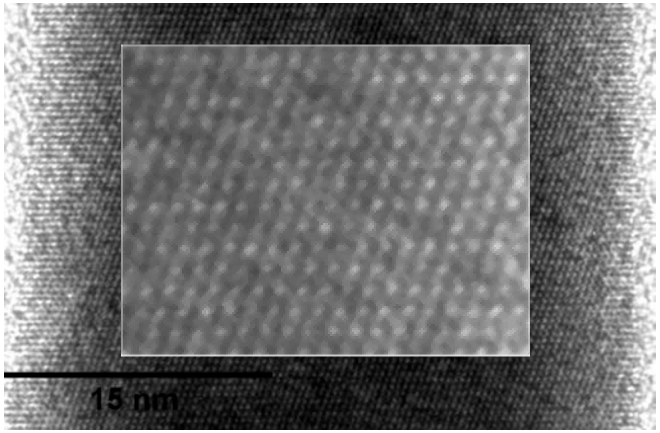
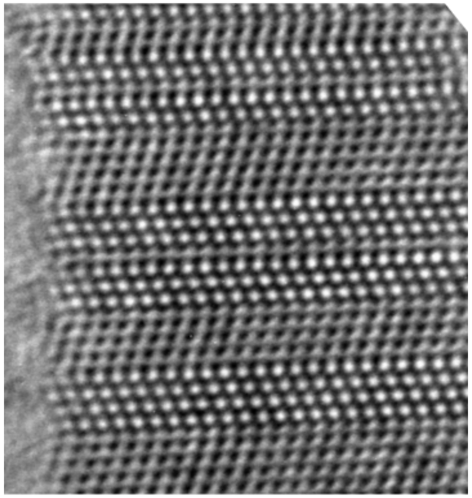
Croissance de matériaux 1D: les nanofils: La Structure Cristalline

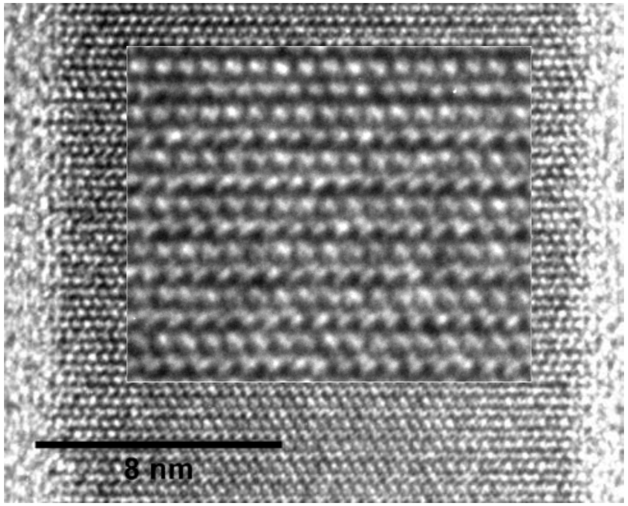
Crystal structure

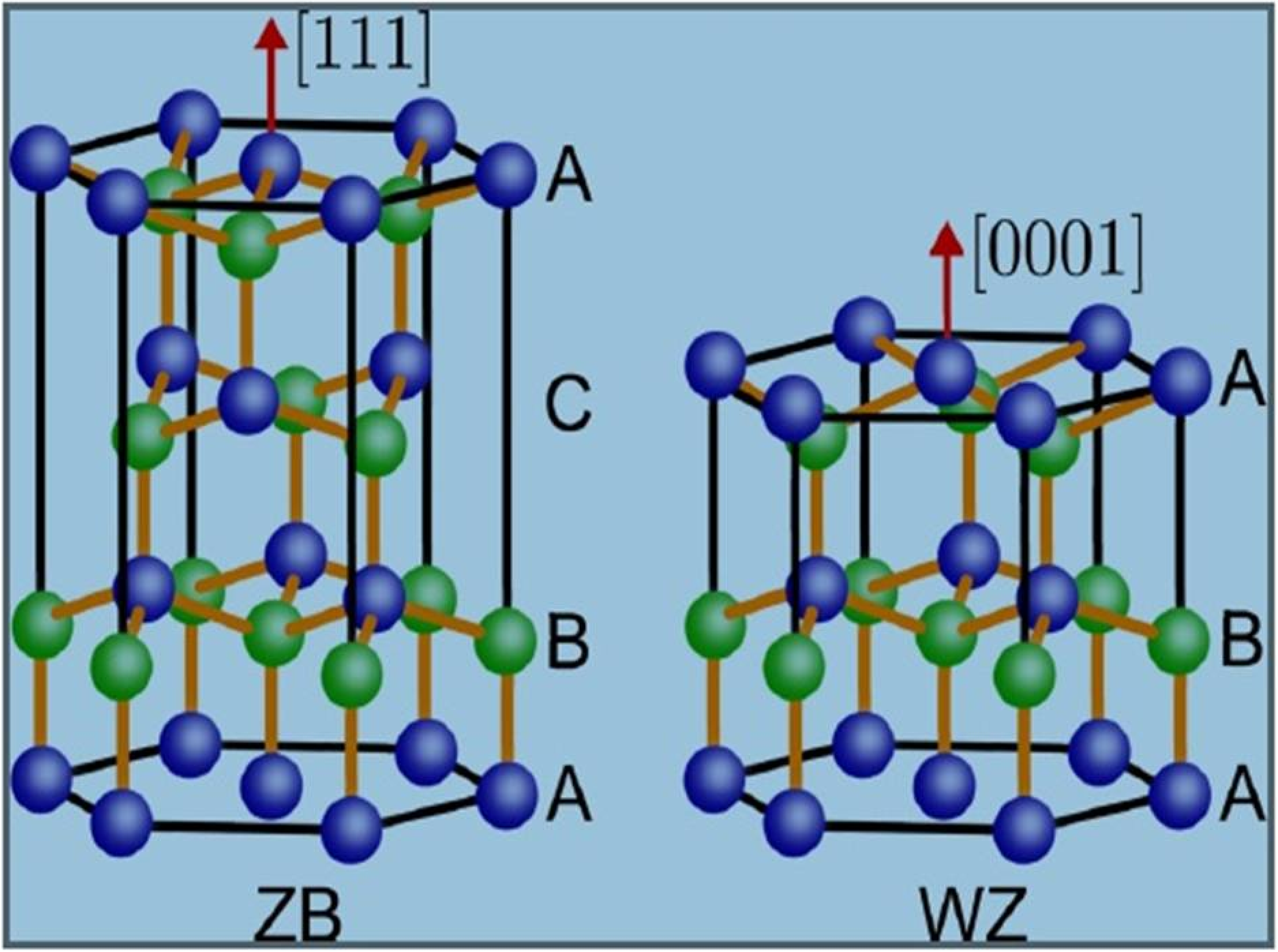
Bulk III-V materials exhibit the cubic zinc blende (ZB) structure.

In nanowires, stacking defects are very common. If these occur in sequence, the hexagonal wurtzite (WZ) structure forms.

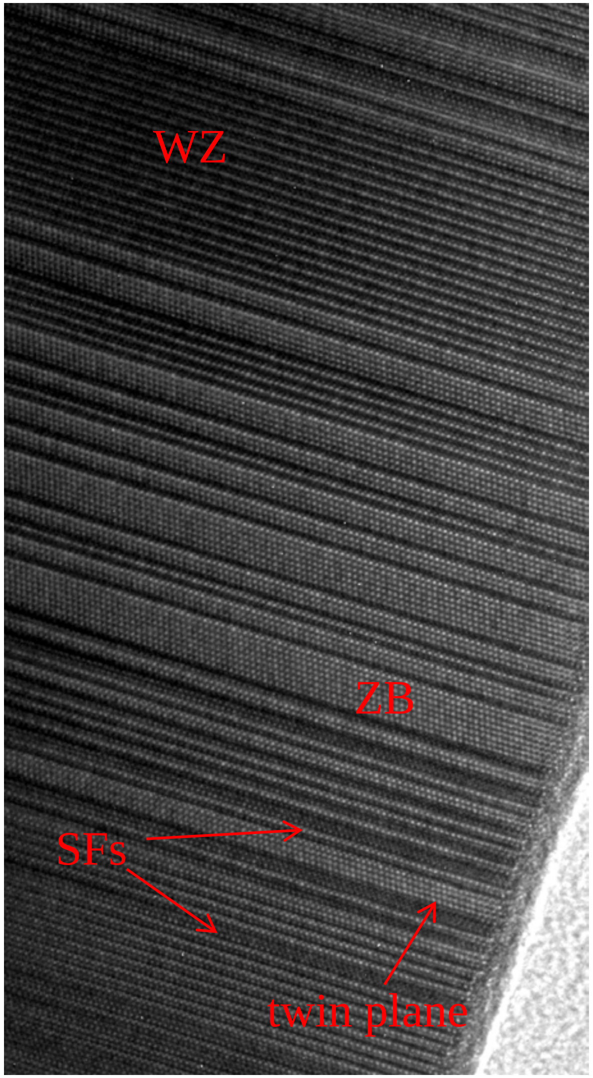


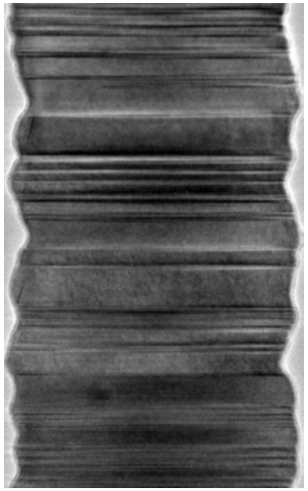





[111]
A
C
B
A
ZB
[0001]
A
B
A
WZ

Crystal Structure: without control...

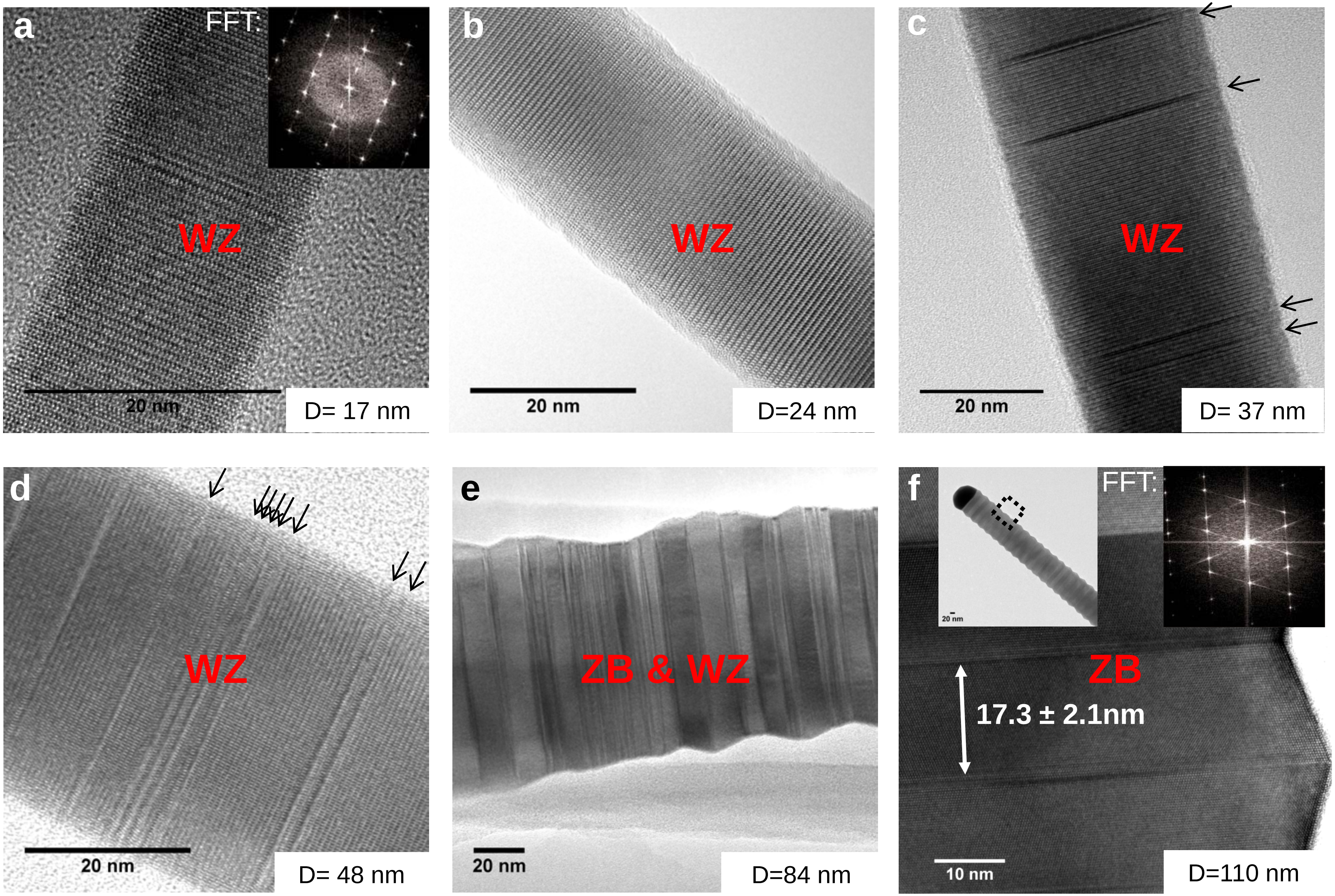




- WZ and ZB phase have different electronic bandstructure
- Stacking defects act as scattering centers for electrons
    - ➢Incompatible with advanced devices! But...
- Heterostructure devices without strain?
- Selective phonon scattering at interfaces?

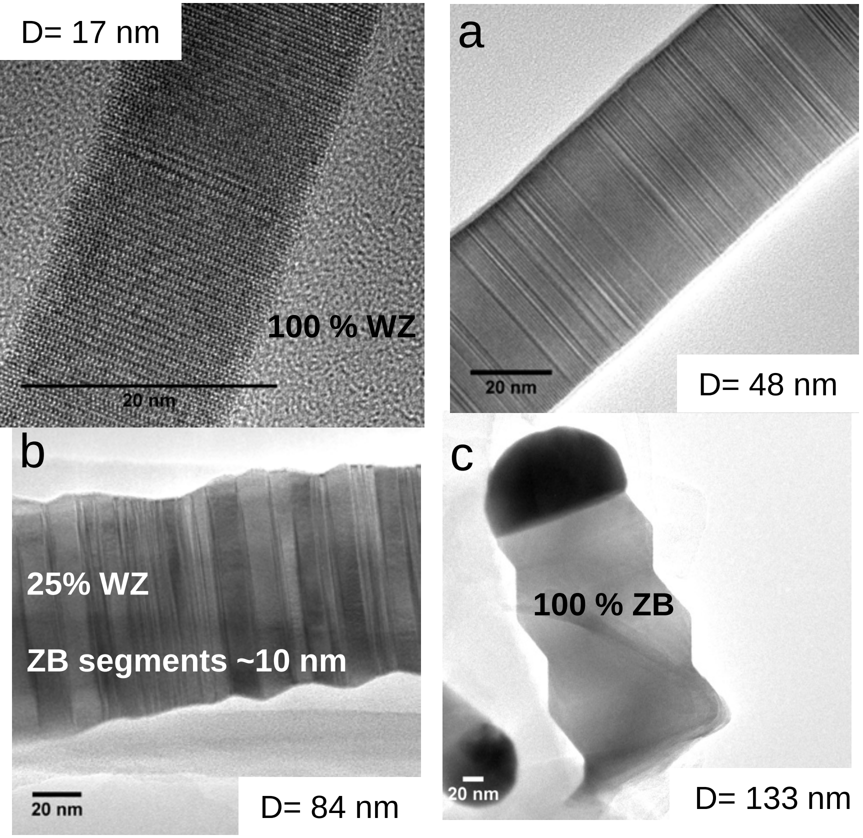
Influence of diameter on the crystal structure of InAs nanowires

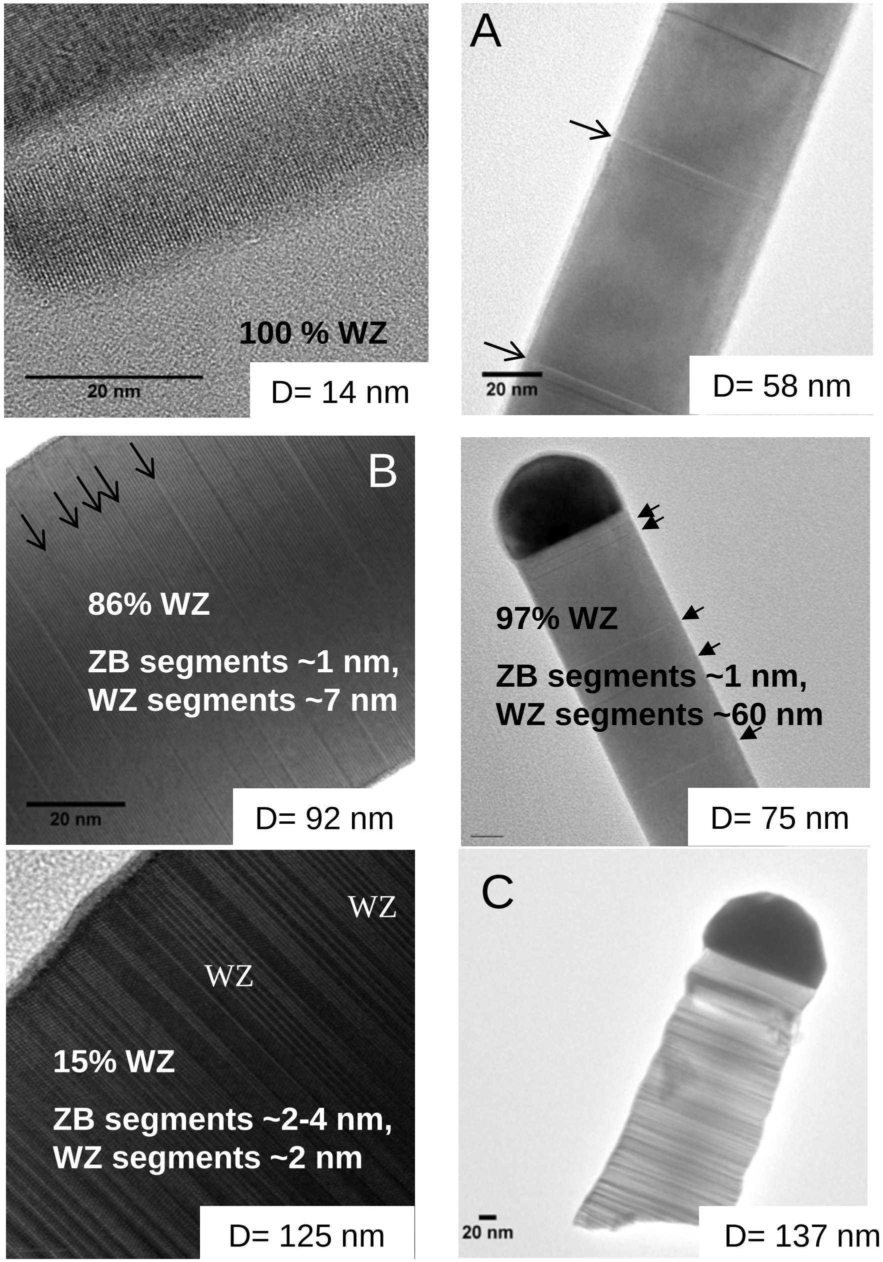
T= 460°C



Influence of temperature on the crystal structure

460°C → **420°C**

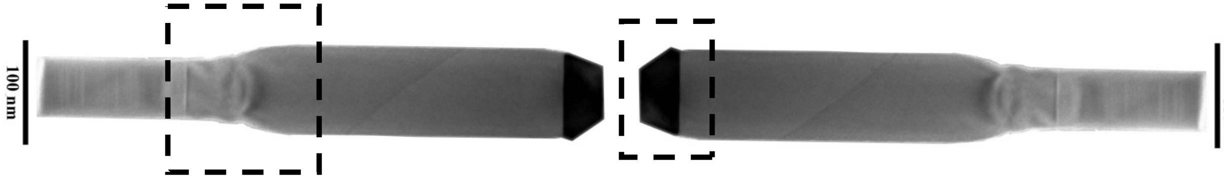




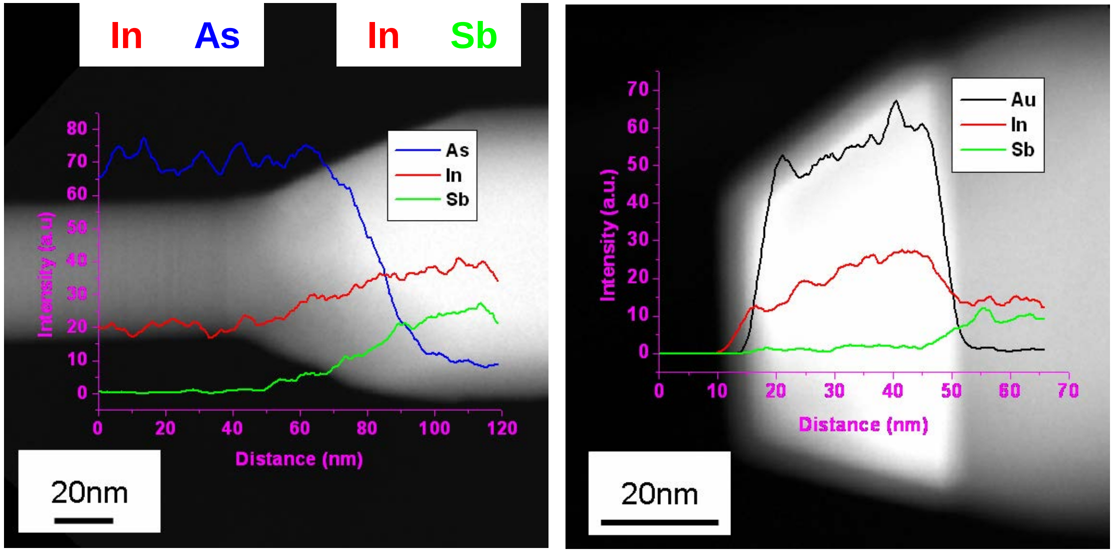
- Small diameters: pure WZ in all cases
- Medium/large diameters:

Lower growth temperature → more pronounced WZ phase

Structural characterization : X-EDS



Line-scan analysis:

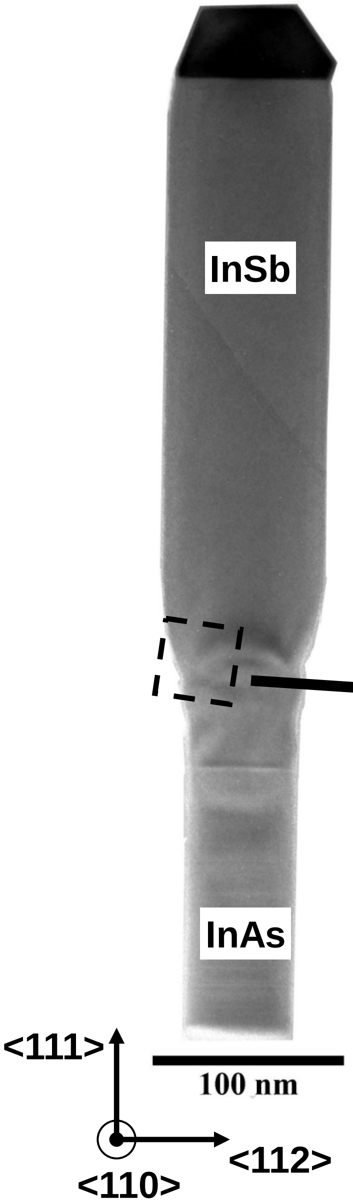


Point analysis:

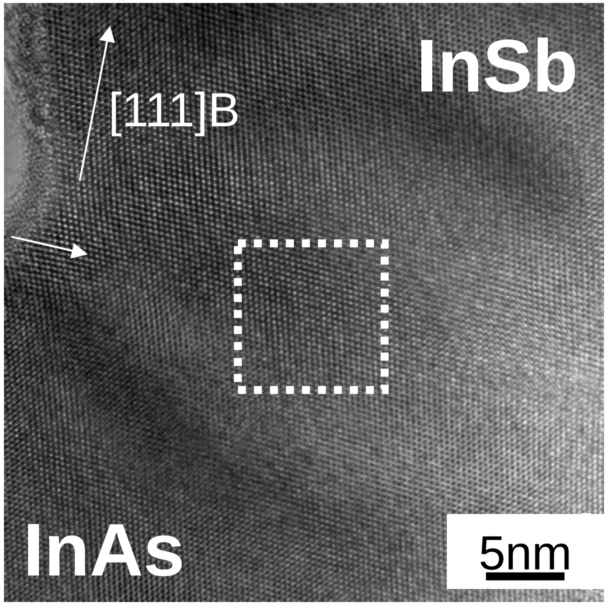
	InAs segment	InSb segment	particle
In (at. %)	49.5 ± 0.6	49.3 ± 1.3	68.0 ± 0.8
As (at. %)	50.5 ± 0.6	2.2 ± 0.3	
Sb (at. %)		48.5 ± 1.1	3.5 ± 0.6
Au (at. %)			28.5 ± 0.8

Pure InAs InSb(As) Close to AuIn$_2$

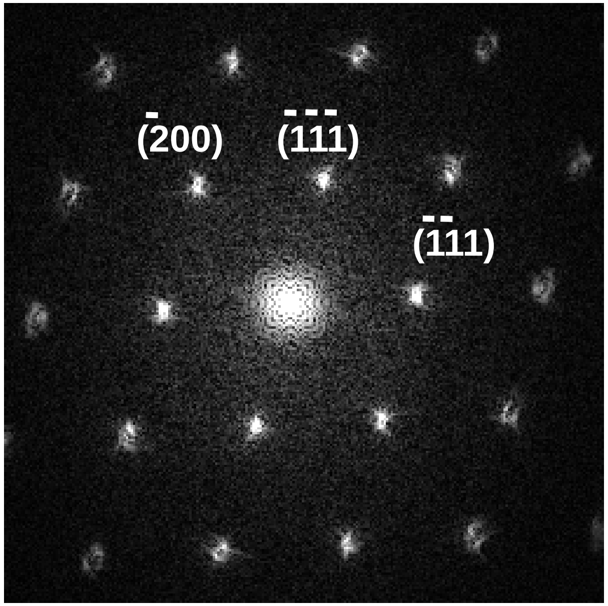
Structural characterization: High Resolution TEM



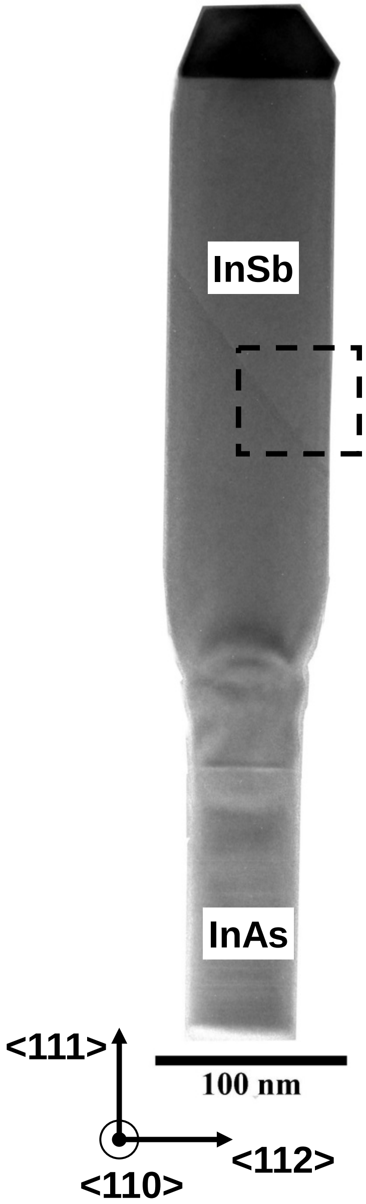
- Strain field visible due to high lattice mismatch (~7%)
- Very abrupt interface between InAs and InSb
- No stacking fault or other defect at the interface in any nanowire investigated



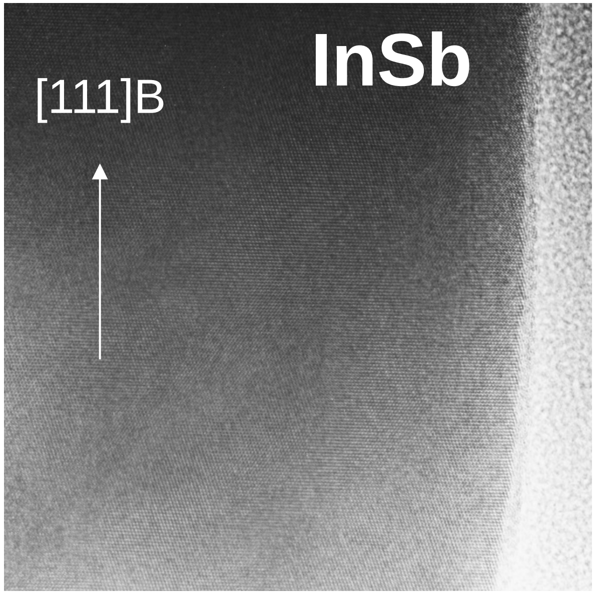
FFT of the selected area

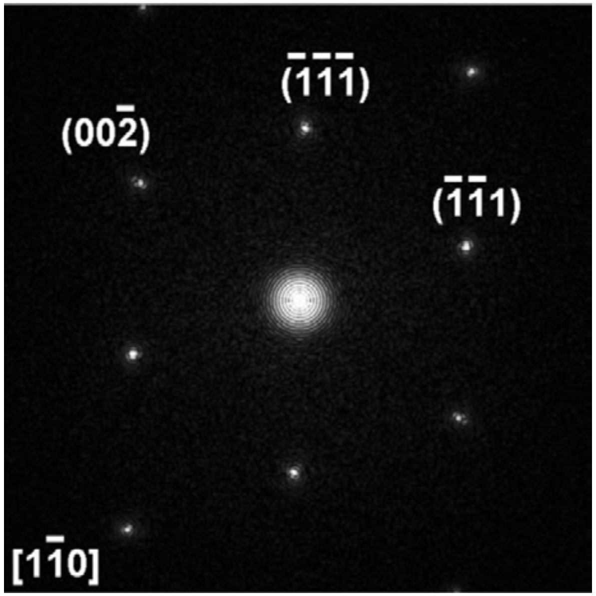


Structural characterization: High Resolution TEM

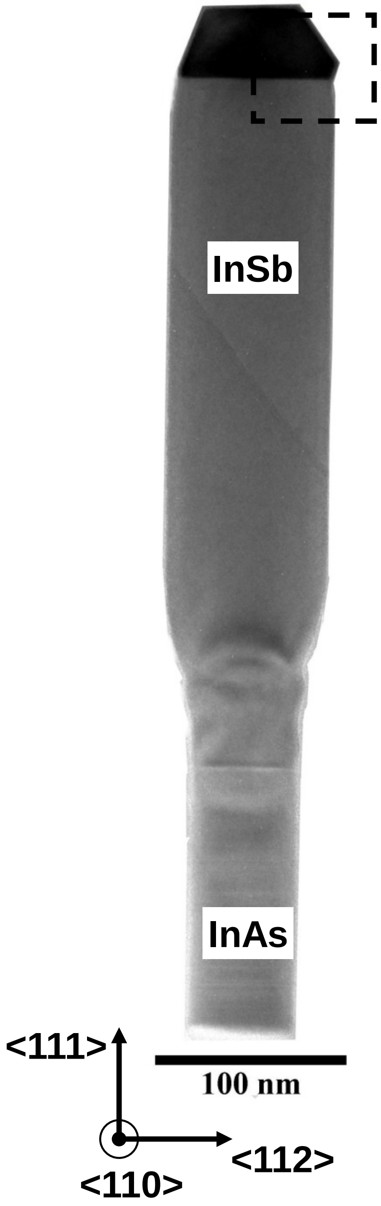


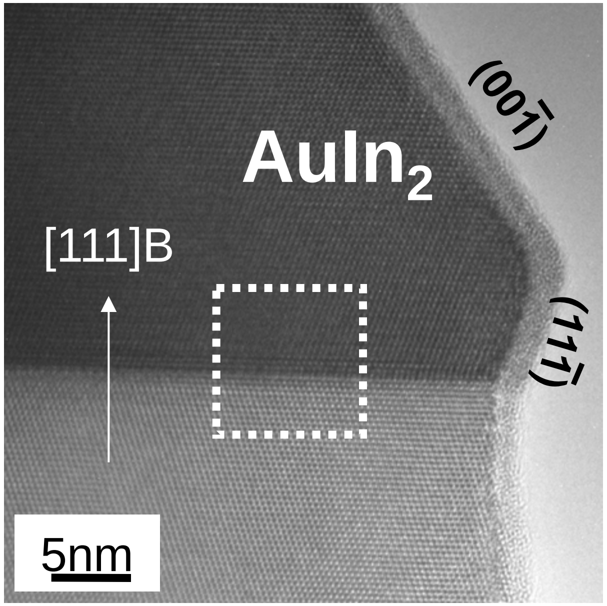
- InSb crystal is in a pure Zinc-Blende (ZB) phase
- No stacking fault or other defects ever observed in InSb

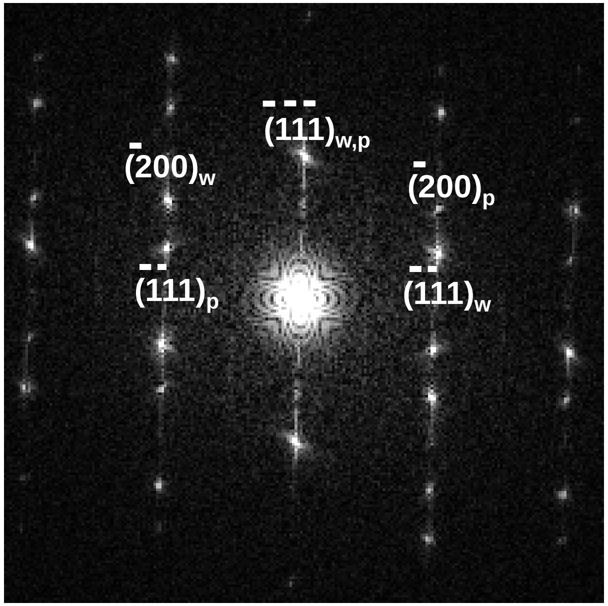




Structural characterization: High Resolution TEM

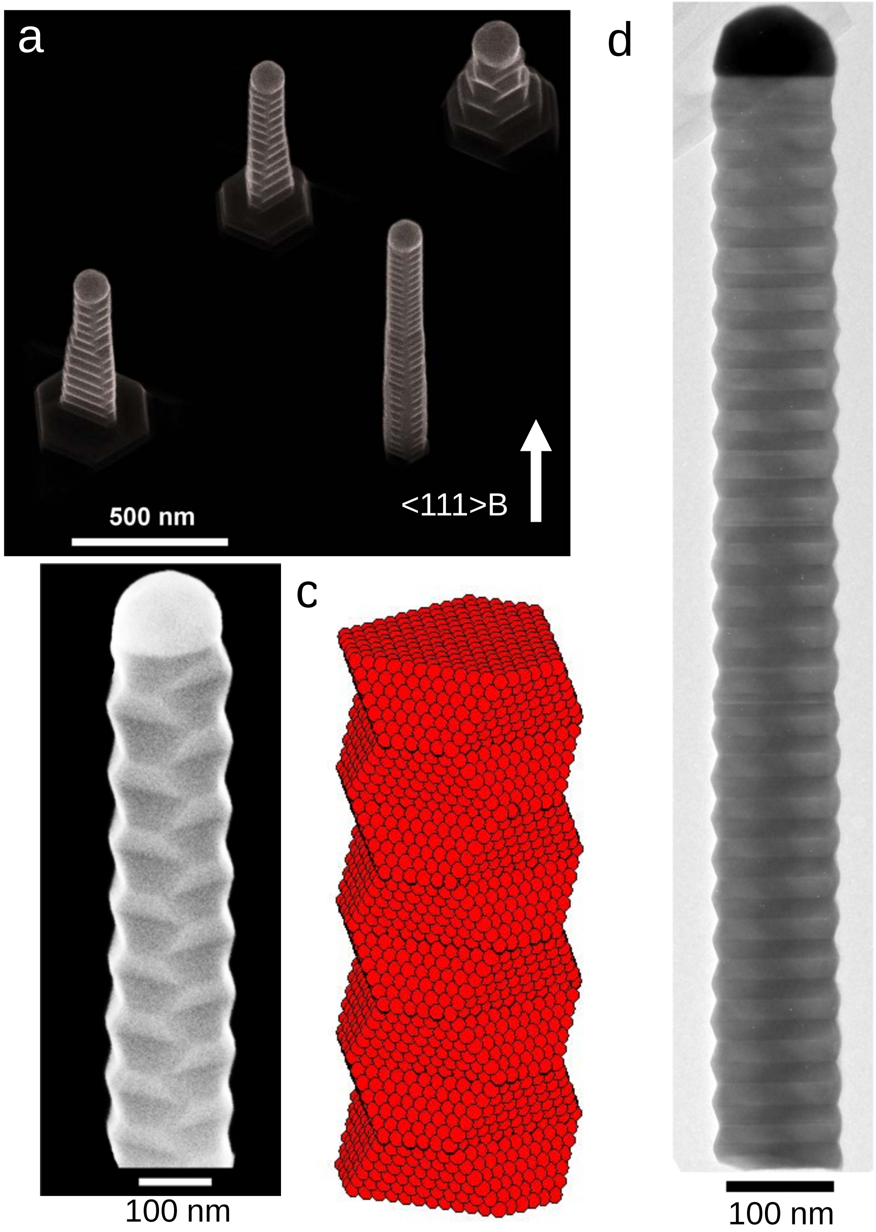


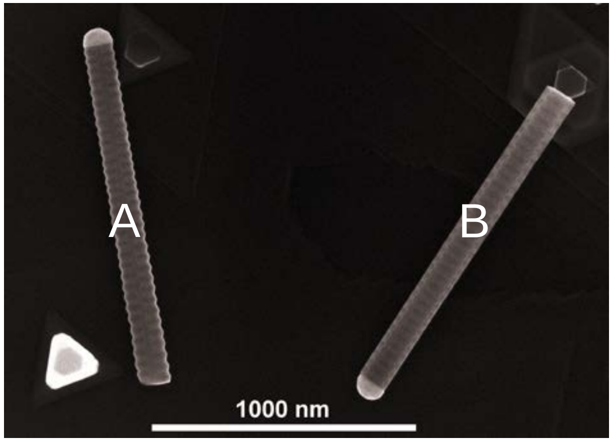


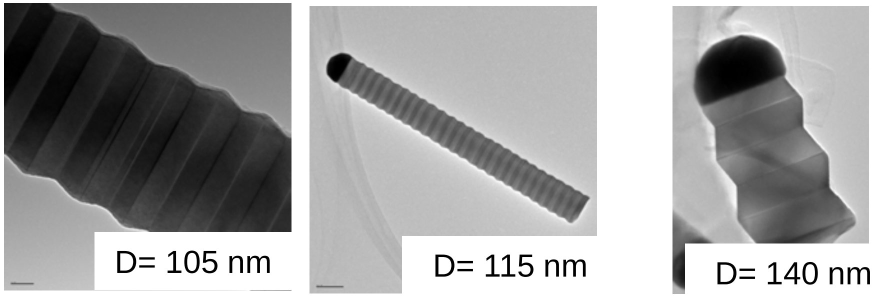


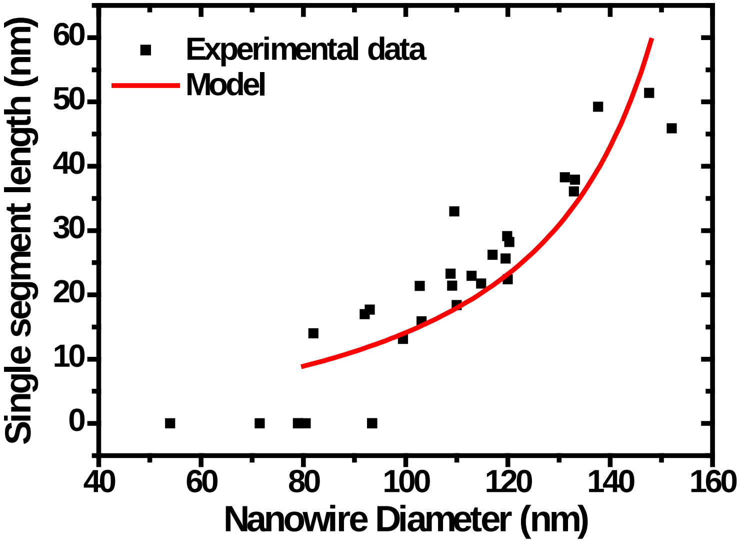
- Single crystalline $AuIn_2$ particle having a cubic structure matching CaF_2 (lattice fringes separation)
- Lattice-matching to the InSb nanowire segment (within 0.4%)

Twin plane superlattices (TPS) in InAs

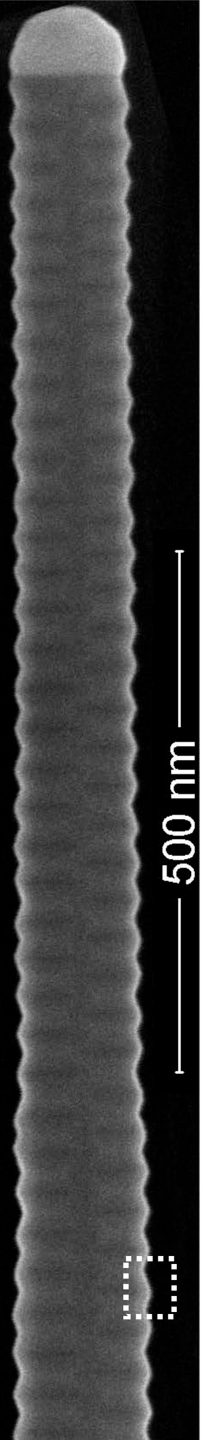


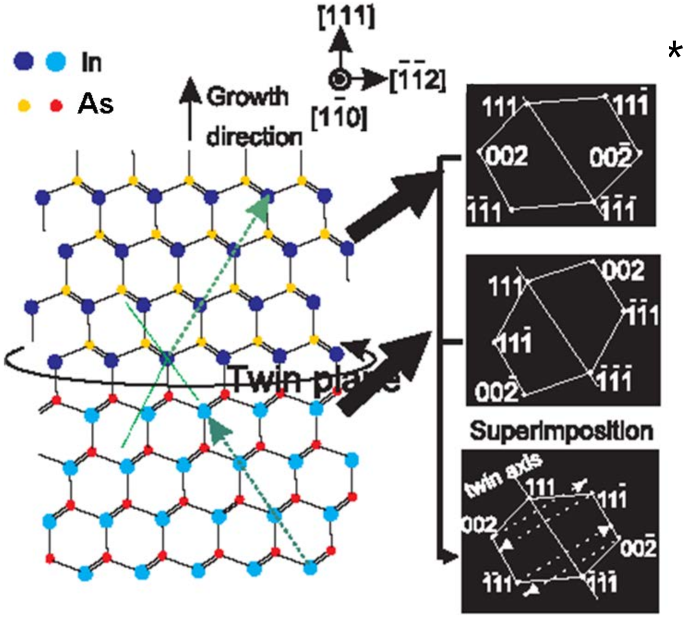


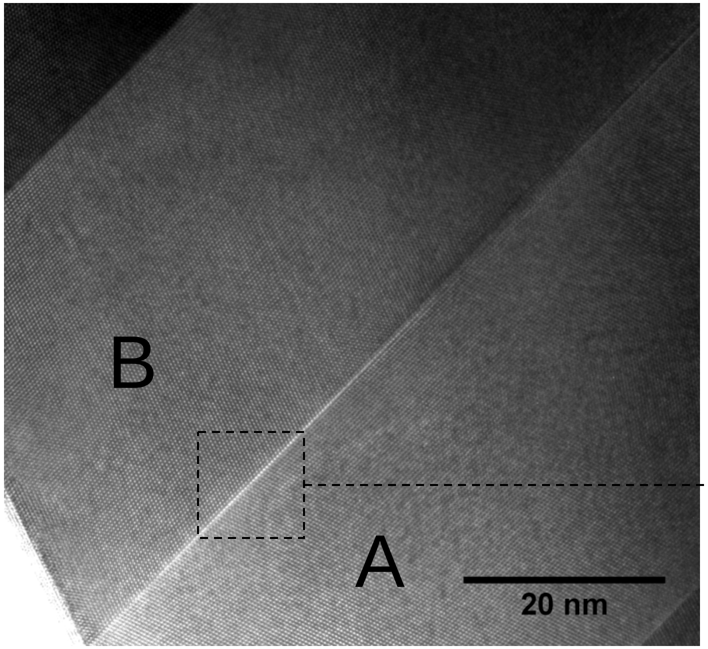




Crystal structure detailed

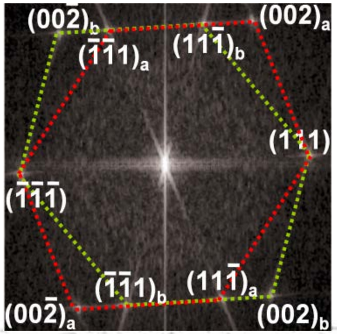


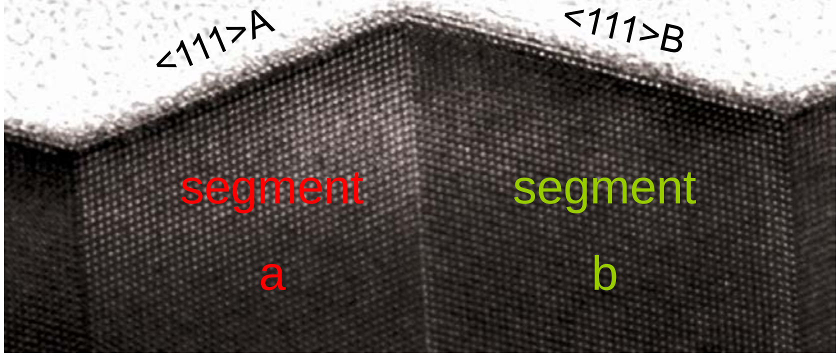


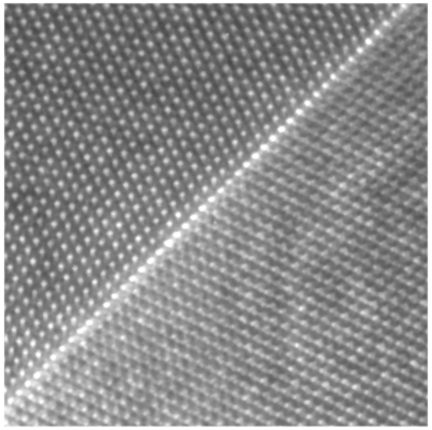


Perfection of the twin plane superlattice <= ± 3 atomic rows along 20 periods

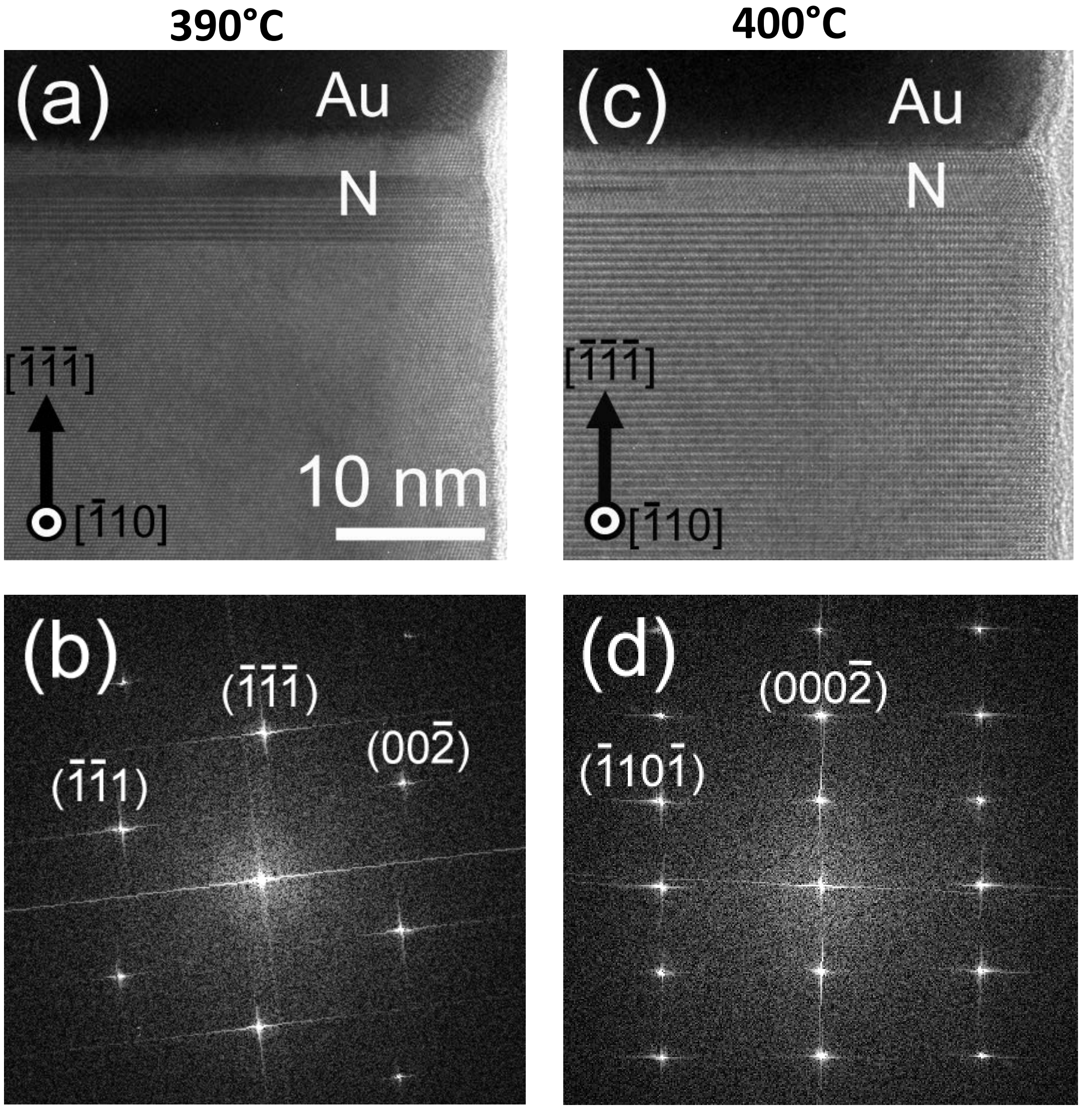
<111>B







Abruptness of structure change

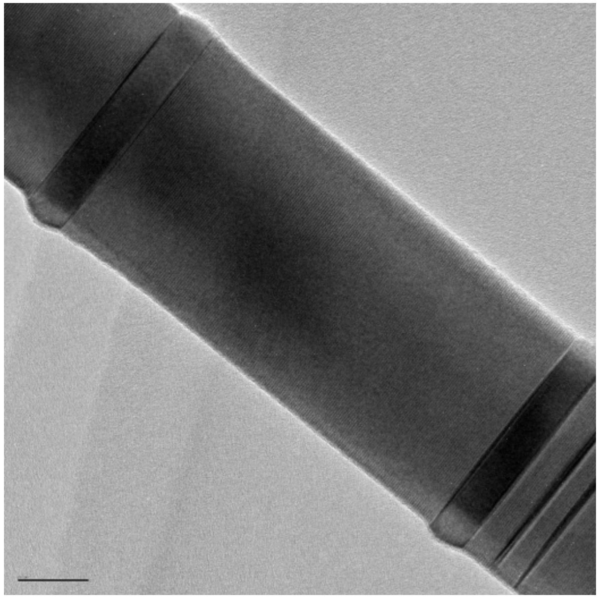


- InAs structure changes from pure ZB to pure WZ over 10 ^{o}C

- This suggest a phase change : either of the particle, or of the side facets/side facet reconstruction

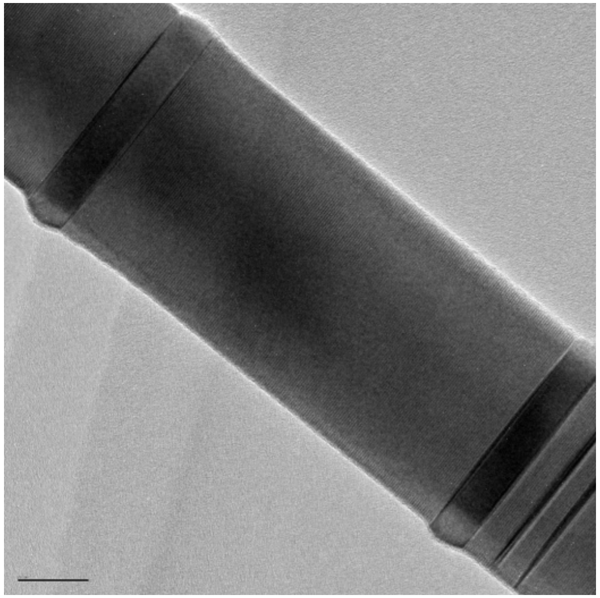
- The region directly below the gold particle (‘neck region’, N) has the opposite crystal structure

Precise structural tuning…



ZB quantum dots in WZ nanowire

Precise structural tuning…



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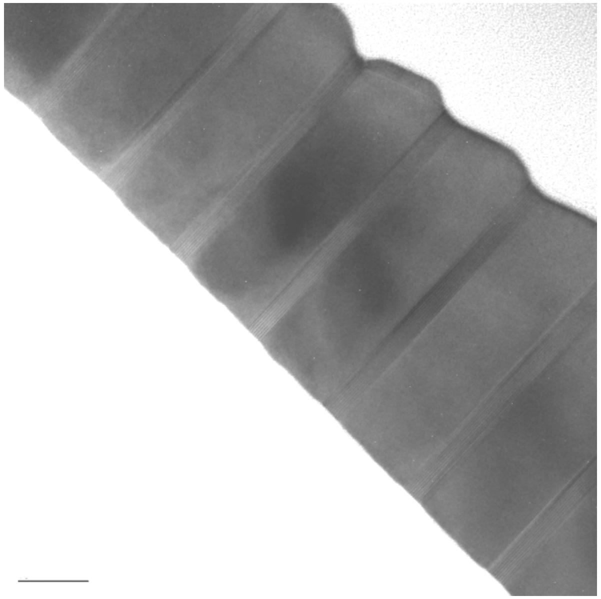
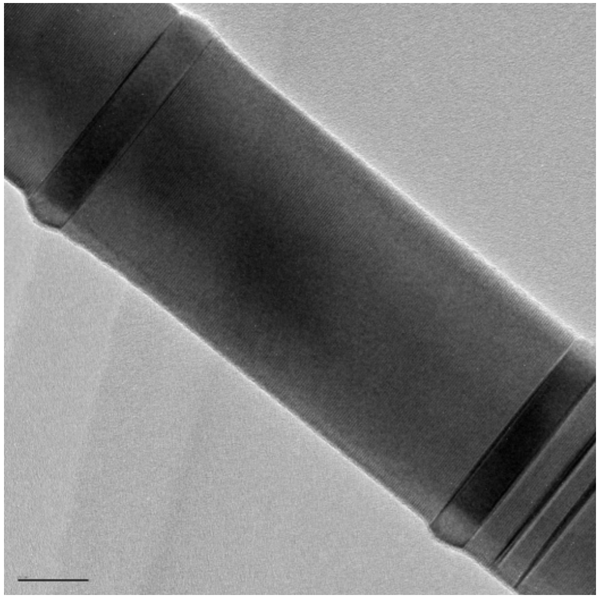


WZ barriers separating ZB quantum dots

Precise structural tuning…



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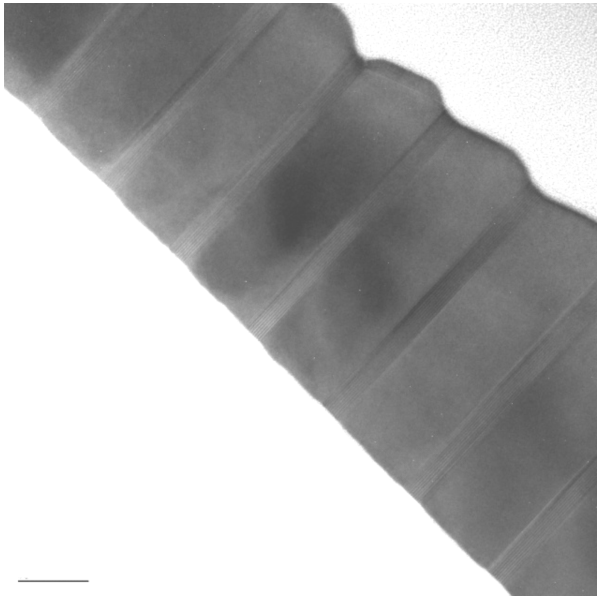

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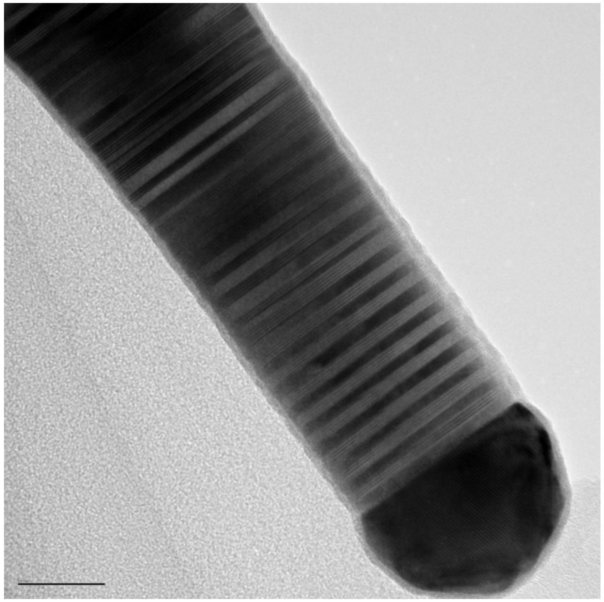
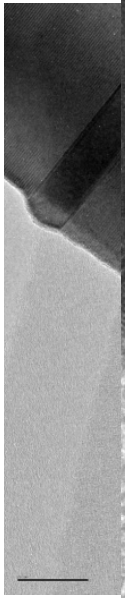
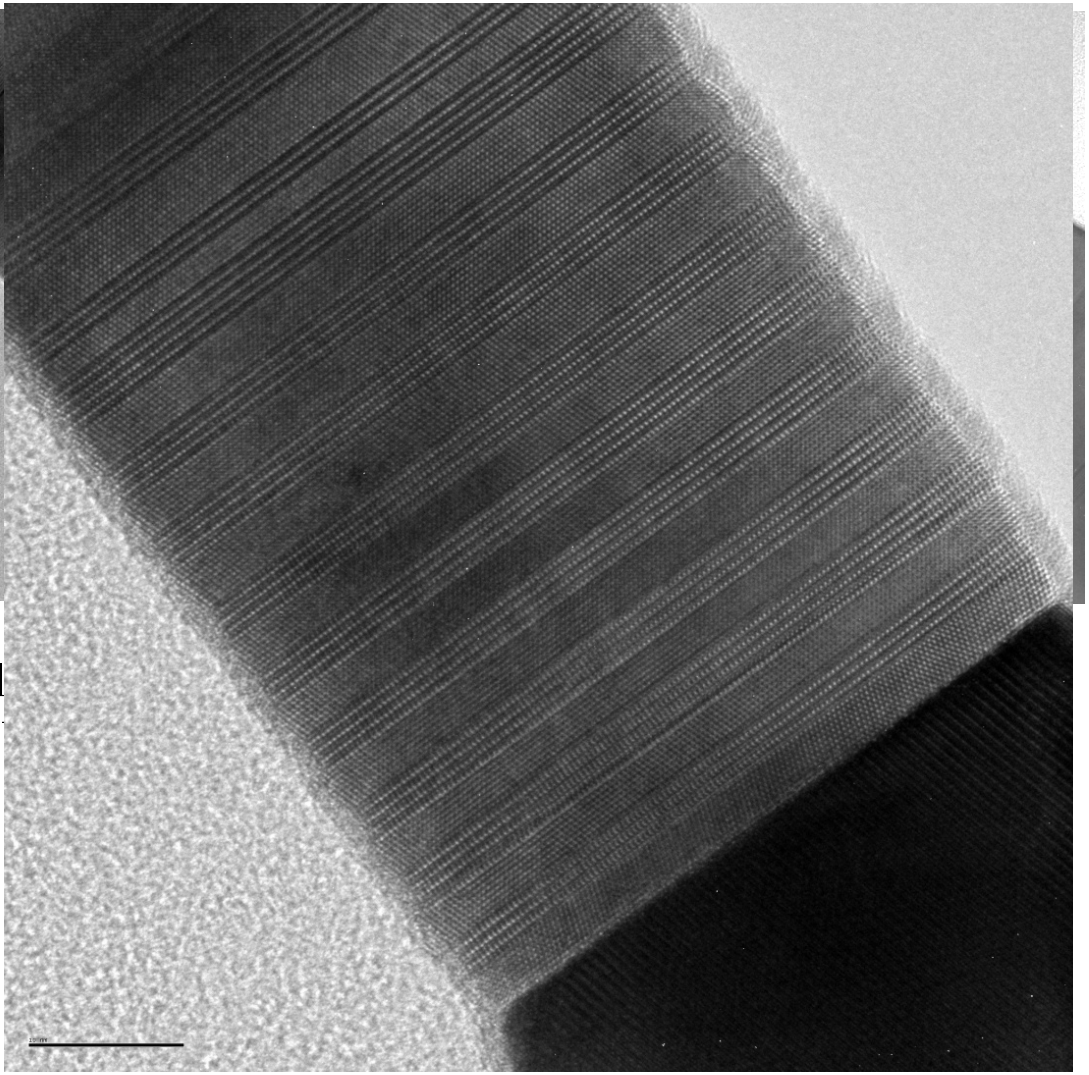


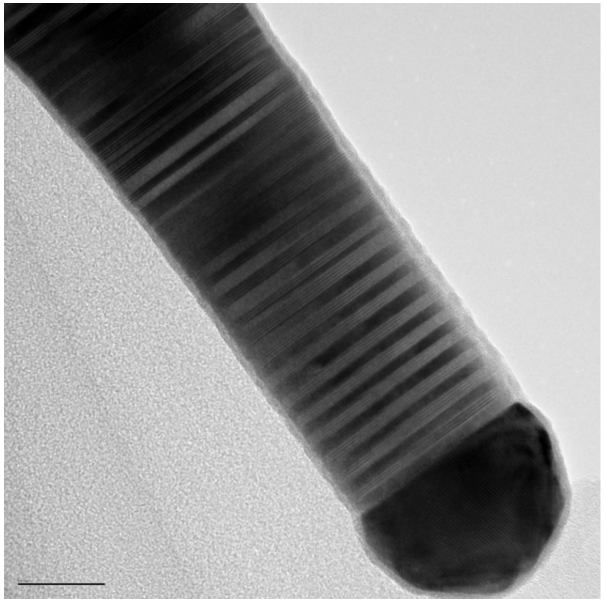
ZB-WZ superlattice

Precise structural tuning…



ZB q
nano



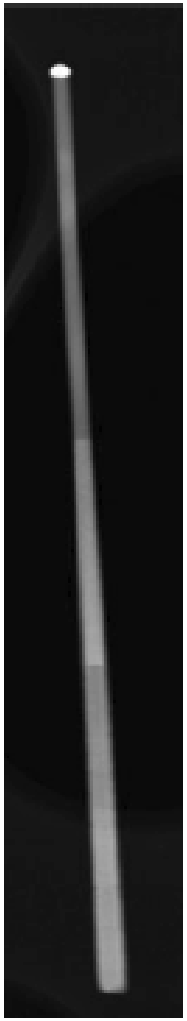


ZB-WZ superlattice

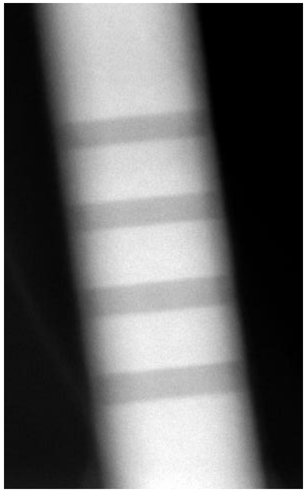
WZ segments 8 atomic bilayers
ZB segments 8 atomic bilayers

Croissance de matériaux 1D: les nanofils:
Les Hétérostructures

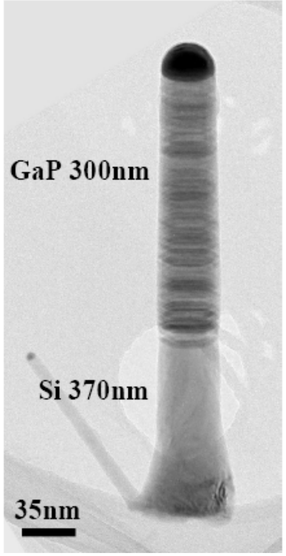
Heterostructures – lattice mismatch



GaAs-GaP



InAs-InP



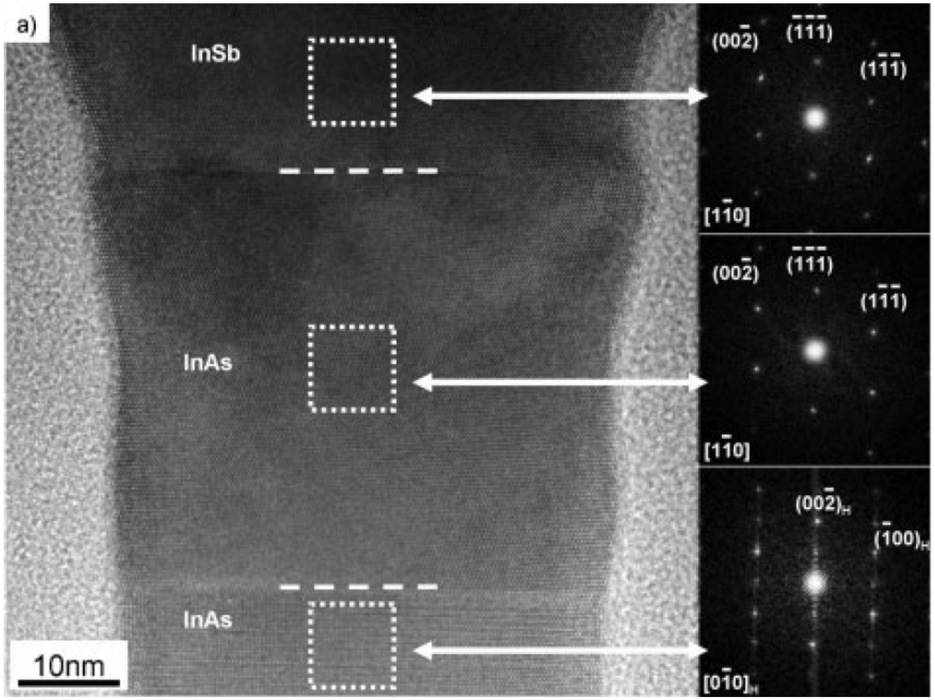
Si-
GaP

Heterostructures combinations not generally limited by lattice matching

Materials such as InAs-InP and GaAs-GaP can be combined (both 3% mismatch)

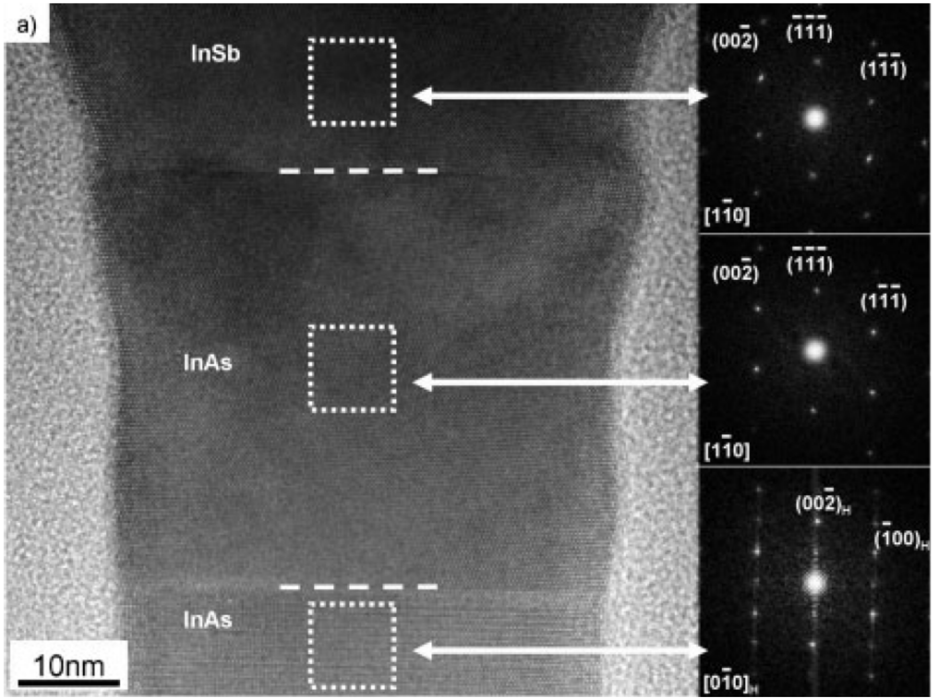
Similarly, materials from different families (such as GaP-Si) can be combined

Limits of mismatch accommodation



InAs-InSb (mismatch 6.9%) : wires with diameter ~50 nm usually have defect-free interfaces

Limits of mismatch accommodation



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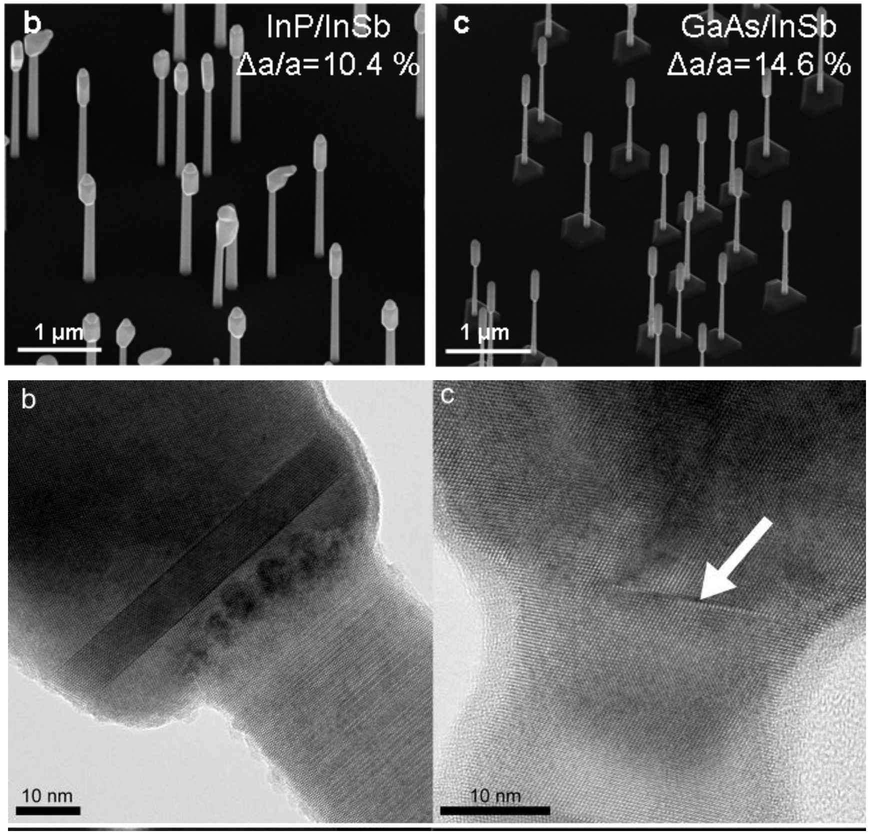
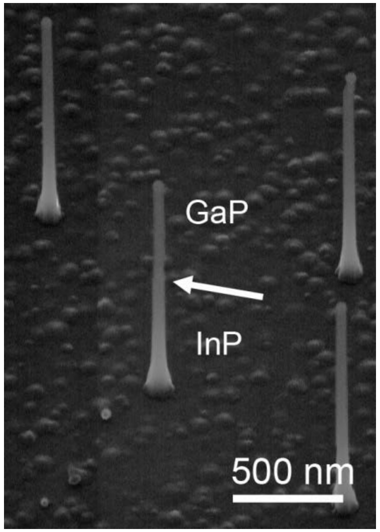
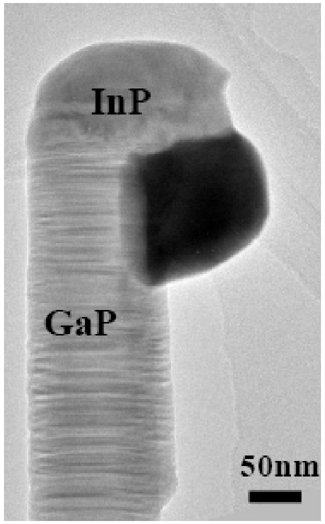


InP-InSb and GaAs-InSb: 50 nm wires most often have interface defects – but still most often straight and epitaxial

Heterostructure Nanowires

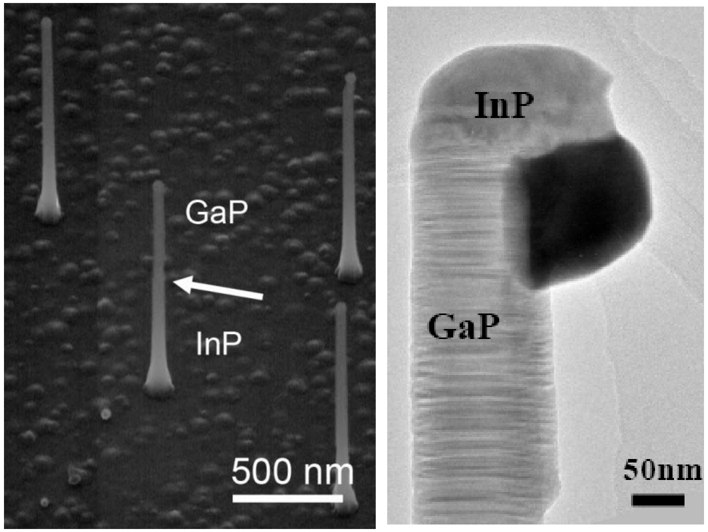


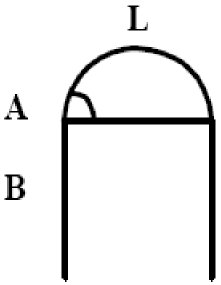


Heterostructure combinations not limited by lattice matching

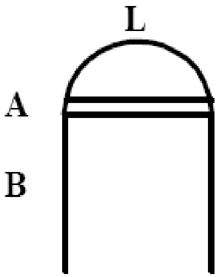
However wires often grow straight in only one direction!

Heterostructure Nanowires





$E_{AL} + E_{AB} > E_{BL}$ **hence kinked wire**



$E_{AL} + E_{AB} < E_{BL}$ **hence straight wire**

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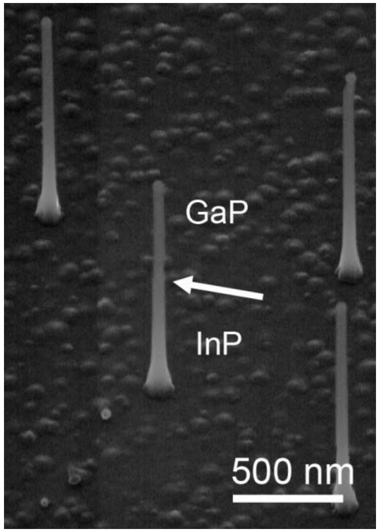
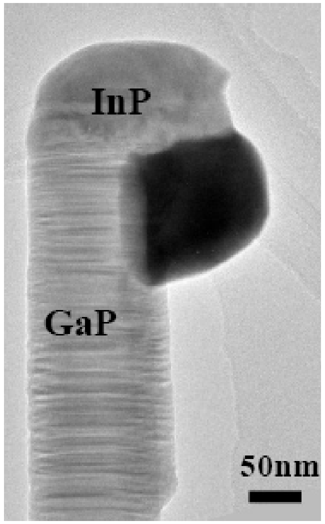
Heterostructure Nanowires





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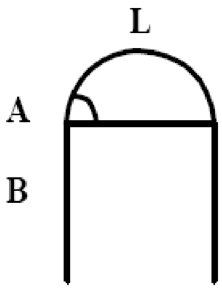

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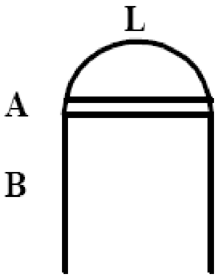

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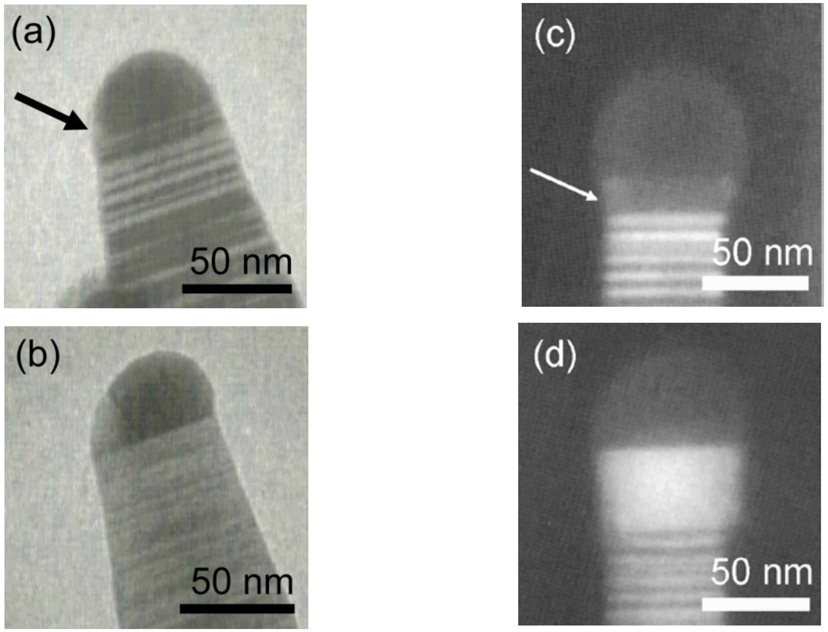
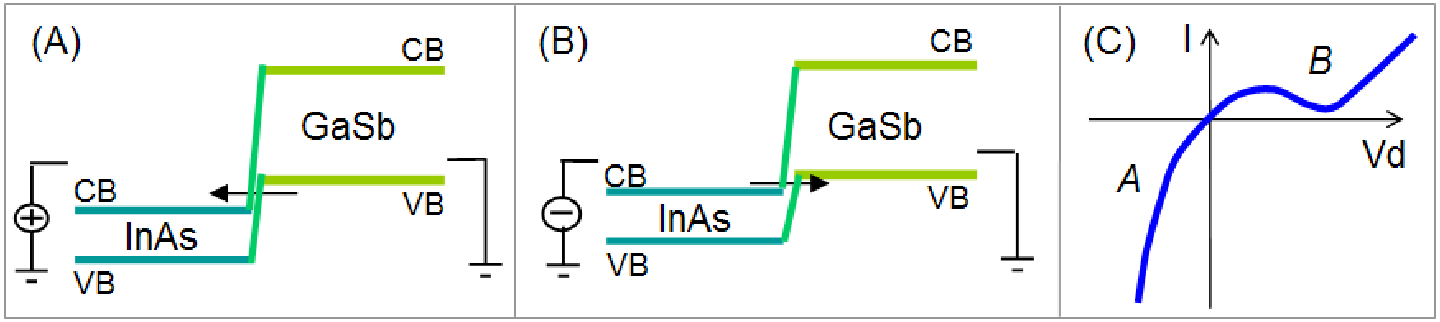


Material combinations

Material A	Material B	Material A Lattice Constant (Å)	Material B Lattice Constant (Å)	Nucleus Type: B on A	Nucleus Type: A on B	Mismatch (%)
AlAs	GaAs	5.6605	5.6533	kinked	straight	-0.13
AlAs	GaP	5.6605	5.4512	kinked	straight	-3.70
AlAs	InAs	5.6605	6.0584	kinked	straight	7.03
AlAs	InP	5.6605	5.8686	kinked	straight	3.68
GaAs	GaP	5.6533	5.4512	straight	straight	-3.57
GaAs	GaSb	5.6533	6.0959	straight	kinked	7.83
GaAs	Ge	5.6533	5.6461	straight	-	-0.13
GaAs	InAs	5.6533	6.0584	kinked	straight	7.17
GaAs	InP	5.6533	5.8686	kinked	straight	3.81
GaAs	InSb	5.6533	6.4790	straight	kinked	14.61
GaAs	Si	5.6533	5.4310	straight	kinked	-3.93
GaP	InAs	5.4512	6.0584	kinked	straight	11.14
GaP	InP	5.4512	5.8686	kinked	straight	7.66
GaP	Ge	5.4512	5.6461	kinked	-	3.58
GaP	Si	5.4512	5.4310	kinked	straight	-0.37
InAs	InP	6.0584	5.8686	straight	kinked/straight[a]	-3.13
InAs	InSb	6.0584	6.4790	straight	kinked	6.94

Example: InAs-GaSb

Lattice-matched - tunnel transistors (broken band alignment)
Nanowires geometry allows gate access, more precise tuning of bandstructure



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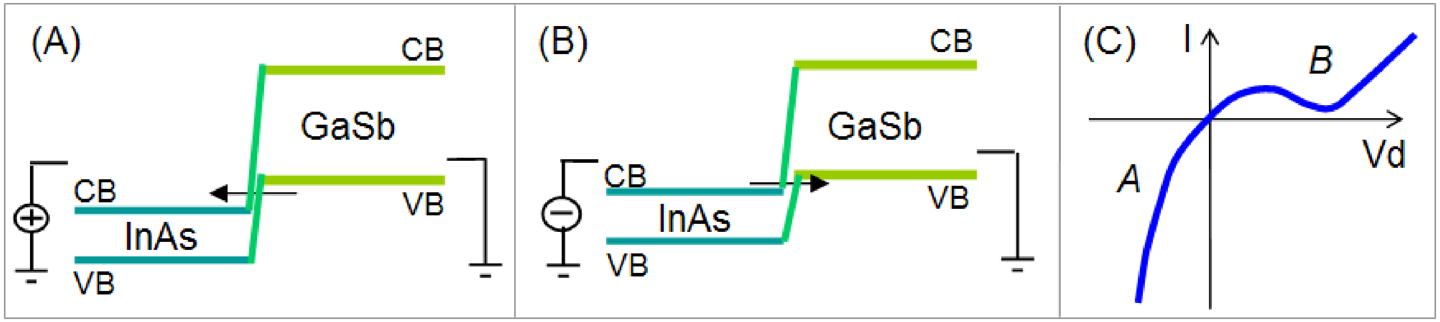
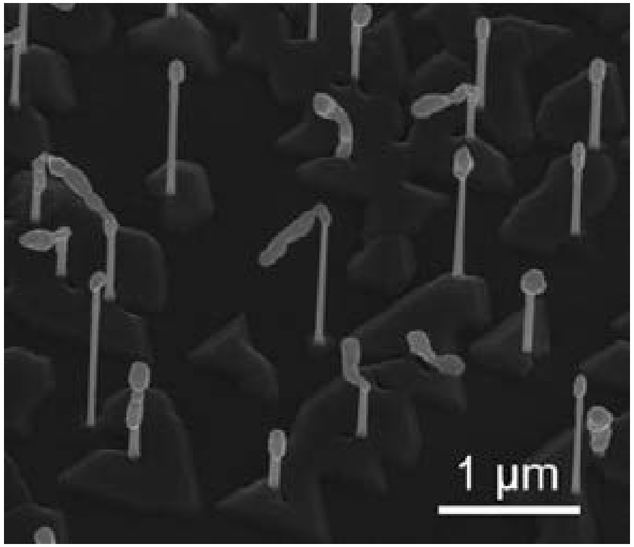
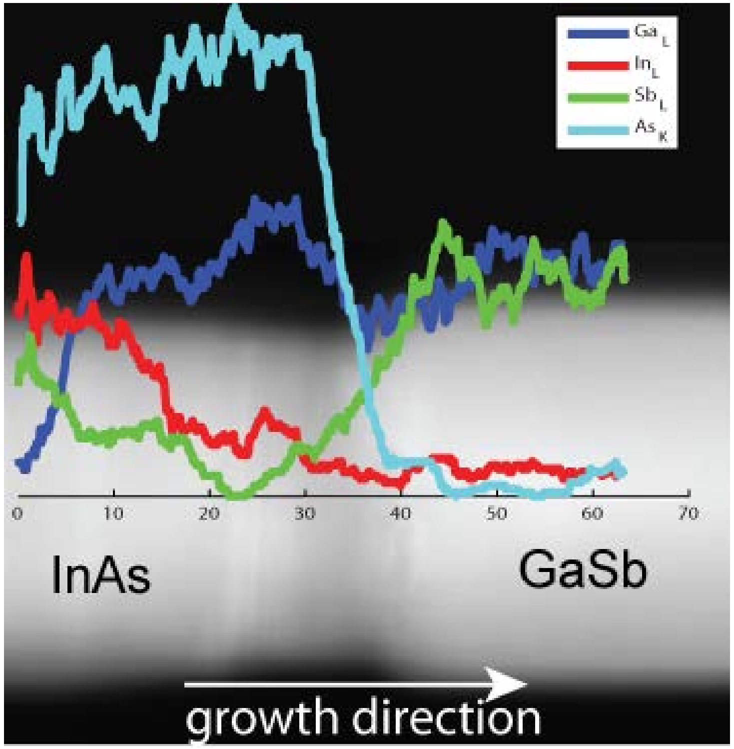


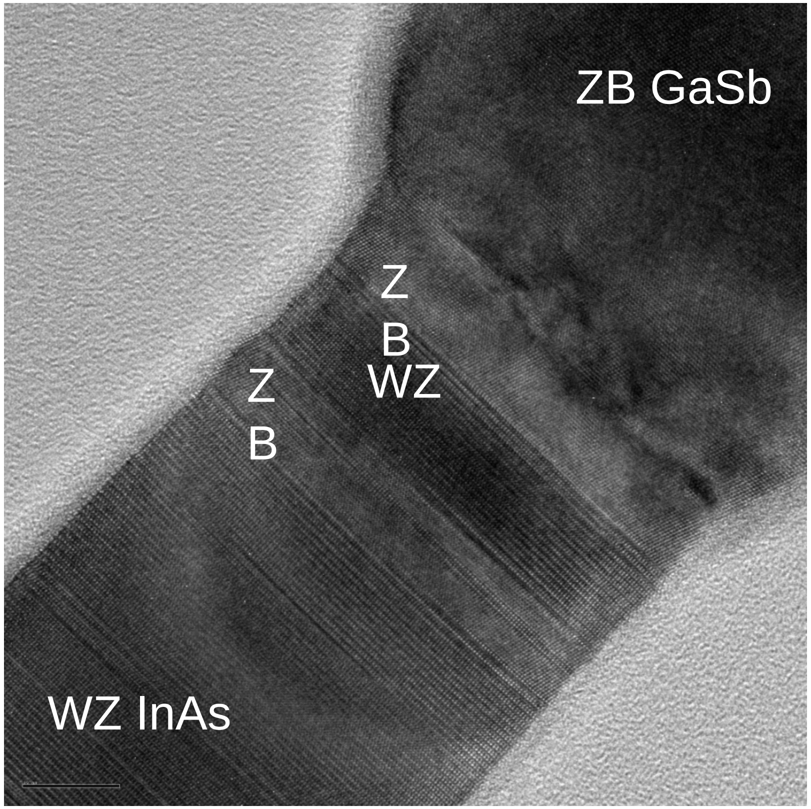
HOWEVER…normally InAs-GaSb heterostructure nanowires kink when the interface is sharp!



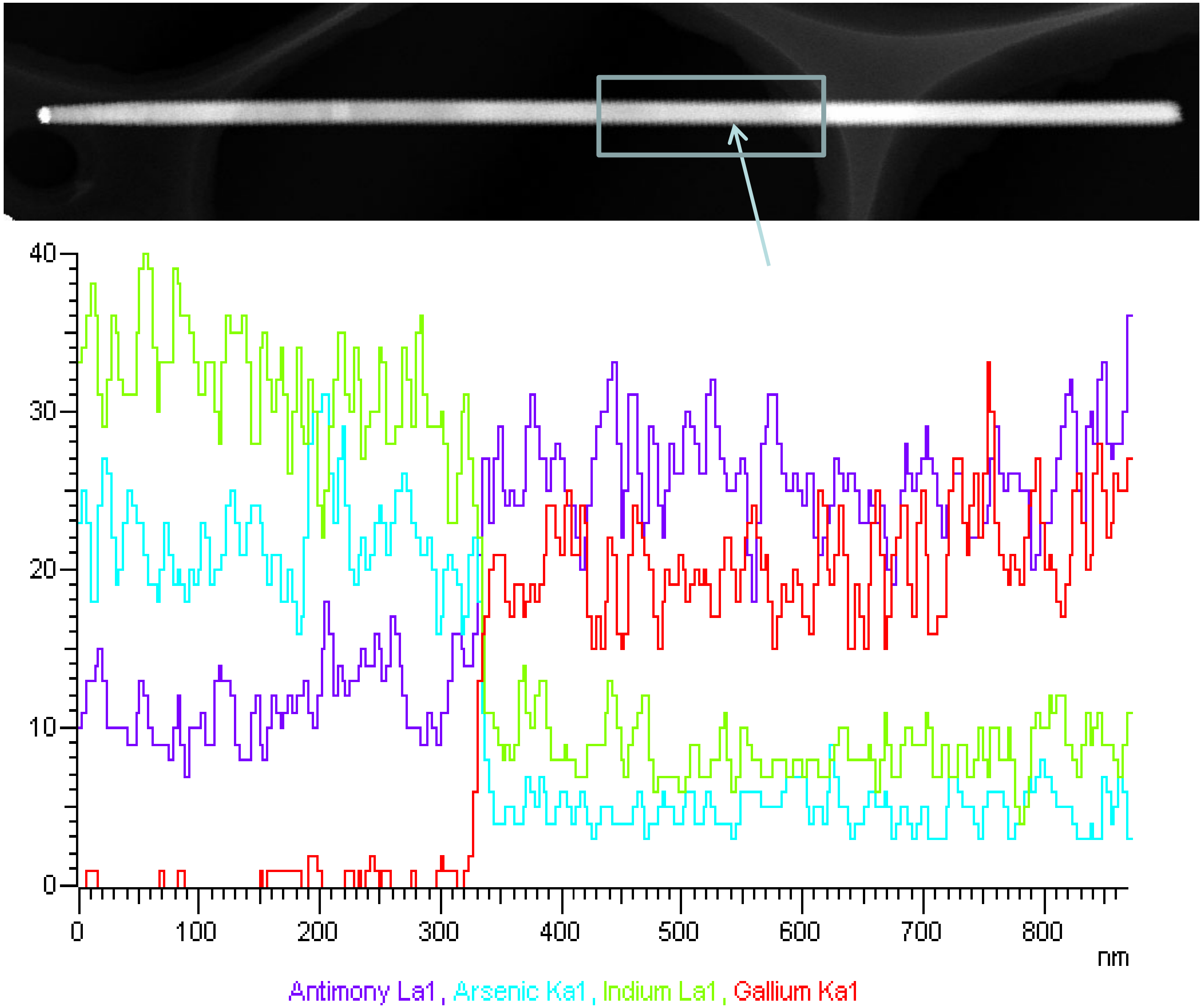
Example: InAs-GaSb

Straight nanowires can be achieved using a diffuse interface (~thin GaAs segment in between)…it is much more difficult to obtain efficient tunnelling behaviour in this case



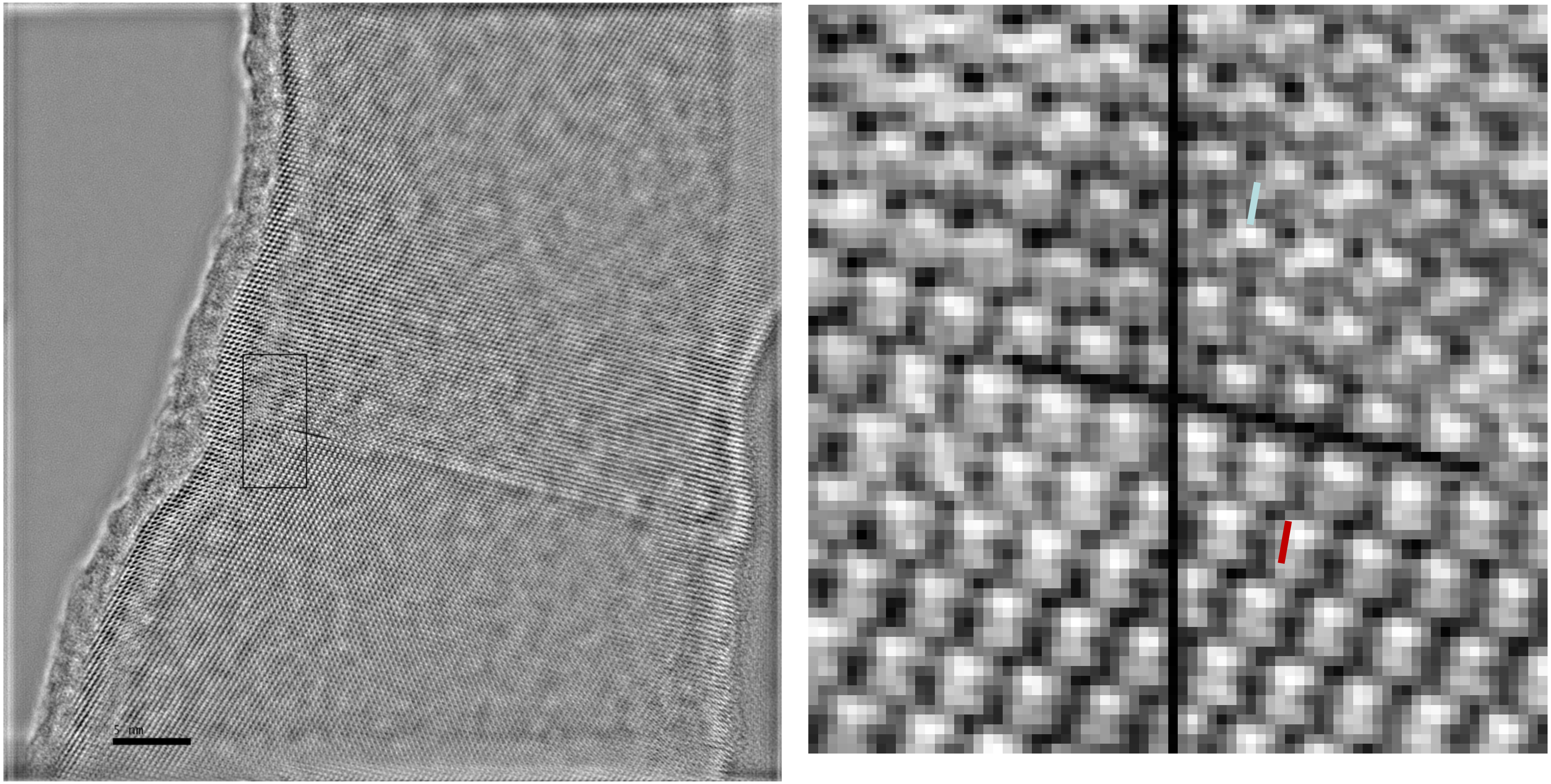


Example: GaSb-InAs



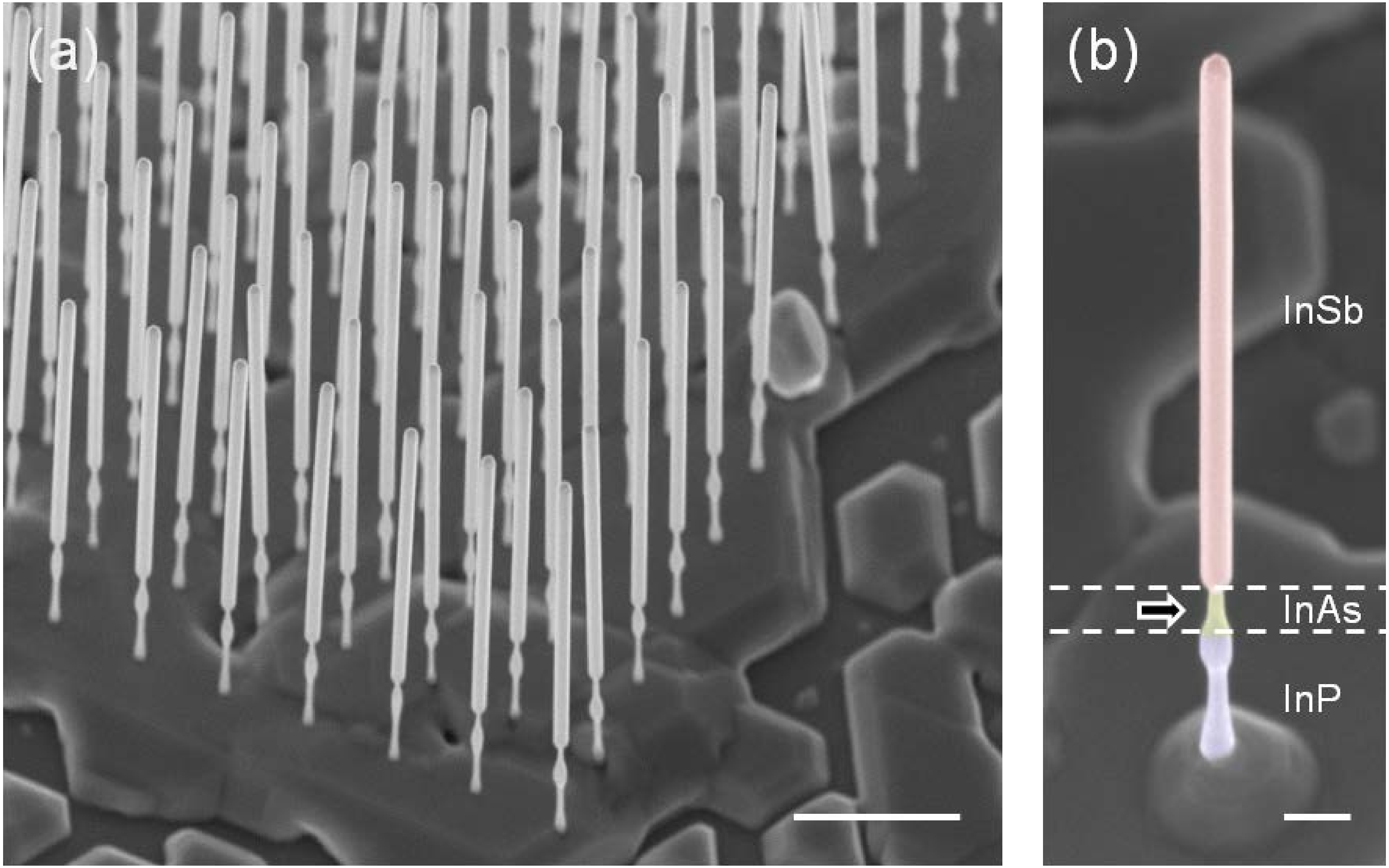
In the opposite direction – sharp interface, no kinking!

GaSb-InAs: atomically sharp!



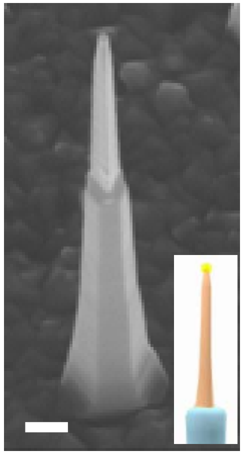
Croissance de matériaux 2D, 3D …

The starting point



Plissard et al. *Nano Lett.* **2012**, 12, 1794-1798

Formation of InSb nanocrosses: A 4 step process

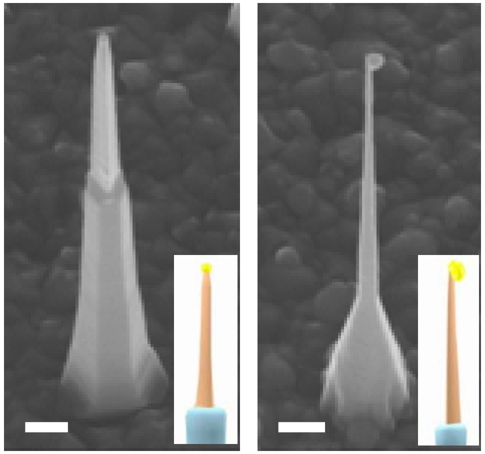


1) InP – InAs nanowire grown on (111) InP substrate

S.R. Plissard & al., *Nature Nanotech.* **2013**, 8, 859-864

all scale bars 200 nm

Formation of InSb nanocrosses: A 4 step process



1) InP – InAs nanowire grown on (111) InP substrate

2) Thermal annealing of InP – InAs nanowire : gold droplet slips on InAs {112} side facet

S.R. Plissard & al., *Nature Nanotech.* **2013**, 8, 859-864

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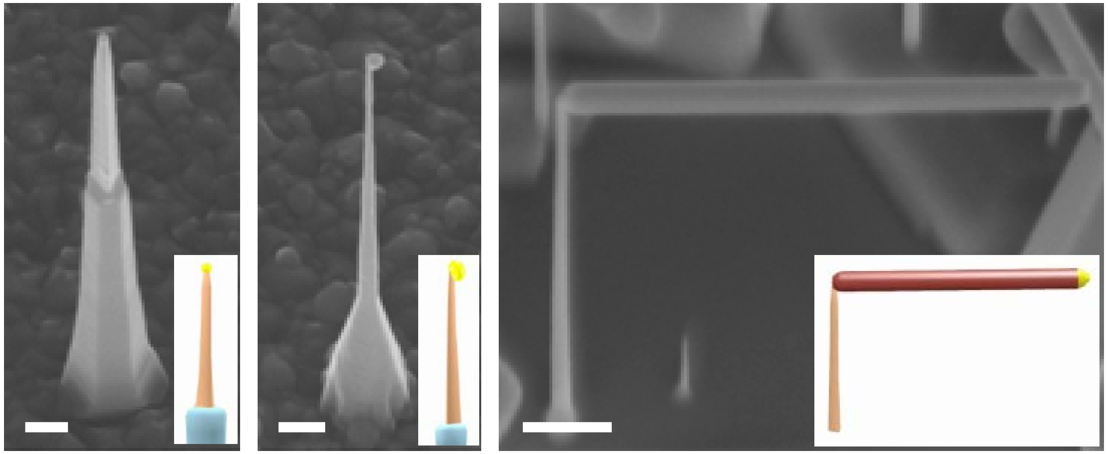
Formation of InSb nanocrosses: A 4 step process



1) InP – InAs nanowire grown on (111) InP substrate

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S.R. Plissard & al., *Nature Nanotech.* **2013**, 8, 859-864

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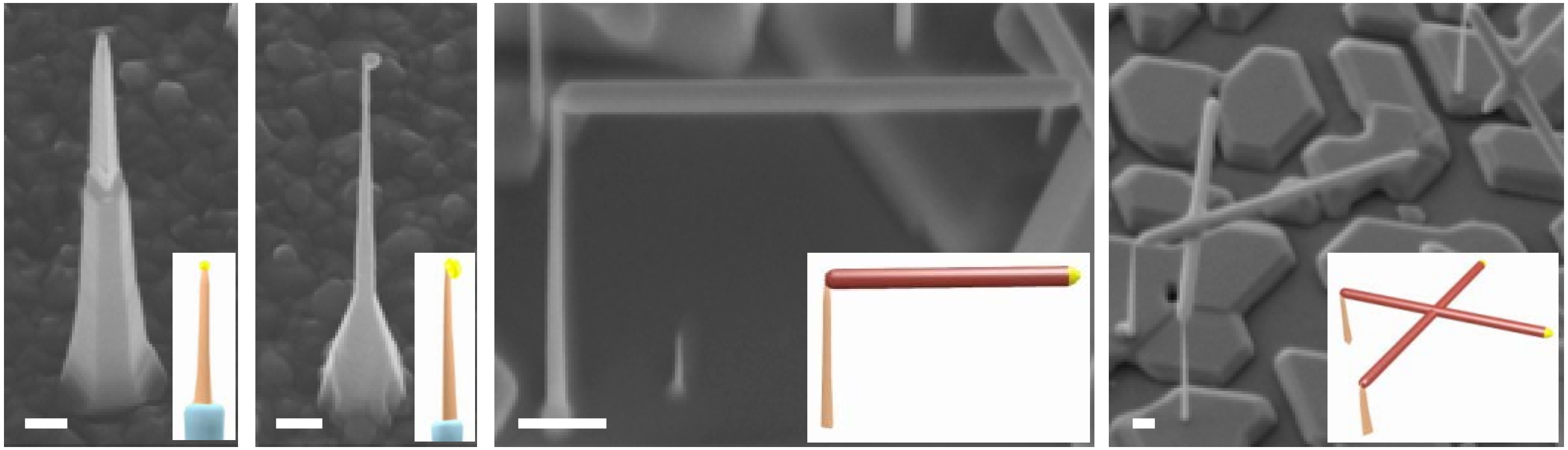
Formation of InSb nanocrosses: A 4 step process



1) InP – InAs nanowire grown on (111) InP substrate

2) Thermal annealing of InP – InAs nanowire : gold droplet slips on InAs {112} side facet

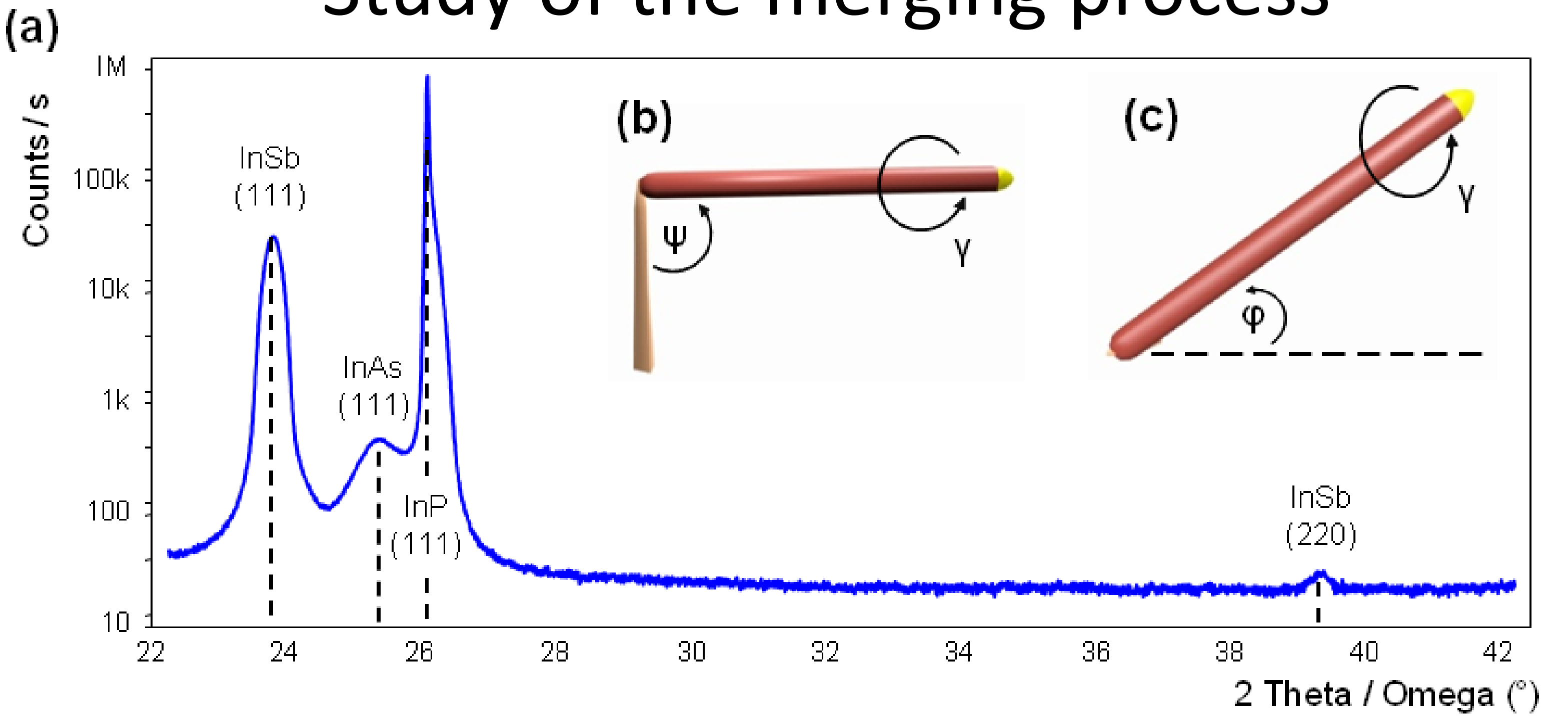
3) InSb nanowire grows parallel to the surface

4) When two nearby nanowires meet, they merge and form a nanocross

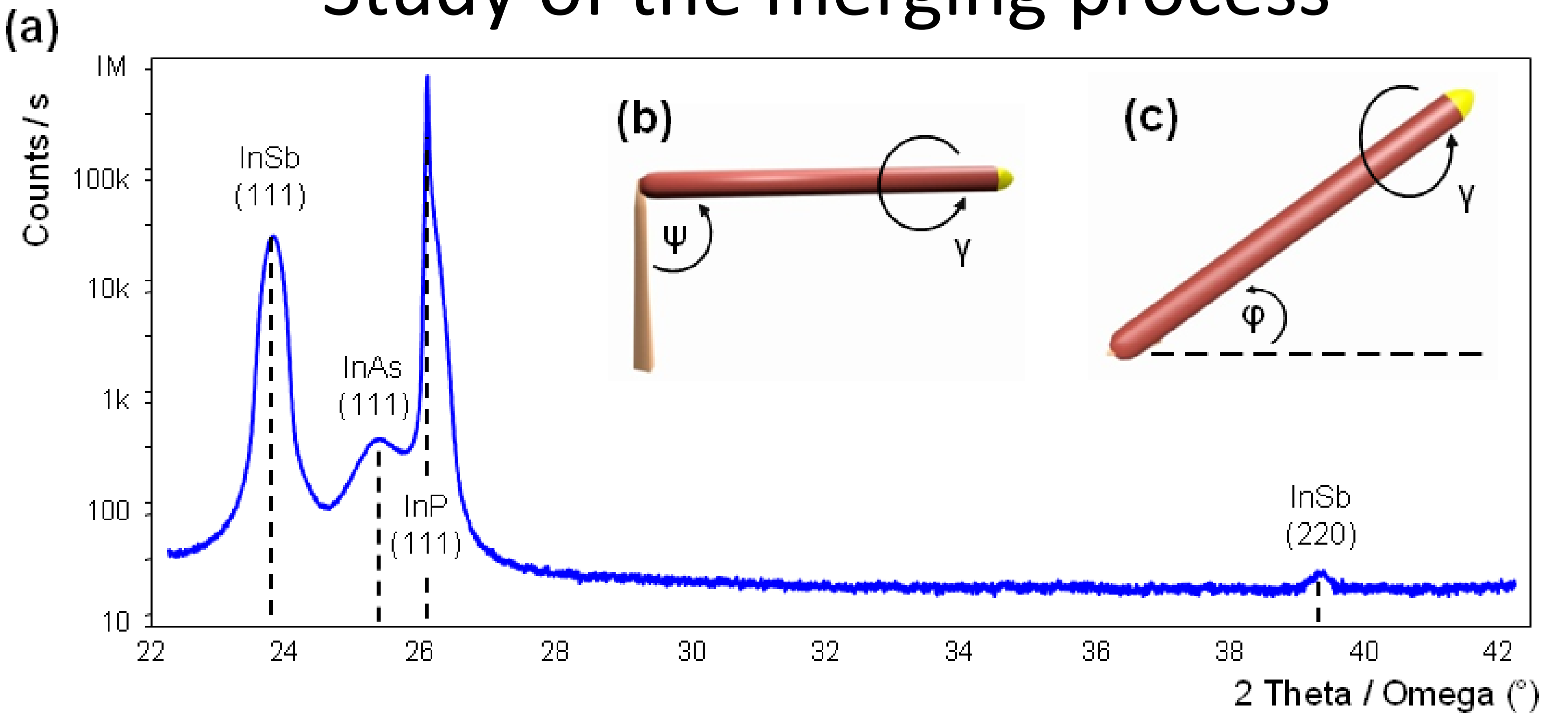
S.R. Plissard & al., *Nature Nanotech.* **2013**, 8, 859-864

all scale bars 200 nm

Study of the merging process



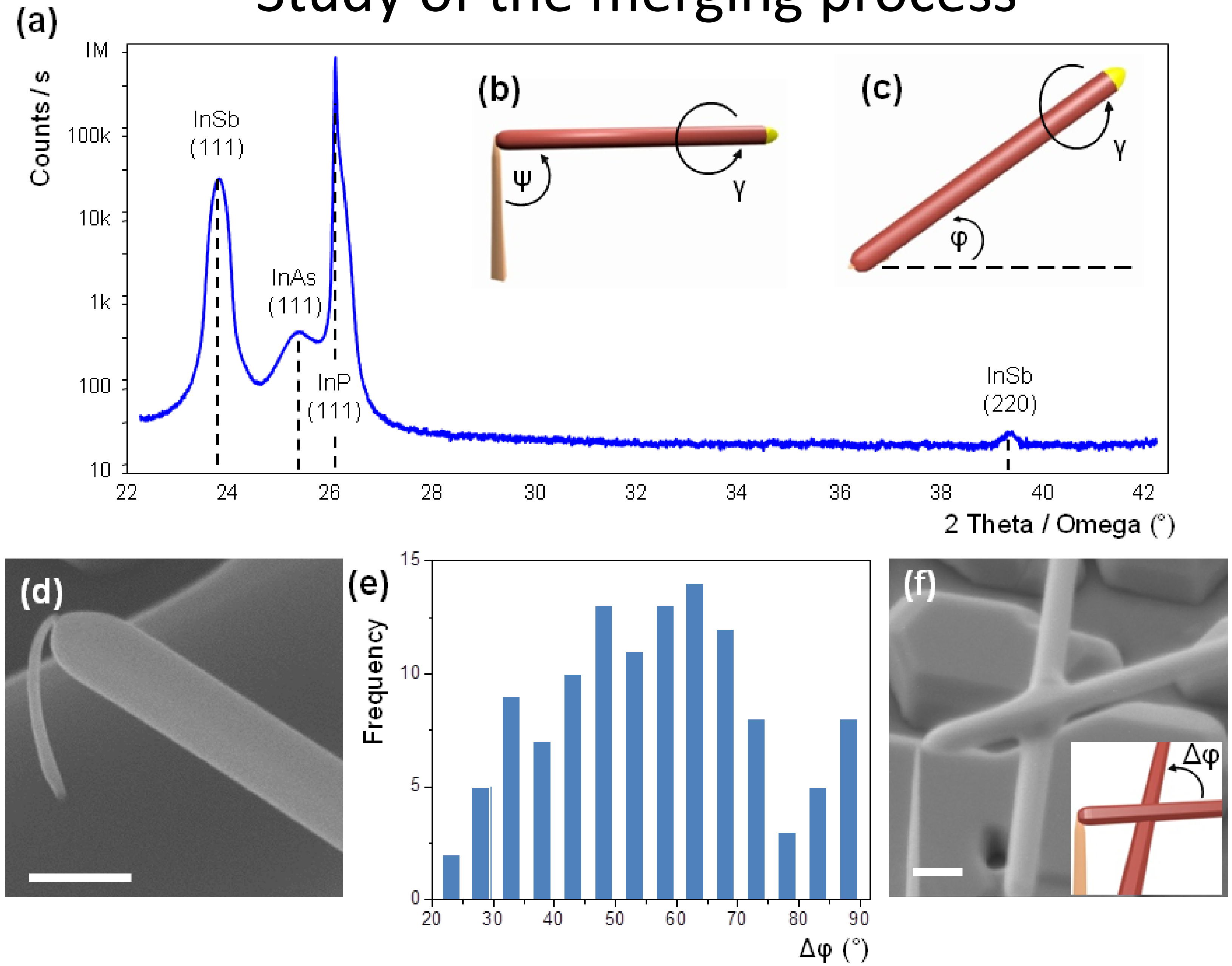
Study of the merging process



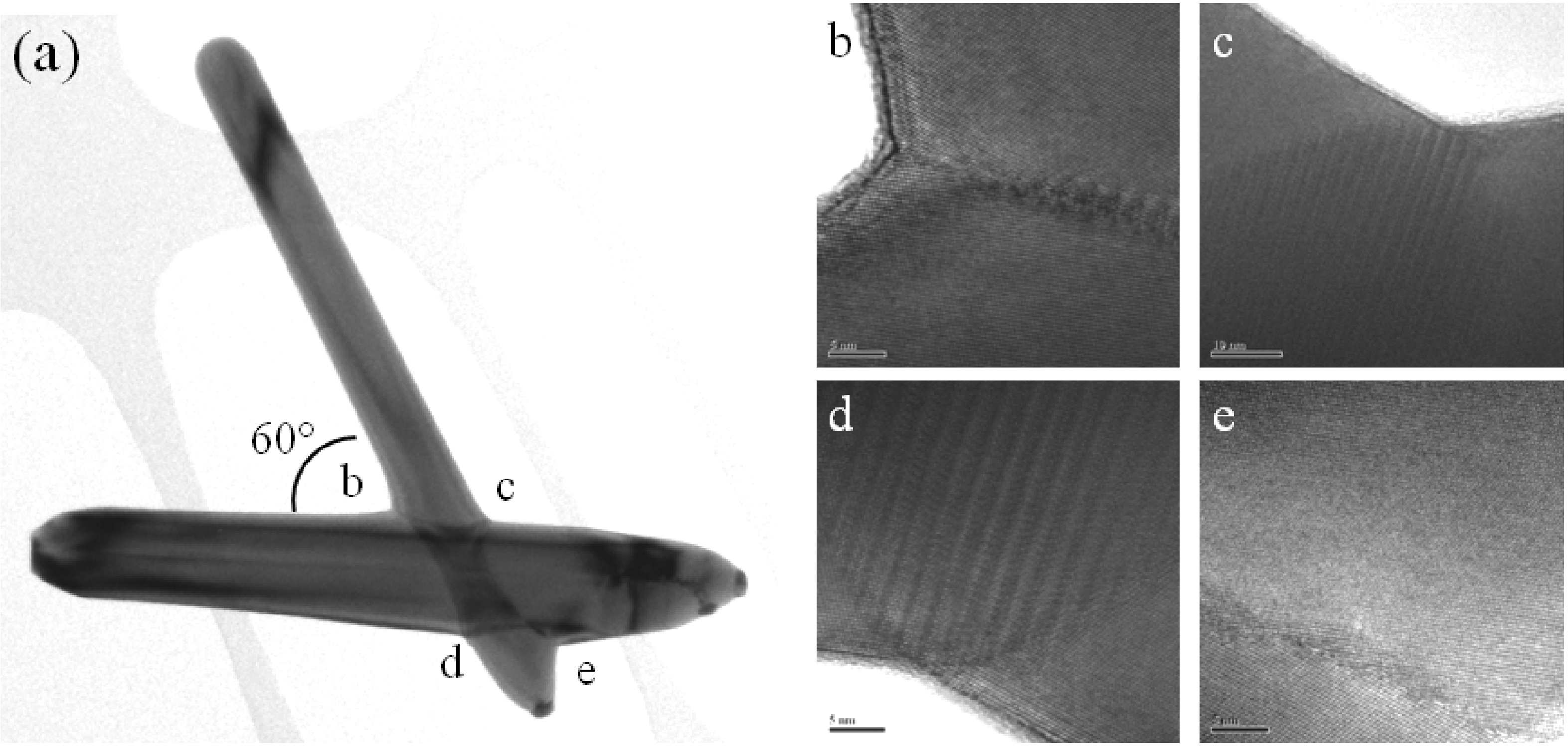
- A peak at 39.3° corresponds to InSb (220) Bragg angle: it originates from the InSb nanowires having one of their {110} side facets parallel to the surface

- Angles ψ and γ are **not random**: they are fixed around ψ = 90° and γ = 0°

Study of the merging process

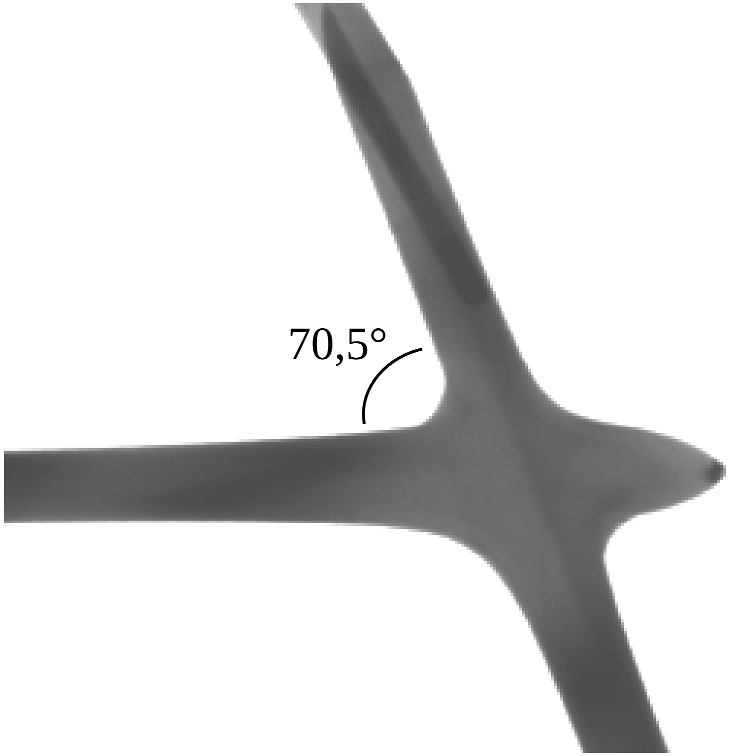


Transmission electron microscopy on a most probable case (δ = 60° nanocross)



- Moiré interference pattern -> a single grain boundary at a junction

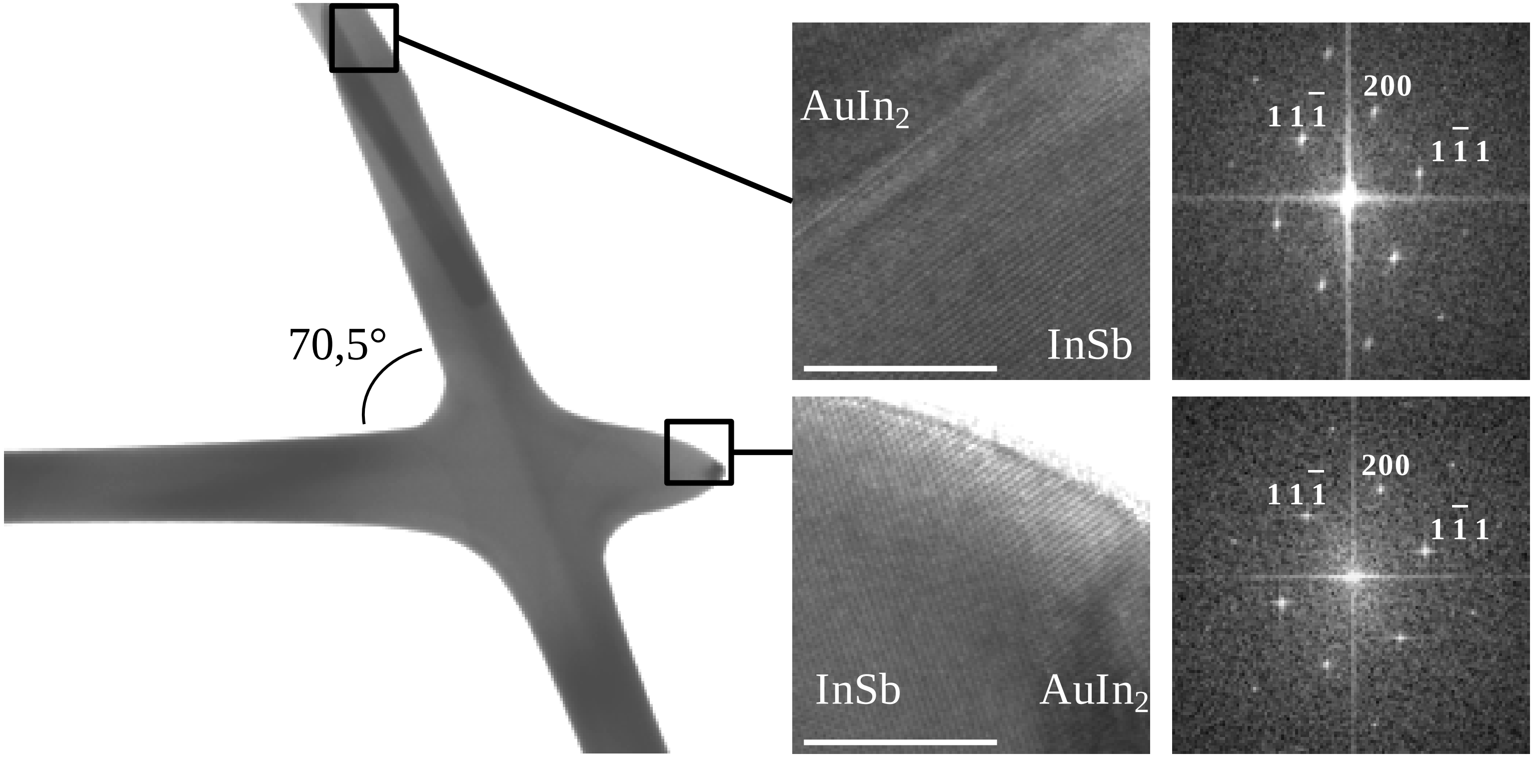
Transmission electron microscopy on a single crystalline nanocross (δ = 70.5°)



- Single crystalline crosses are formed when the meeting angle between the two nanowires is δ = 70.5°

all scale bars 5 nm

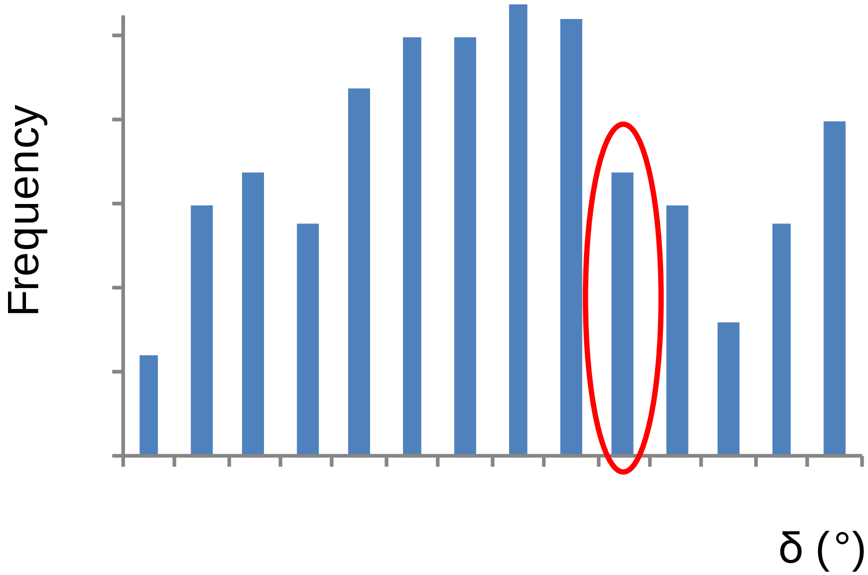
Transmission electron microscopy on a single crystalline nanocross (δ = 70.5°)



- Single crystalline crosses are formed when the meeting angle between the two nanowires is δ = 70.5°

all scale bars 5 nm

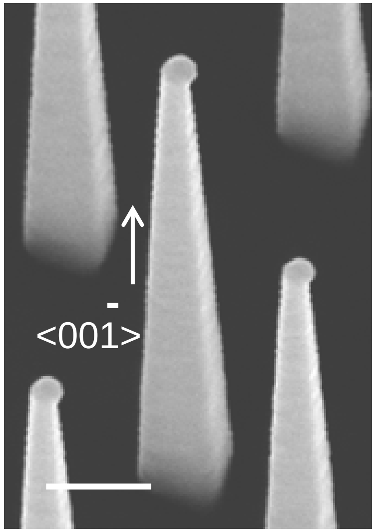
Yield of single crystalline InSb nanocrosses: 8 %



- Can we further improve the yield?

Yes, we can !

InSb nanowires on InP (001) substrate

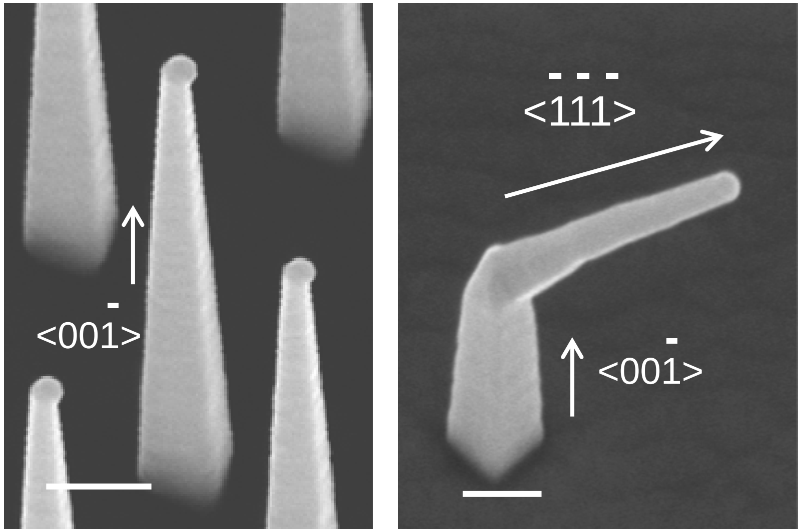


1) InP (001) nanowires grown on InP (001) substrate

J. Wang & al., *Nano Lett.* **2013**, 8, 3802-3806

all scale bars 200 nm

InSb nanowires on InP (001) substrate



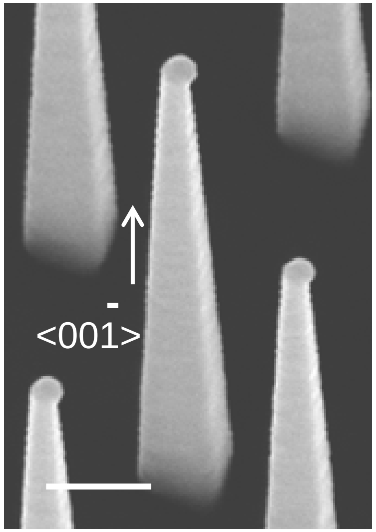
1) InP (001) nanowires grown on InP (001) substrate

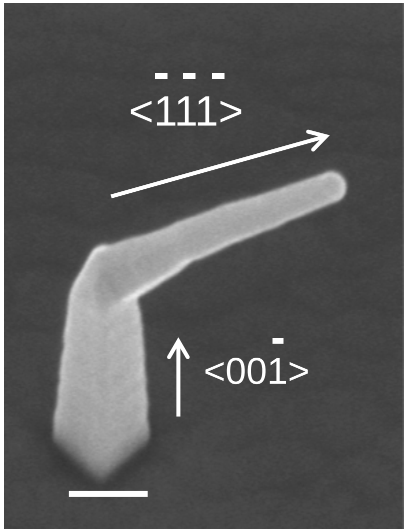
2) By changing the contact angle of the catalyst Au droplet, nanowire growth direction is switched from <001> to <111>.

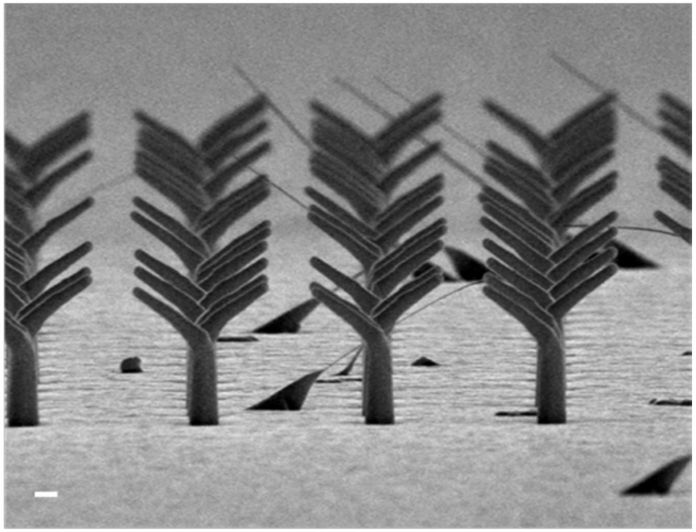
J. Wang & al., *Nano Lett.* **2013**, 8, 3802-3806

all scale bars 200 nm

InSb nanowires on InP (001) substrate







1) InP (001) nanowires grown on InP (001) substrate

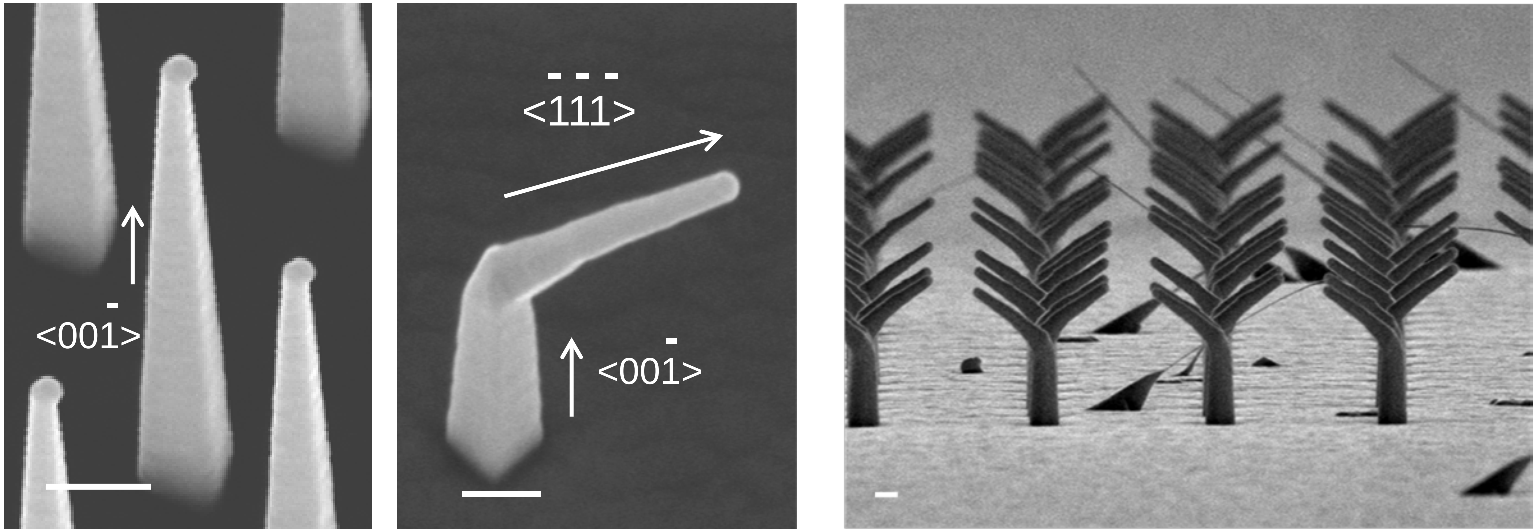
2) By changing the contact angle of the catalyst Au droplet, nanowire growth direction is switched from <001> to <111>.

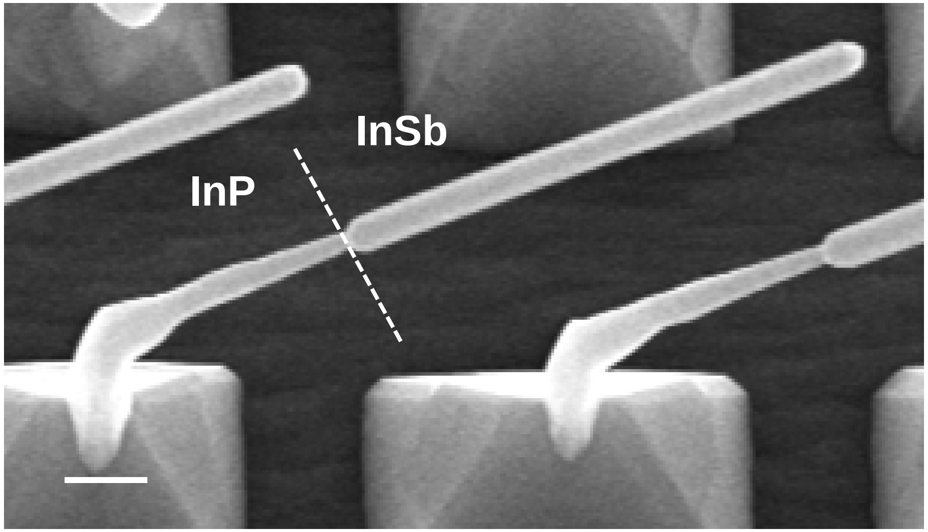
3) As two <111>B directions are available on a (001) substrate , 50 % of the wires will kink in the <11-1> and 50 % in the <-1-1-1> direction.

J. Wang & al., *Nano Lett.* **2013**, 8, 3802-3806

all scale bars 200 nm

InSb nanowires on InP (001) substrate



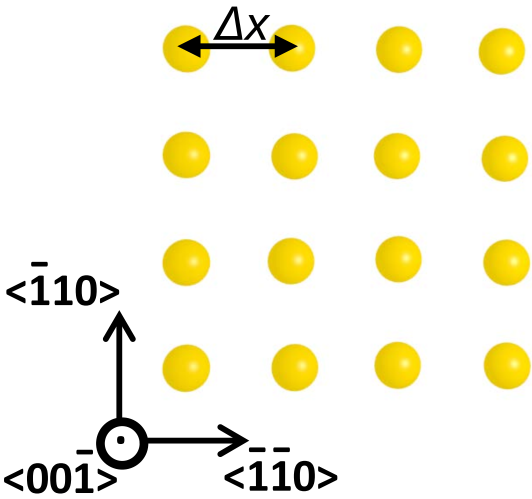


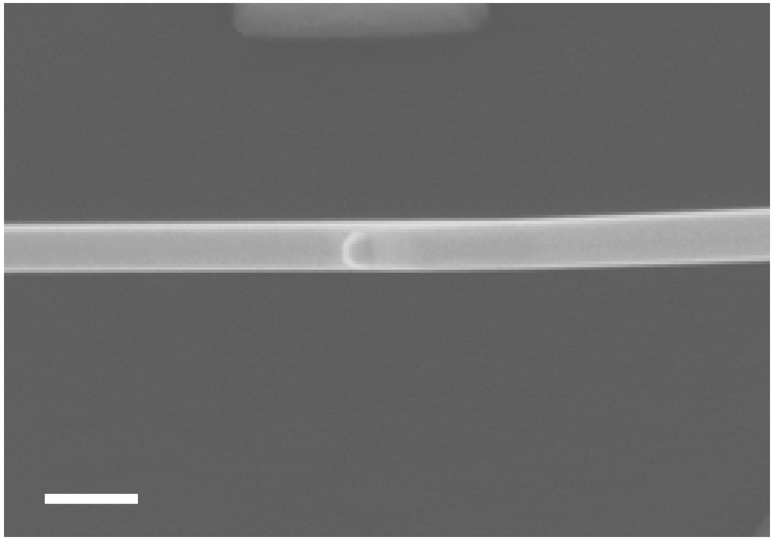
- InSb <111> nanowire on top of kinked InP structure

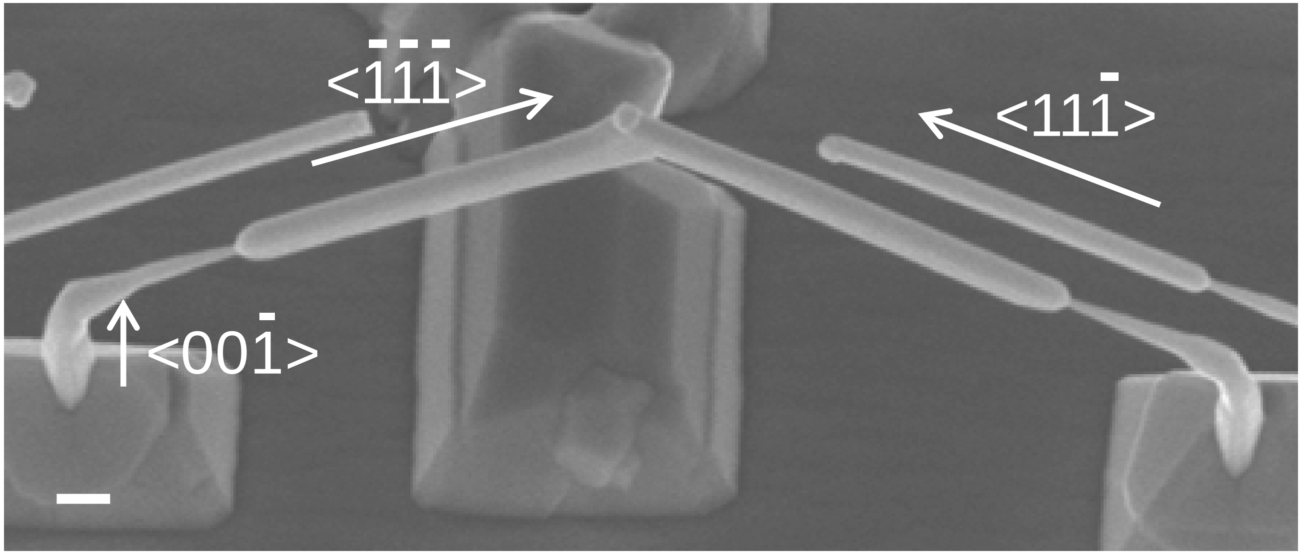
J. Wang & al., *Nano Lett.* **2013**, 8, 3802-3806

all scale bars 200 nm

InSb nanowires on (001) InP substrates

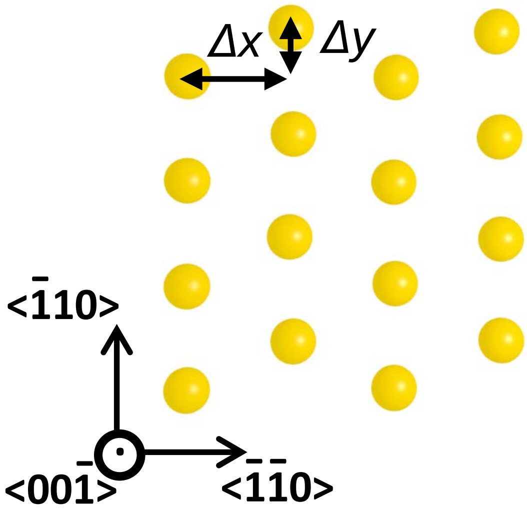


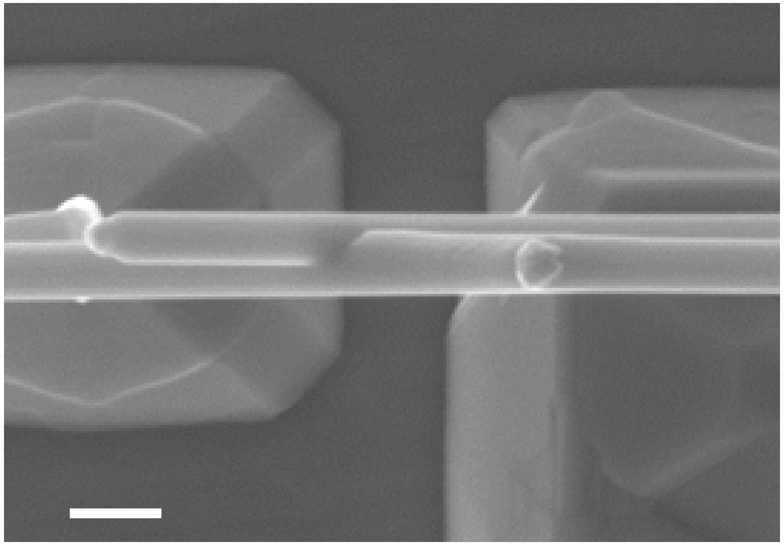


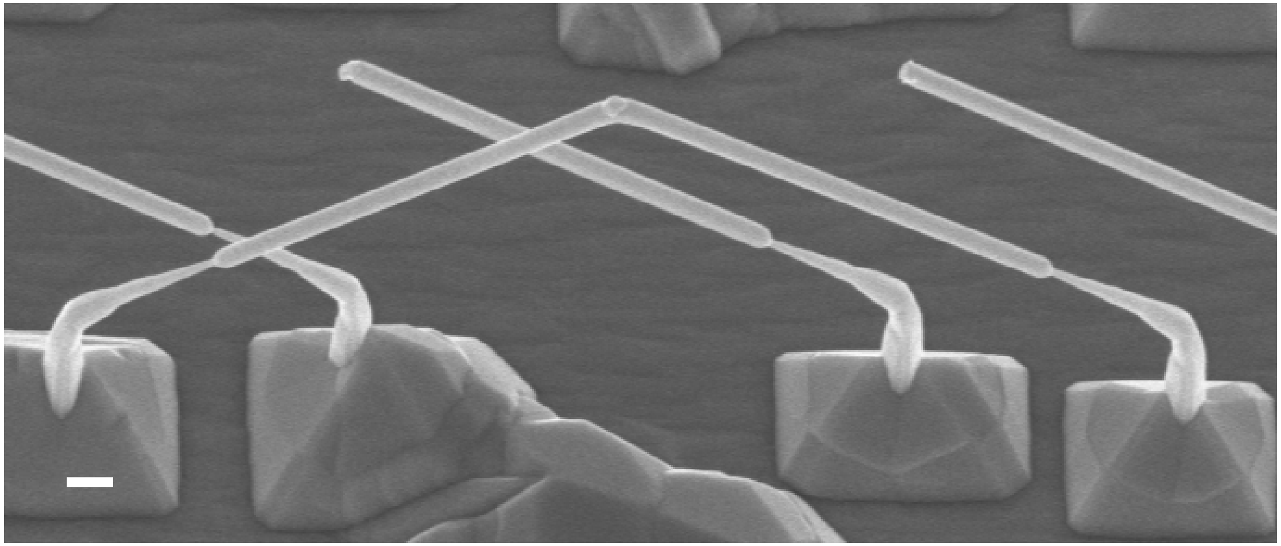


D. Car & al., *Adv. Mat.* **2014**, Early view: DOI: 10.1002/adma.201400924

InSb nanowires on (001) InP substrates

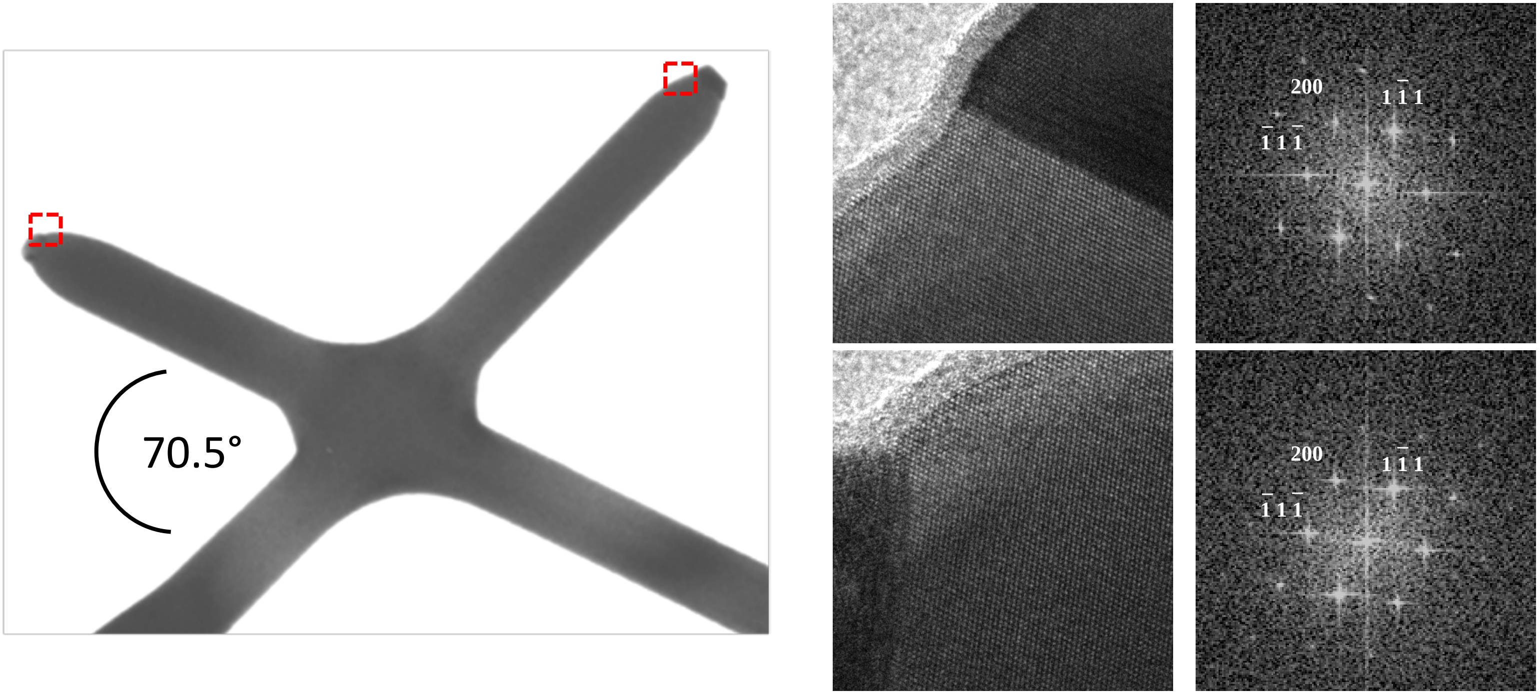




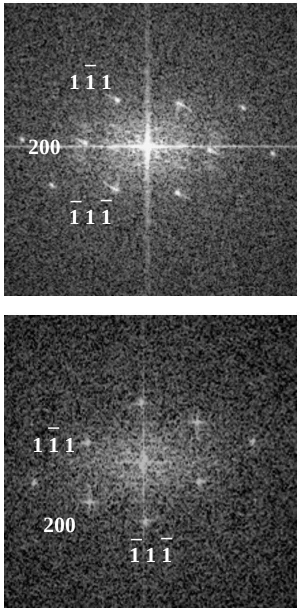


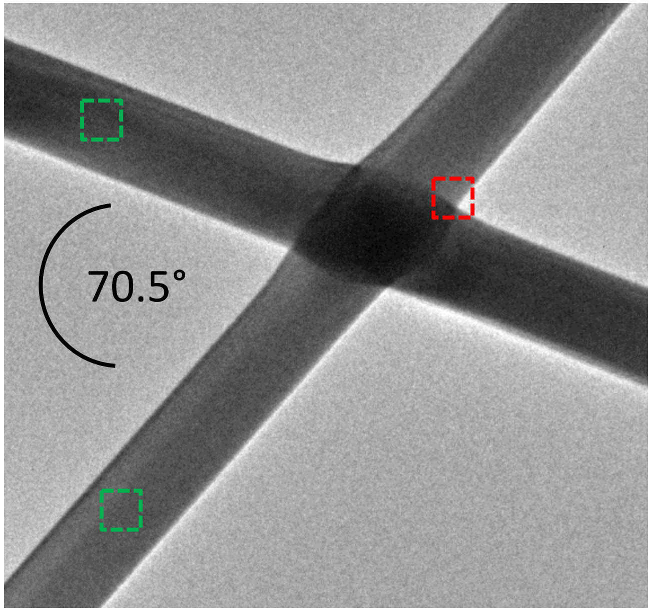
D. Car & al., *Adv. Mat.* **2014**, Early view: DOI: 10.1002/adma.201400924

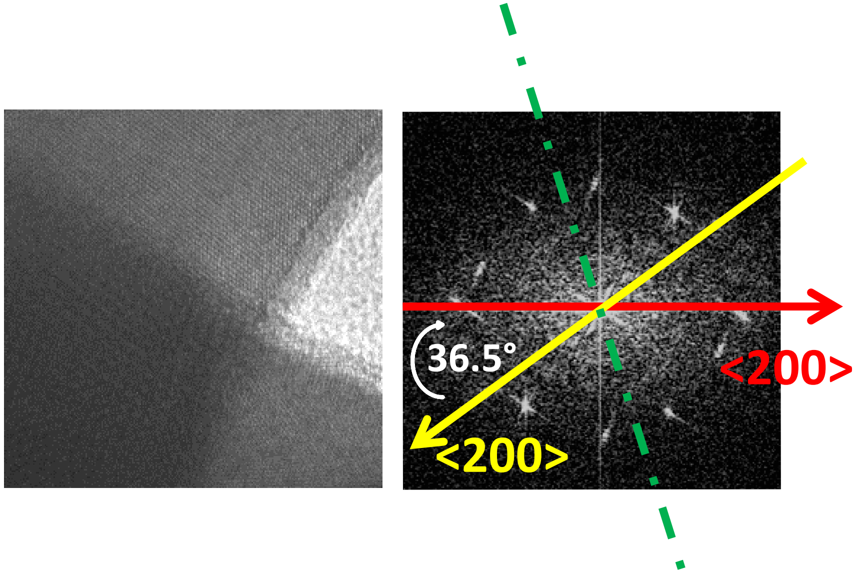
Transmission electron microscopy: A single crystalline nanocross (δ = 70.5°)



Transmission electron microscopy:
A nanocross with a grain boundary (δ = 70.5°)

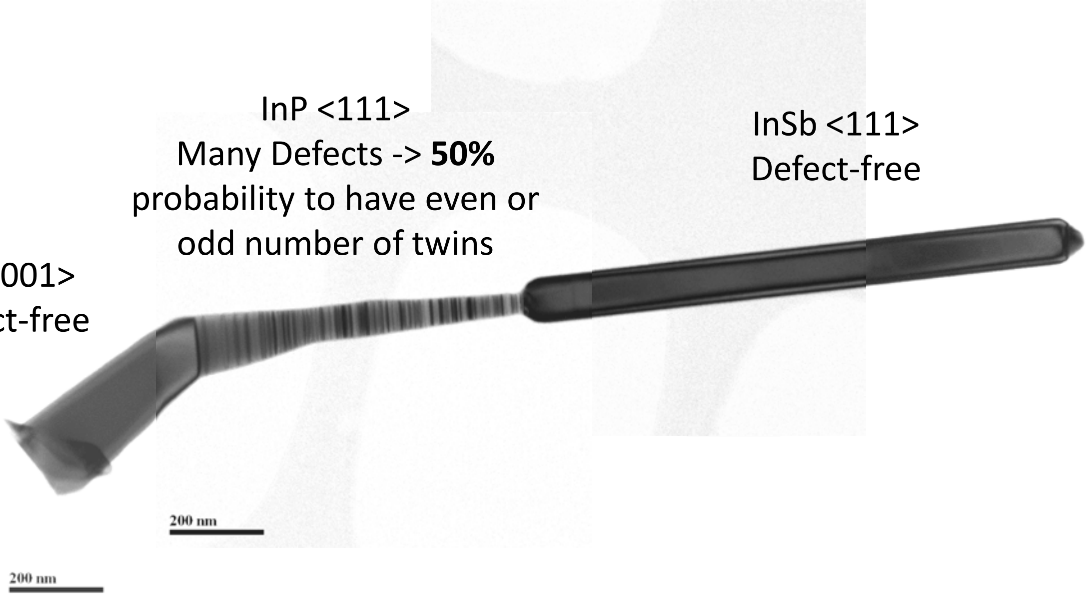






- A twinned FFT diffraction pattern with a 36.5° angle between the <200> directions of two nanowires

Twinning

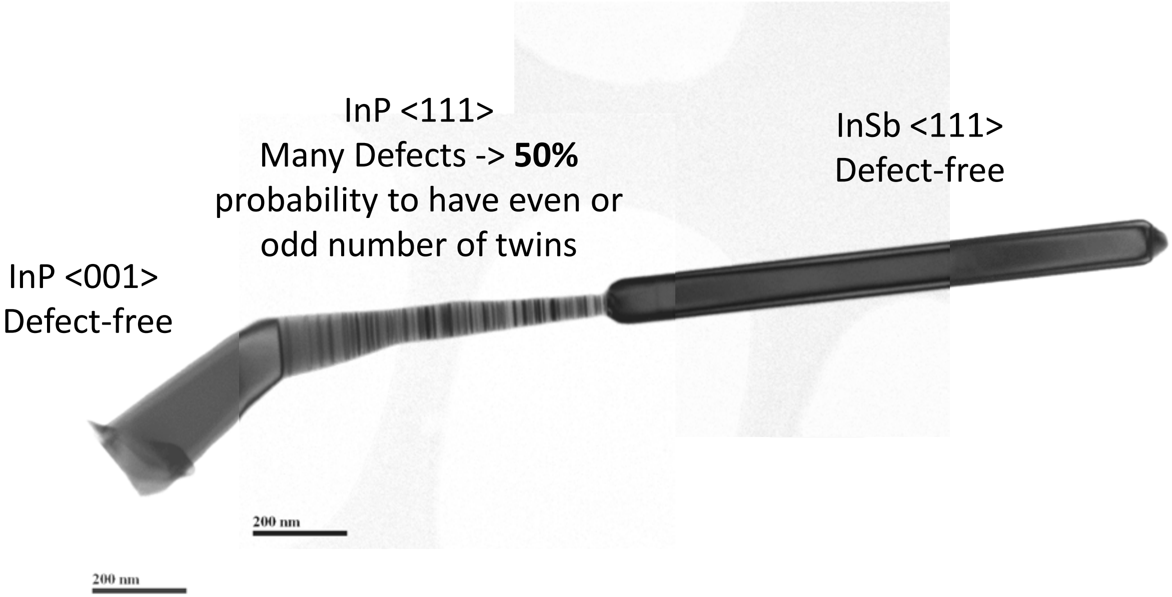


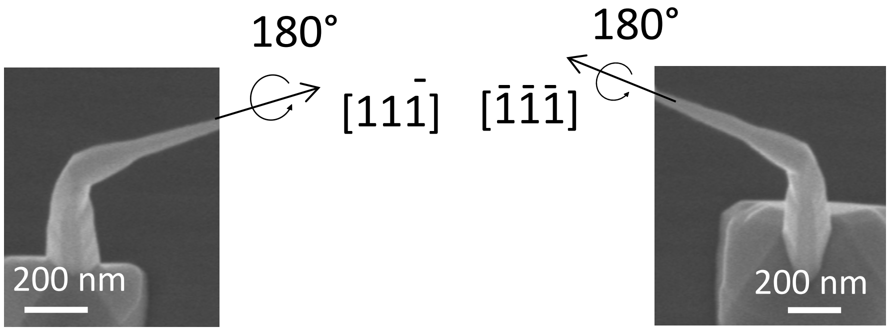
InP <111>
Many Defects -> **50%** probability to have even or odd number of twins

InSb <111>
Defect-free

InP <001>
Defect-free

Twinning

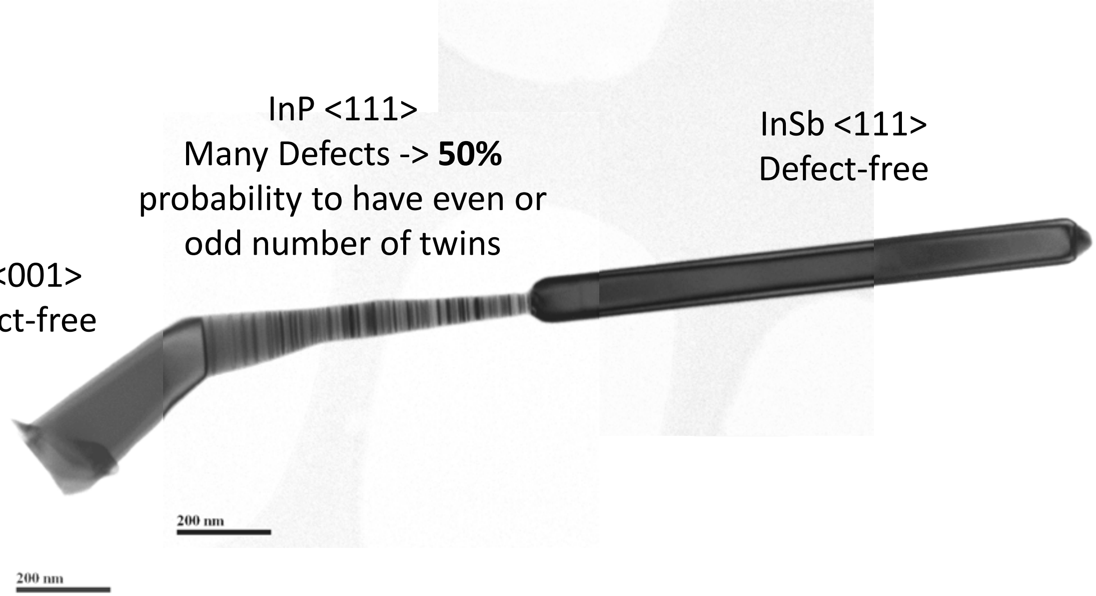




Odd number of twins: Orientation of the nanowire is rotated by 180° around the <111> growth axis

Even number of twins: Orientation of the nanowire remains the same (rotation of 360° around the <111> growth axis)

Yield of single crystalline nanocrosses: 25 %



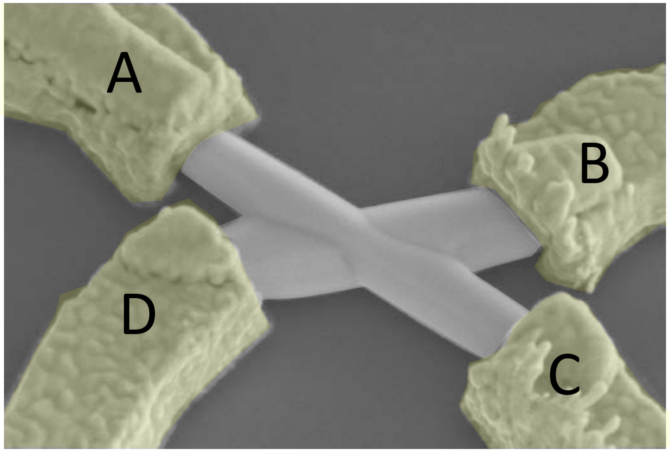
InP <001>
Defect-free

InP <111>
Many Defects -> **50%** probability to have even or odd number of twins

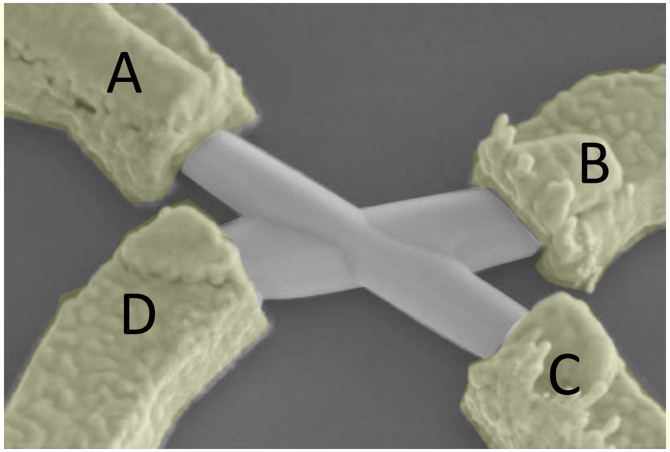
InSb <111>
Defect-free

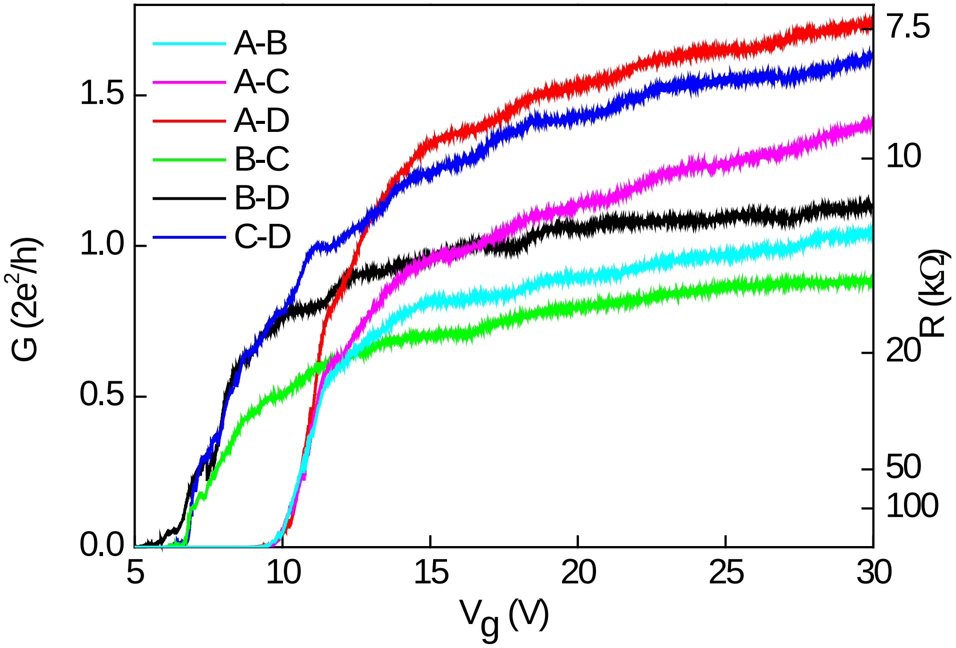
$N_{[111]}$	$N_{[111]}$	Junction	Angle between <200> directions	Probability
even	even	**Single Crystal**	0°	**25%**
odd	even	Twinned	109.5°	50%
even	odd			
odd	odd	Twinned twin	36.5°	25%

Transport through a nanocross

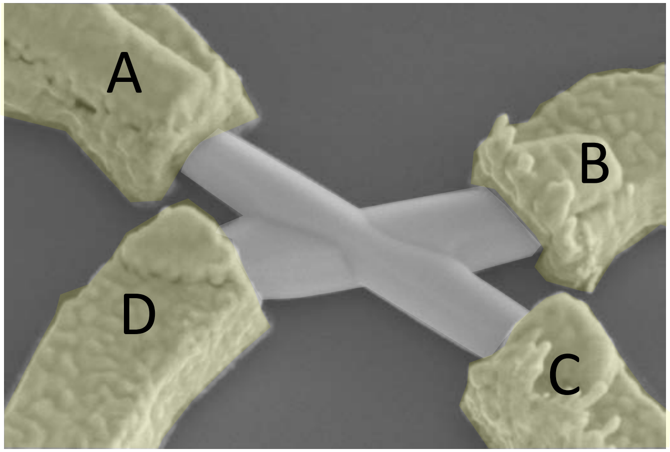


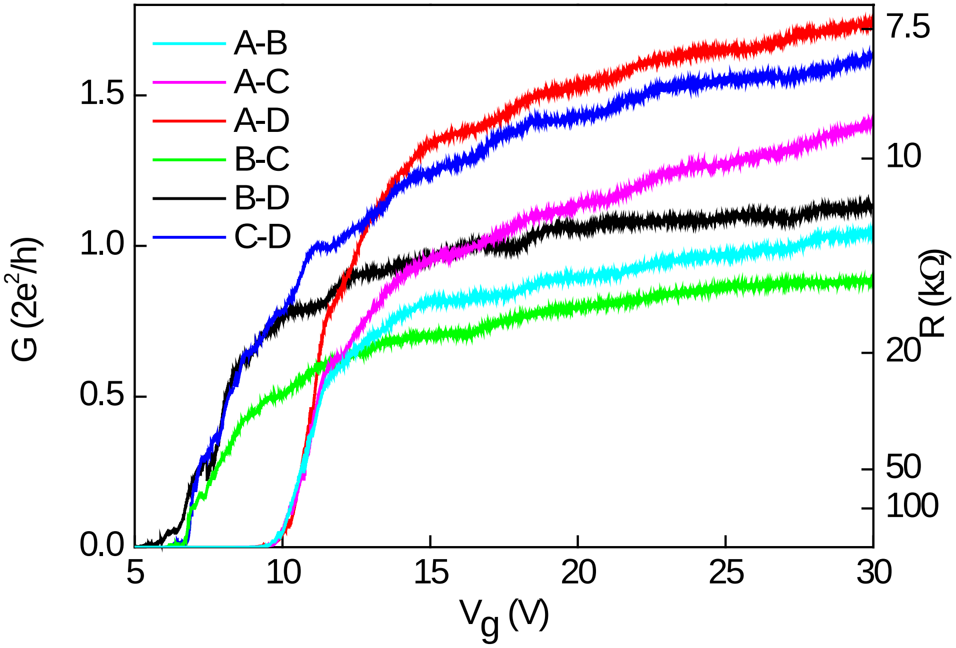
Transport through a nanocross

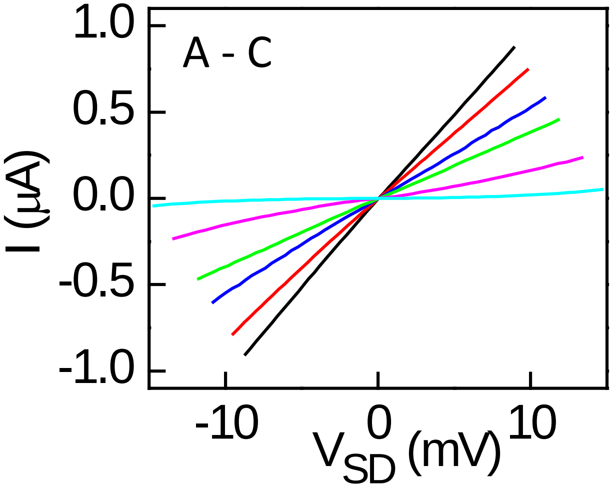


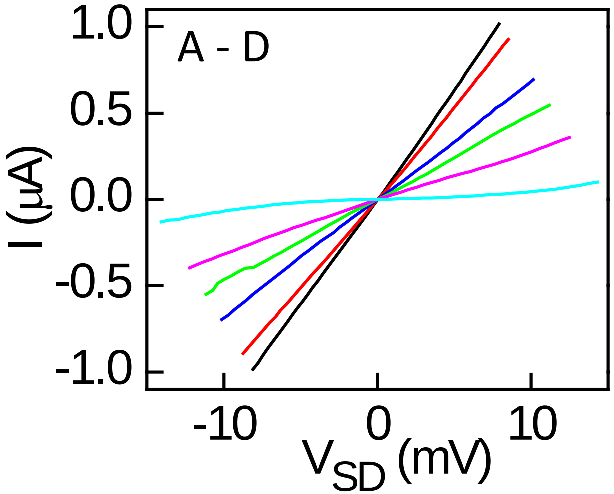


Transport through a nanocross





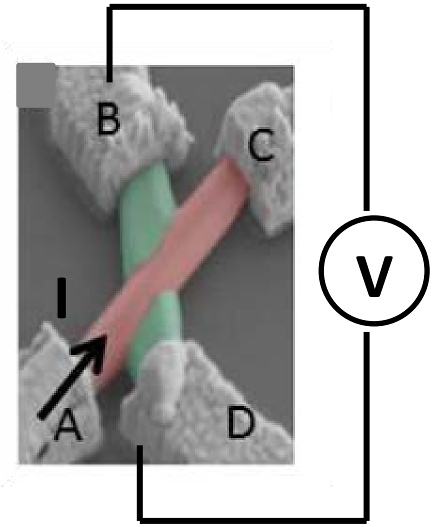




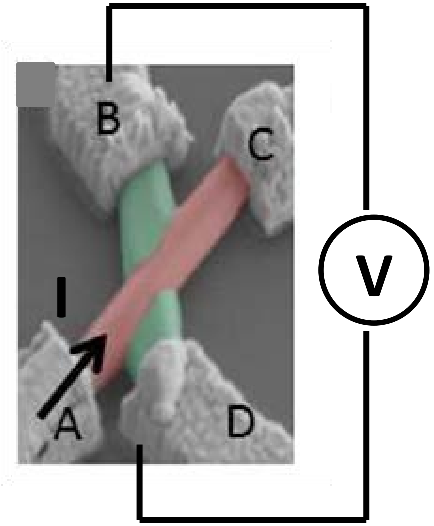
Junction is transparent:

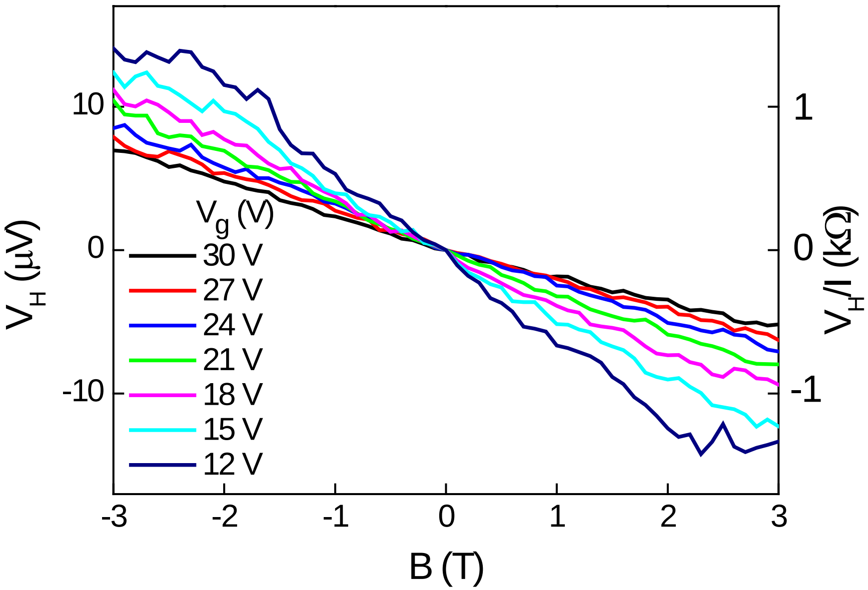
Transport from
wire to wire
without a
tunneling barrier

Nanocross Hall measurements

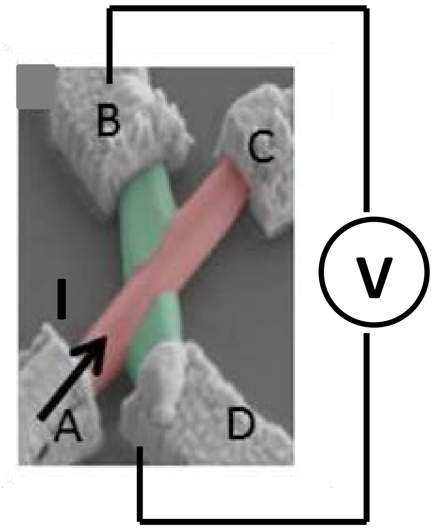


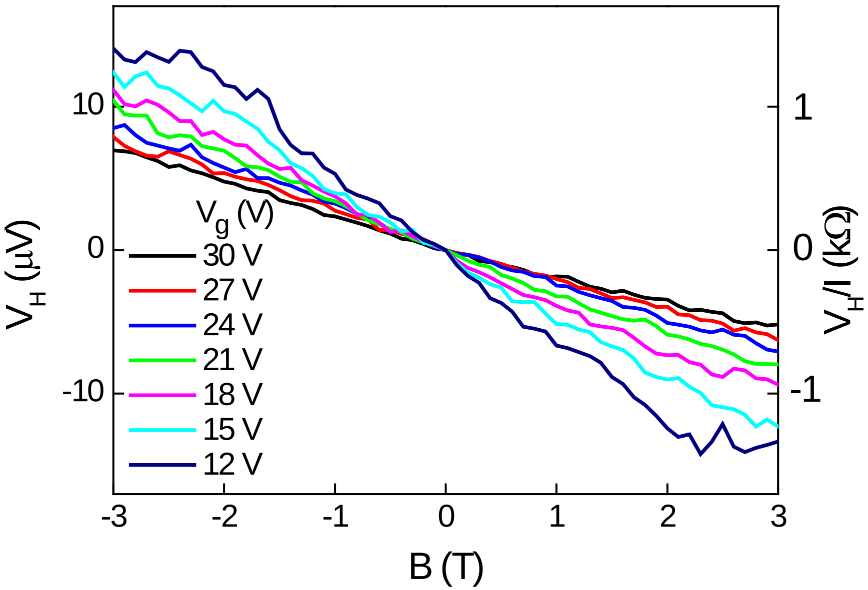
Nanocross Hall measurements

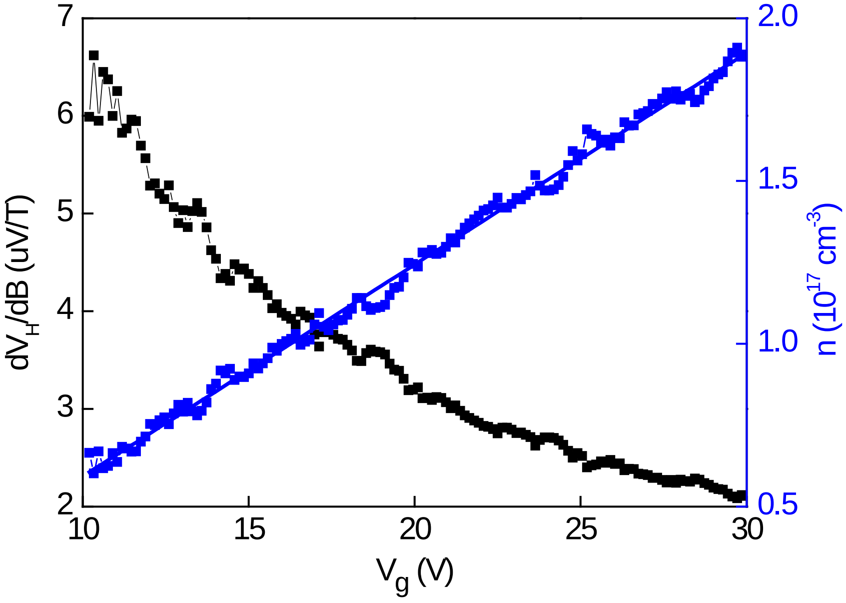




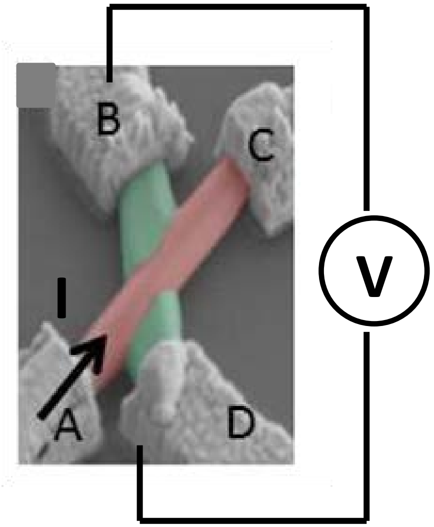
Nanocross Hall measurements

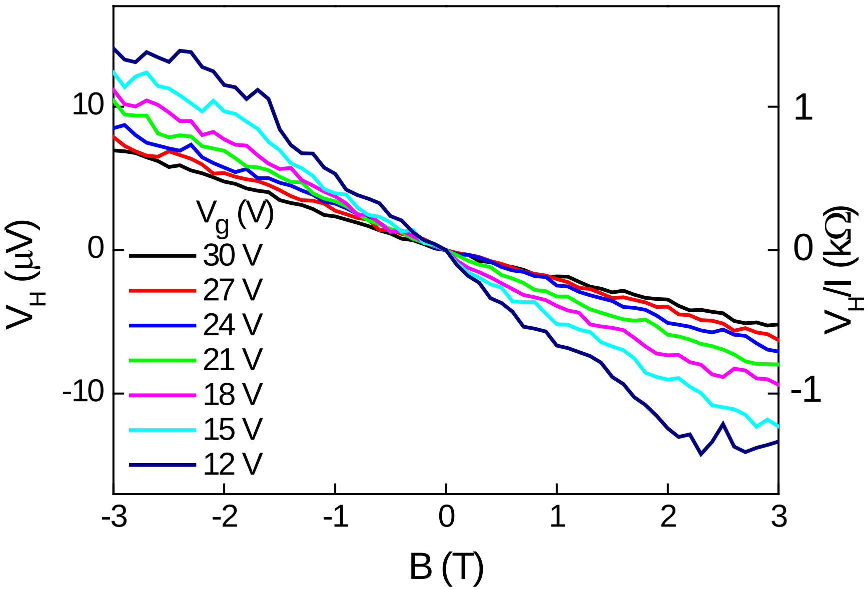


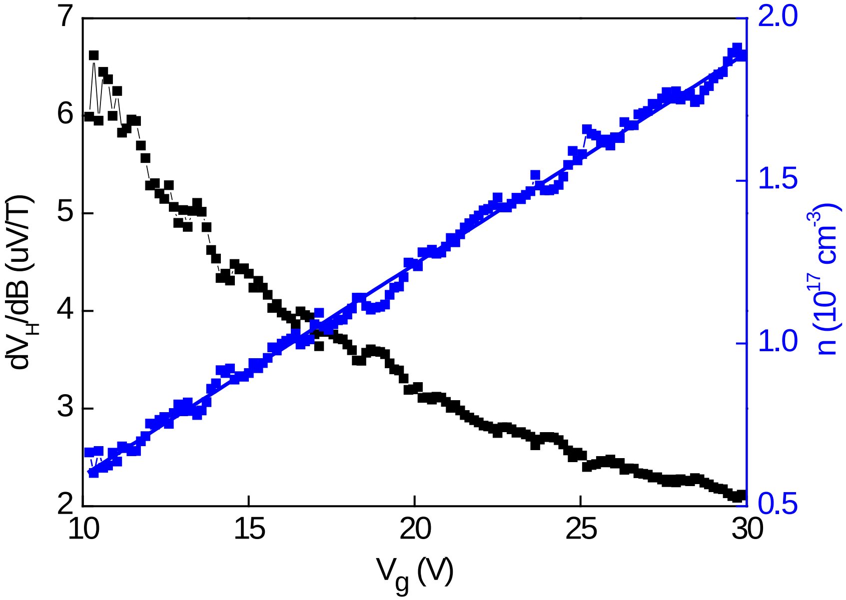


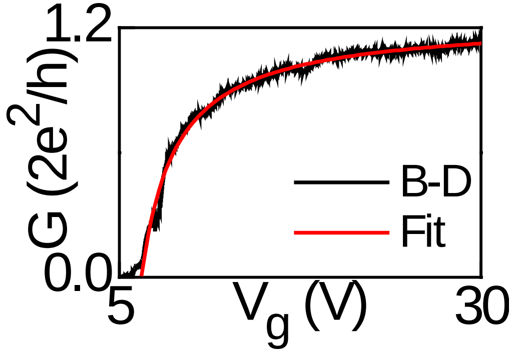


Nanocross Hall measurements



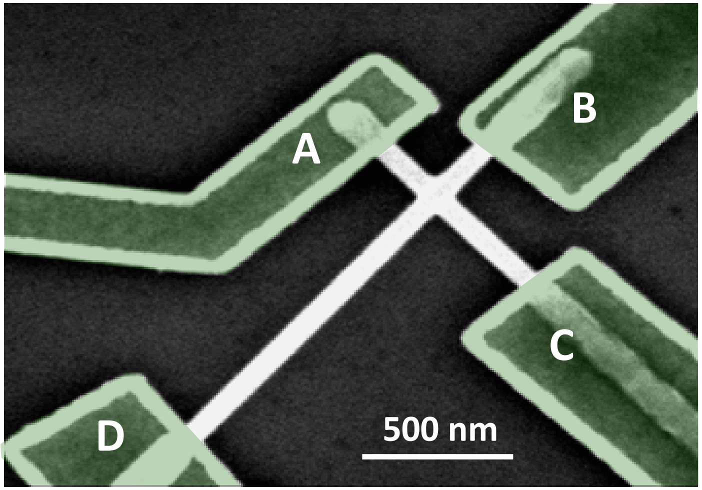


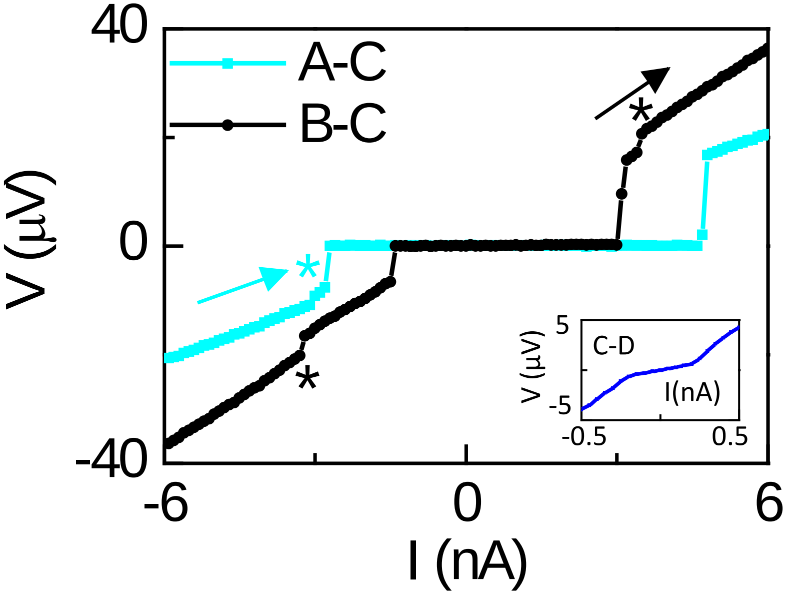




- Hall mobilities: 6500 - 10 000 cm^2/Vs

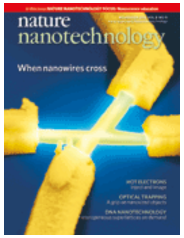
Gate-tunable supercurrent through a nanocross





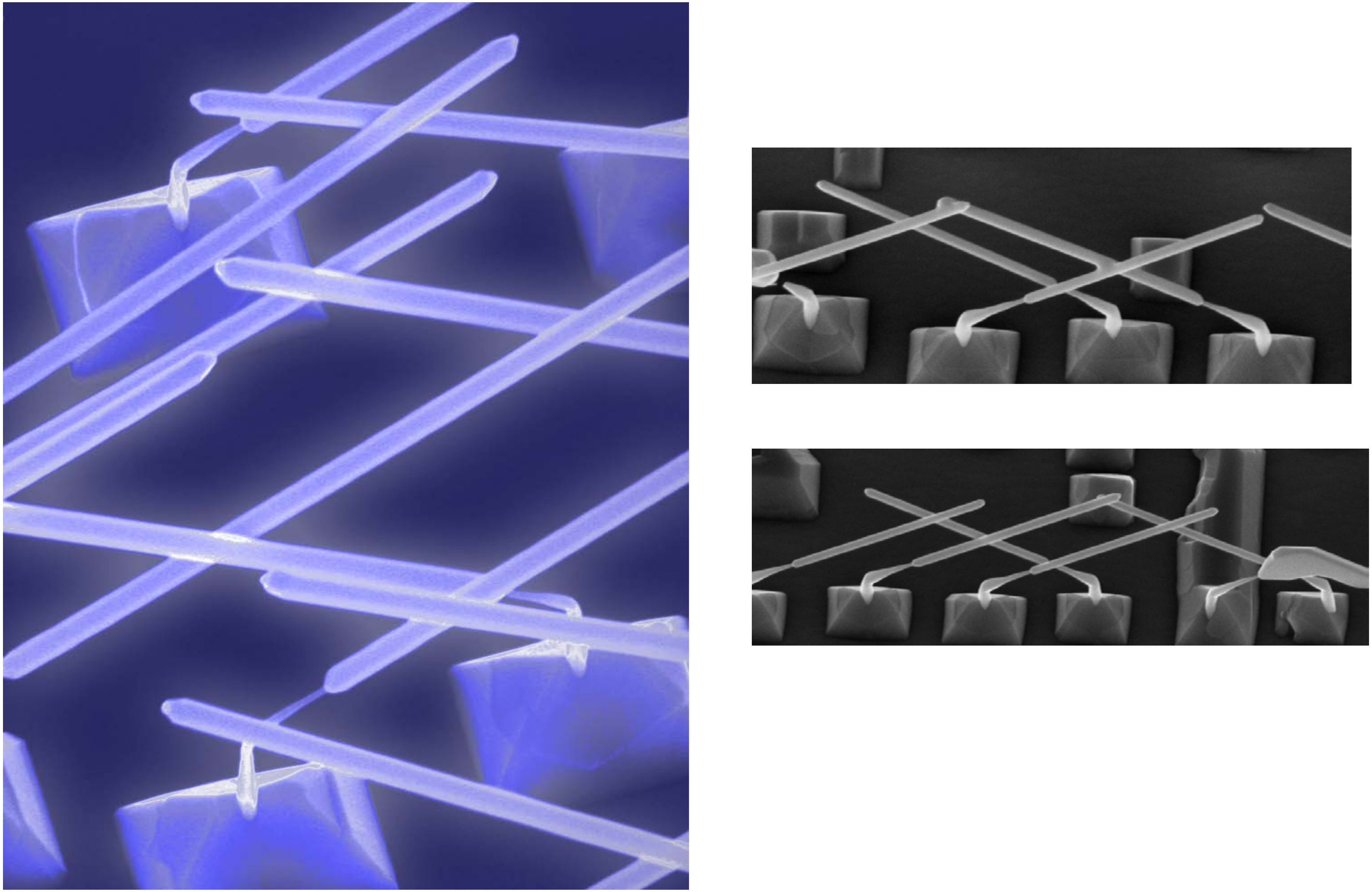
- Proximity induced supercurrent through the junction, over the distance of ~ 1.5 μm at 20 mK

•InSb nanocrosses are suitable for future Majorana fermion experiments



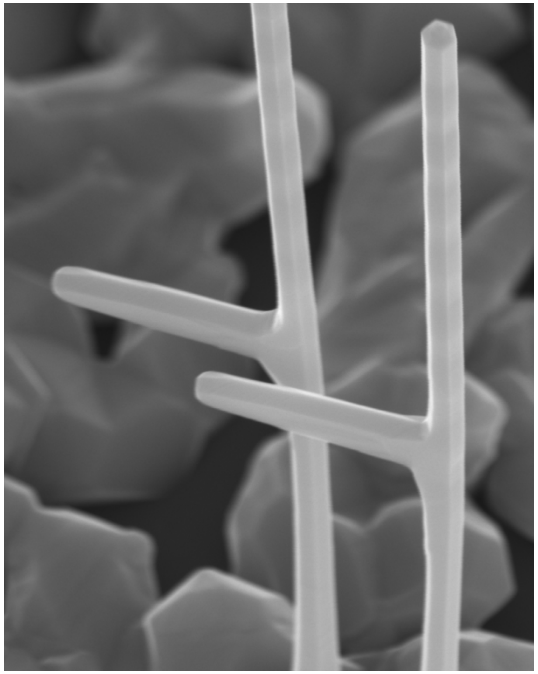
S.R. Plissard & al., *Nature Nanotech.* **2013**, 8, 859-864

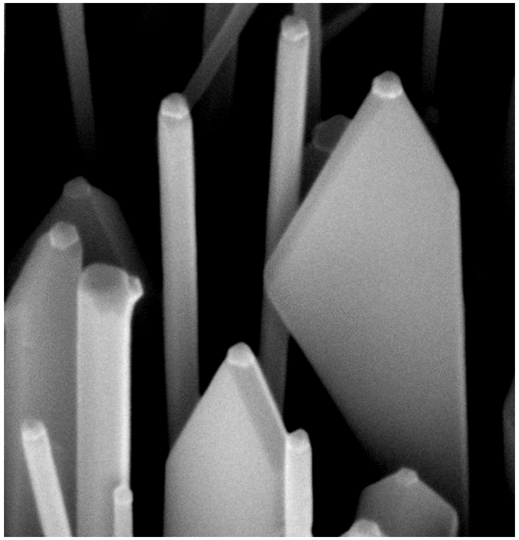
Nanowire Networks



A few alternatives …

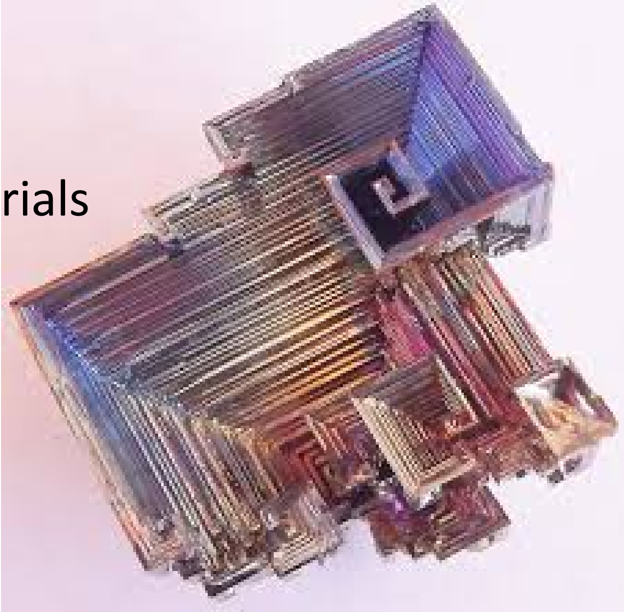
- An alternative method to grow nanowire networks





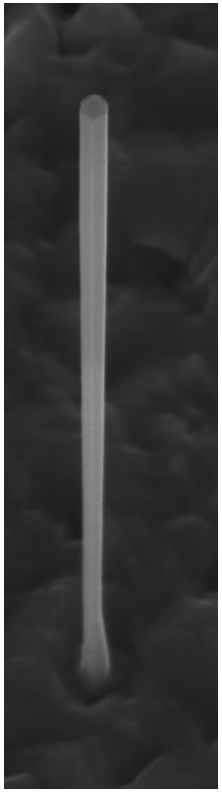
- Alternative shapes

- New nano-materials



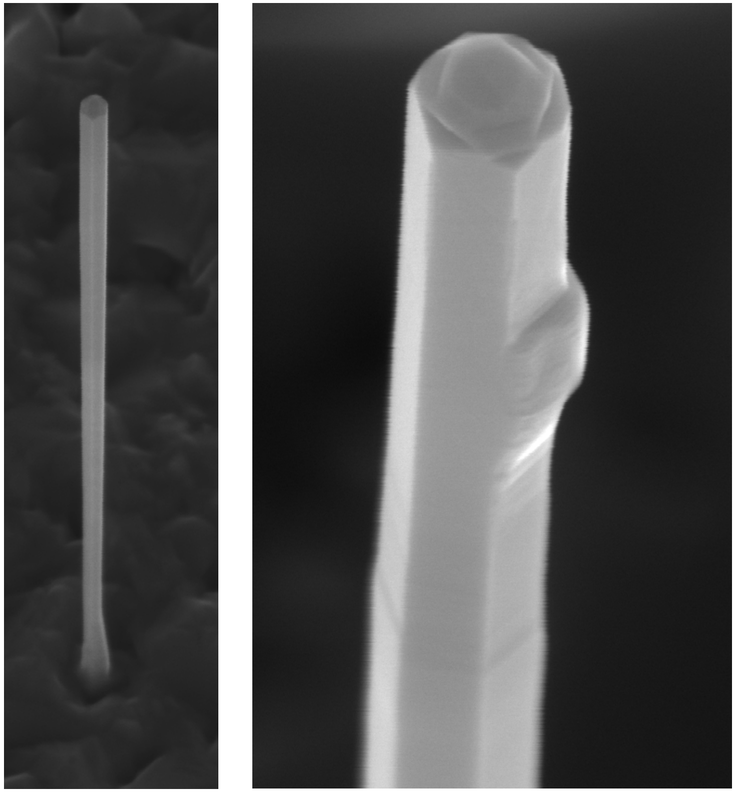
Self-catalysed nanotrees via droplet engineering

1) Self-catalysed growth of nanowires



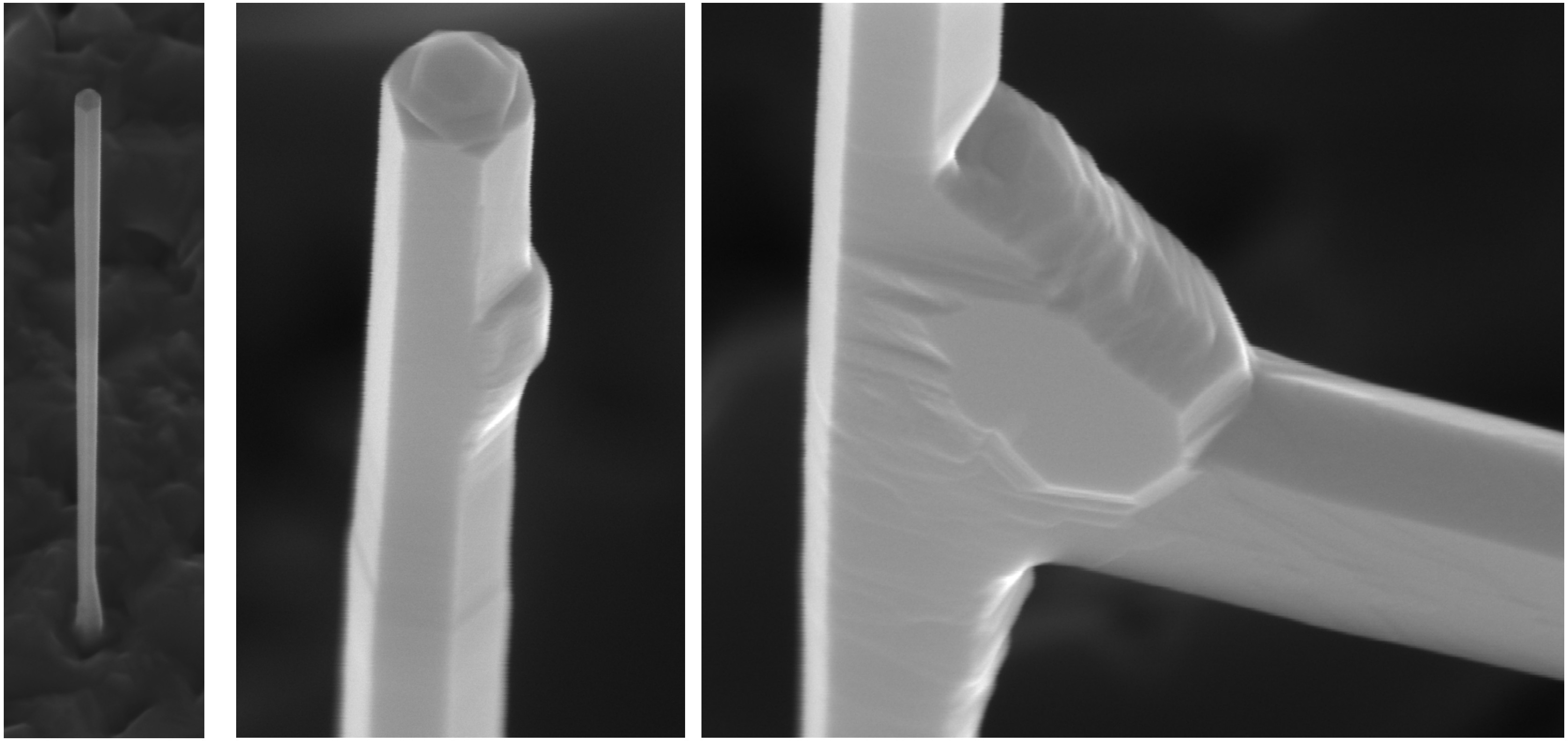
Self-catalysed nanotrees via droplet engineering

1) Self-catalysed growth of nanowires
2) Creation of a droplet on a side-wall

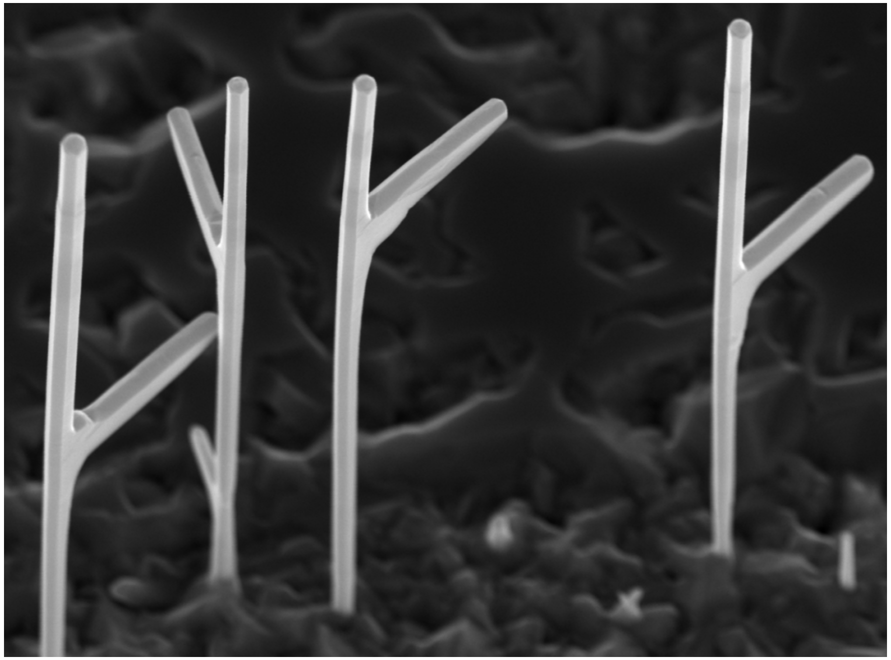


Self-catalysed nanotrees via droplet engineering

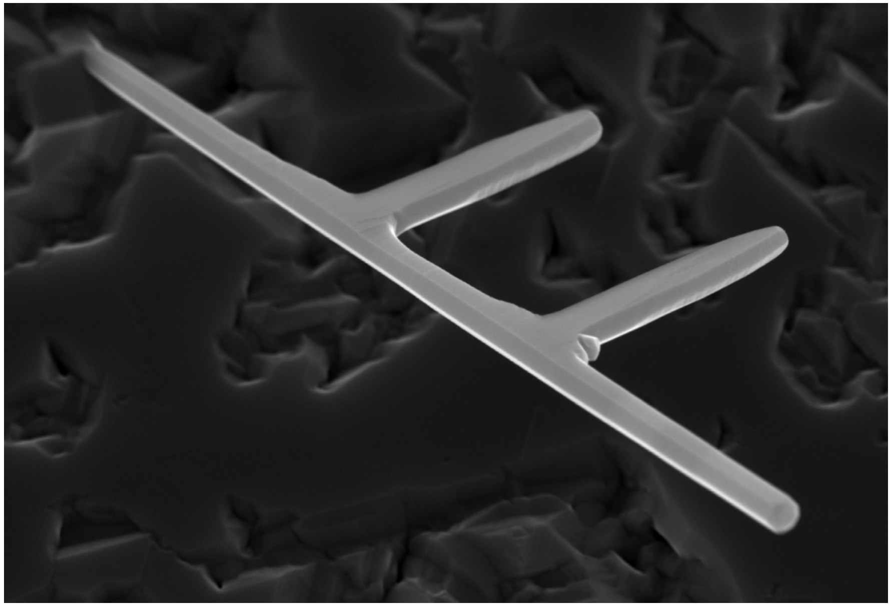
1) Self-catalysed growth of nanowires
2) Creation of a droplet on a side-wall
3) Growth of a new branch



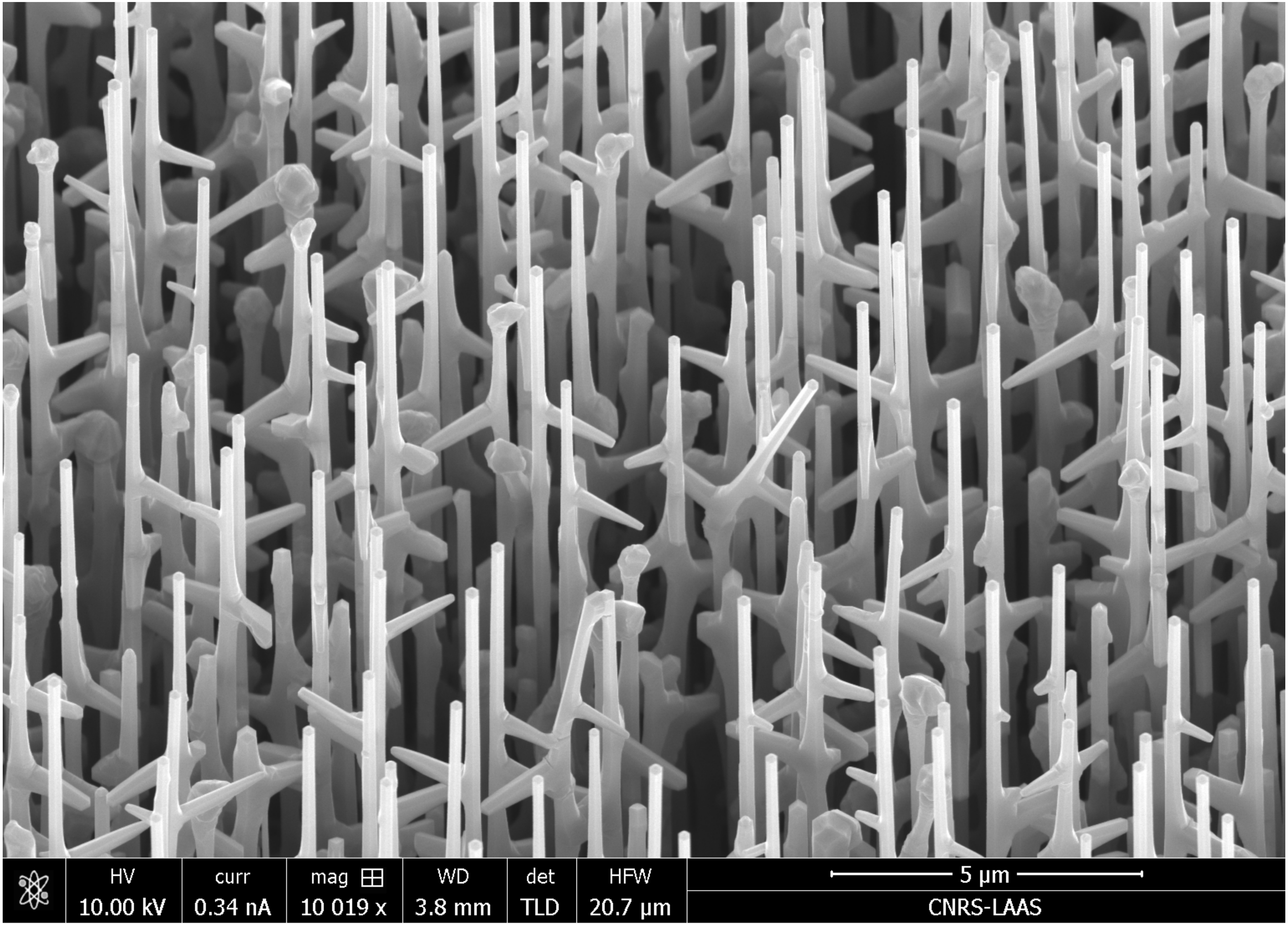
Self-catalysed nanotrees via droplet engineering



- Multiple branches can nucleate from the same nanowire



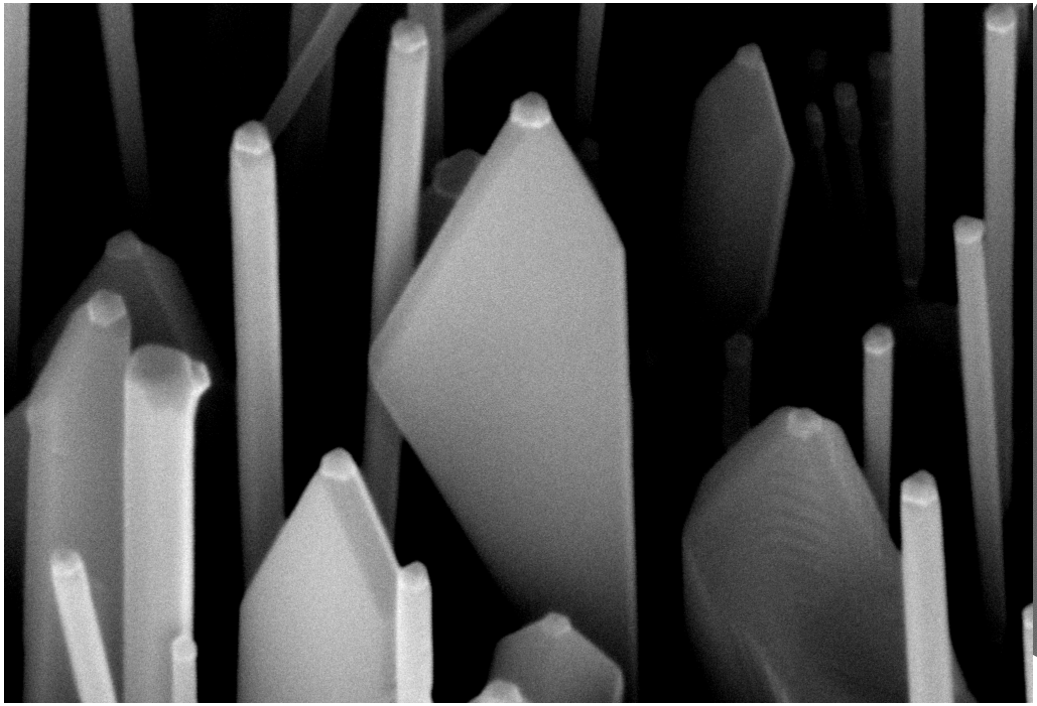
- Possibility to grow π-structures

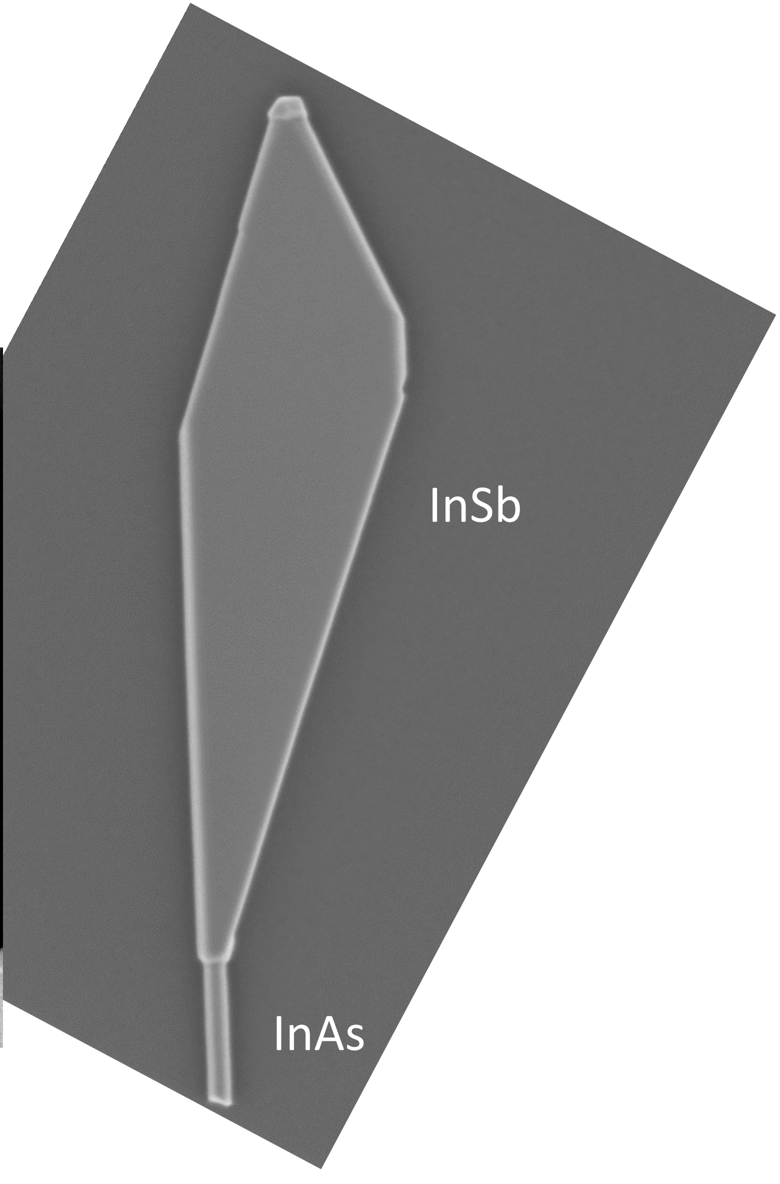

HV
10.00 kV
curr
0.34 nA
mag
10 019 x
WD
3.8 mm
det
TLD
HFW
20.7 µm
5 µm
CNRS-LAAS

Alternative InSb shapes

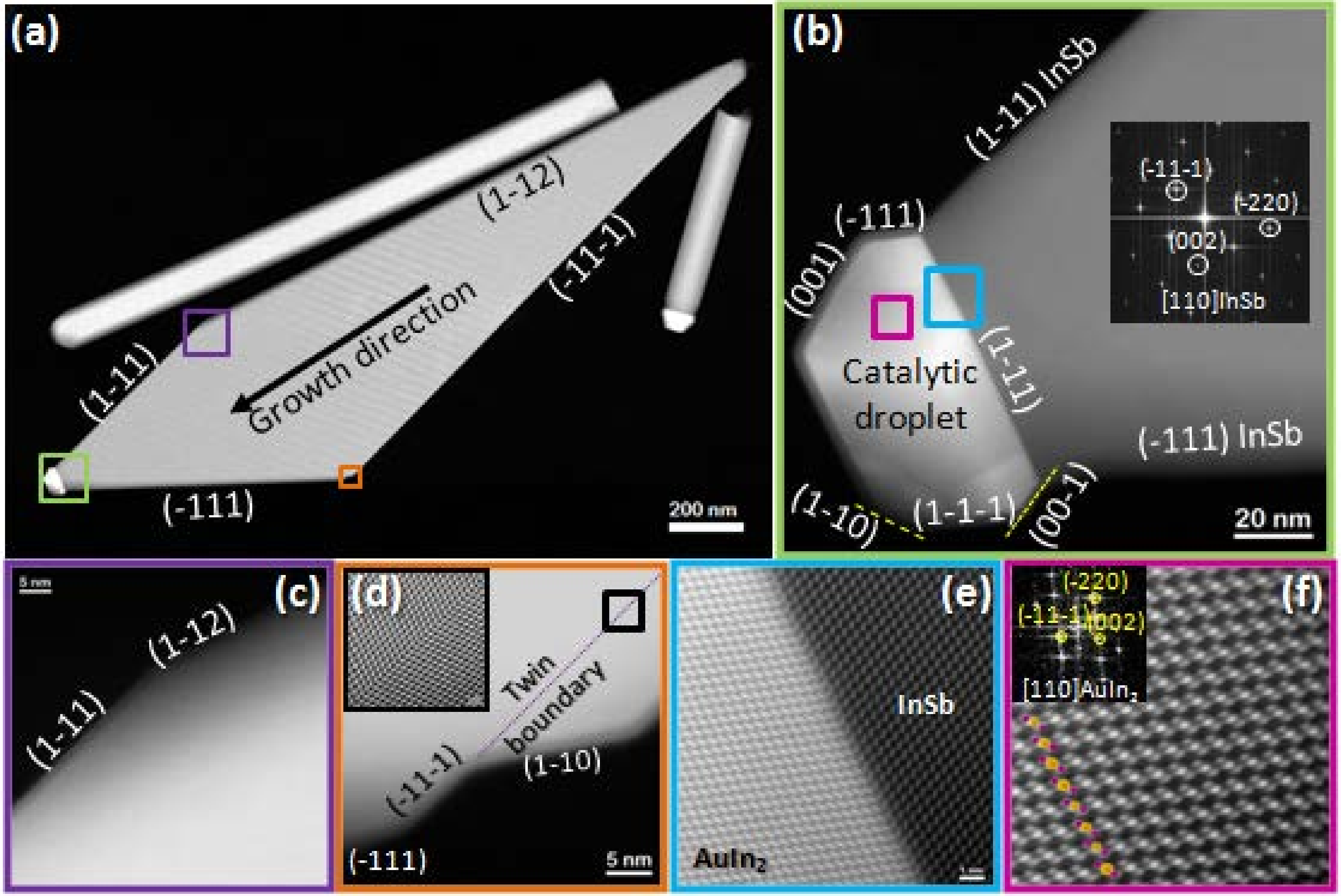
Growth of InSb 2D nano-structures

(thickness ~ 100 nm)





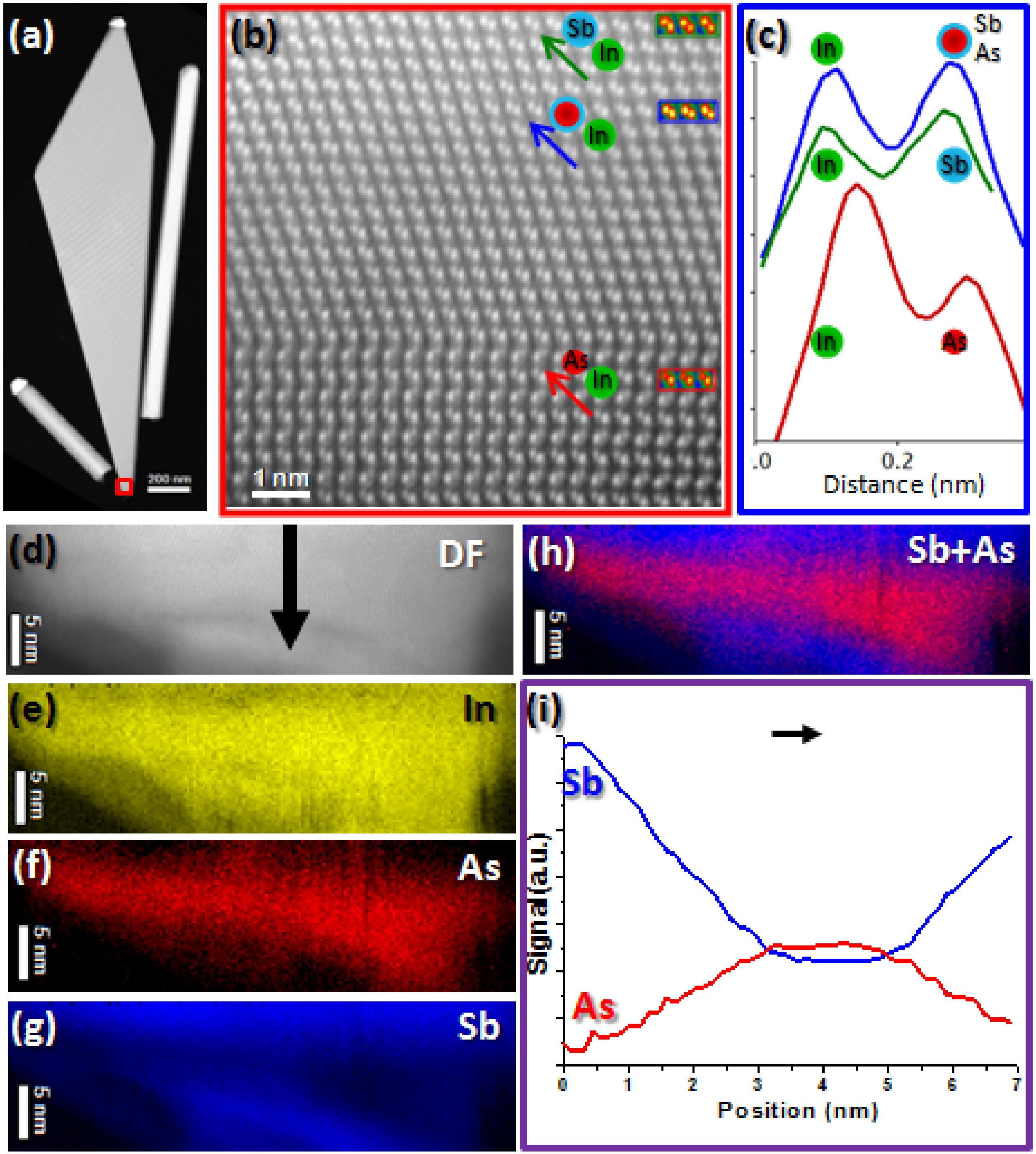
Alternative InSb shapes



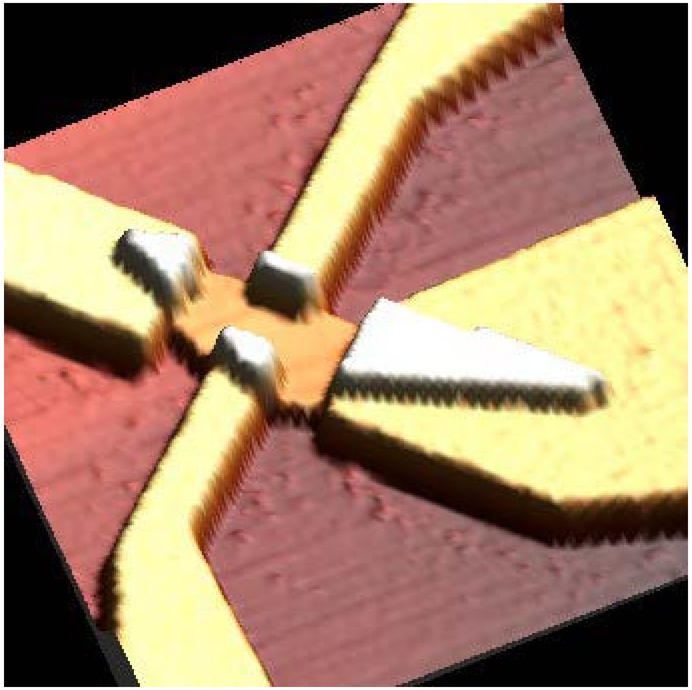
No diffusion of As in the InSb nanoflake

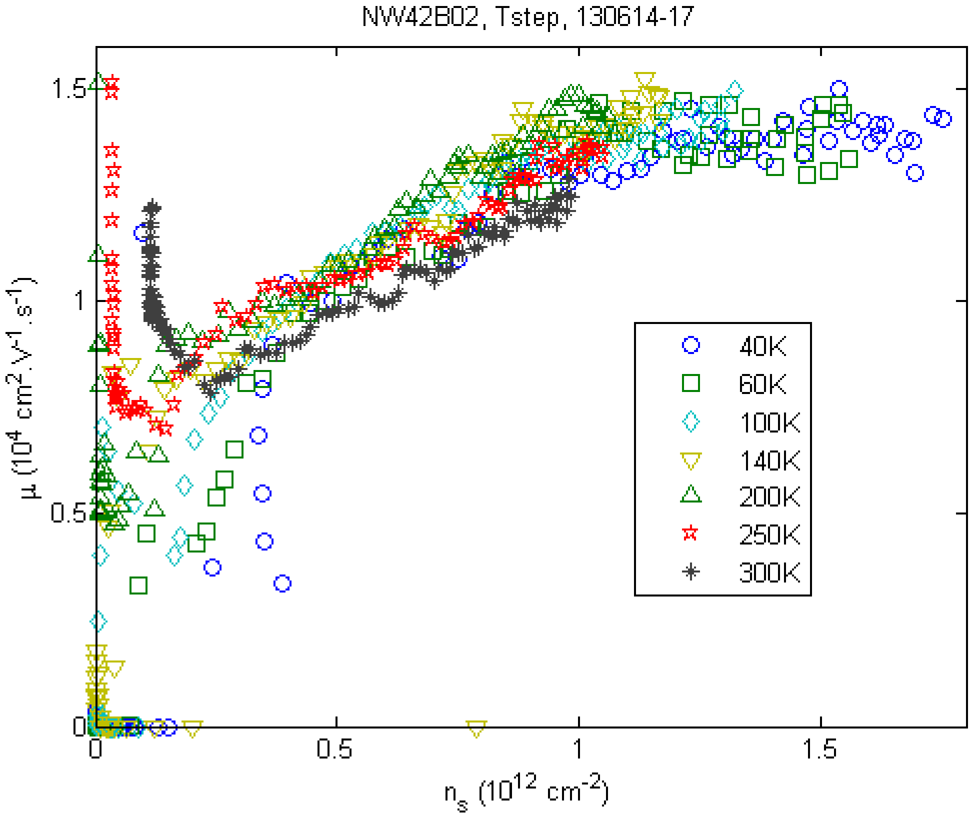
+

No gold found in InSb



Electrical measurement of the InSb nanoflakes

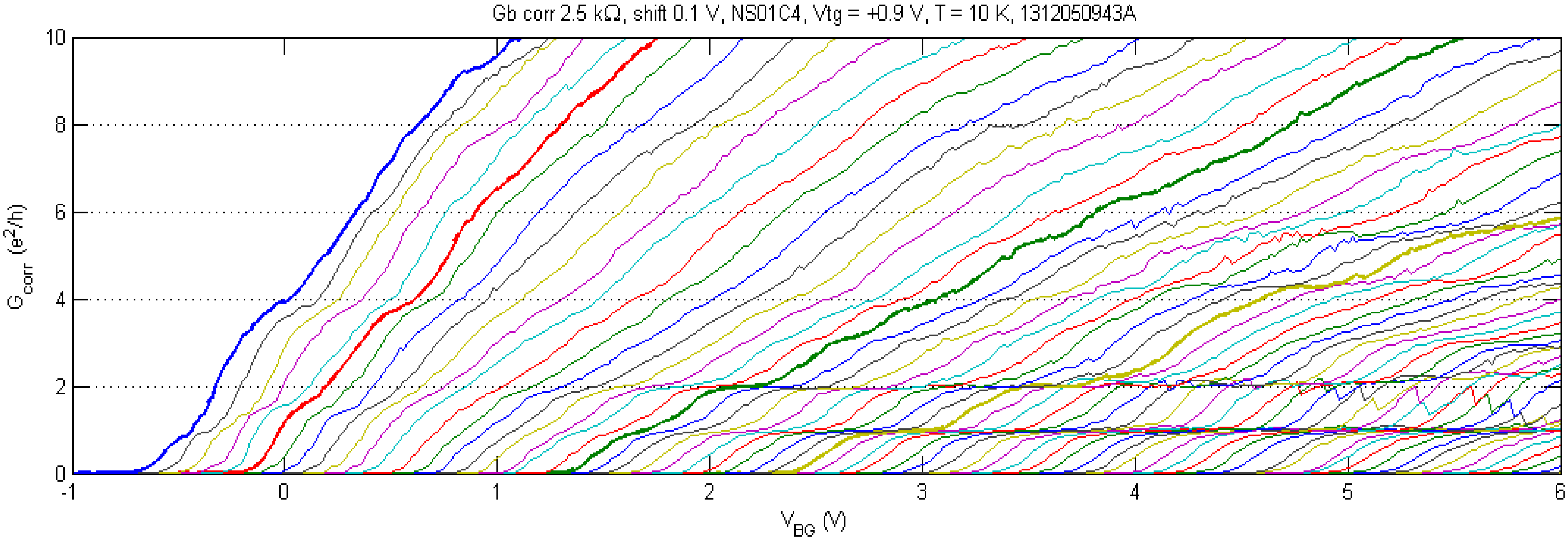




High electron mobility in these nanostructures ~ 10 000 cm².V^{-1}.s^{-1}

Not influenced by the Temperature

First QPC devices



First hints of quantized conductance in these structures