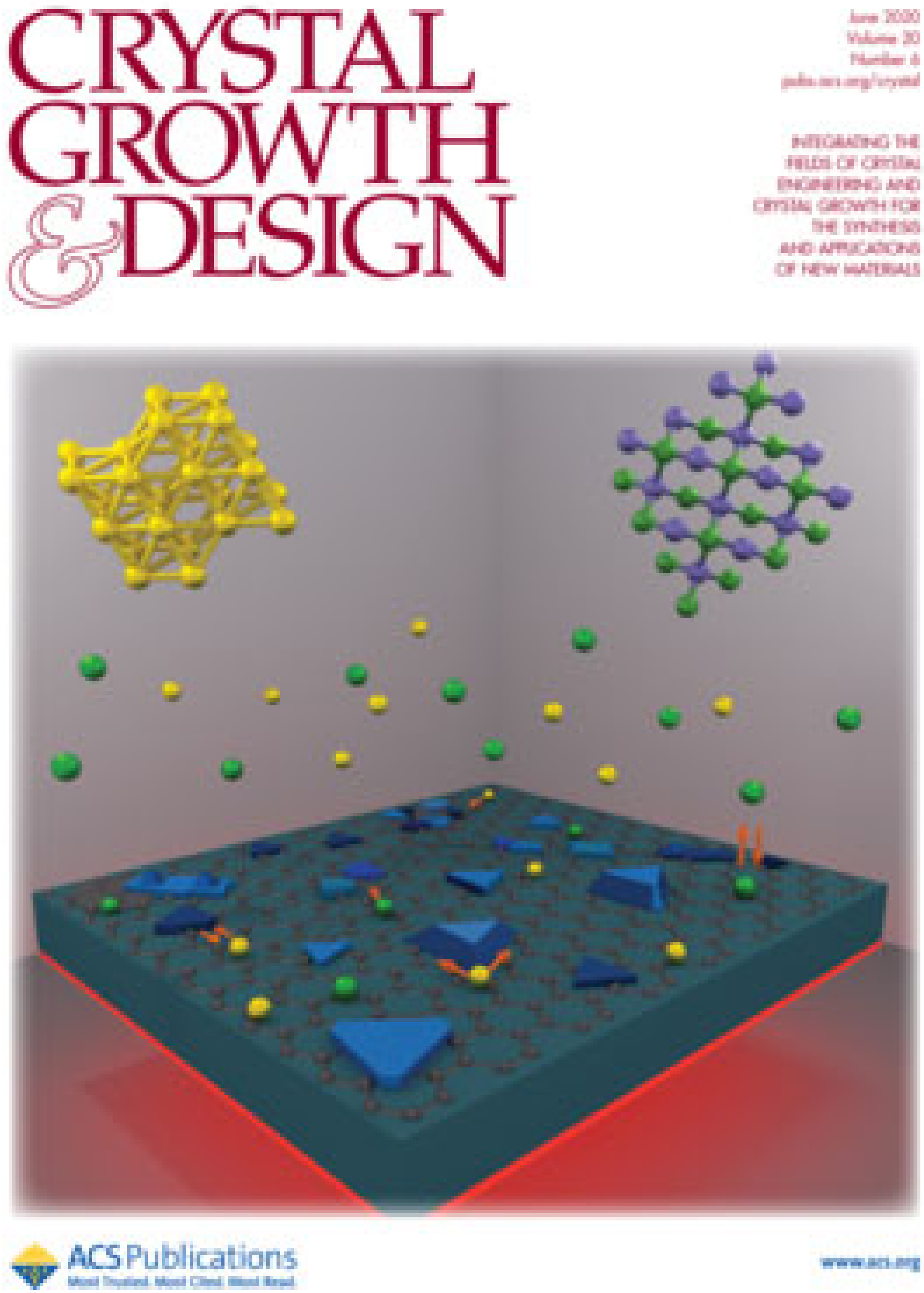
M. Heiss et al, Nature Mater 12, 439 (2013)

Structural characterization



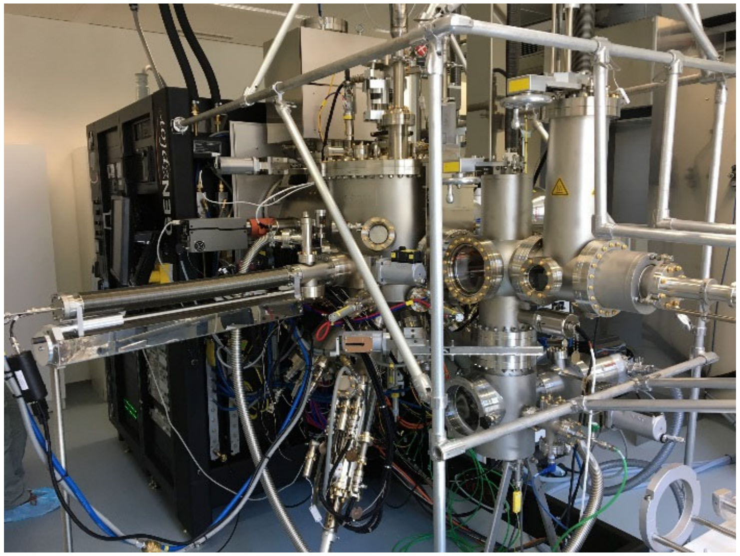
S. Conesa-Boj

M. Heiss et al Nature Mater 12, 439 (2013)

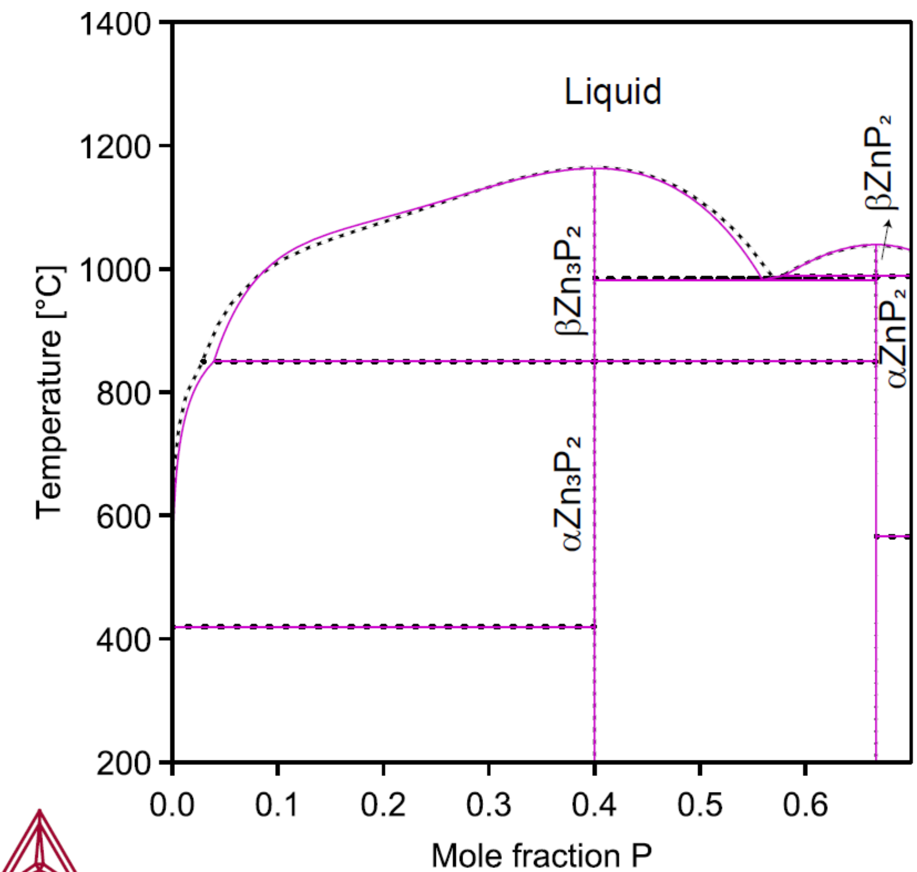


Towards more exotic materials

A new effort on Zn_3P_2



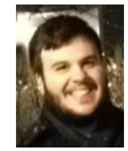
Material sources: Zn, P_2 (g)
Doping: Ag, Mg
Forms: thin film, nanowires




J.B. Leran


E. Stutz


M. Zamani


S. Escobar

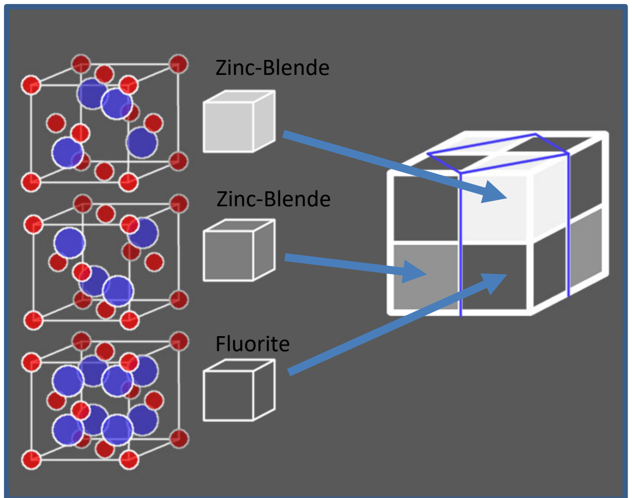

R. Paul

Cooperation with M Ghasemi (CALPHAD)

EPFL

LMSC
LABORATOIRE DES MATERIAUX SEMICONDUCTEURS

New materials, new tools



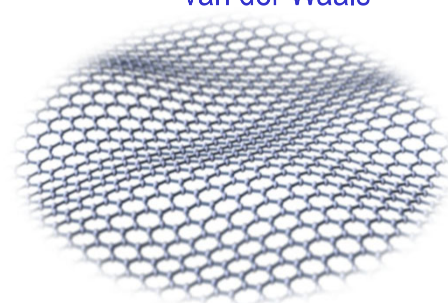
Tetragonal: a = 8.097 Å, c = 11.45 Å

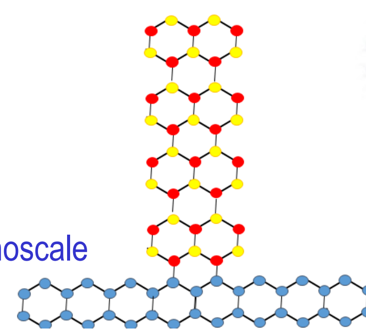
Properties:

- Direct bandgap at 1.5 eV
- Carrier diffusion length (5 – 10 µm)
- Carrier mobility ($10^2 – 10^3$ cm^2/Vs)
- Absorption coefficient ($10^4 – 10^5$ cm^{-1})
- Good thermoelectric material

Challenges:

- Thermal expansion mismatch
- Lattice mismatch
- Doping

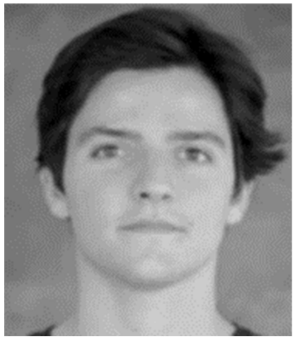




EPFL

LMSC LABORATOIRE DES MATERIAUX SEMICONDUCTEURS

Rajrupa Paul



Nicolas Humblot

van der Waals Epitaxy of Earth-Abundant Zn_3P_2 on Graphene for Photovoltaics

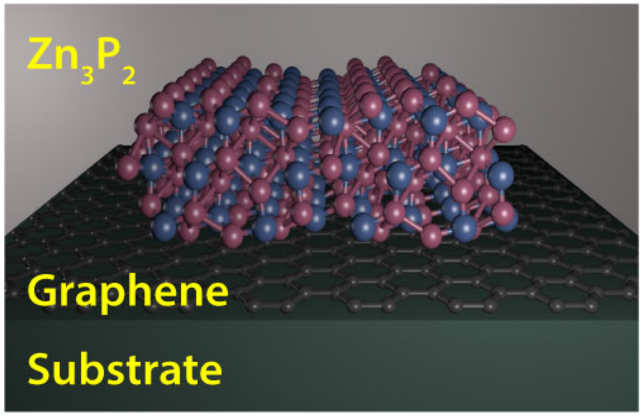
Rajrupa Paul[1], Nicolas Humblot[1,2], Simon Escobar Steinvall[1], Elias Zsolt Stutz[1], Shreyas Sanjay Joglekar[1], Jean-Baptiste Leran[1], Mahdi Zamani[1], Cyril Cayron[3], Roland Logé[3], Andres Granados del Aguila[2], Qihua Xiong[2], Anna Fontcuberta i Morral[*1,4]

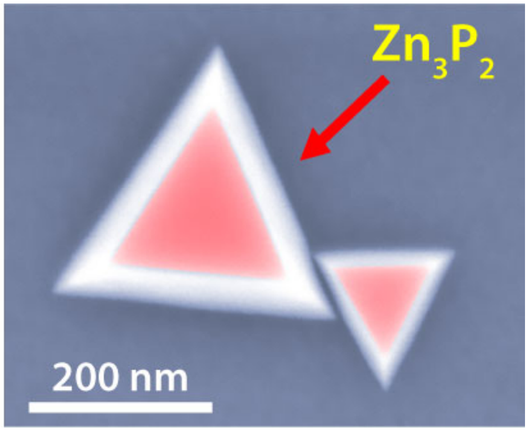
[1]Laboratory of Semiconductor Materials, Institute of Materials, School of Engineering, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

[2] Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, 637371, Singapore

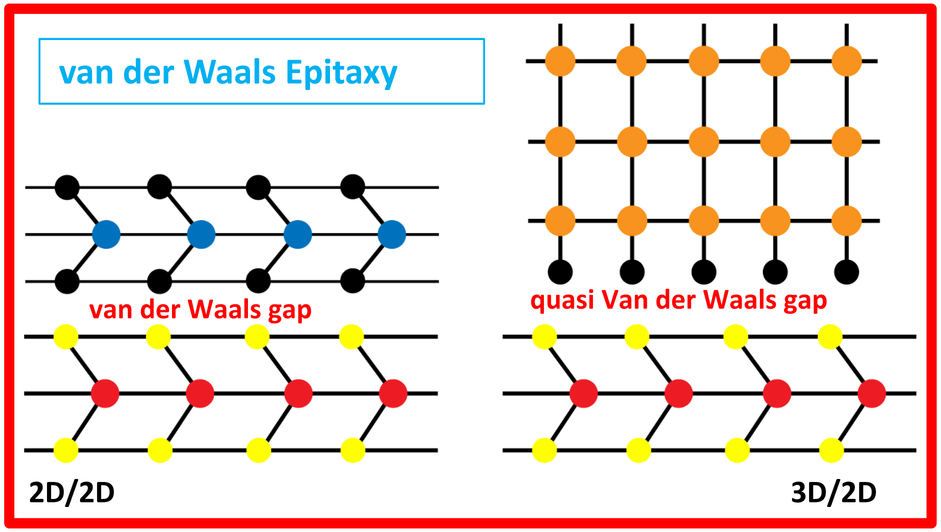
[3] Laboratory of Thermomechanical Metallurgy, School of Engineering, Ecole Polytechnique Fédérale de Lausanne, 2002 Neuchâtel, Switzerland

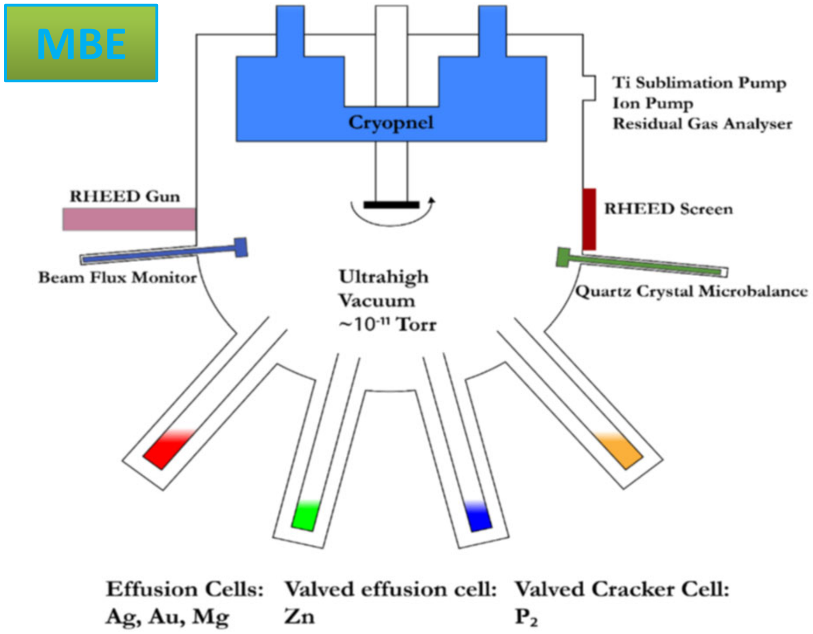
[4] Institute of Physics, School of Basic Sciences, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

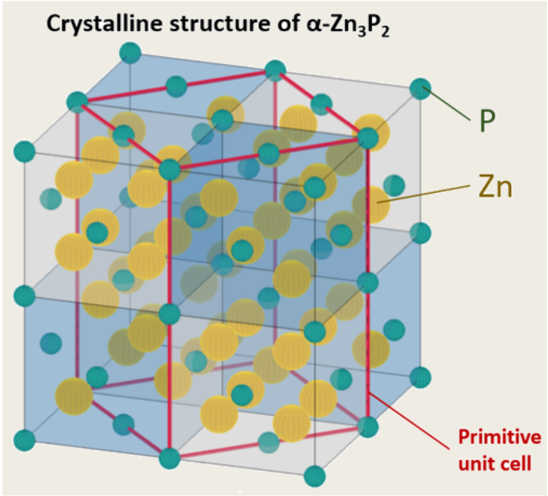




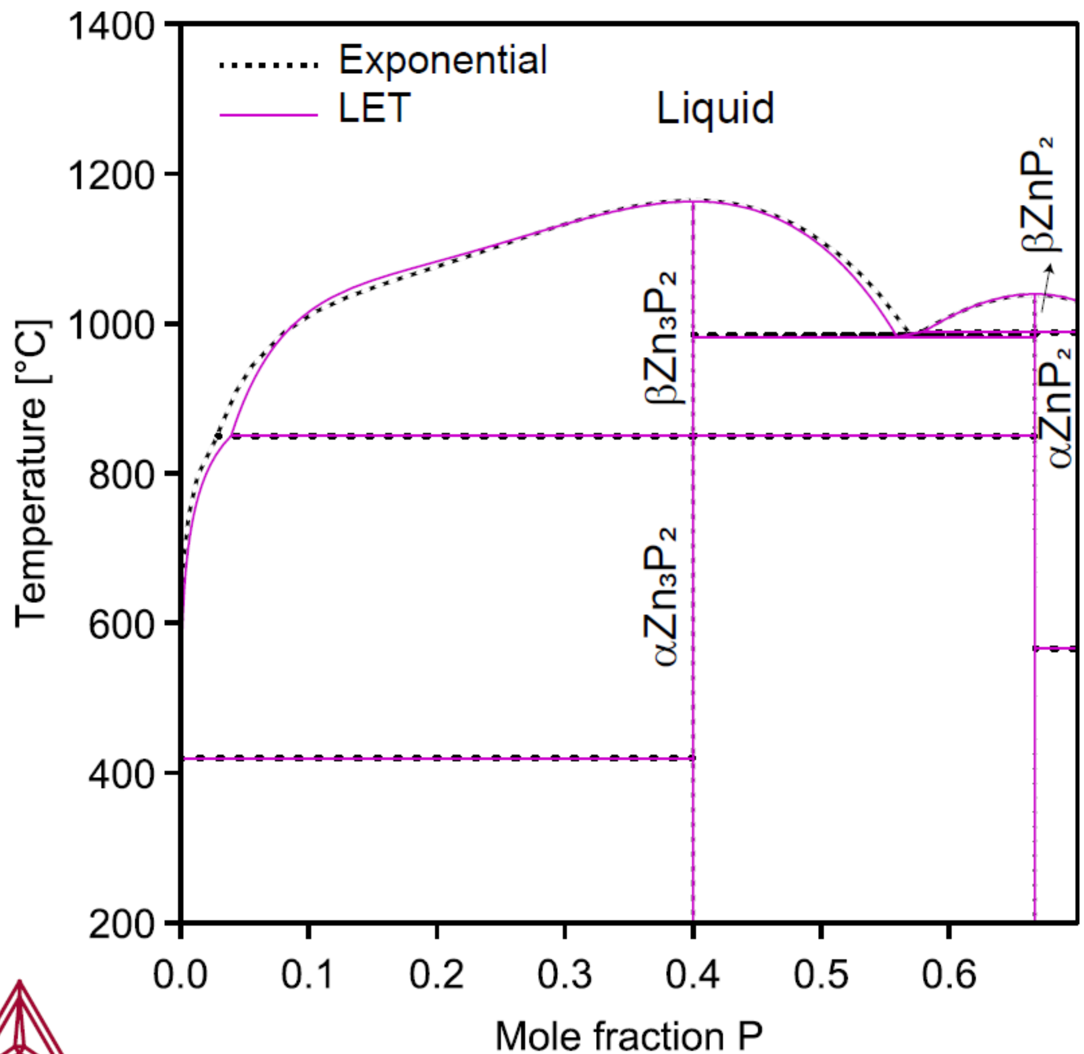
van der Waals Epitaxy of Zn_3P_2 on Graphene





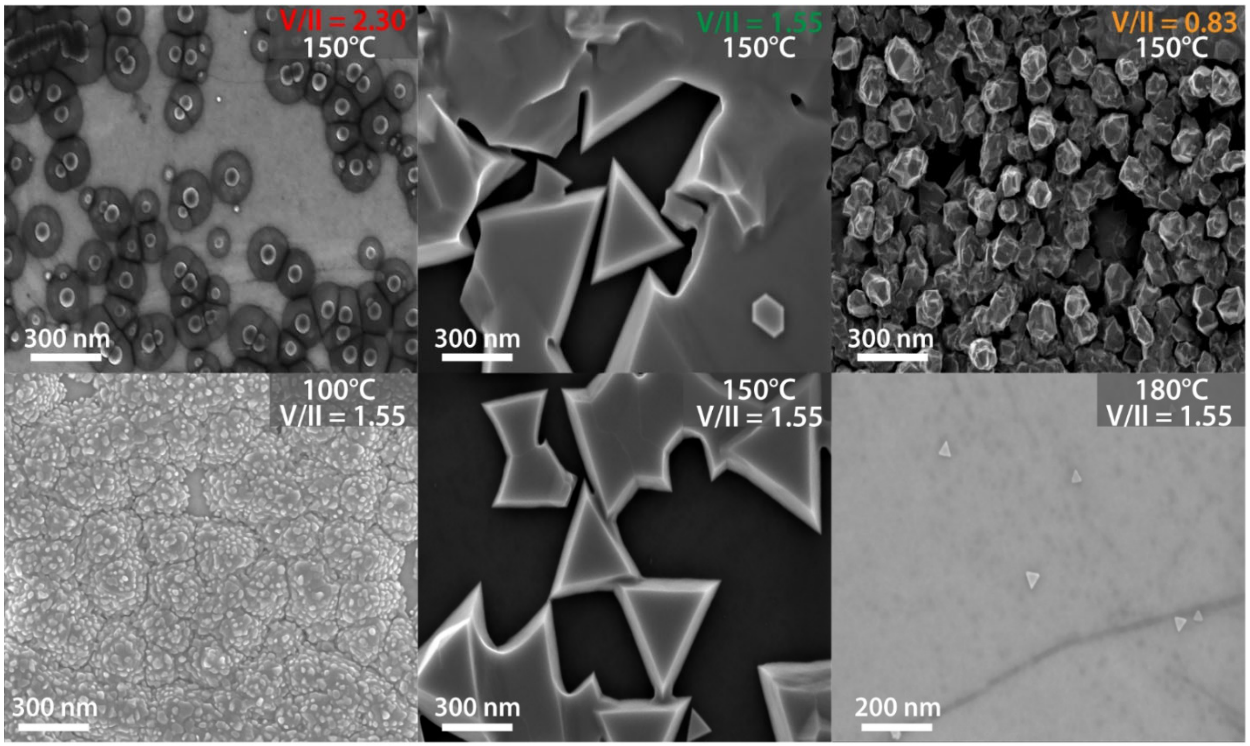


- Thermal expansion coefficient = $1.24 \times 10^{-5} K^{-1}$
- Tetragonal crystal structure : a = b = 8.097 Å and c = 11.45 Å

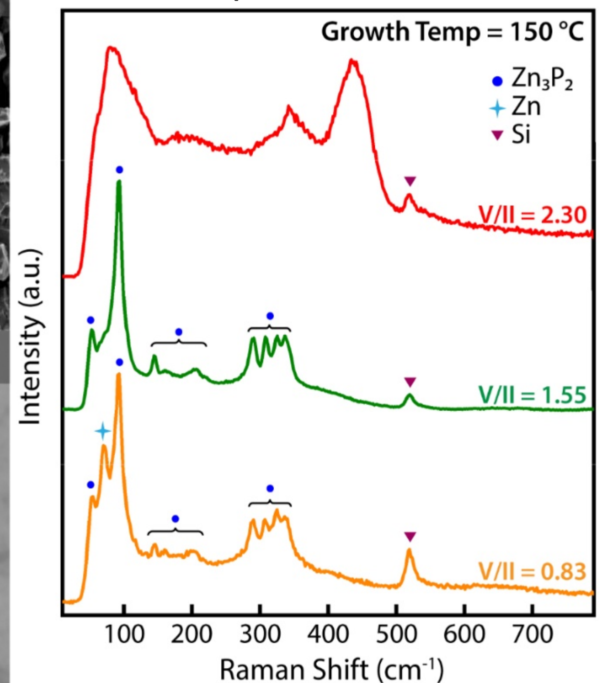


Exponential
LET
Liquid
βZnP₂
βZn₃P₂
αZnP₂
αZn₃P₂
Temperature [°C]
Mole fraction P
1400
1200
1000
800
600
400
200
0.0
0.1
0.2
0.3
0.4
0.5
0.6

Effect of Growth Parameters

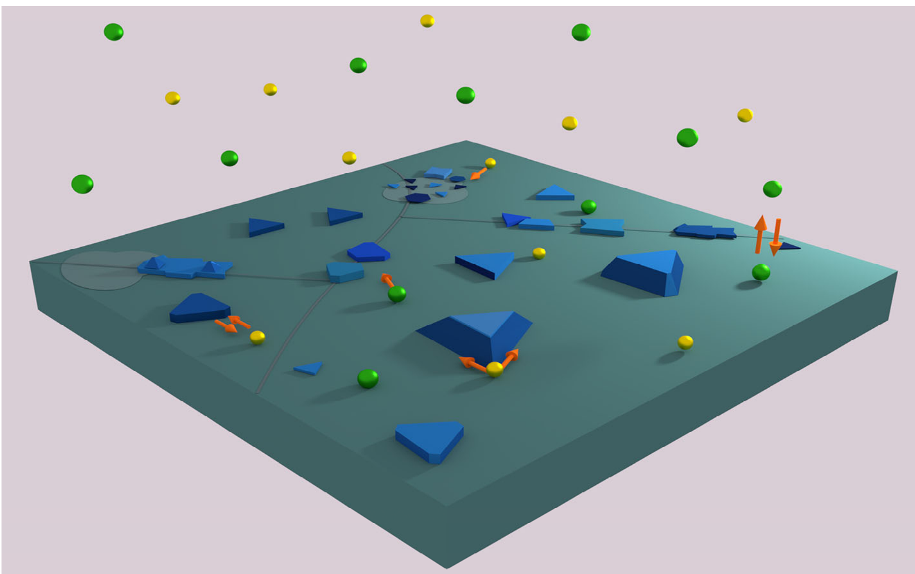


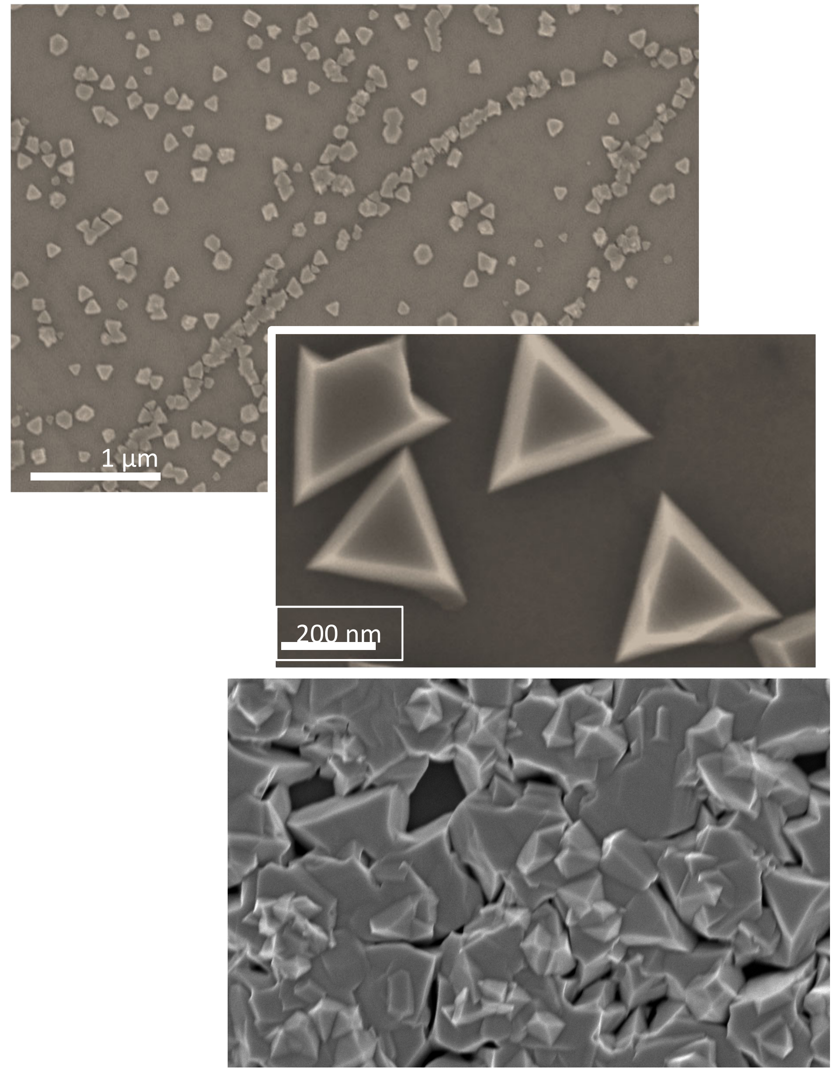
Raman spectra



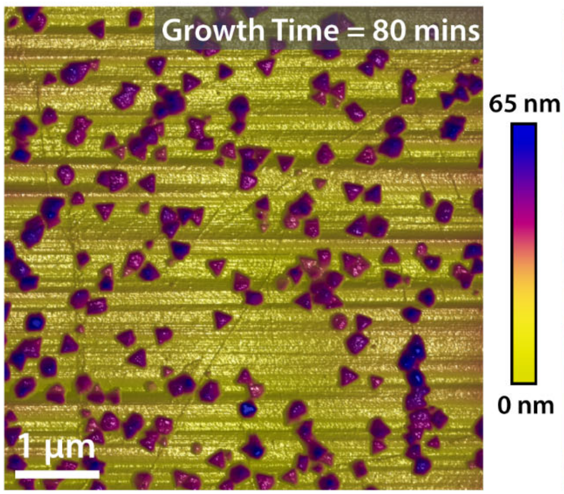
- Crystalline Zn_3P_2 observed at 150 °C and V/II = 1.55
- Temperature, V/II ratio, and total flux influences the morphology and composition

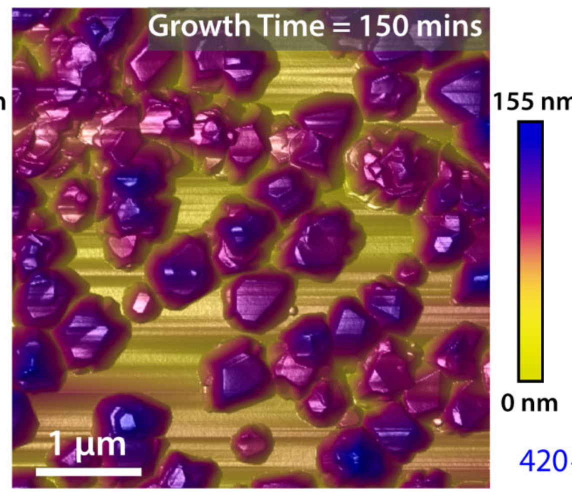
Growth Mechanism

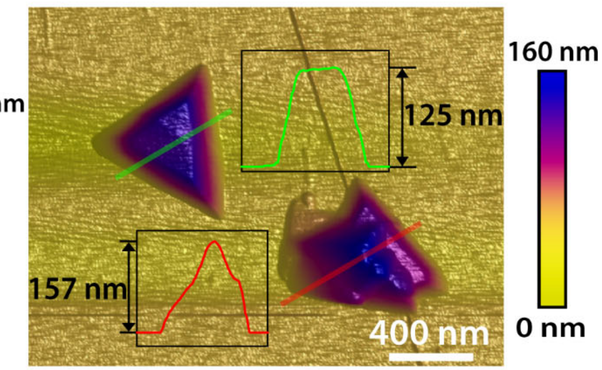


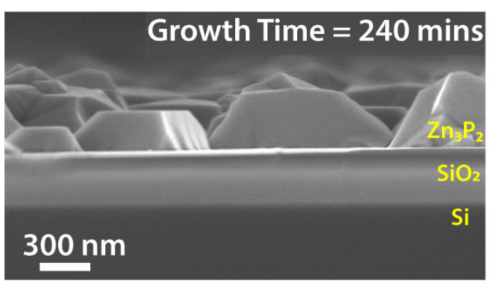


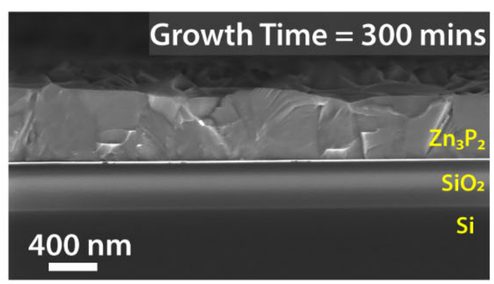
Growth Mechanism

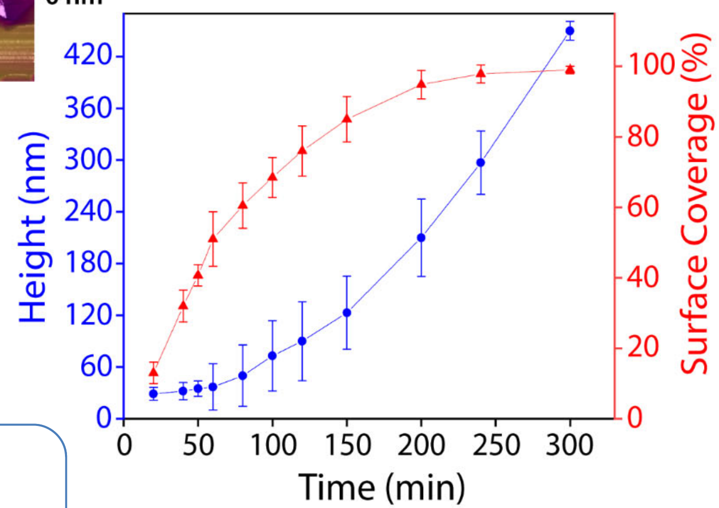






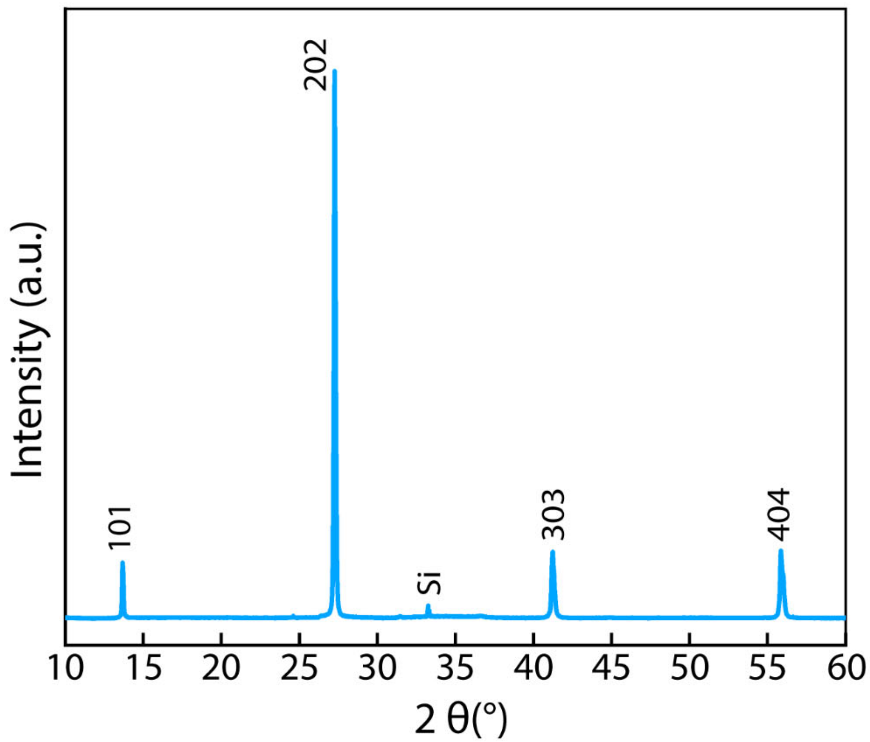


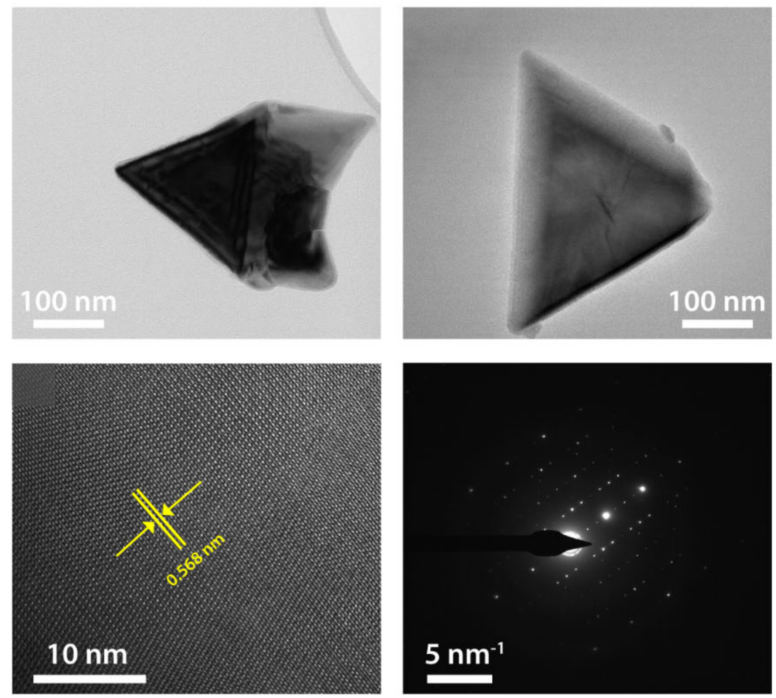




- The defects on graphene play a critical role in adsorption, and nucleation of adatoms

Structural Analysis





- The Zn_3P_2 triangular flakes, which merge to form a thin film has a strong (101) crystallographic texture