

Полупроводниковые нитевидные кристаллы: рост и физические свойства

Г.Э.Цырлин

*Санкт-Петербургский академический университет – научно-образовательный центр нанотехнологий
РАН, ул. Хлопина д.8/3, Санкт-Петербург.*

Физико-Технический Институт им.А.Ф.Иоффе РАН, Политехническая 26, Санкт Петербург, Россия

Институт Аналитического Приборостроения РАН, Рижский 26, С.Петербург, Россия

Санкт-Петербургский Государственный Университет, С.Петербург, Петергоф, ул. Ульяновская 3, Россия

e-mail: cirlin@beam.ioffe.ru

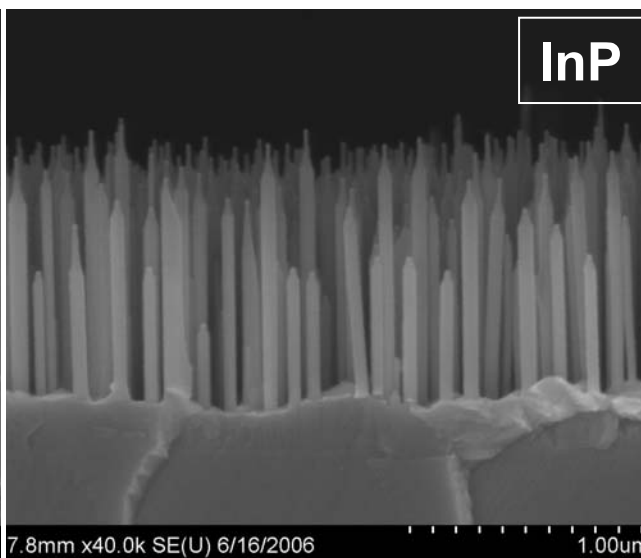
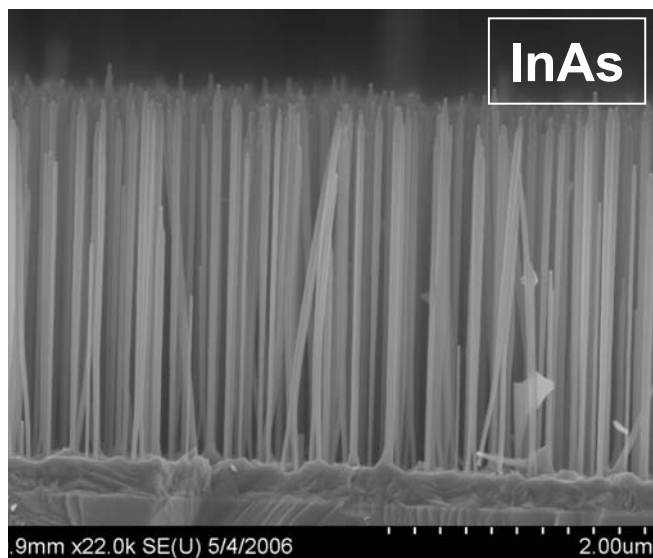
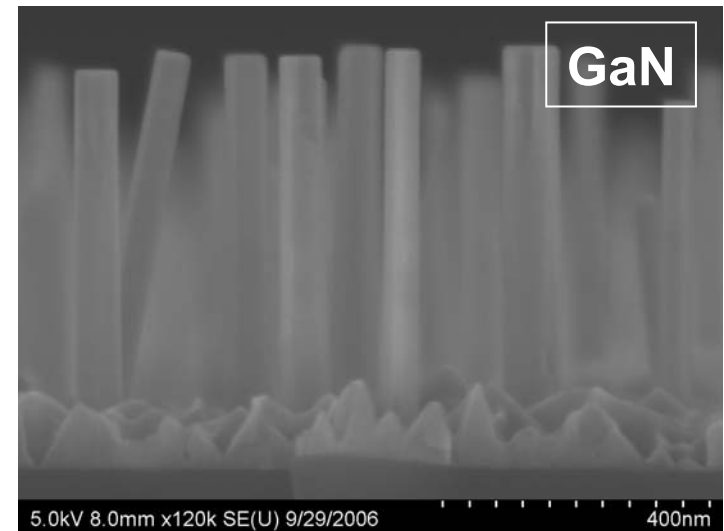
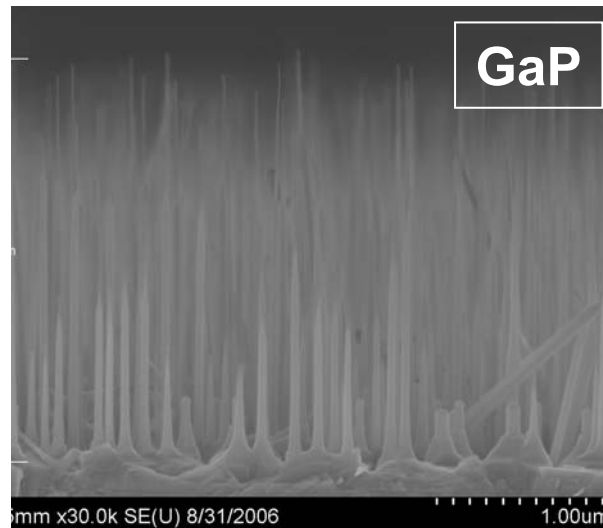
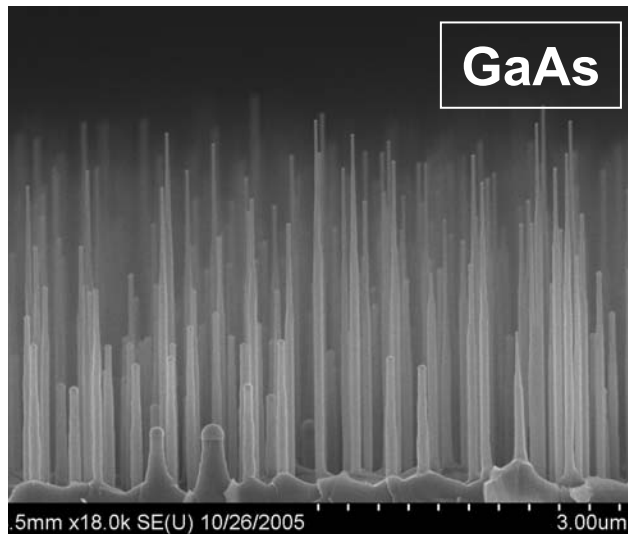
Нижний Новгород, 6 декабря 2012 г.



Outline

- ❑ Au-assisted MBE growth of GaAs nanowires
- ❑ MBE growth of A3B5 nanowires on silicon
- ❑ InAs, InP nanowires and InP/InAsP/InP heterostructures
- ❑ GaAs quantum dots inside AlGaAs nanowires
- ❑ Photovoltaic properties of p-type GaAs NWs on GaAs(111)B n-type substrate
- ❑ Few other examples of NWs (GaAs NWs on tungsten STM tips)

Self-organized III-V nanowires by MBE



Nanowire parameters

- ❑ d from 20 to 200 nm
- ❑ h up to 50 μm
- ❑ hexagonal cross-section
- ❑ density $\sim 10^6 - 10^{10} \text{ cm}^{-2}$



GaAs nanowires

Au assisted nanowire growth

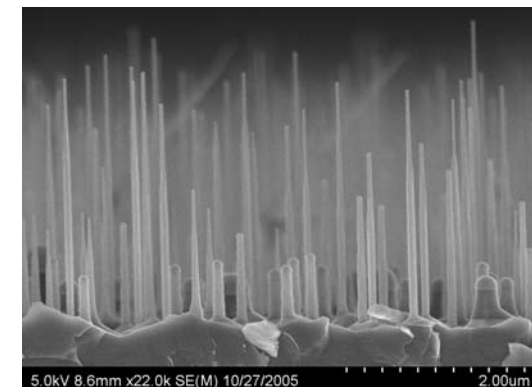
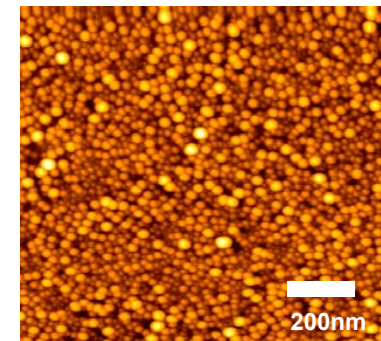
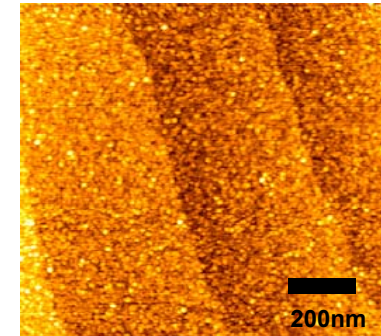
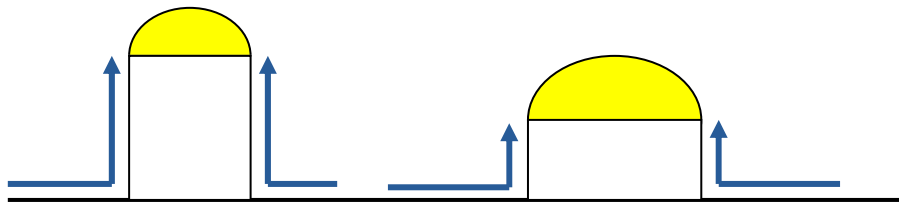
- ❑ (111)B oriented substrate
- ❑ Buffer layer ~100 nm
- ❑ Au deposition in the growth chamber (h up to 1 nm)



- ❑ Annealing $\Rightarrow$ Au – metal alloying
- Droplet size and density depends on h and $T_{\text{annealing}}$

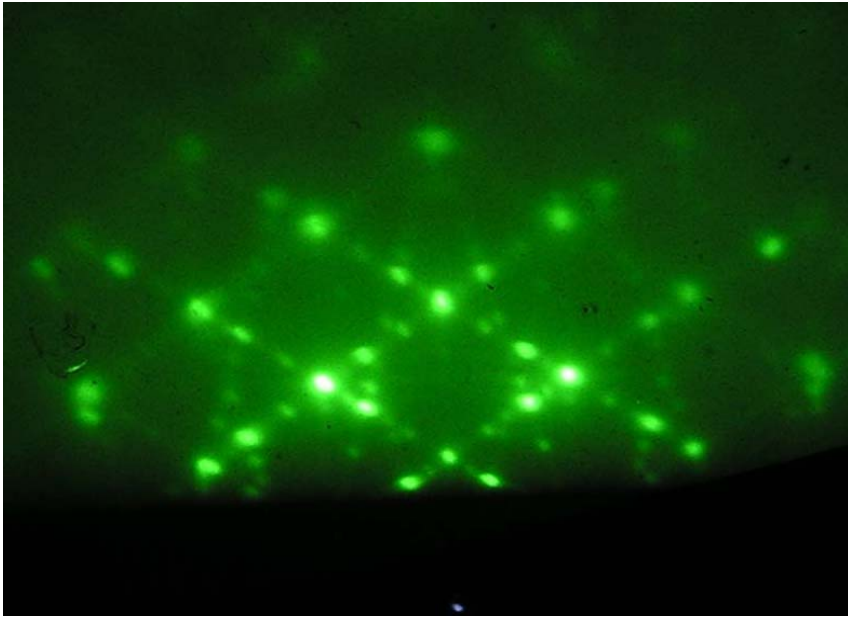


- ❑ Nanowire growth (surface diffusion of the species up to the catalyst, super-saturation, precipitation)

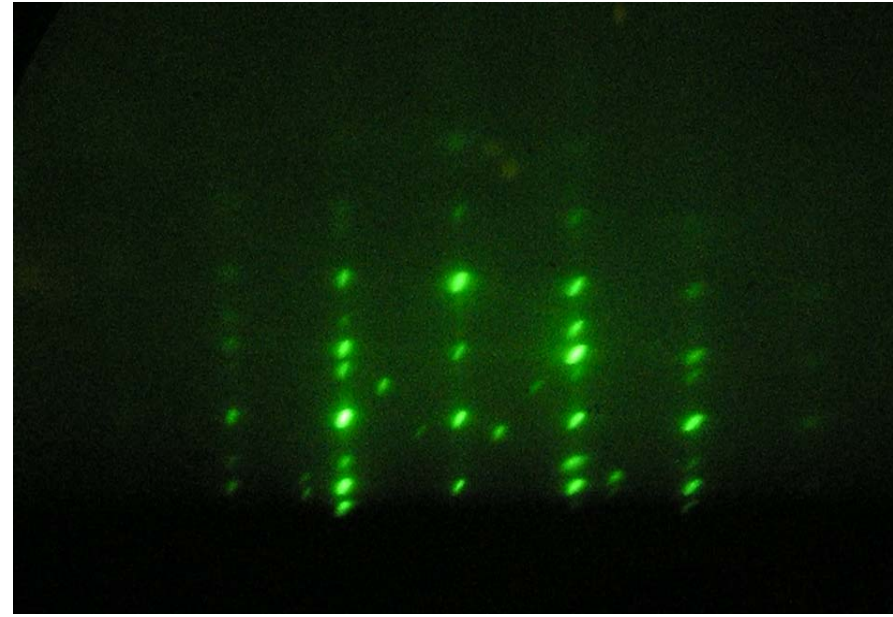




In situ RHEED control



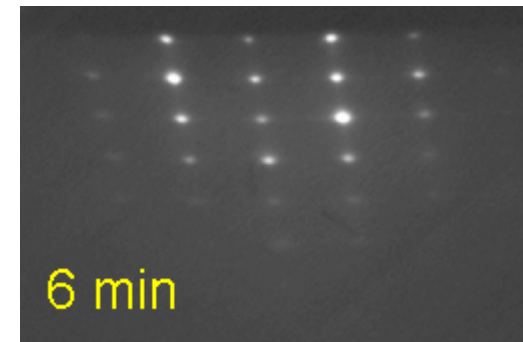
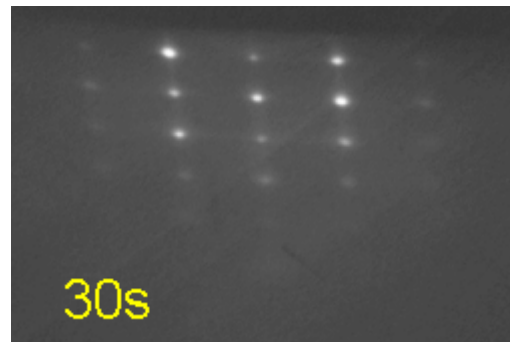
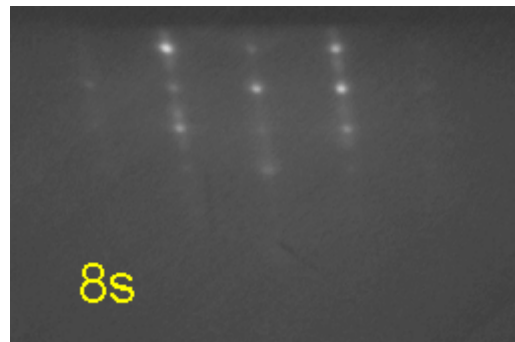
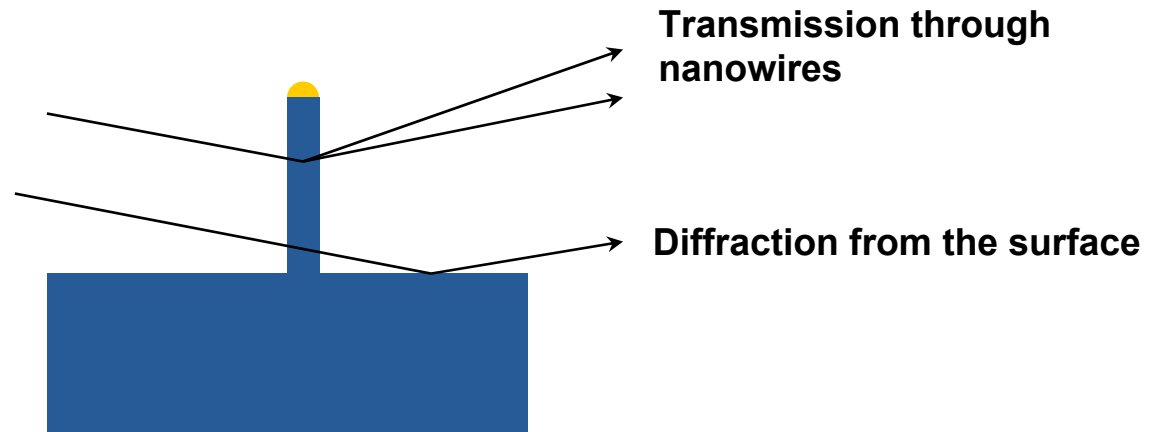
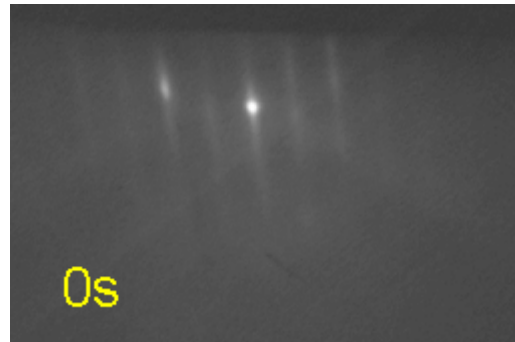
**200 nm
GaAs/Si(001)**



**200 nm
GaAs/GaAs(111)B**

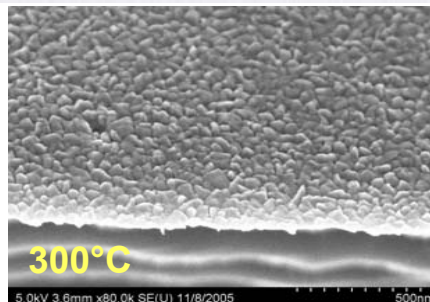
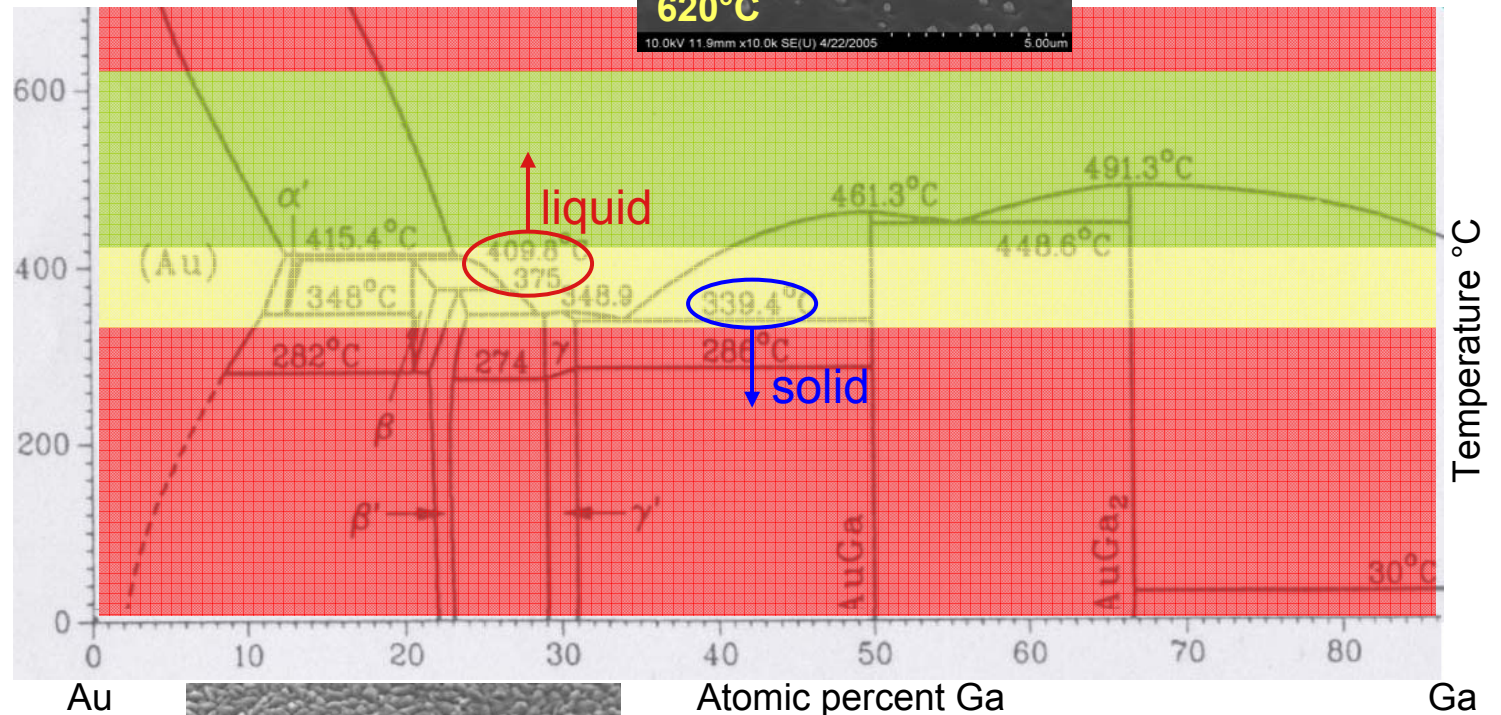
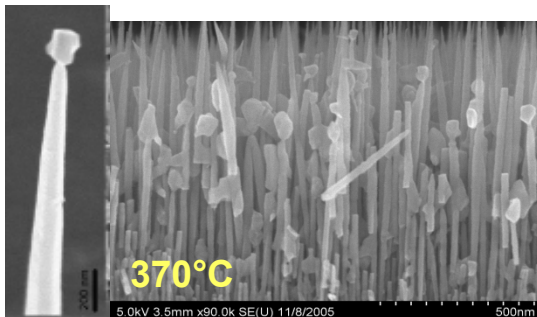
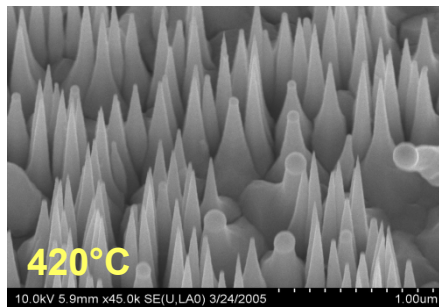
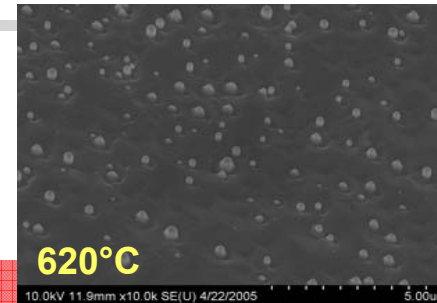
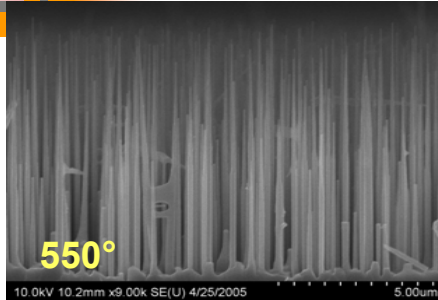
RHEED dynamics: CB to WZ transition

GaAs (111)B + Au
450°C



Hexagonal phase

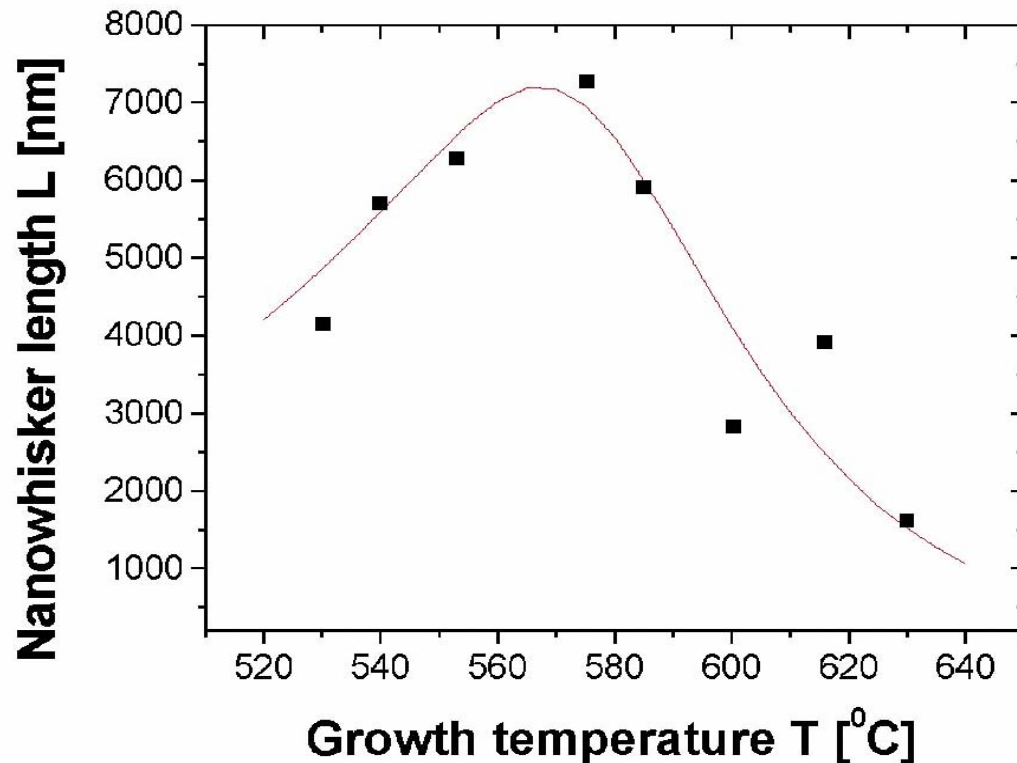
Temperature domain for NW growth



Journal of Crystal Growth,
2007, v.301–302, p.853–856.

Growth rate with temperature

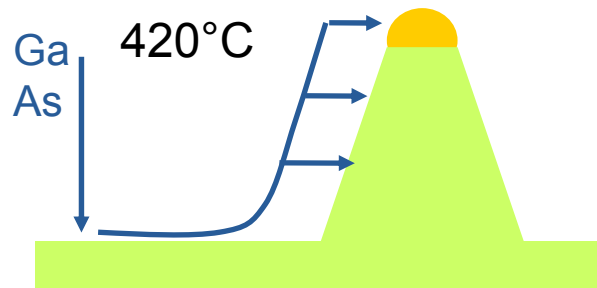
Temperature domain for regular GaAs nanowires : 410°C – 620°C



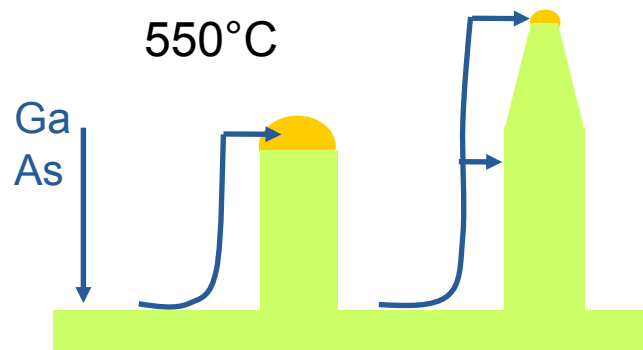
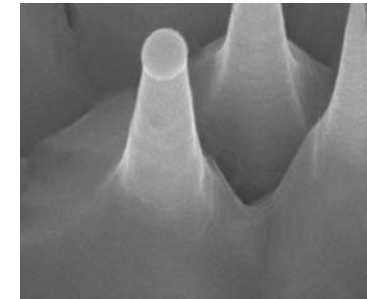
□ Nucleation is faster at the liquid/solid interface than at the vapor/solid interface – increase of the growth rate

□ Increase of $T_g \Rightarrow$ enhancement of adatom surface migration $\Rightarrow$ higher NW growth rates

NW morphology with temperature



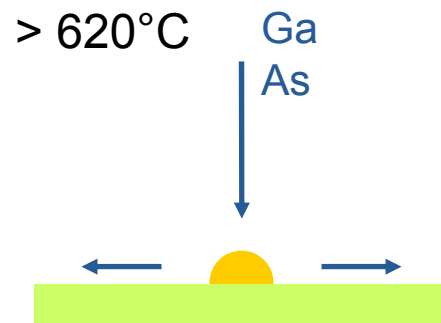
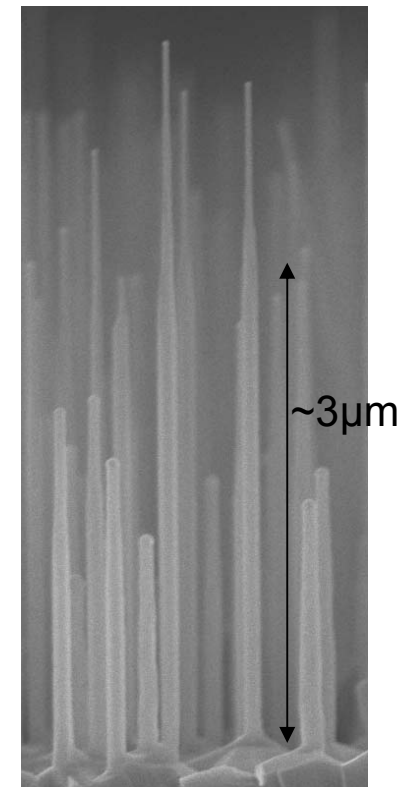
Nucleation on the sidewalls
Conical shape



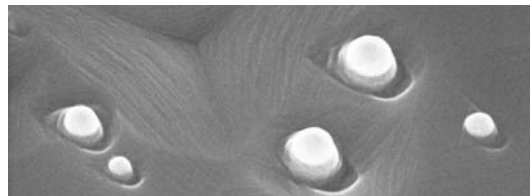
$h < \lambda \Rightarrow$ No nucleation on the sidewalls
Cylindrical shape

$h > \lambda \Rightarrow$

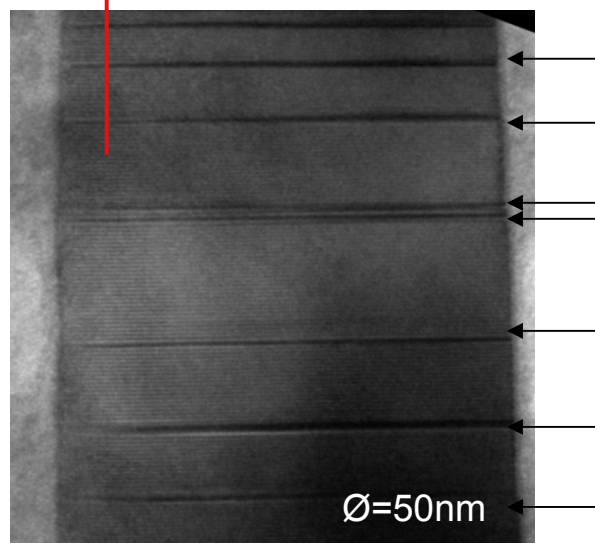
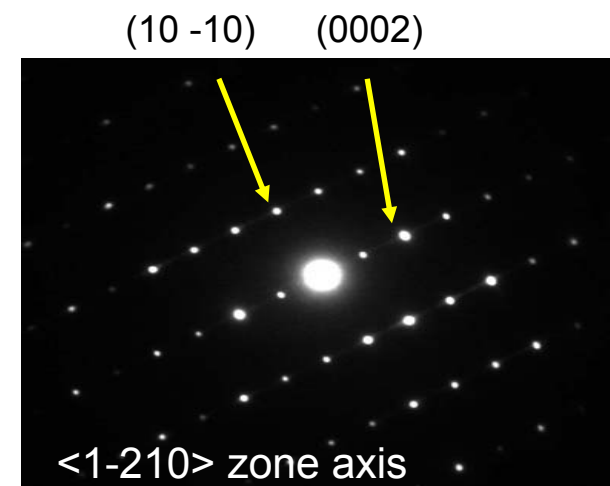
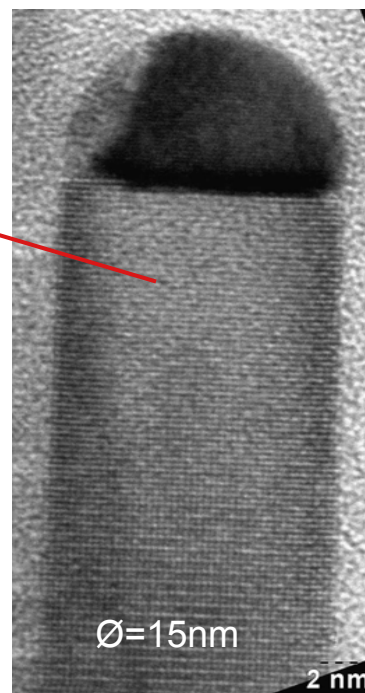
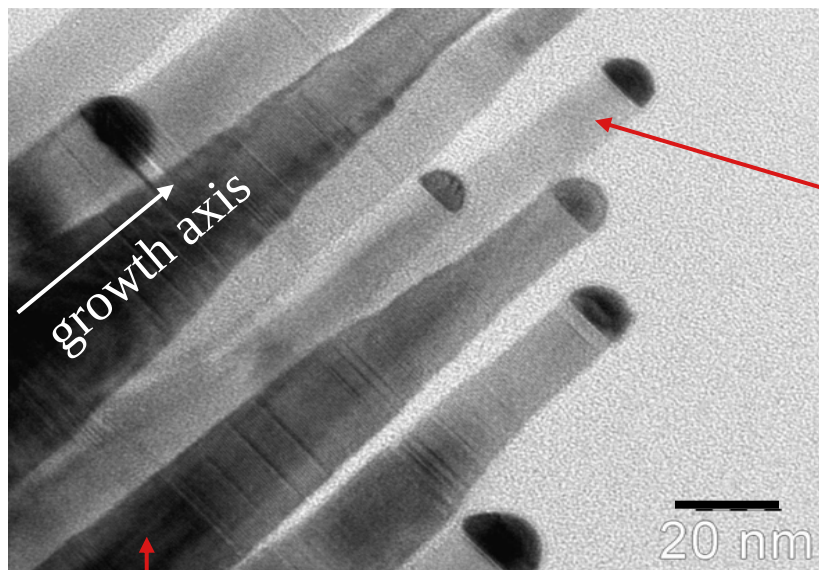
- Possible nucleation on the sidewalls
- Reduction of Ga content in the catalyst
Tapering of the nanowire



Chemical potential $\mu_{\text{liq}} > \mu_{\text{ads}}$
No nanowire growth



TEM study of crystalline phase

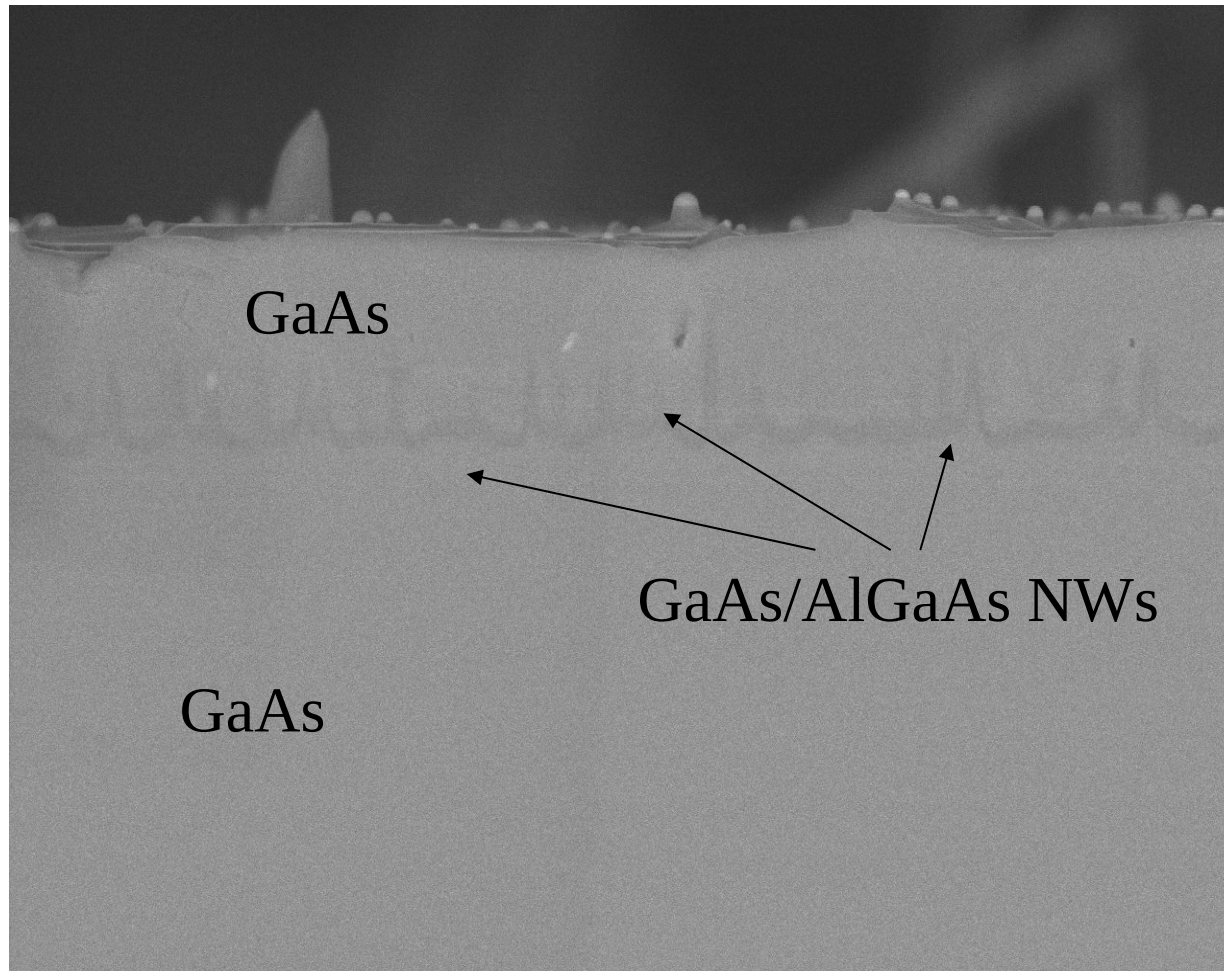


Stacking
faults
(density $\uparrow$
when $T \downarrow$)

**Wurtzite structure
 $\neq$ bulk GaAs**

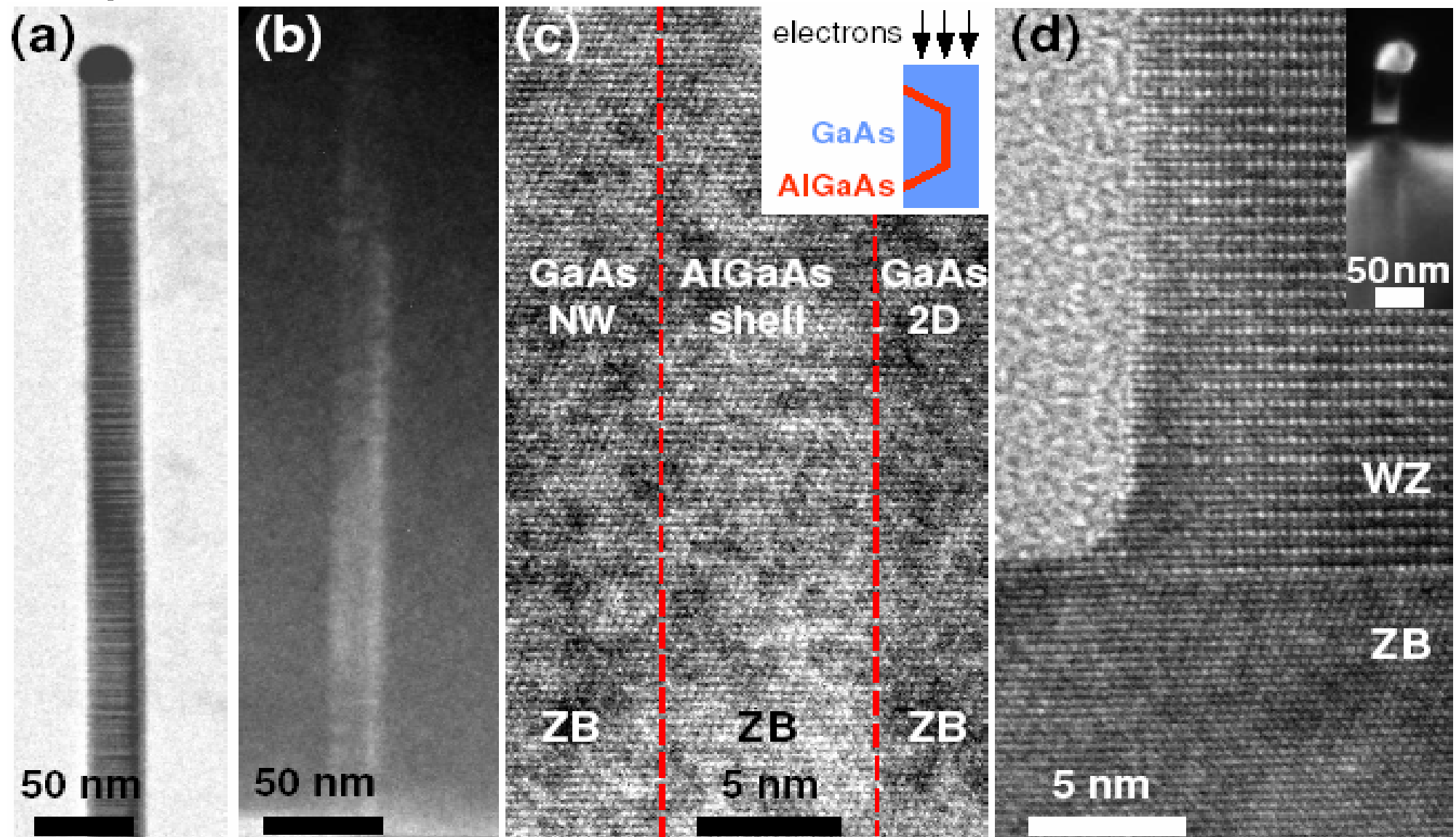
Hexagonal phase is predominant

GaAs/AlGaAs nanowires embedding in GaAs matrix



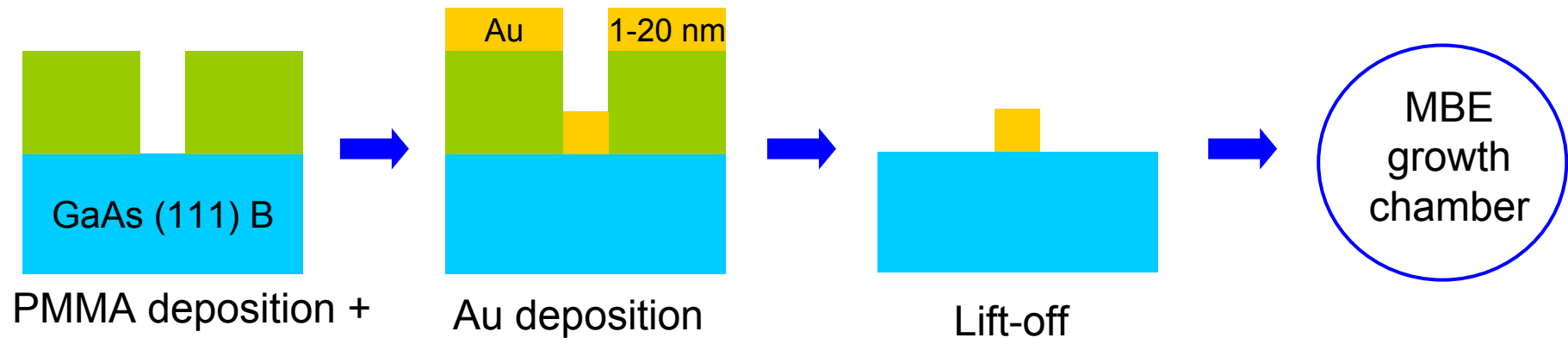
Nano Lett., 2008, v. 8, p.1638-1643

Embedding: WZ to ZB transition, twins disappearance



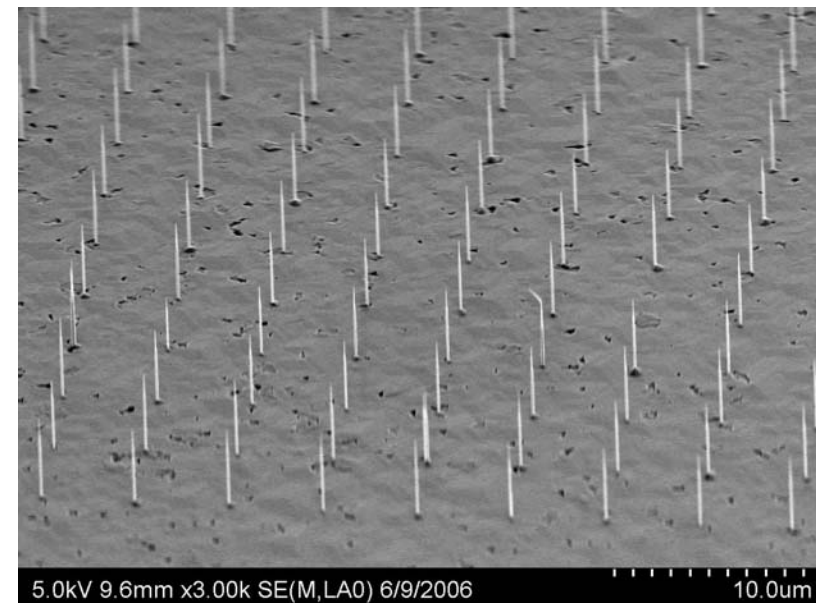
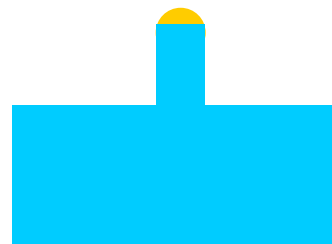
Ordering of GaAs nanowires using e-beam lithography

Fabrication procedure

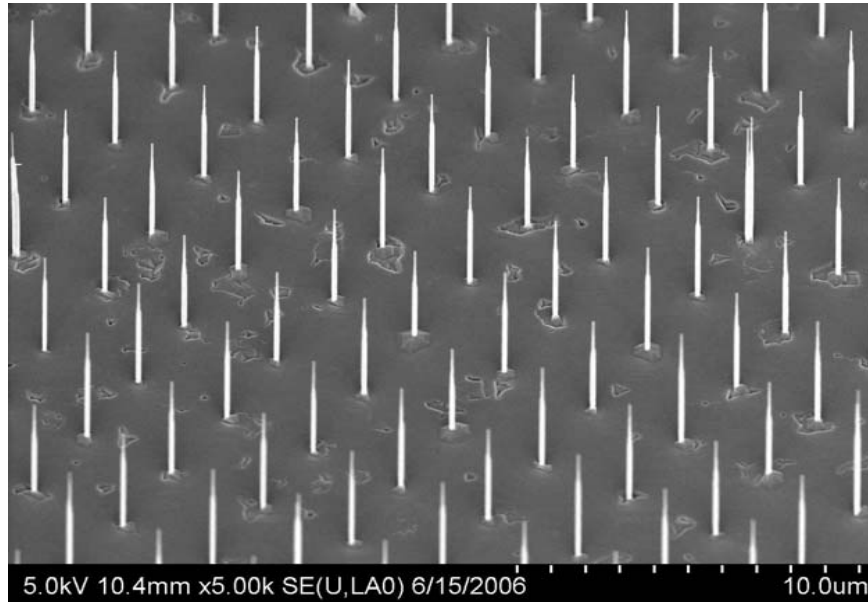


Surface cleaning at
300°C under H plasma

GaAs nanowire
growth at 550 °C



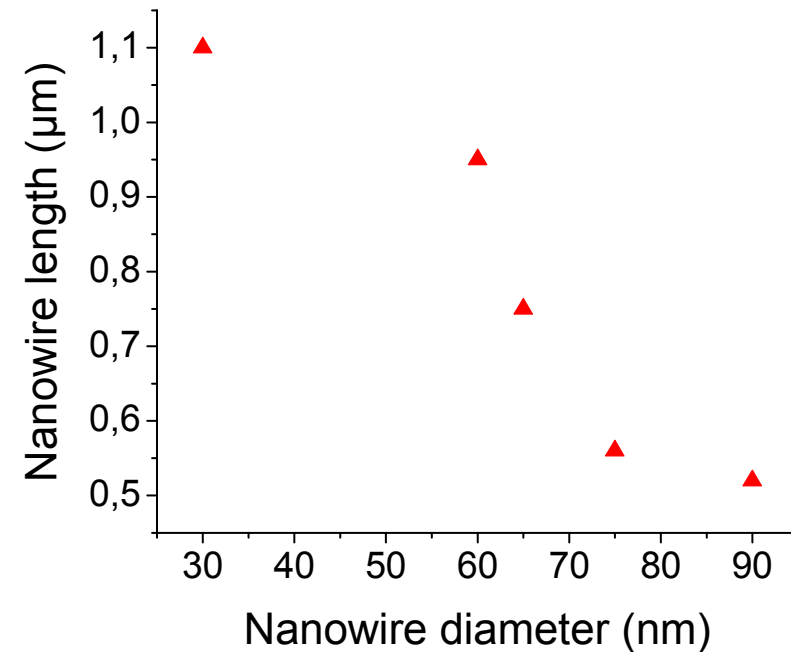
2D Arrays of GaAs nanowires



Mask with different Au dot diameters :
decrease of the nanowire length with diameter



Step 3μm
Wire length 5μm
Wire diameter 120nm
Tapering after 3-μm height

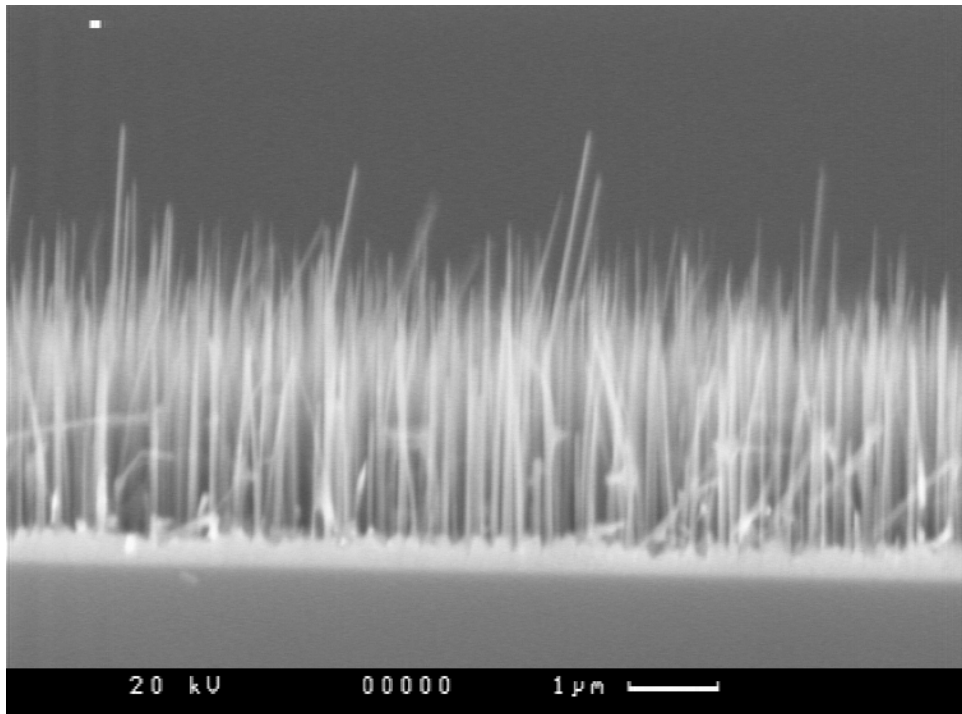


NW growth is fed by surface diffusion

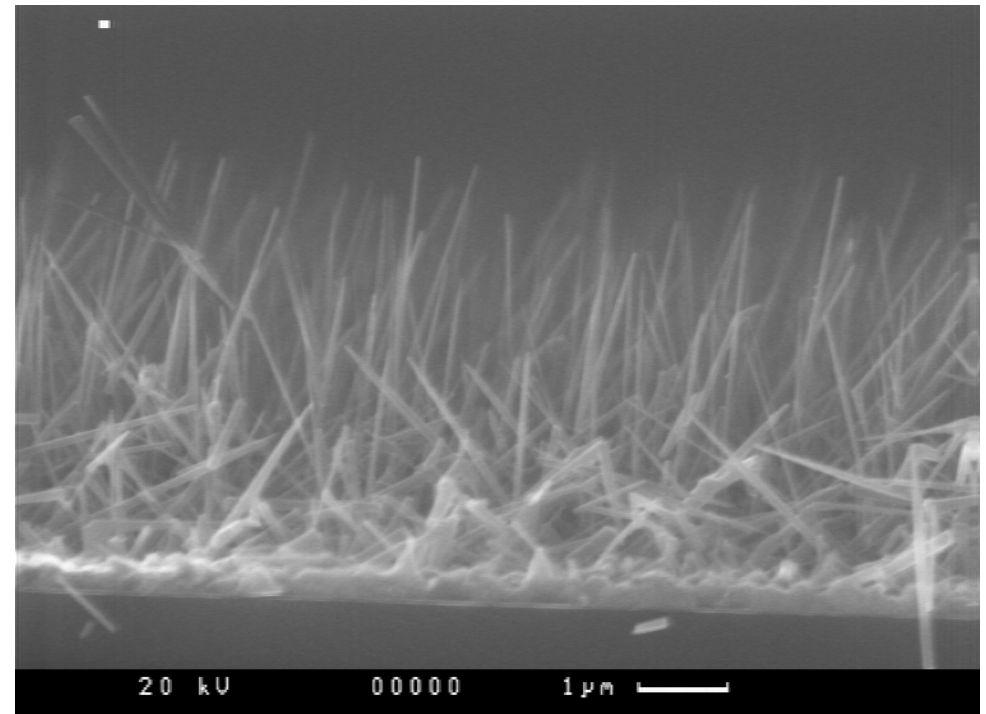


A3B5 nanowires on Si

GaAs NWs on Si: SEM observation

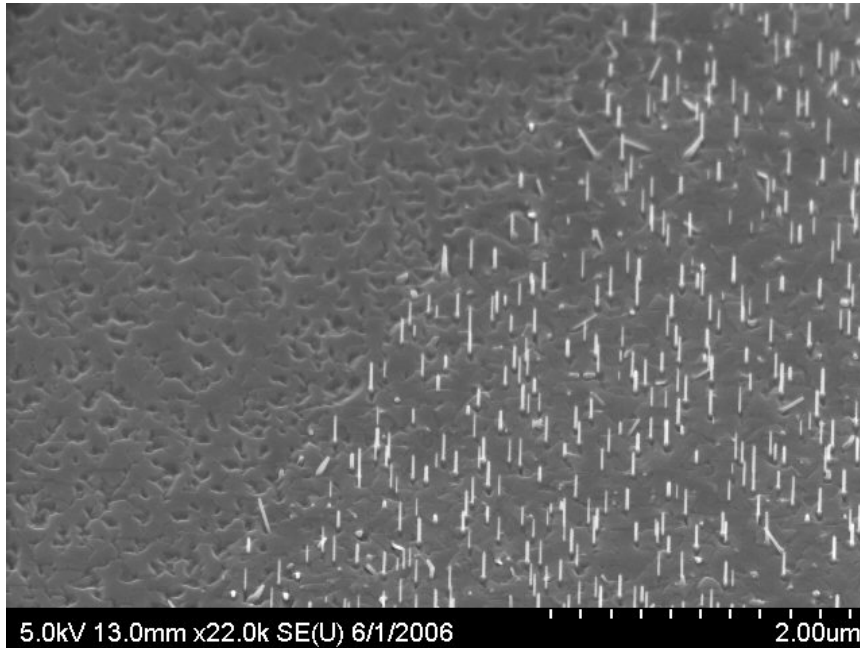


GaAs/Si(111), 700 nm

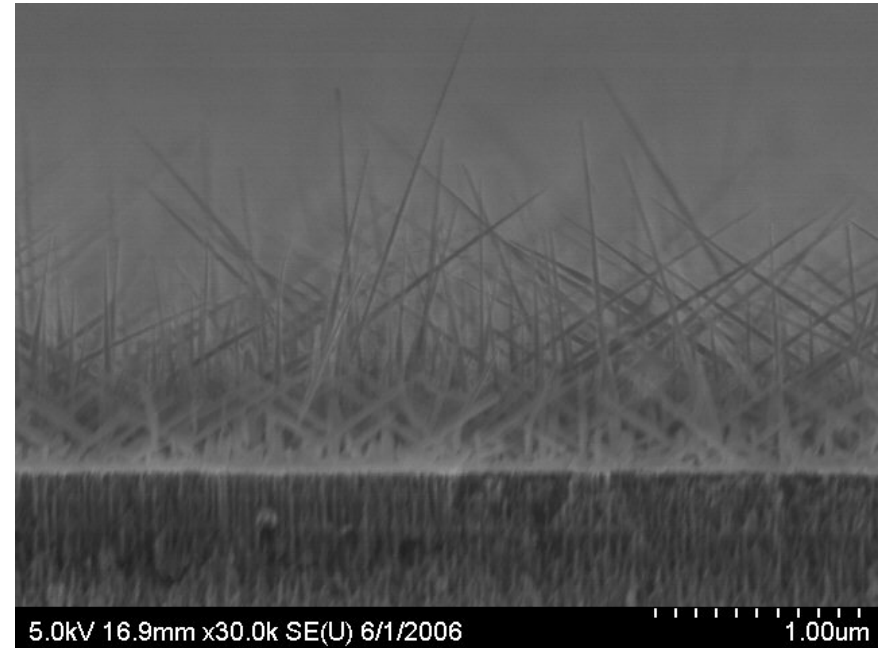


GaAs/Si(001), 700 nm

GaAs NWs on Si: effect of porosity

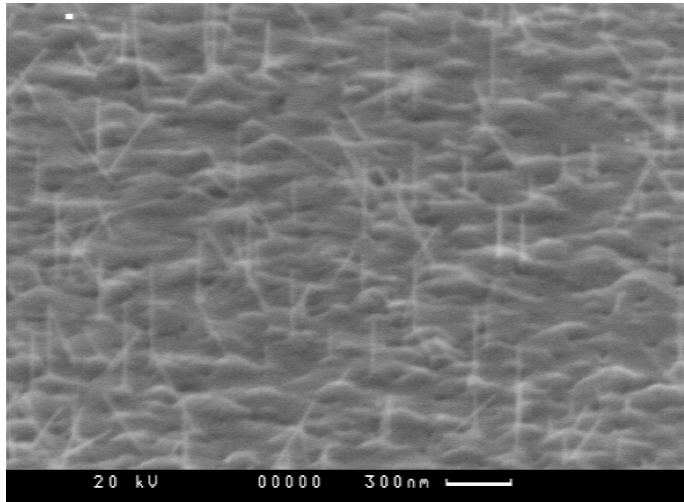


GaAs NWs on Si(111)

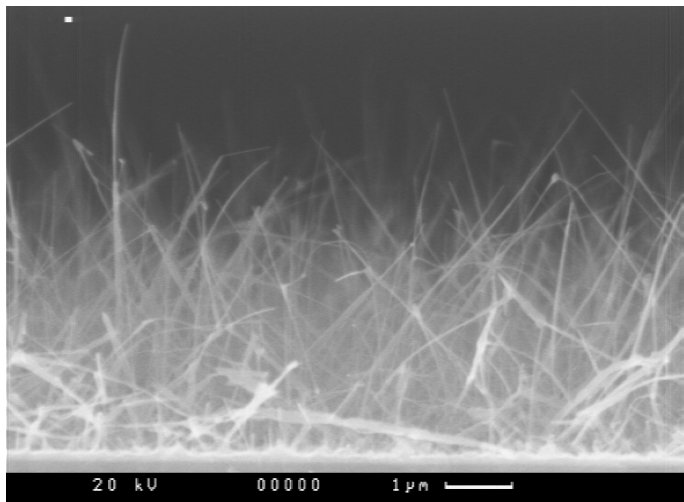


GaAs NWs on Si(001)

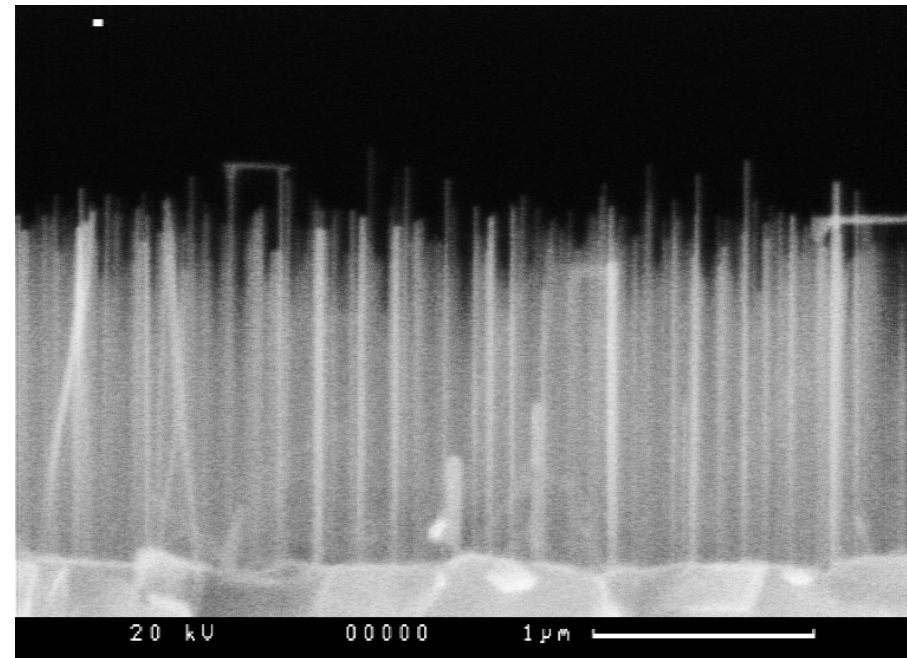
InAs NWs on Si(111) and GaAs(111)B



InAs/Si(111)

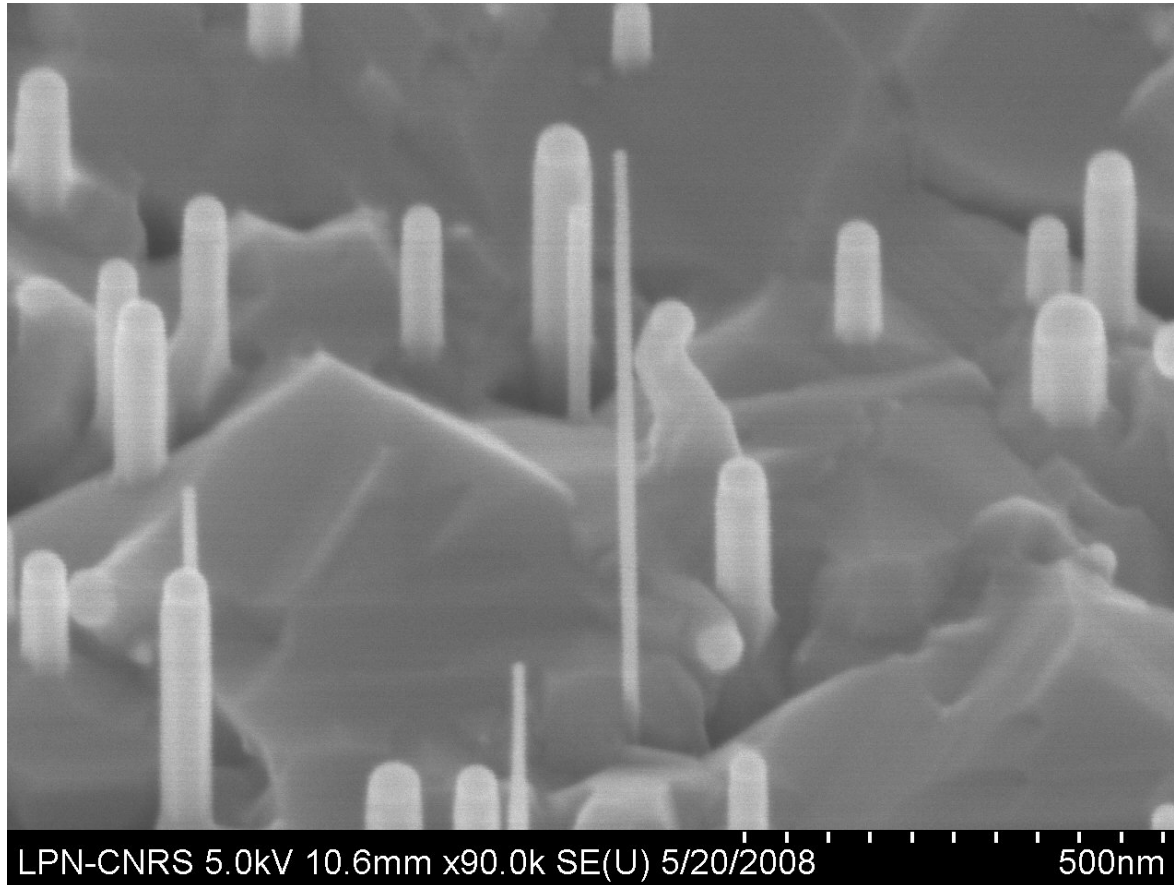


InAs/Si(001)

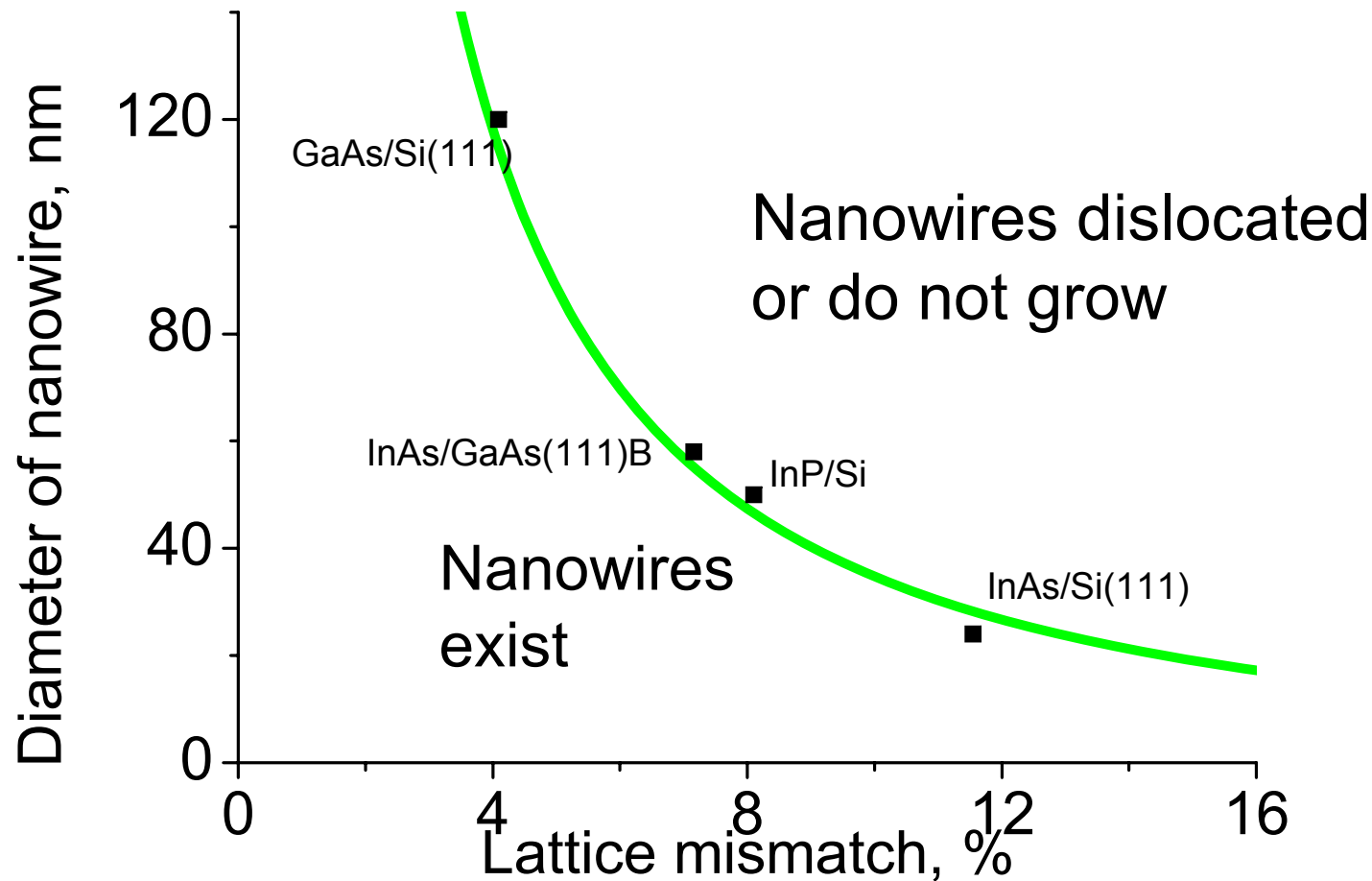


InAs/GaAs(111)B

InP NWs on Si(111)



CRITICAL DIAMETER OF A3B5 NANOWIRES

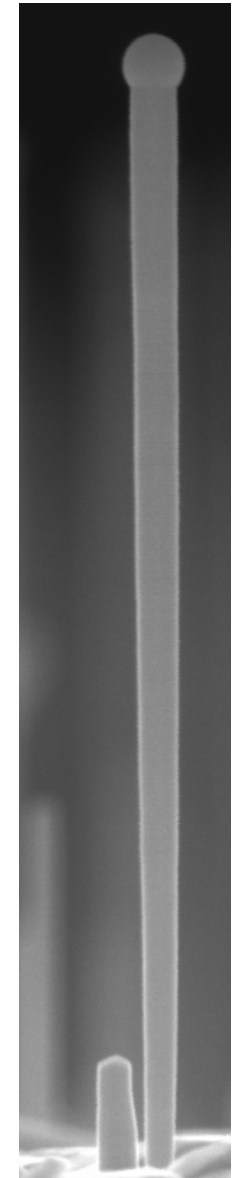
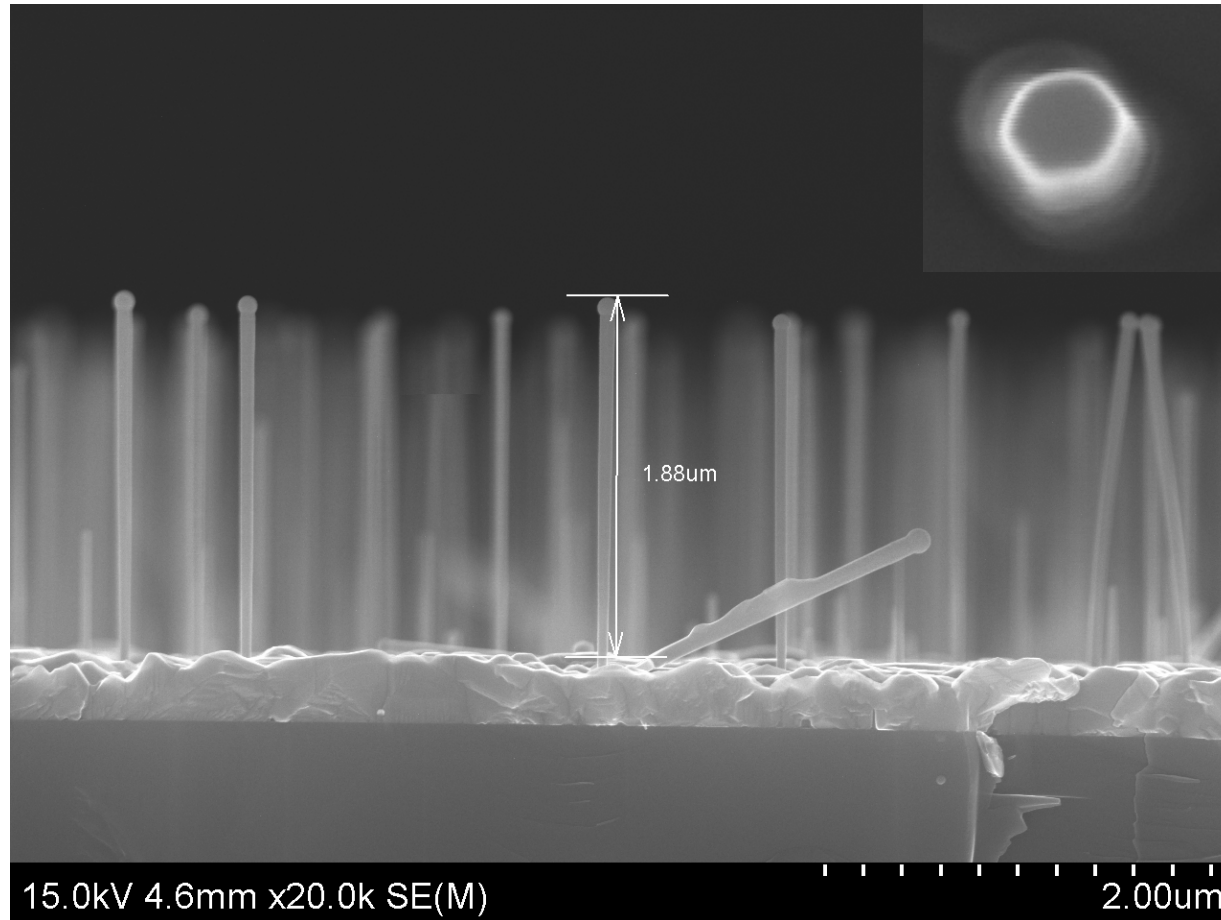


Phys. Status Solidi RRL 3, No.4, 112–114 (2009)



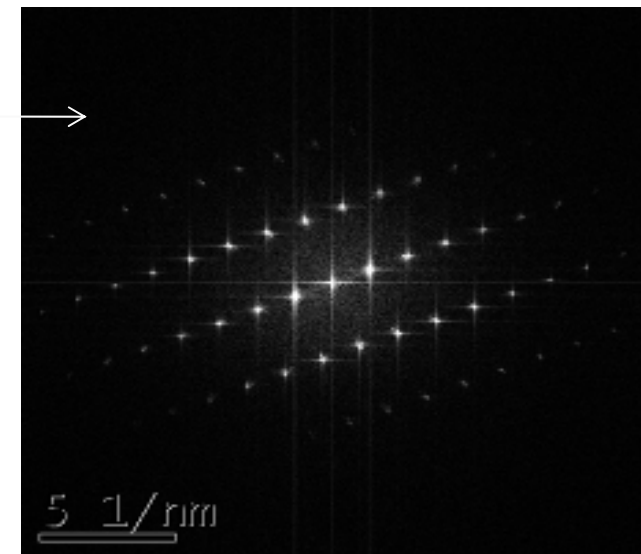
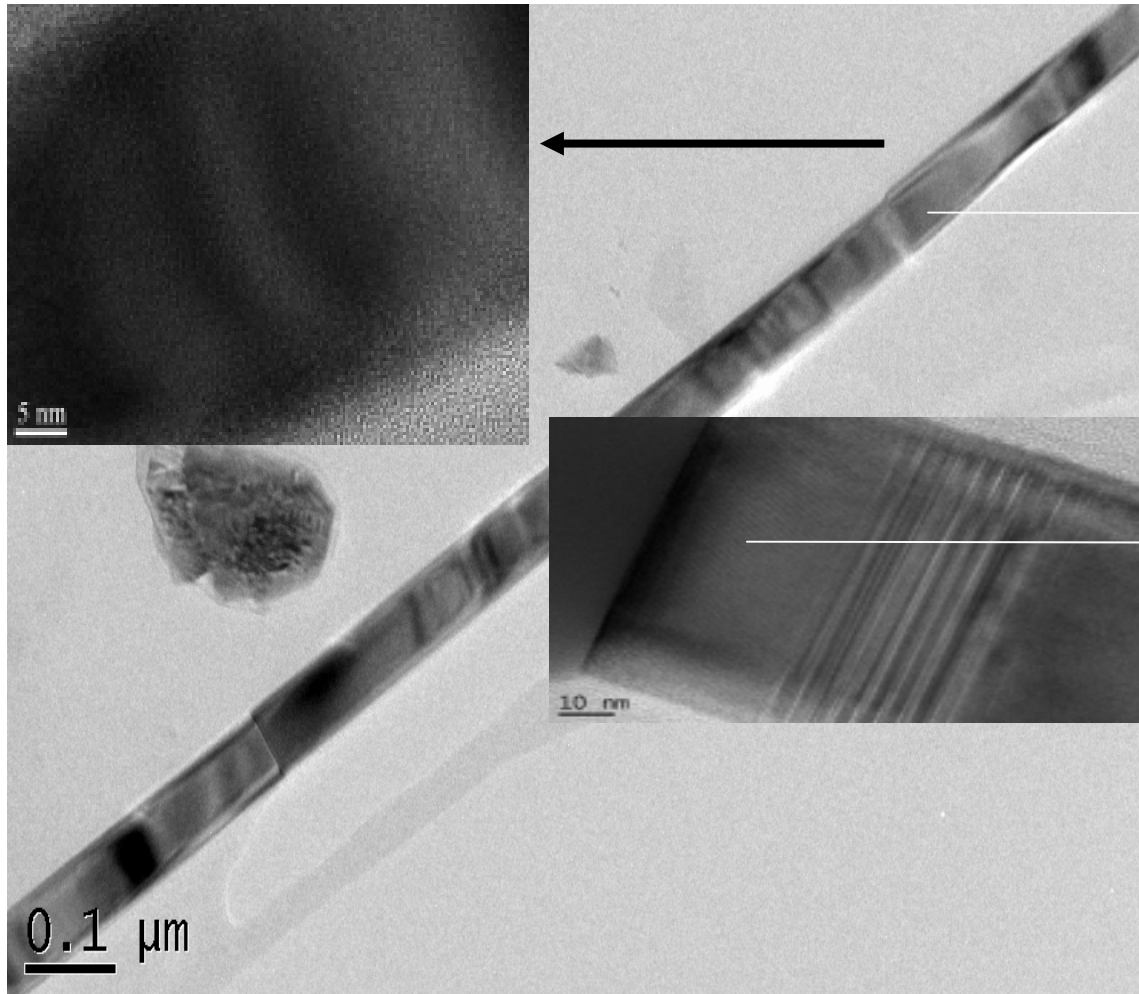
Self-catalysed GaAs NWs on Si(111)

Ga-catalised GaAs/Si(111)

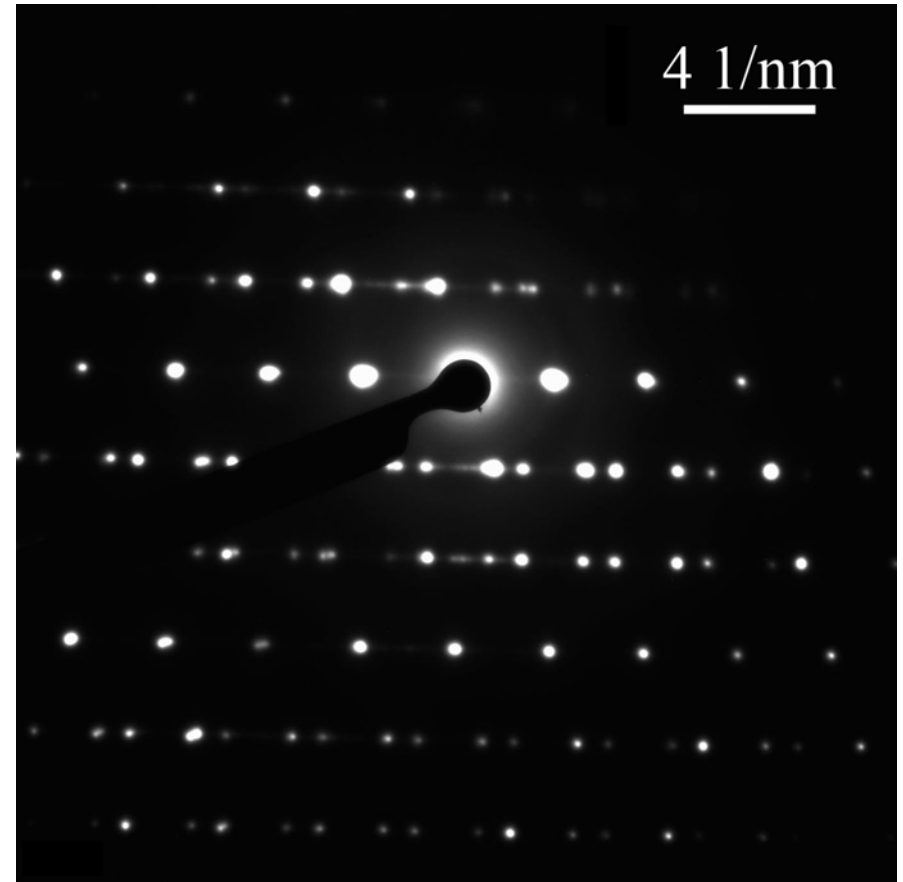
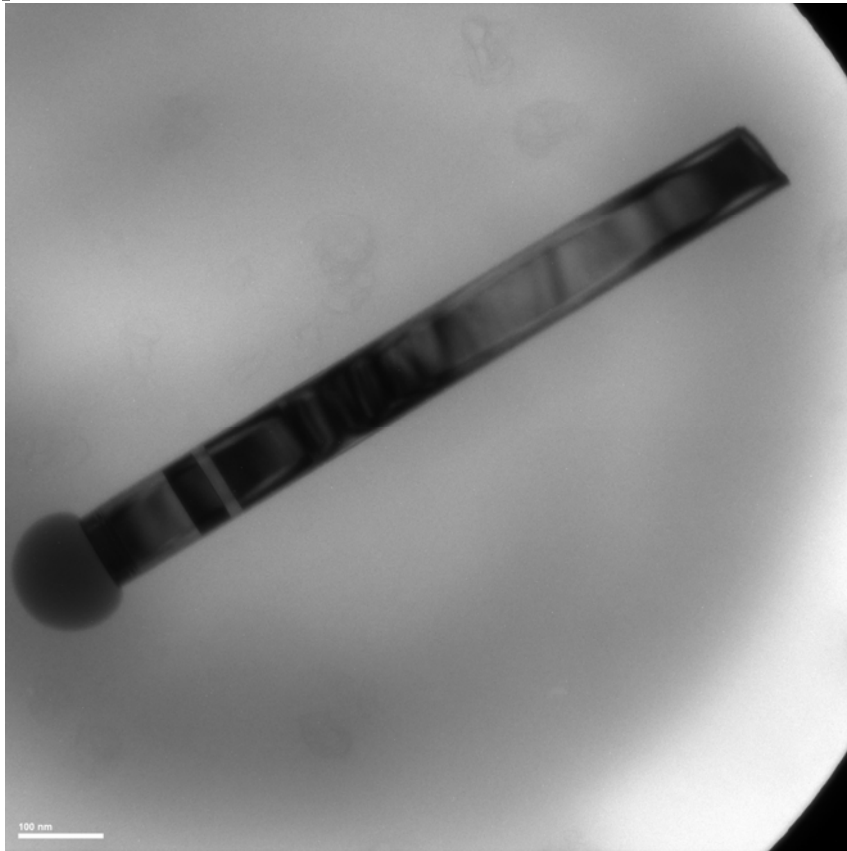


Phys.Rev.B, 2010, v.82, 035302

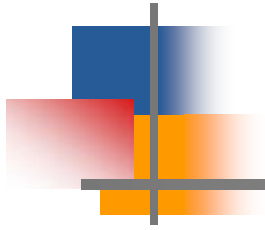
Cubic phase!



Pure cubic phase: approach



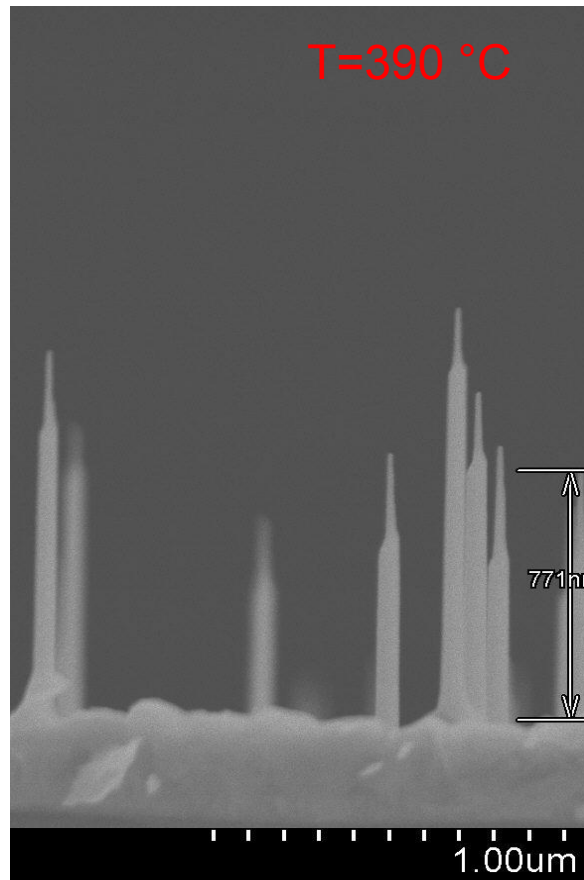
Pure ZB: if stop/reinitiate the growth or end the growth under Ga flux (no As)!



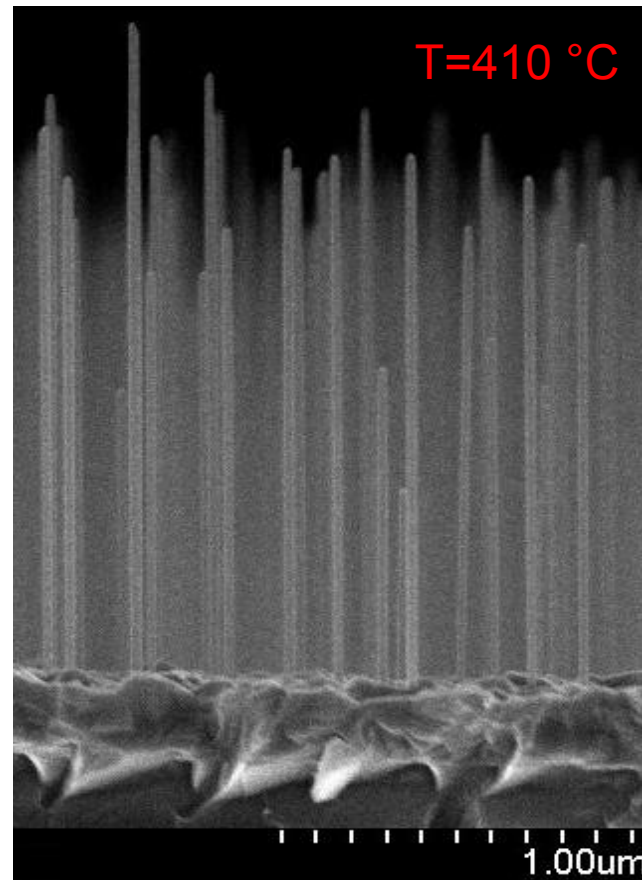
InAs and InP nanowires

InP/InAsP/InP heterostructures

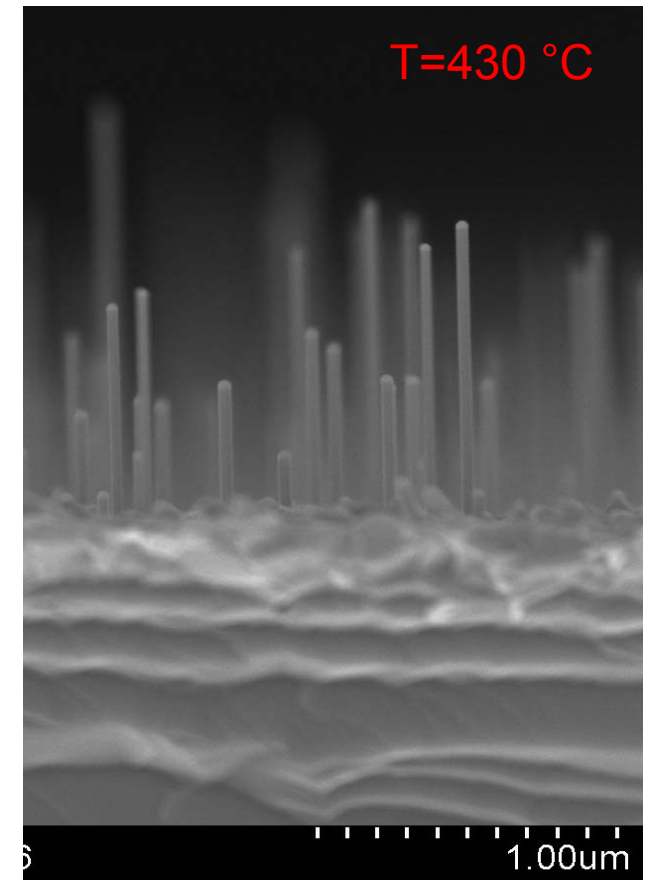
InAs nanowires: morphology



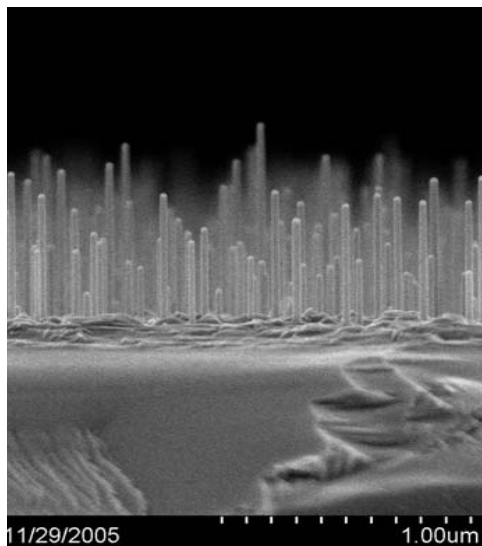
Pencil-like



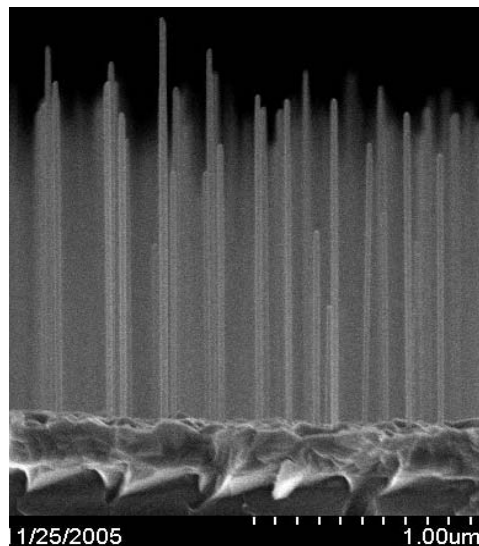
Cylindrical shape



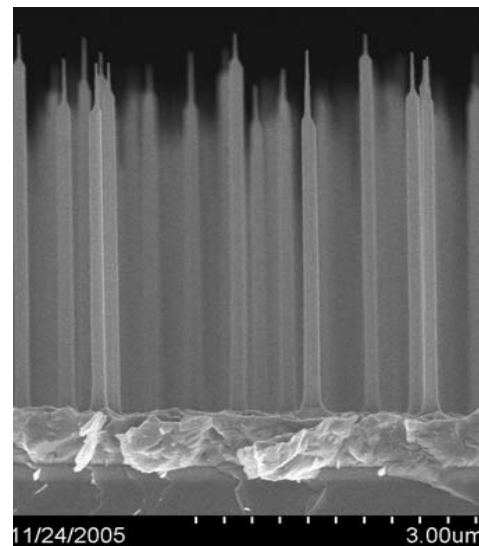
InAs nanowires: growth duration



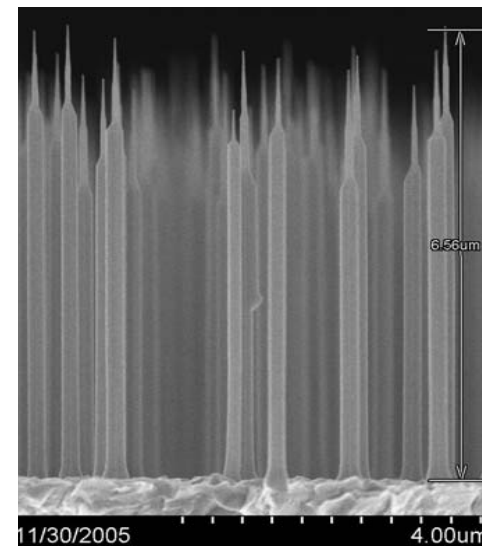
10 min
 $h \sim 0,35 \mu\text{m}$
 $d \sim 30 \text{nm}$



20 min
 $h \sim 1,5 \mu\text{m}$
 $d \sim 40 \text{nm}$

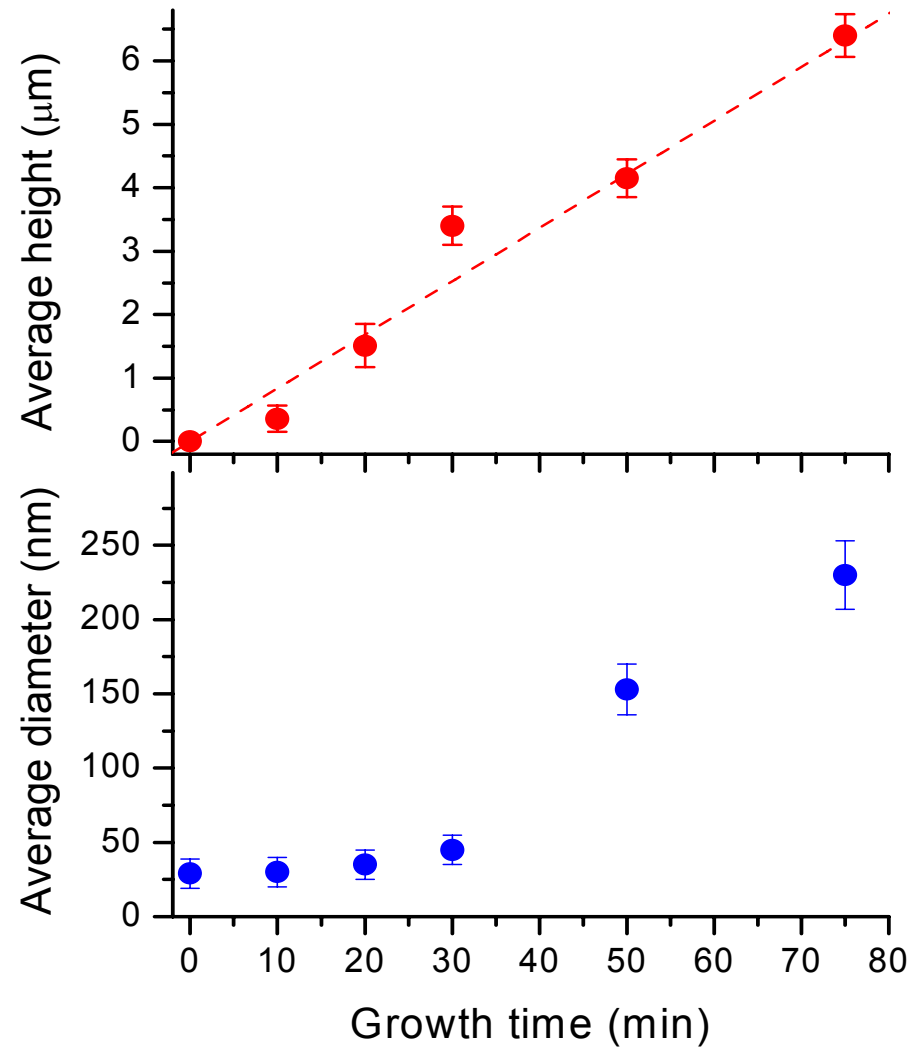


50 min
 $h \sim 4,2 \mu\text{m}$
 $d \sim 150 \text{nm}$



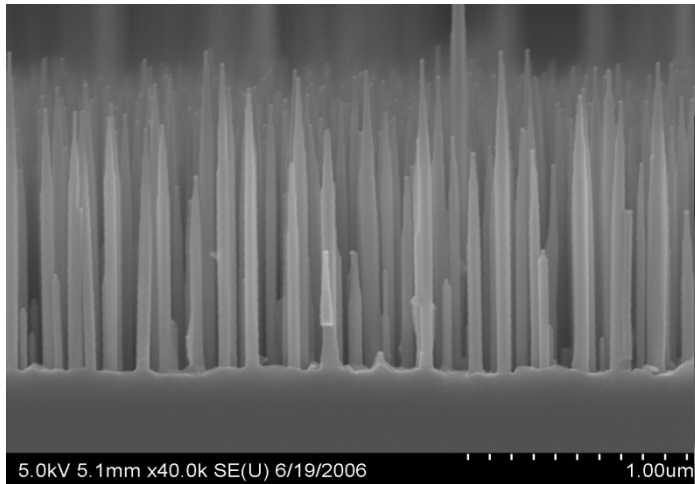
75 min
 $h \sim 6 \mu\text{m}$
 $d \sim 220 \text{nm}$

Axial/lateral growth: effect of growth duration

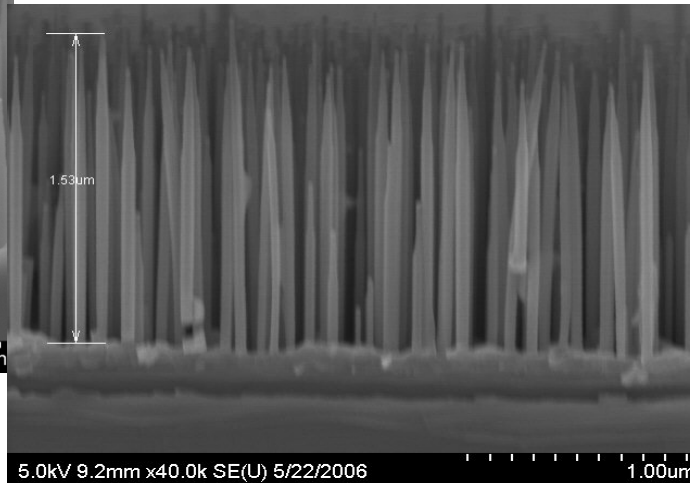


J. Appl. Phys., 2007,
v. 102, 094313

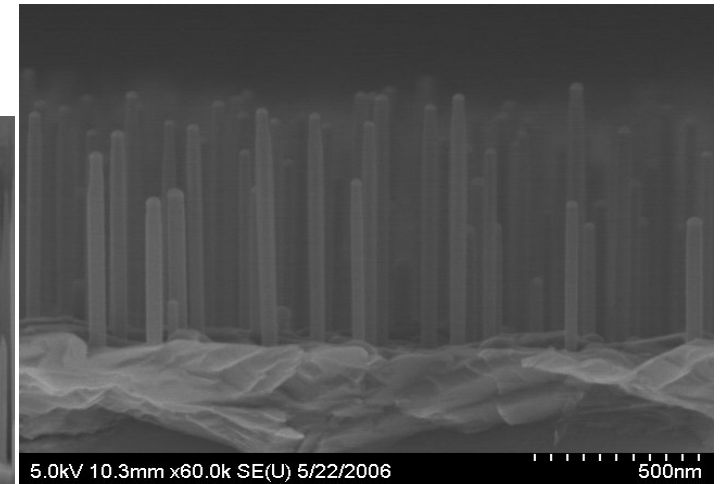
InP nanowires: morphology



T=350 °C

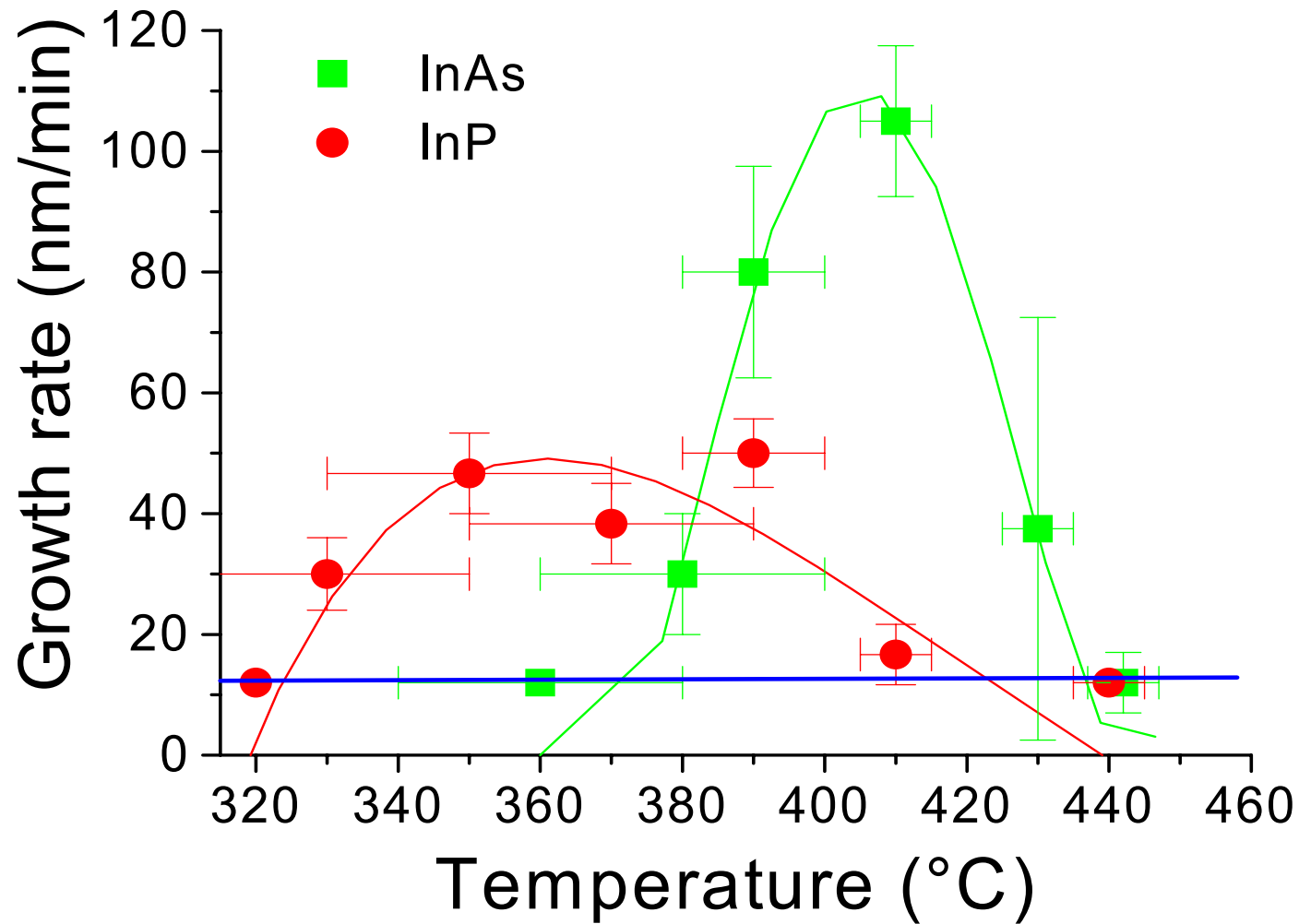


T=390 °C

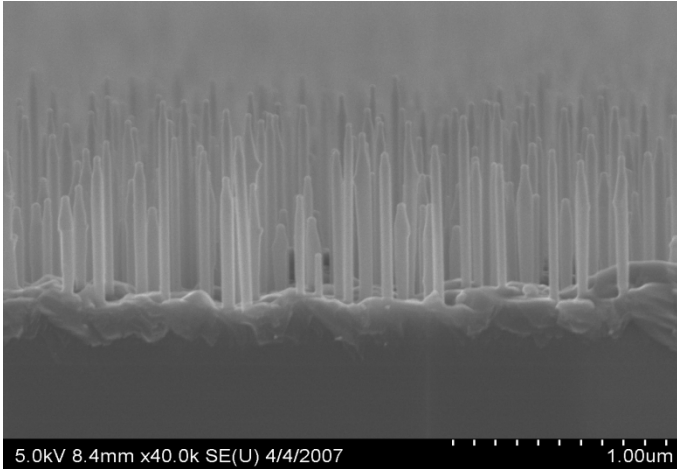


T=410 °C

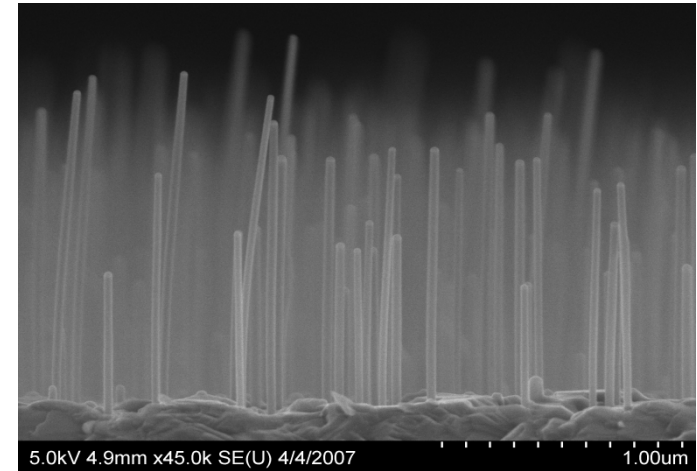
Temperature limits and NWs growth rate



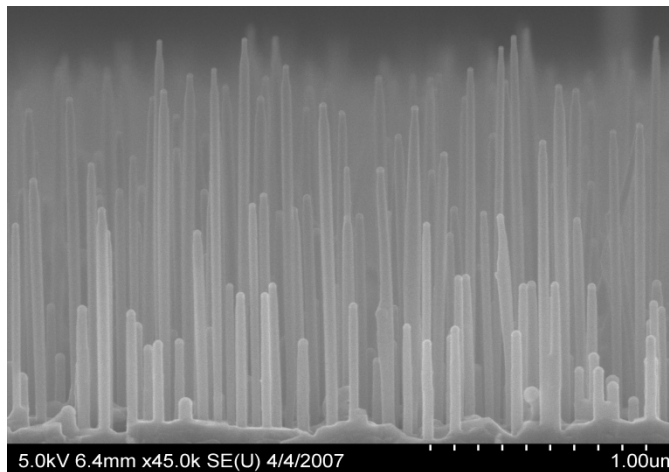
InP/InAsP/InP heterostructures: morphology



390°C



390°C + 430°C

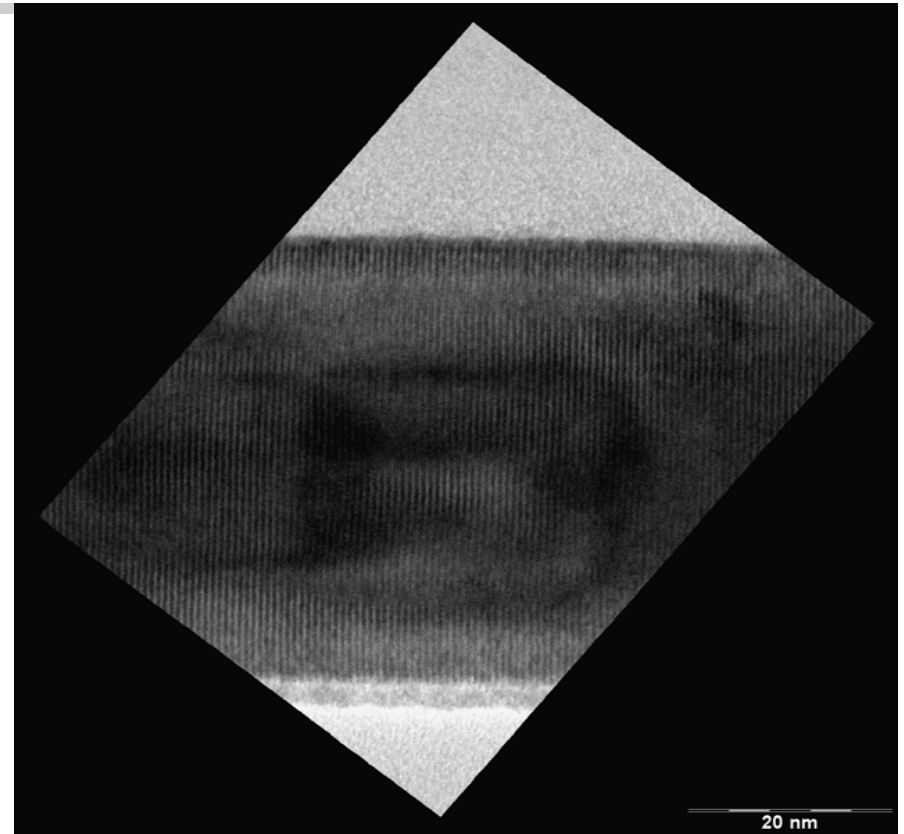


390°C+430°C+390°C

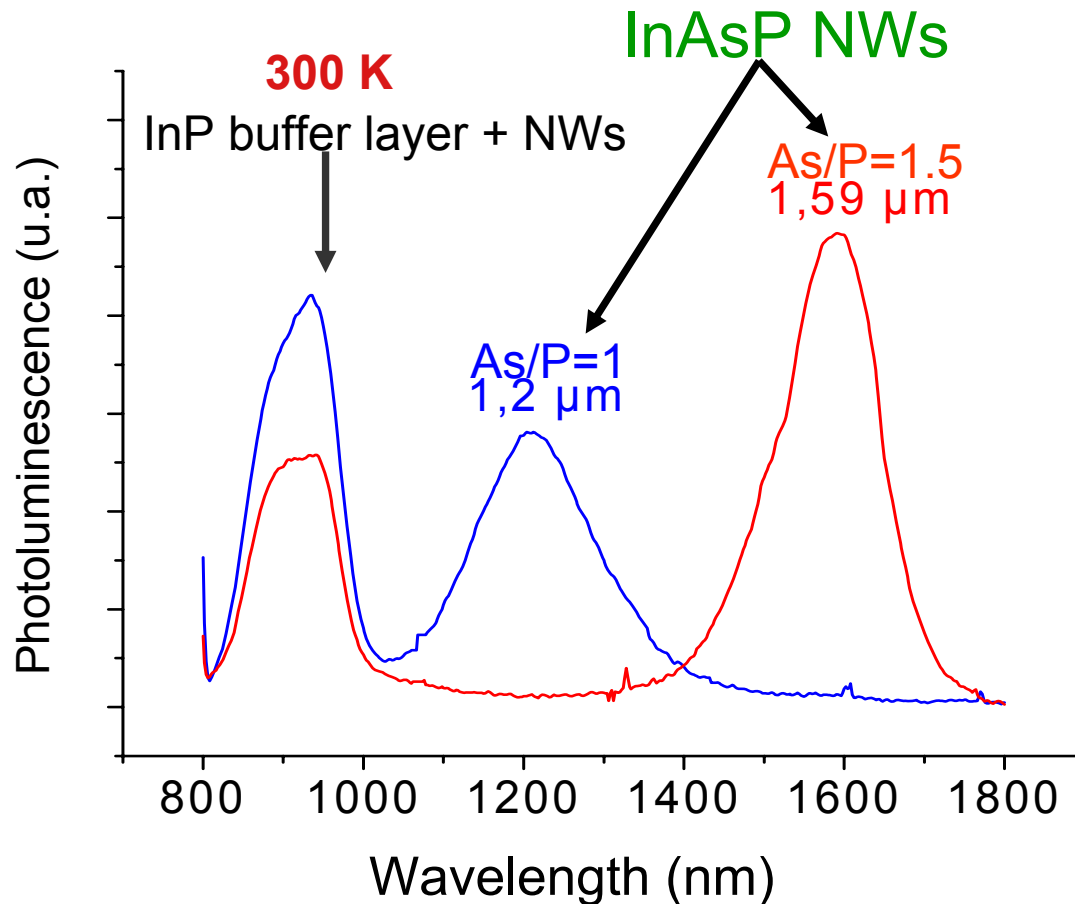
Optimized growth procedure

Three steps procedure

- *Start of InP NW growth at 390°C*
- *Growth of the InP/InAsP/InP heterostructure at 430°C – straight interfaces*
- *Growth of the InP shell at 390°C*



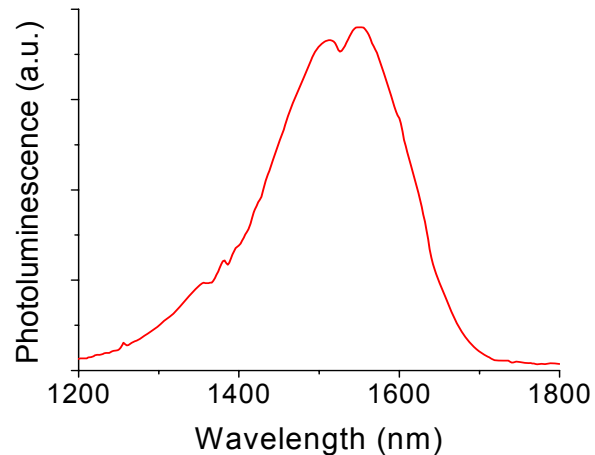
Room-temperature PL of InP/InAsP/InP NWs



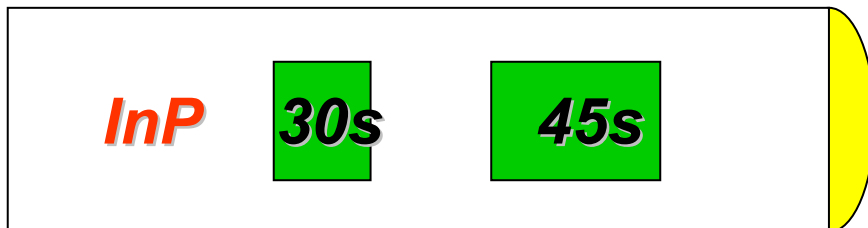
1. By changing As flux from As/P=1.5 to As/P=1 the PL peak is tuned from 1.2 to 1.6 μm – possibility to cover telecom wavelengths
2. FWHM = 150 meV – inhomogeneous broadening is due to the insertion size and composition dispersion
3. Positive effect of InAsP embedding – almost no PL signal for NWs without InP shell.

Macro- and micro-PL of InP/InAsP/InP NWs

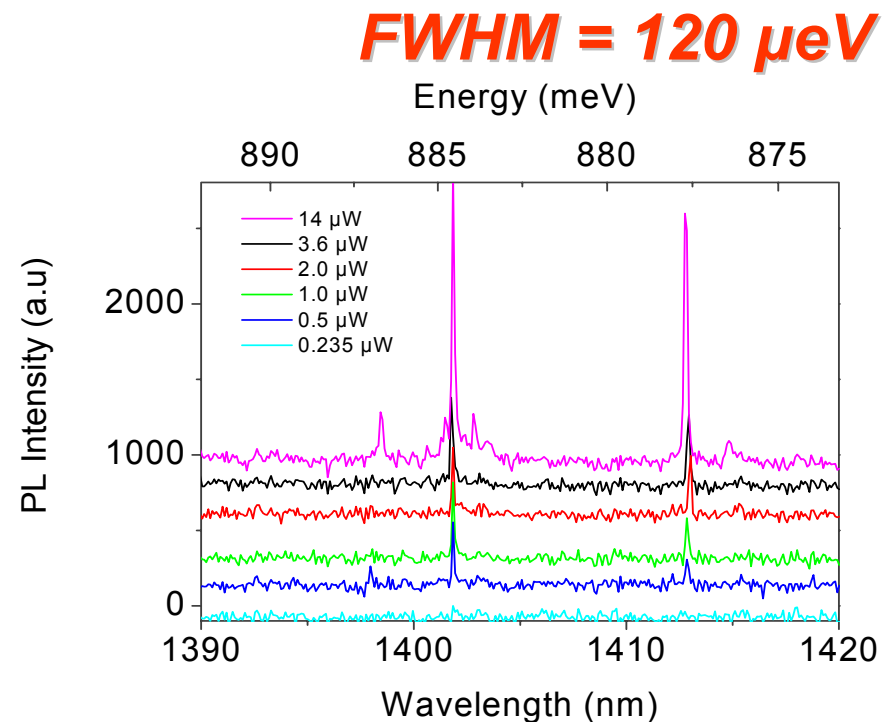
Room-temperature macro-PL



Structure with 2 InAsP segments



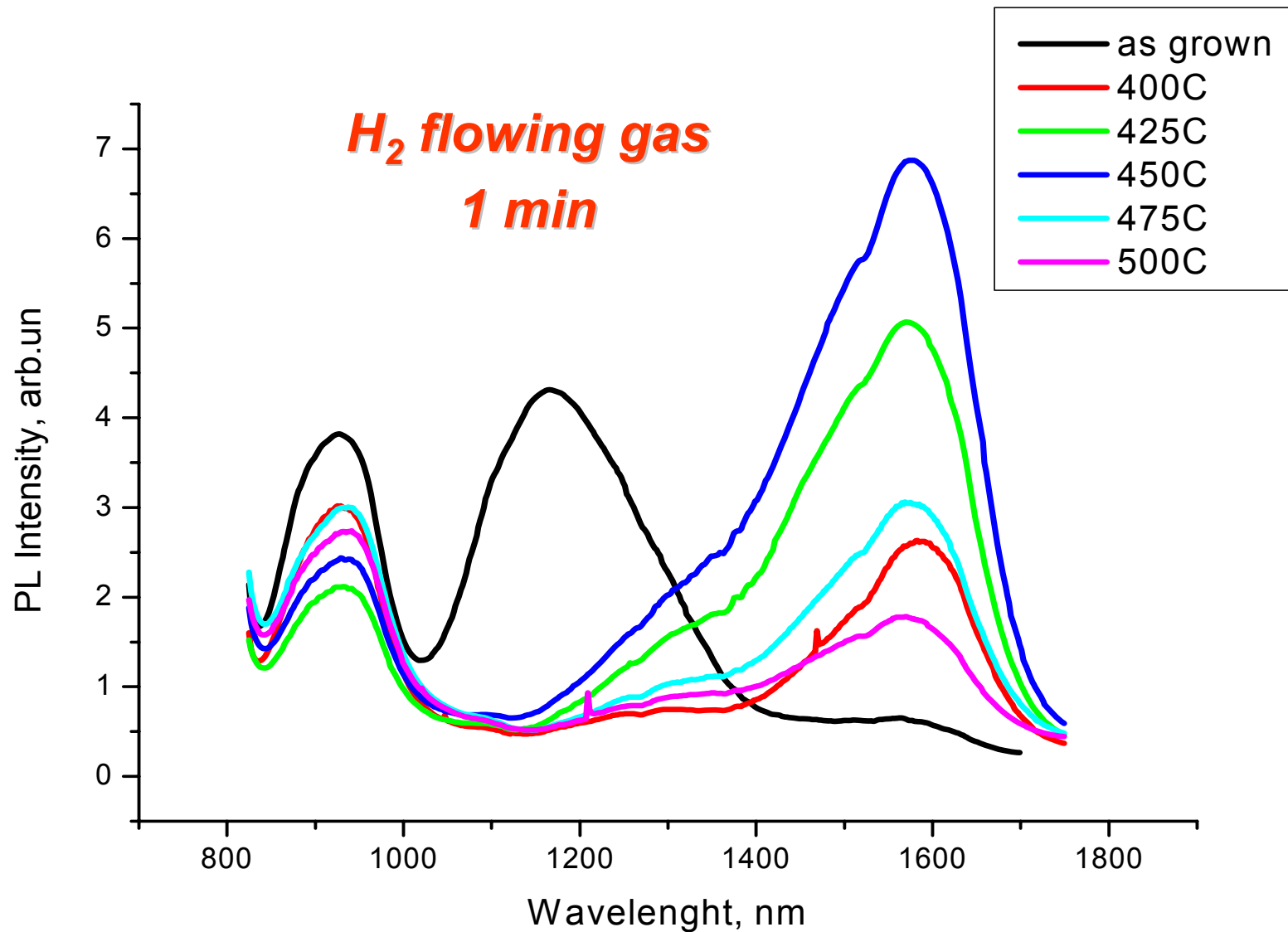
Micro-PL at 10K of a single wire

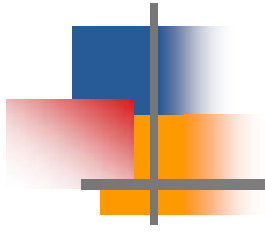


*Valery Zwiller
Delft University of Technology*

Nano Lett., 2007, v. 7, p. 1500-1504.

InP/InAsP/InP LT grown NWs: post growth annealing

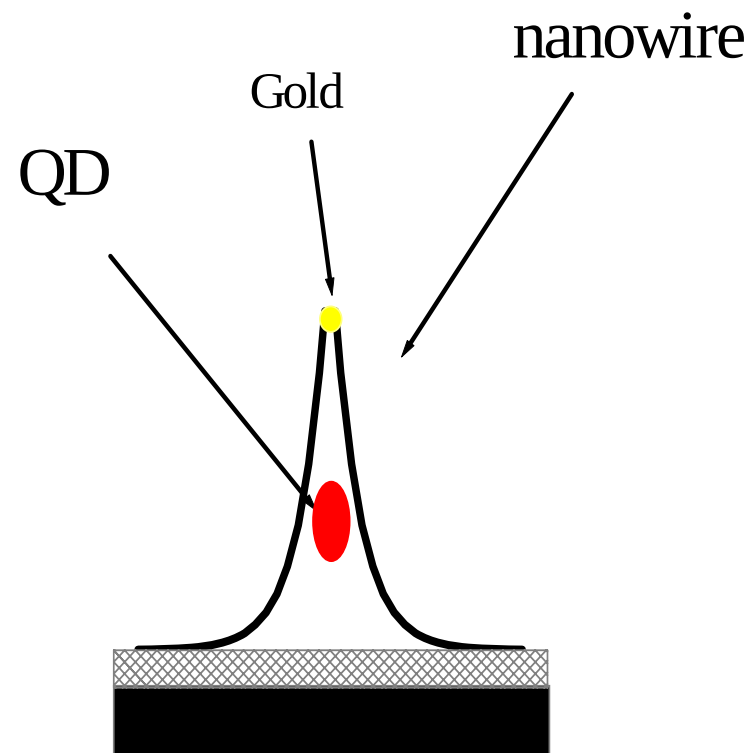




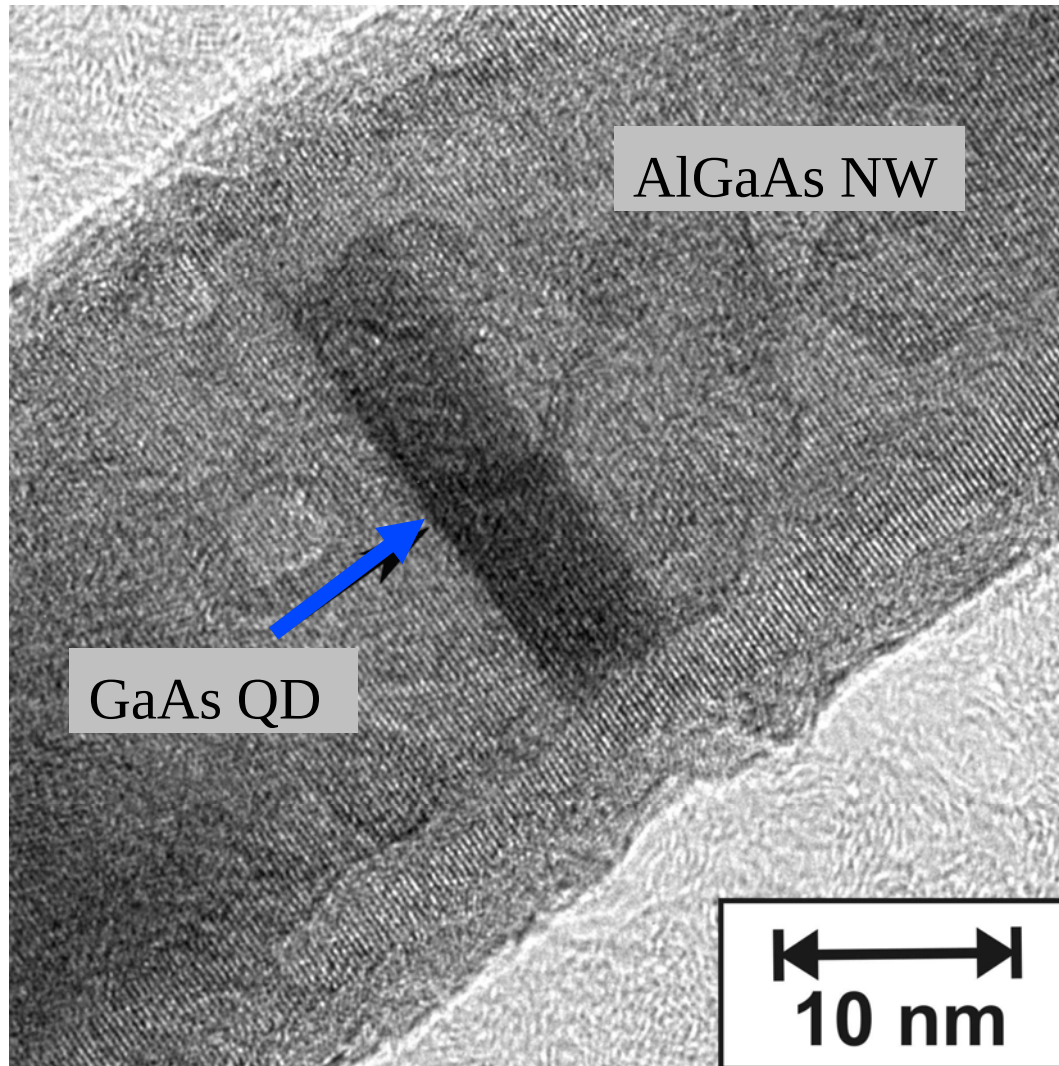
GaAs quantum dots in AlGaAs nanowires

Samples preparation

- AlGaAs NWs were grown on the GaAs (111)B semi-insulating substrate in an MBE system
- Al concentration in NW was 30%, according to the two-dimensional growth rate
- For AlGaAs/GaAs/AlGaAs quantum dot formation, the growth started with 15 min of AlGaAs, and then the Al source was closed for 5 sec in order to form a GaAs segment in each NW.
- The growth was completed with 2 min. deposition of GaAs at 530 °C to avoid oxidation.



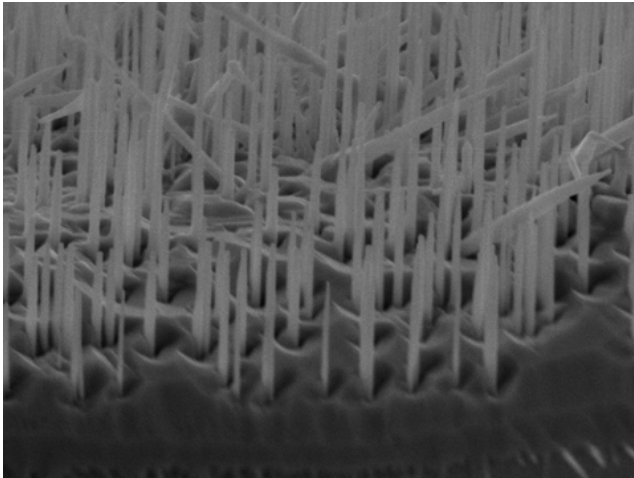
TEM image of GaAs QD in AlGaAs NW



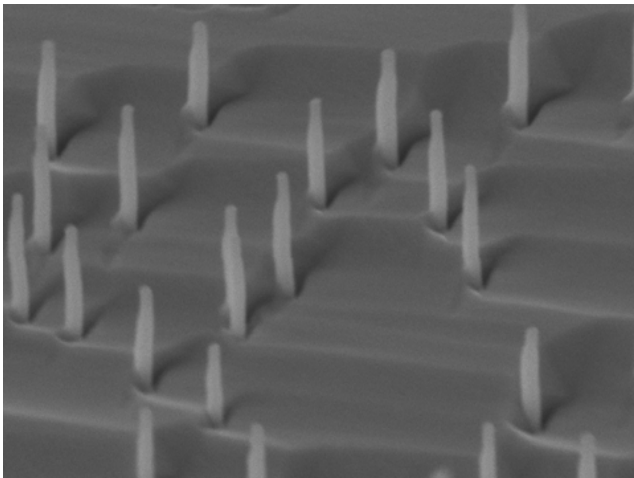
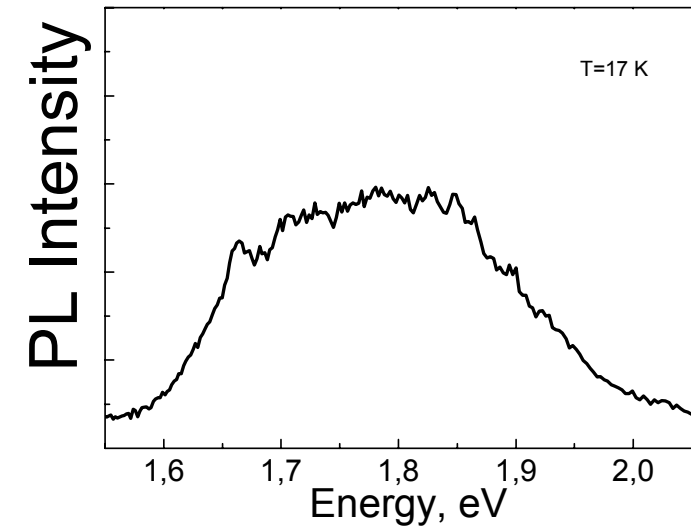
- QD height is 5 nm and diameter is 20-30 nm

- Sharp interfaces

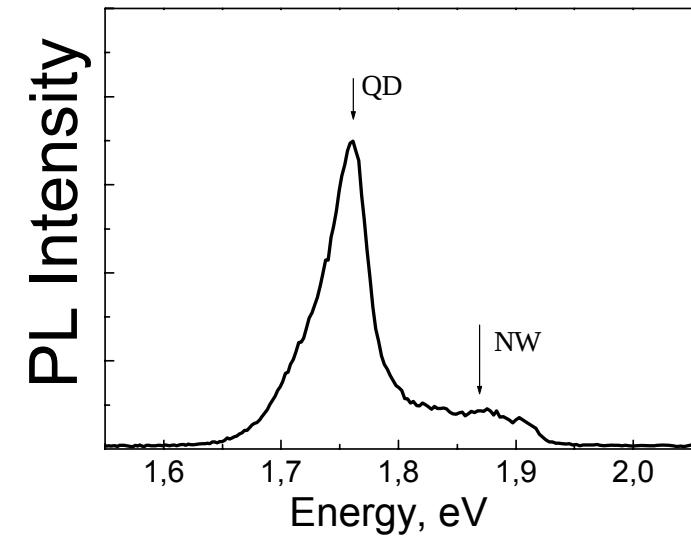
Growth at low and high substrate temperature



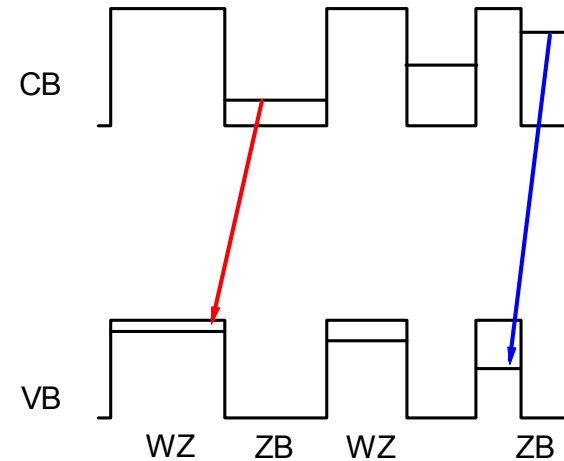
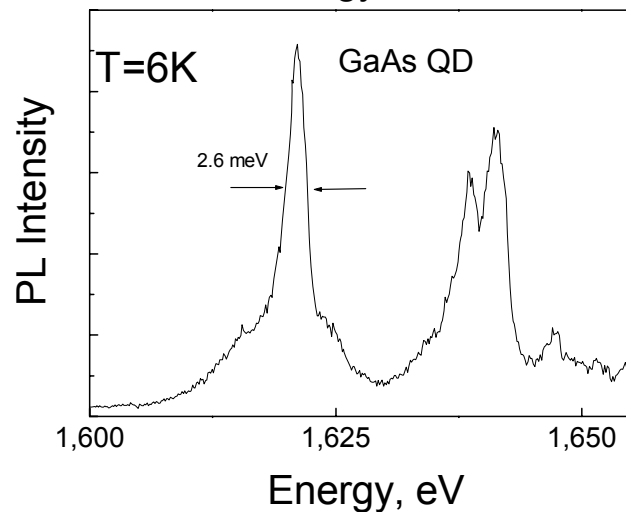
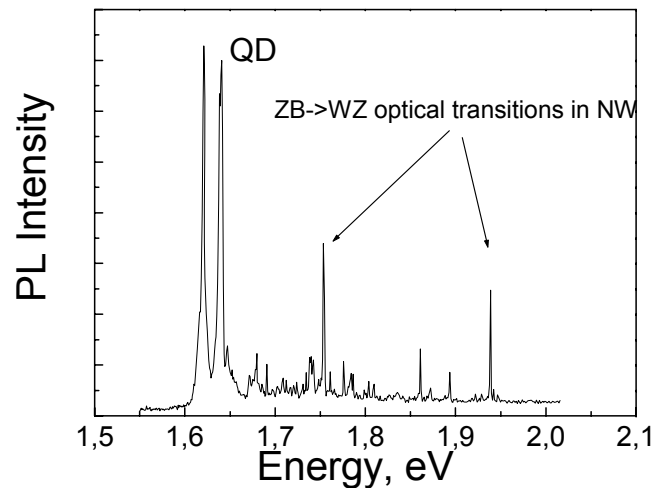
$T = 550^{\circ}\text{C}$



$T = 580^{\circ}\text{C}$

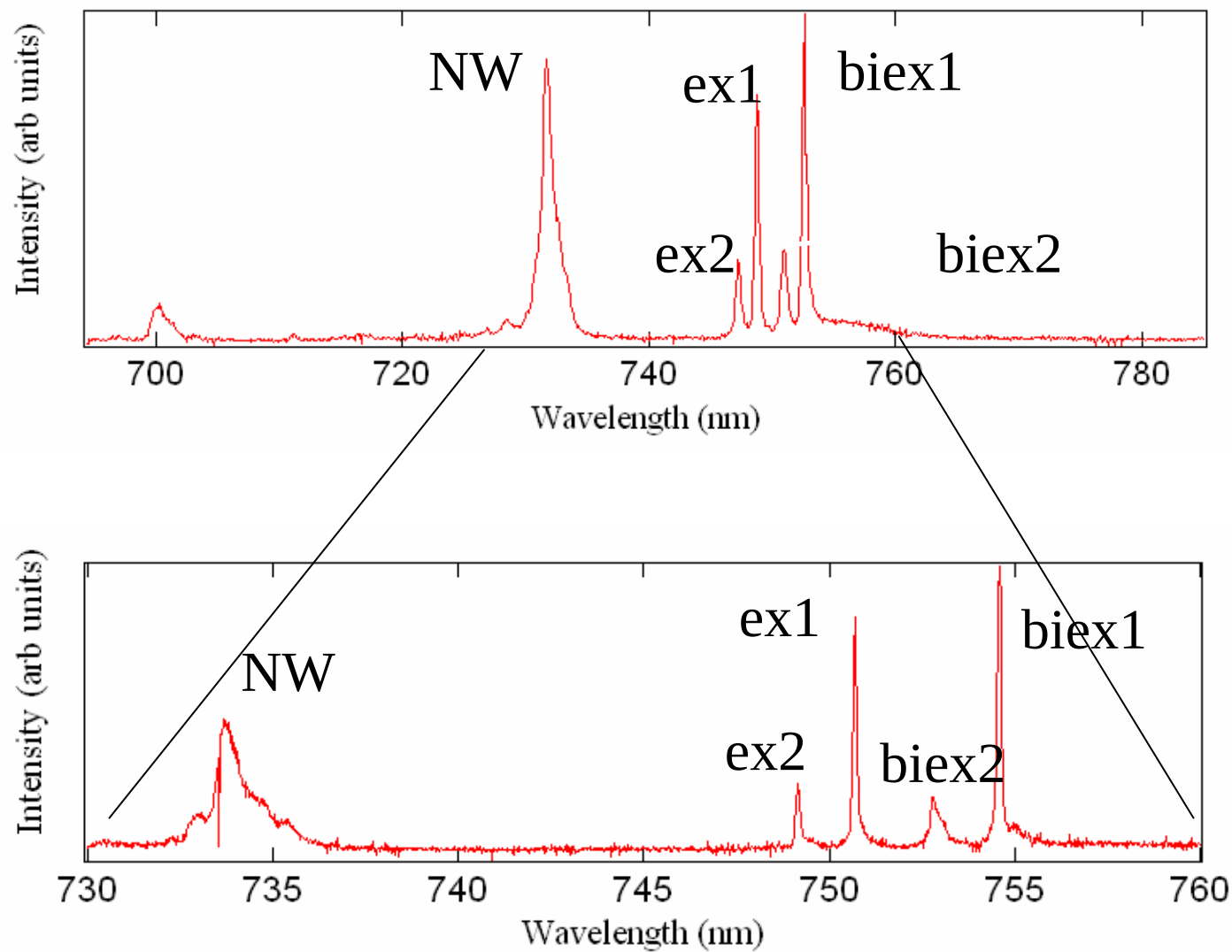


PL features in AlGaAs/GaAs NW-QD structures

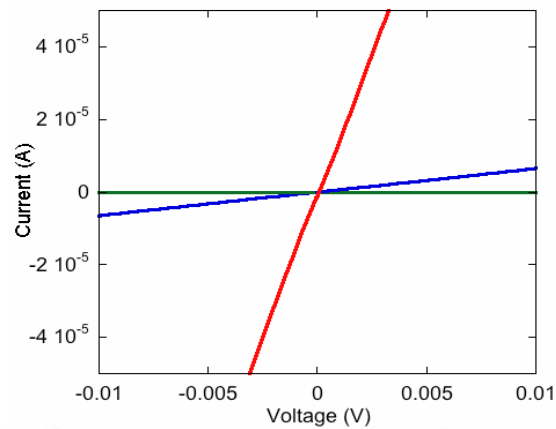


In AlGaAs nanowire, the crystalline structure can switch spontaneously from the zinc-blende (ZB) to the wurtzite (WZ) structure. The alternation in crystalline structure leads to the formation of type -II superlattice along the growth direction and therefore the carrier spectrum become quantized along the axis.

Micro PL of 2 NWs

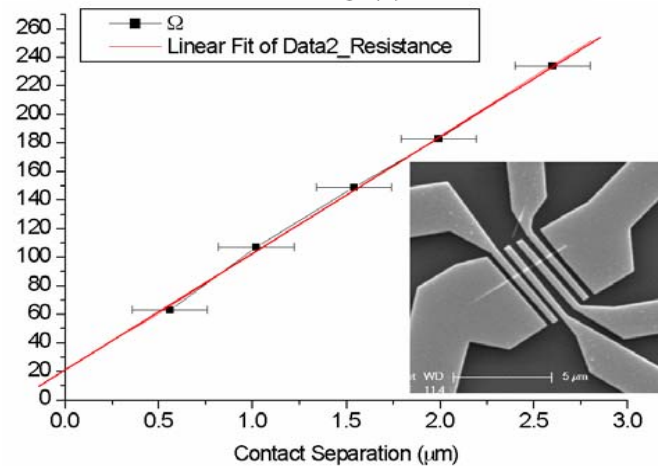


Локальные вольт-амперные характеристики

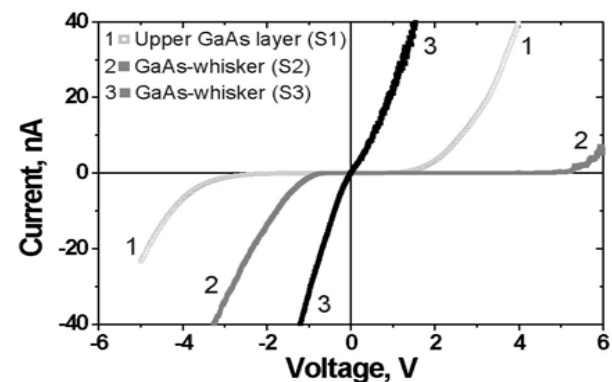
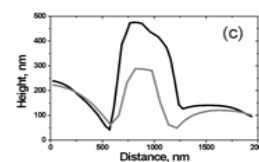
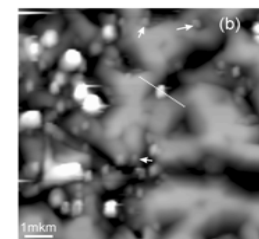
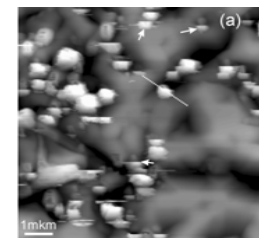


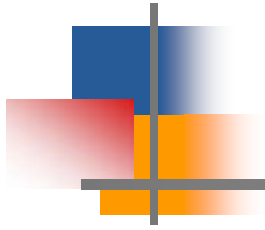
InP:Si

GaAs:Si

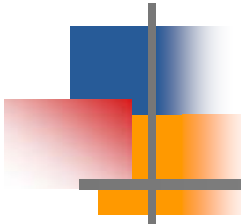


undoped	no conduction
Low Si doping ($T_{si}=1040^{\circ}\text{C}$)	$1.9 \pm 0.4 \times 10^{-4} \Omega\text{cm}$
Hi Si doping ($T_{si}=1150^{\circ}\text{C}$)	$1.6 \pm 0.3 \times 10^{-5} \Omega\text{cm}$





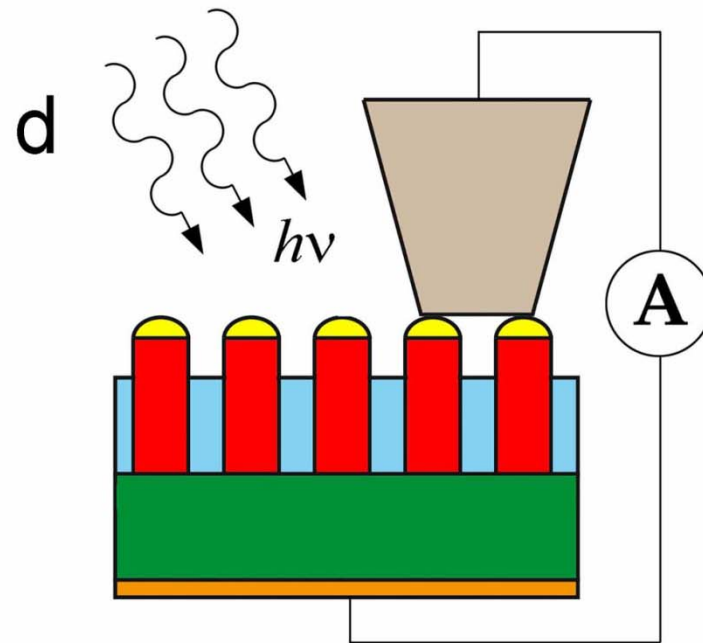
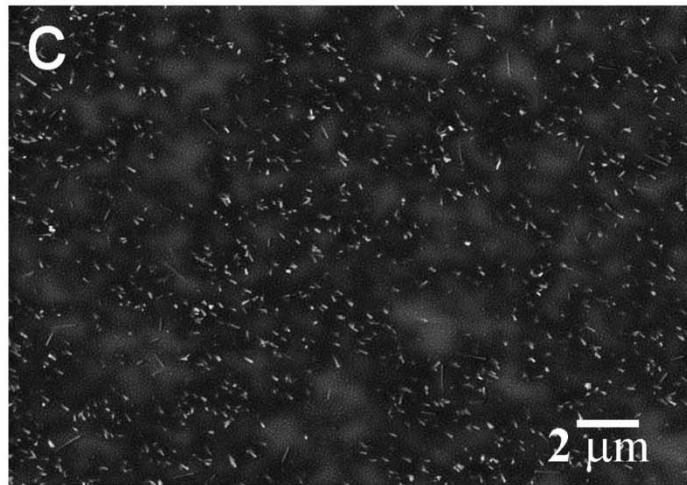
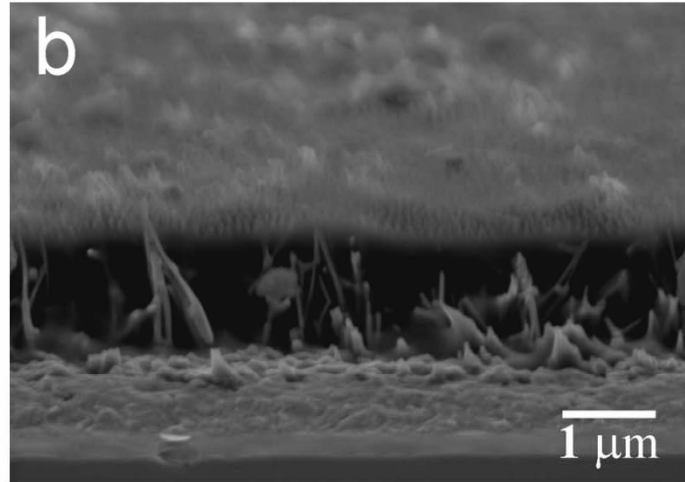
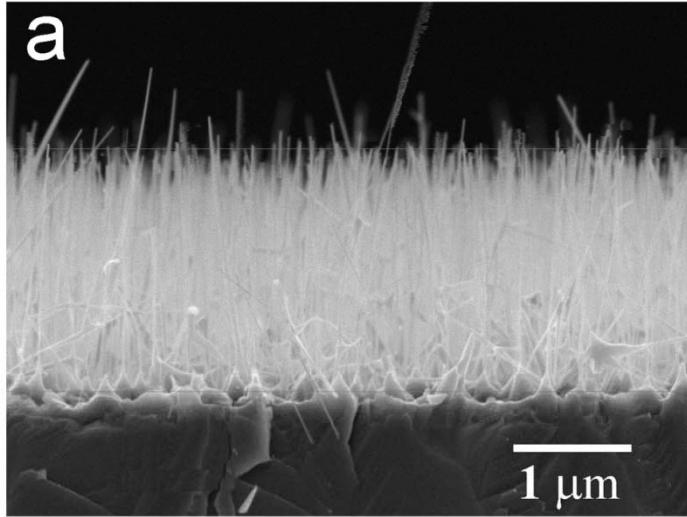
Photovoltaic properties of p-type GaAs NWs on GaAs(111)B n-type substrate



Samples description

- **MBE growth of GaAs:Be NWs on n-type GaAs(111)**
- **Back (substrate side) metallic contact by electron-beam deposition of AuGe-30 nm+ Ni/Au 10/150nm**
- **Filling the space between the NWs with PMMA**
- **Partial removing of PMMA and the top of NWs in O₂ plasma**

SEM images taken at different stages of device structure preparation





Measurement details

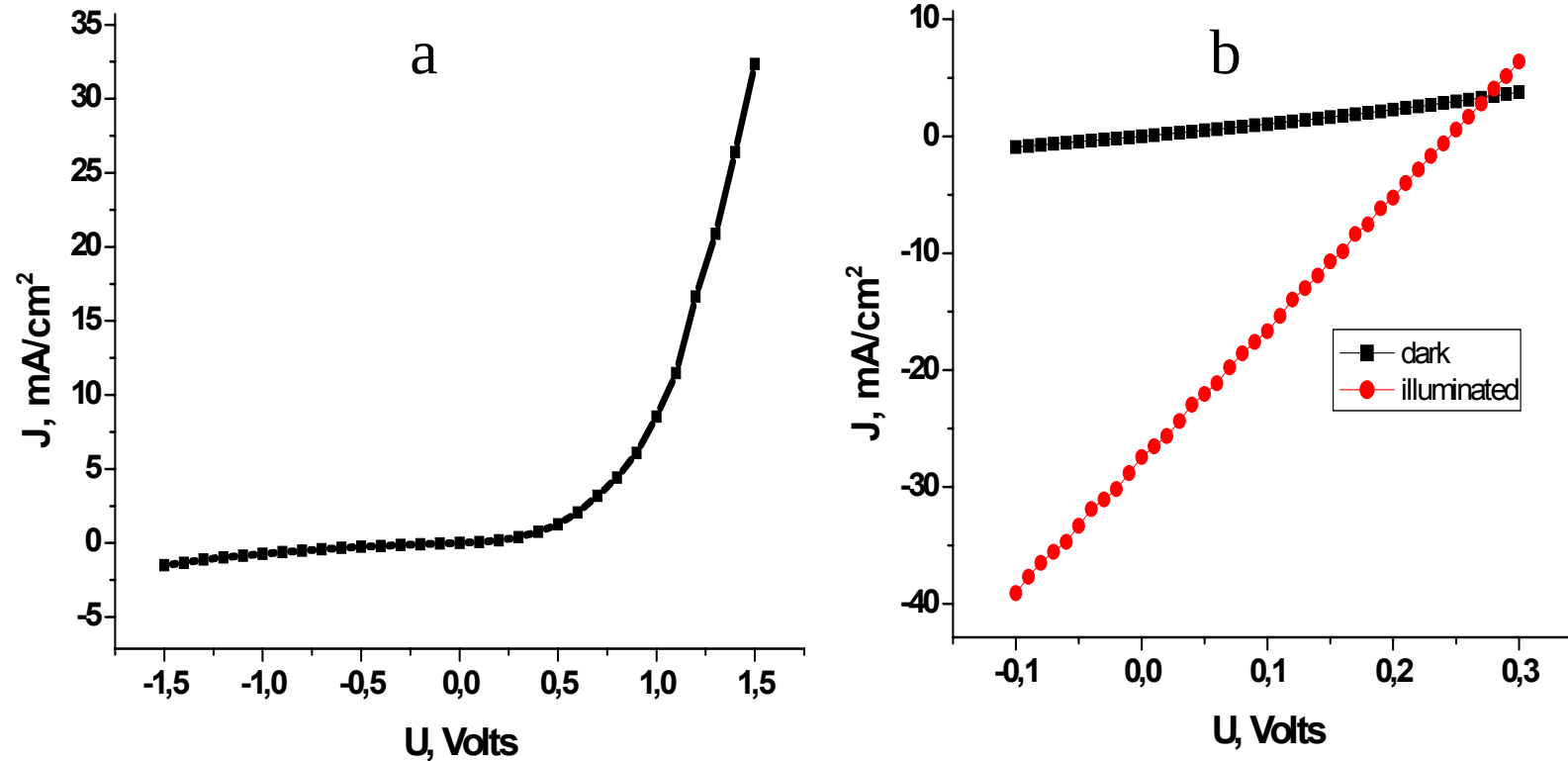
- I-V characteristics are measured using a Keithley 238 source meter. The samples are placed on a copper base from a backside; a metallic sharp tip ($D \sim 0.5\text{mm}$) is used as a top contact to the NWs/PMMA array. The energy conversion efficiency was determined by illuminating the structures using halogen arc-lamp with a calibrated power density of $P = 100 \text{ mW/cm}^2$.
- Fill factor (FF) and power conversion efficiency (η) are calculated according to the following equations:

$$FF = V_M J_M / V_{OC} J_{SC}$$

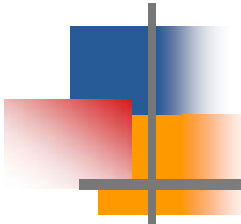
$$\eta = V_M J_M / P$$

V_{OC} and J_{SC} are the open-circuit voltage and short-circuit current and V_M and J_M are the voltage and current density at the maximum power output, respectively, and P is the incident power density

J-V characteristics



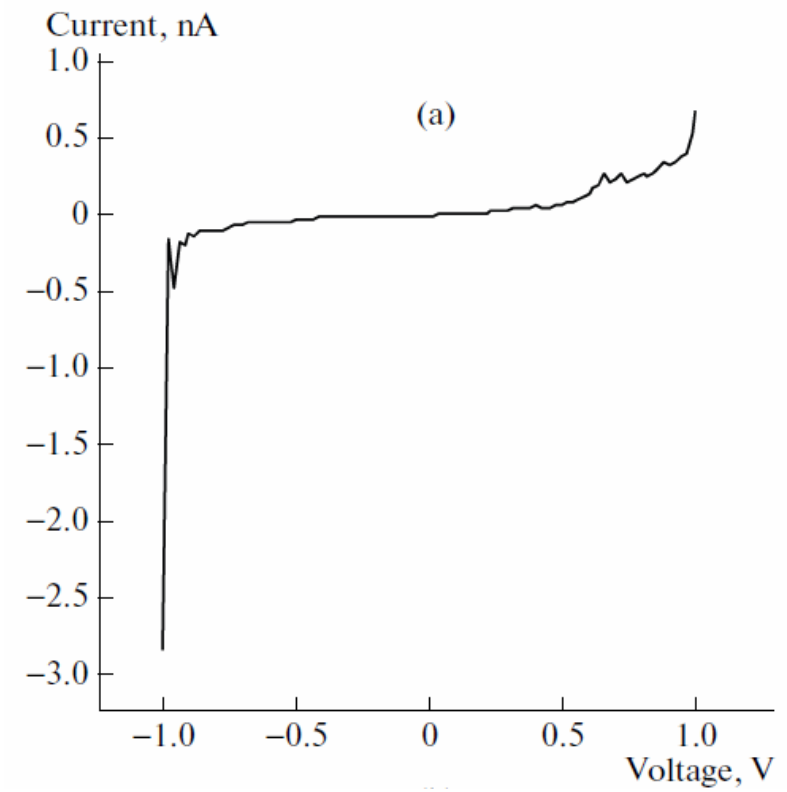
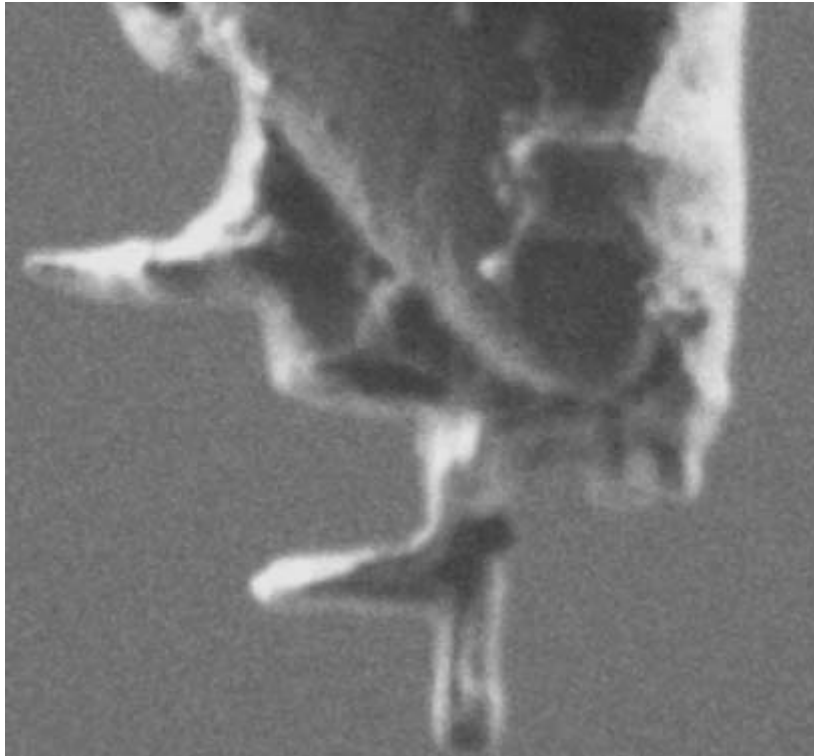
The rectification ratio is greater than 10^2 at ± 0.5 V, implying a reasonable p-n junction



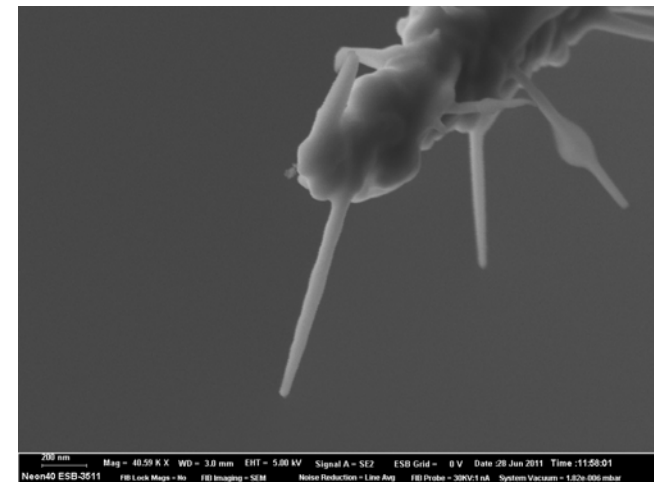
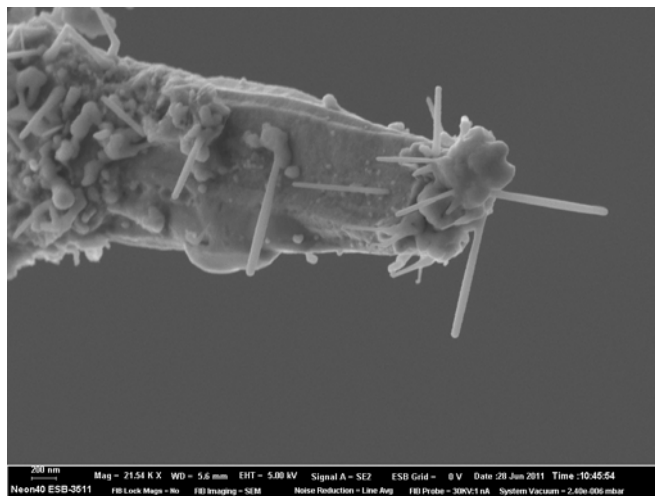
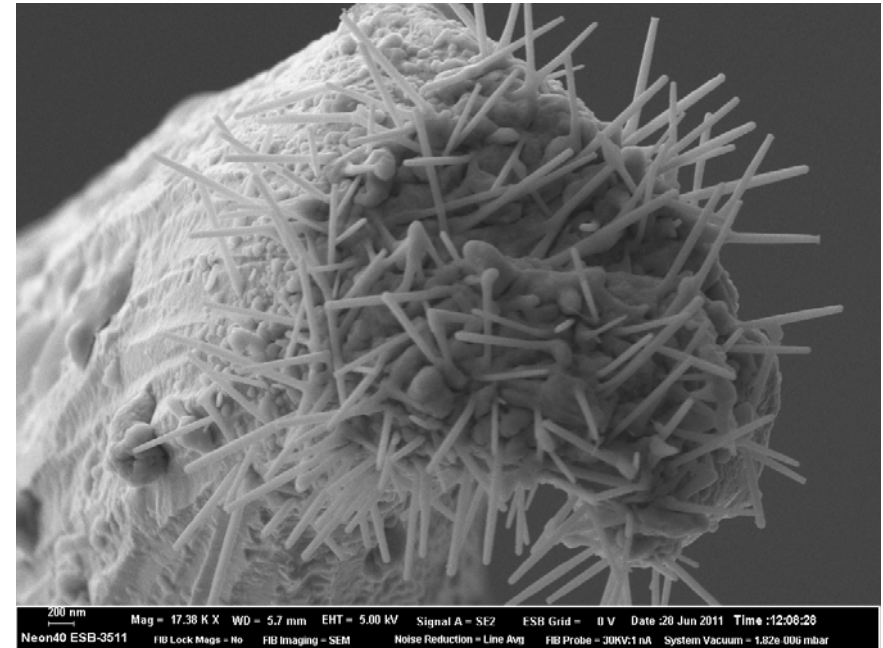
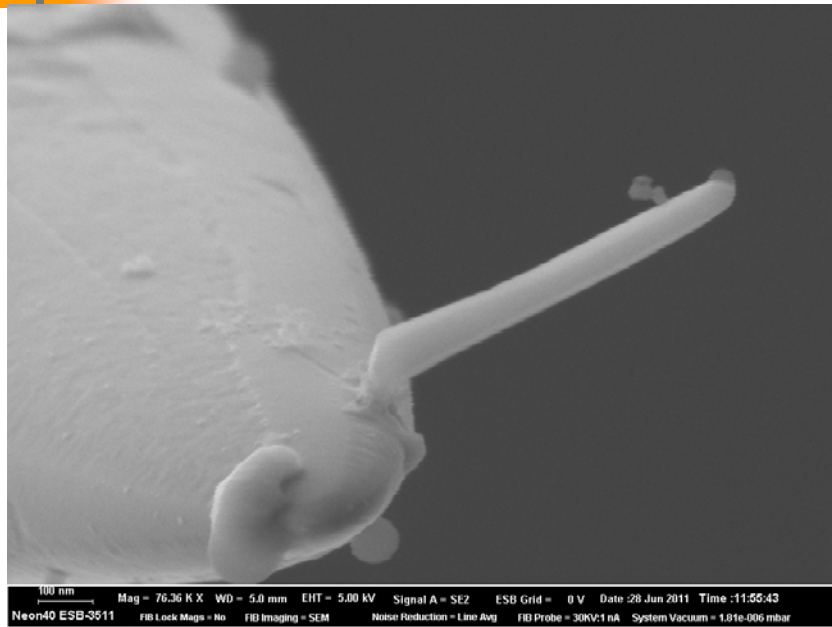
Efficiency vs NWs array properties

T_s, C	NWs surface density, cm⁻²	NWs height, mkm	Conversion efficiency, % (FF, %)
520	1*10⁹	1.7	0.08 (29)
535	1*10⁹	1.9	0.27 (27)
550	1*10⁹	2.2	1.65 (25)
580	5*10⁸	1.7	0.29 (28)

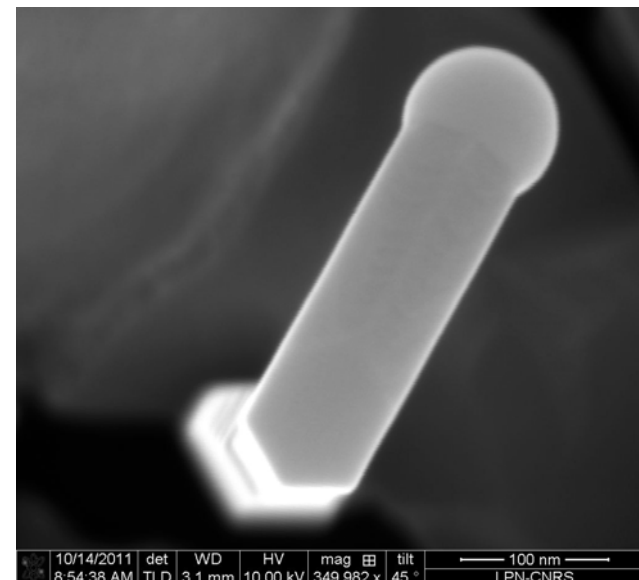
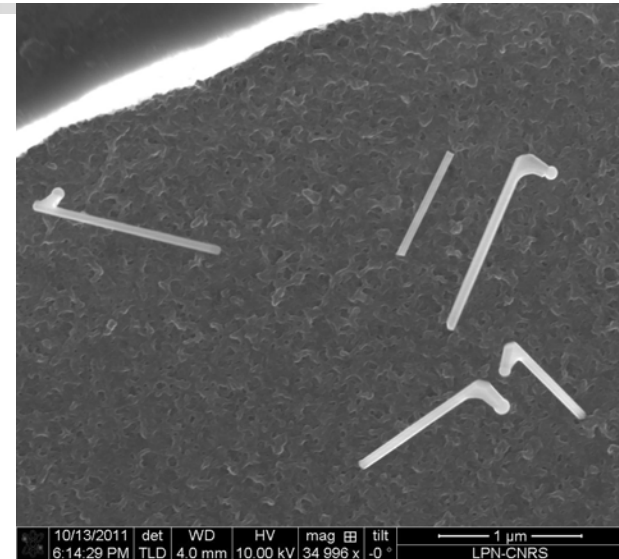
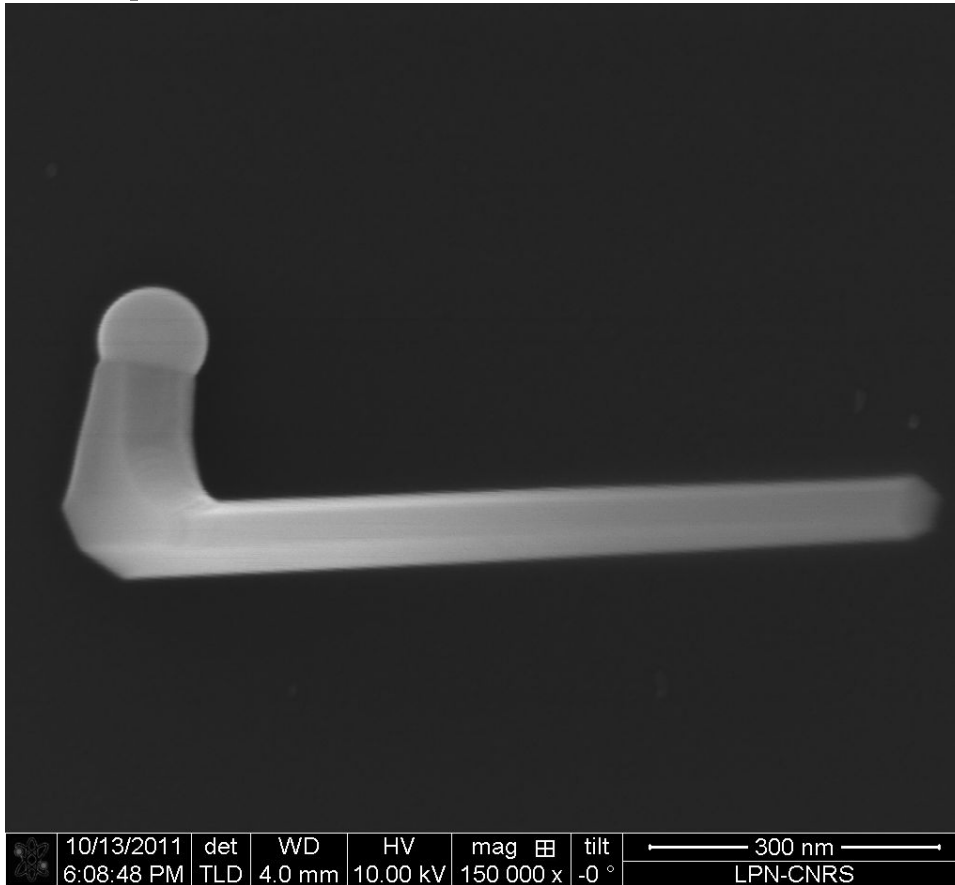
Single NW grown on tungsten tip



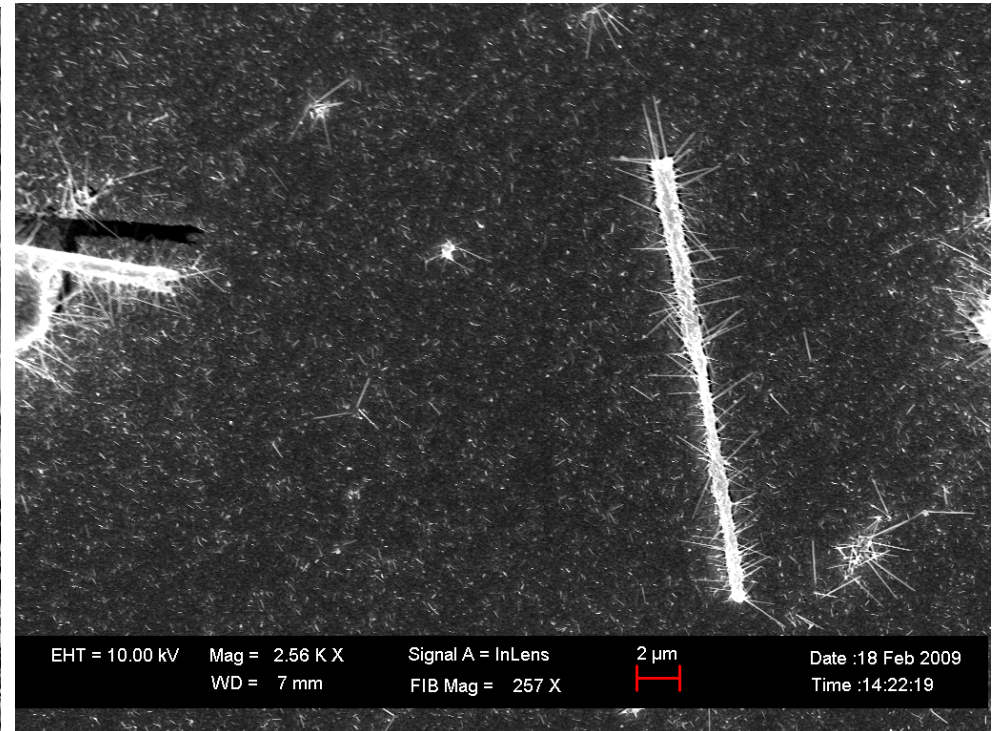
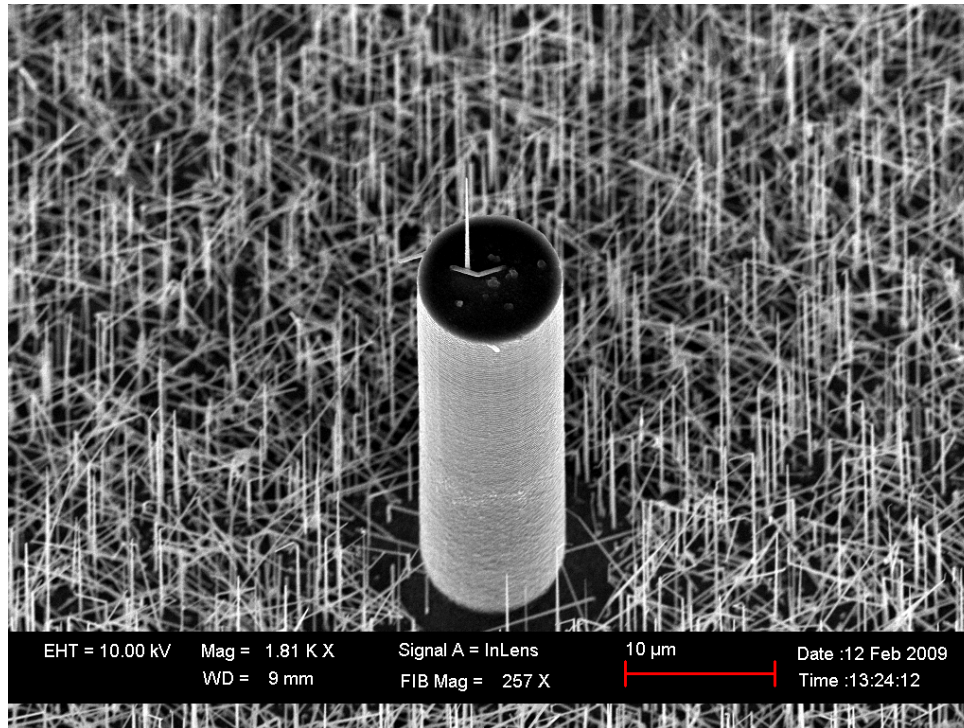
Self catalysed GaAs NW on a STM W tip



NWs with controllable change of the growth direction



GaAs NWs grown on micro pillars





Спасибо за внимание!