# Physical, Chemical, and Electronic Properties of Nanostructured Photocathodes: **III–V nanowires**

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LUND UNIVERSITY

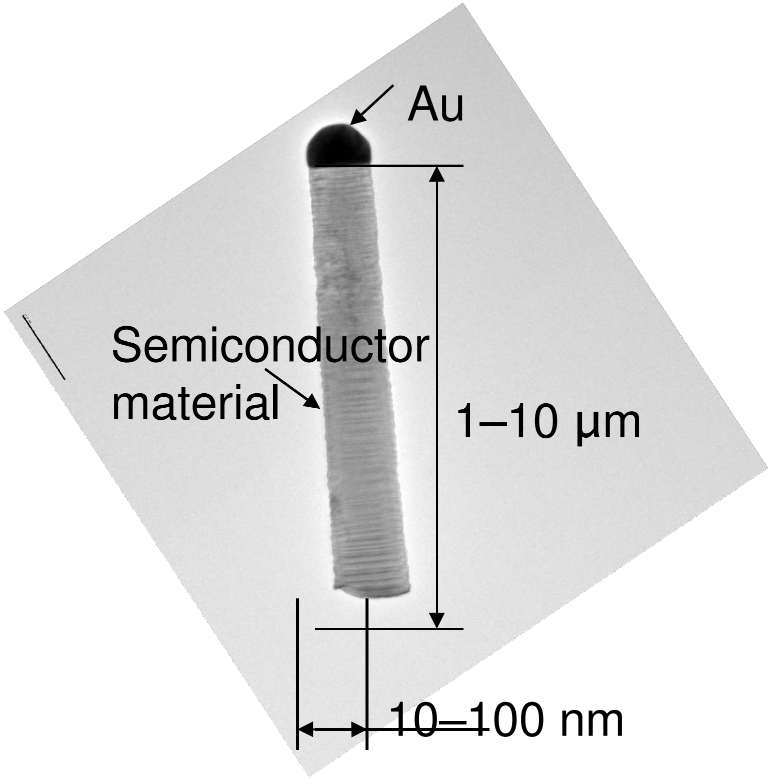
structures

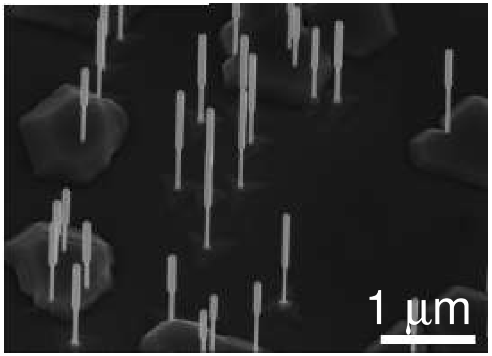
# Outline

- Introduction to nanowires and their formation
- Morphology and crystal structure
- Heterostructures
  - Axial
  - Radial (core/shell)
- Doping and pn-junctions
- Patterned growth
- Processing (including applications)

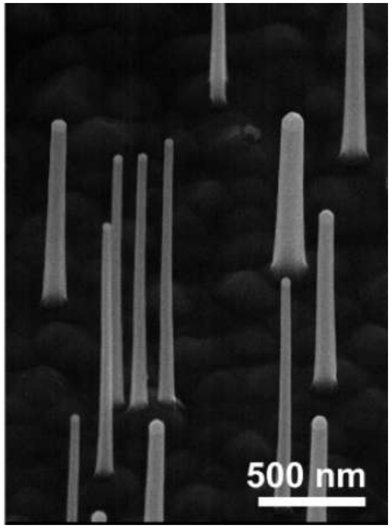
# Introduction to nanowires

- Nanowires in most III–V combinations
- Gold particle seeded growth (and gold–free growth)
  - Aerosol particles
  - Lithography, evaporation, and lift–off
- Growth by
  - Metal Organic Vapor Phase Epitaxy
  - Chemical Beam Epitaxy



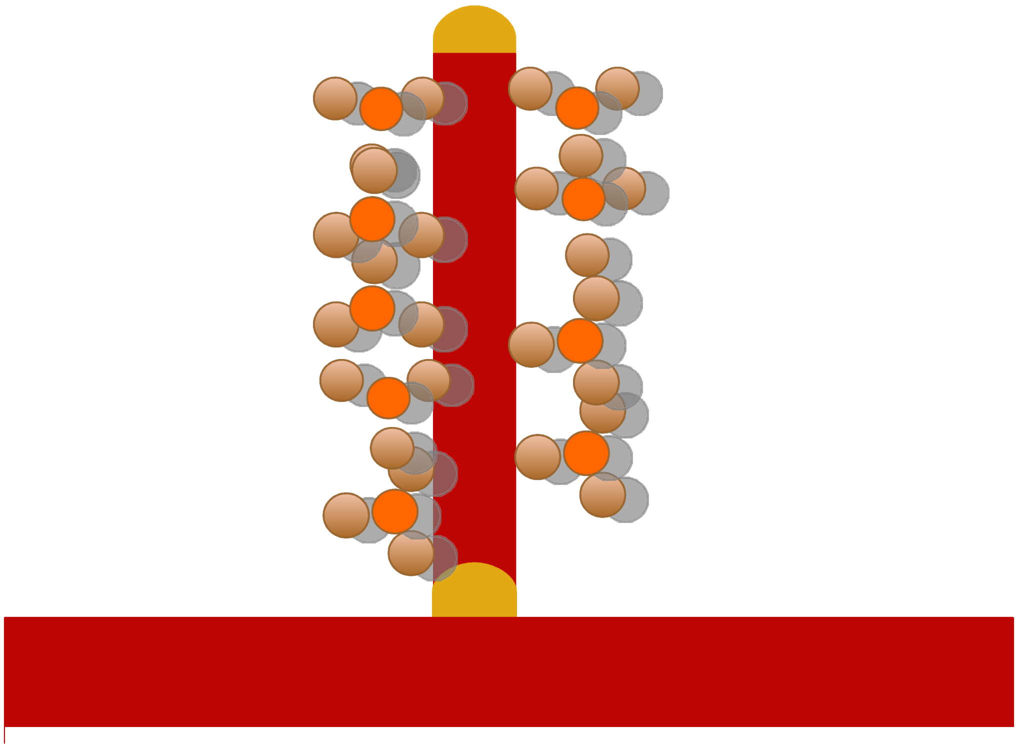

**InSb**
P. Caroff, ICMOVPE-XIV, France, 2008

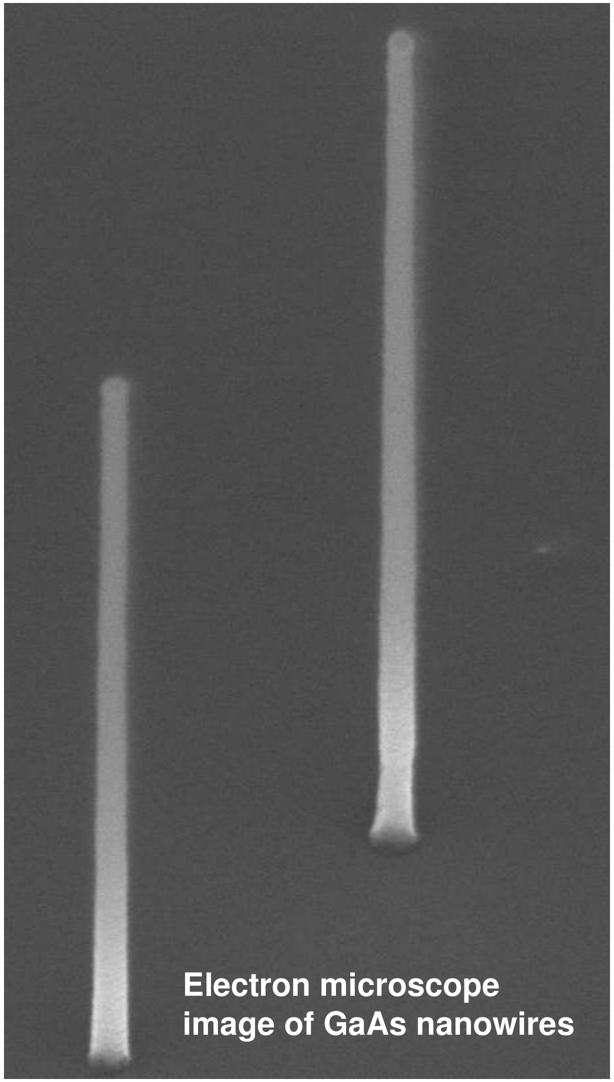



**GaP**

# How nanowires grow

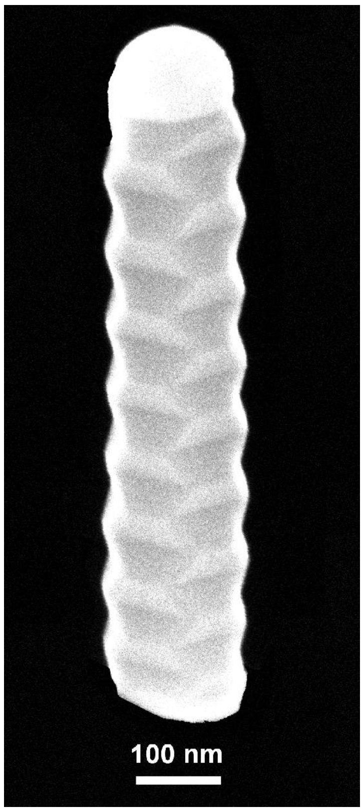
1. Deposit size-selected Au nanoparticle
2. Supply precursors of the relevant materials
3. The nanowire grows under the Au particle



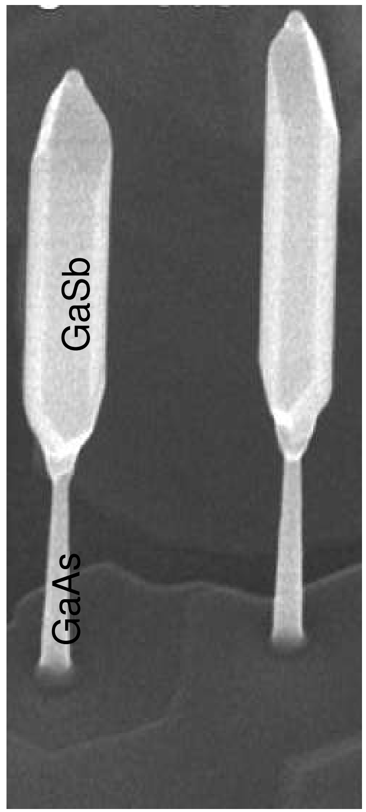


# What is so special with nanowires?

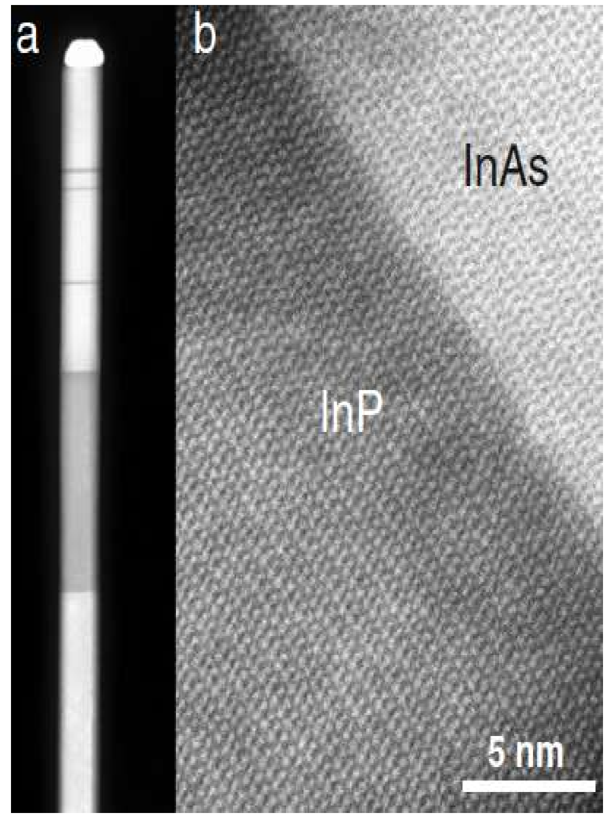
**1. Perfect crystal structures**



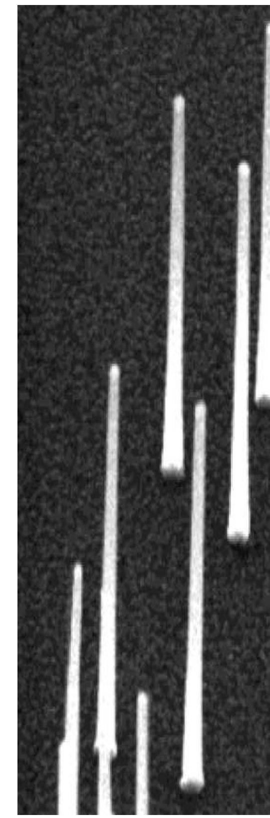

**2. Mismatched material combinations**



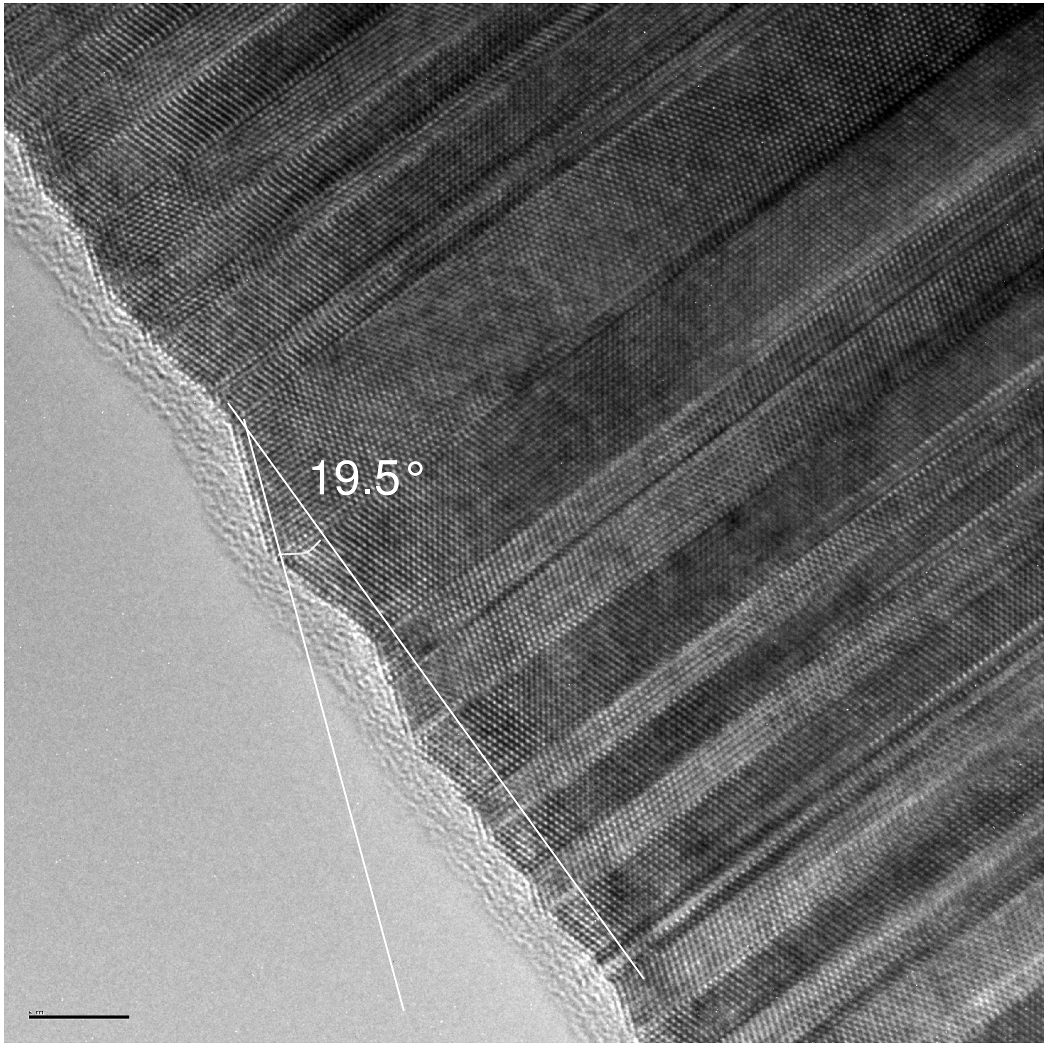

**3. Atomically sharp interfaces**




**4. On low-cost silicon**

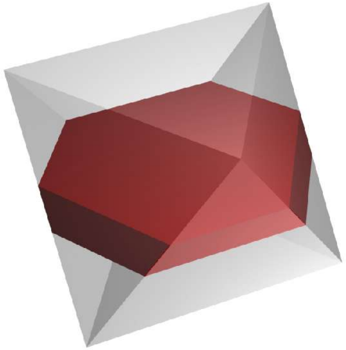


**Potential for many applications, including high-efficiency and low-cost sola light-emitting structures, 1D electronic devices, as well as photocathode st**

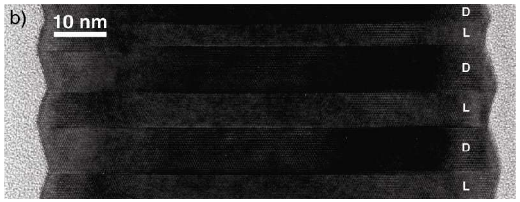



- The same angle as for regular octahedra
- Straight when rotated 30°

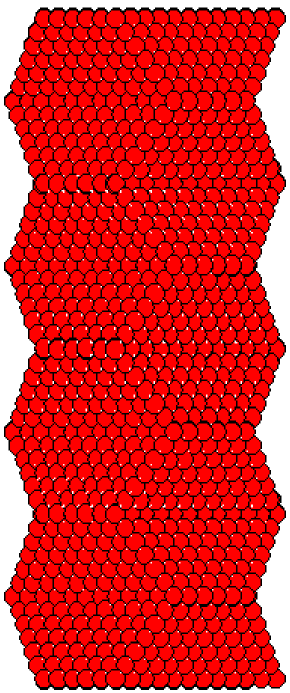
- The wire is built of ”octahedron slices” and is consequently limited by {111} side facets



# Geometric model







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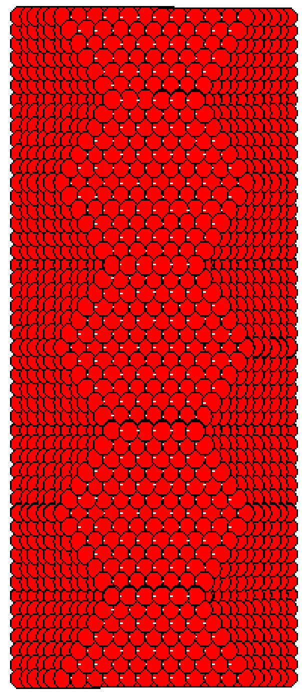

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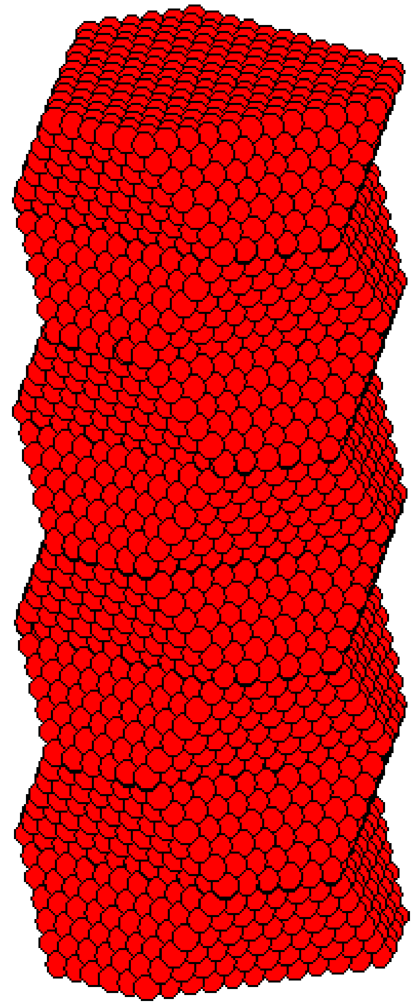
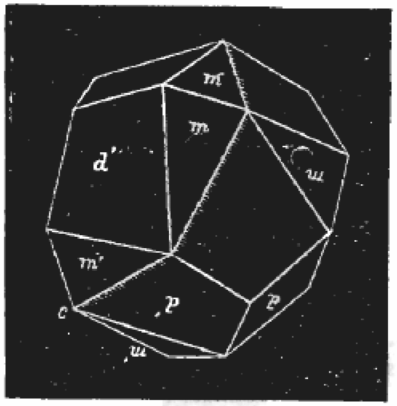


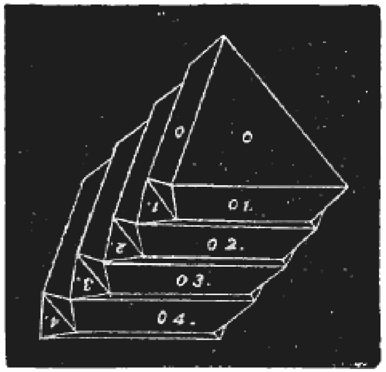
3D perspective view

- Models built with ATOMS

# In nature

*Pyrite* in pale-coloured crystalline coatings, and on blende.
Brown *blende* in twins of *d m* arranged as a coating, and in linear ag-

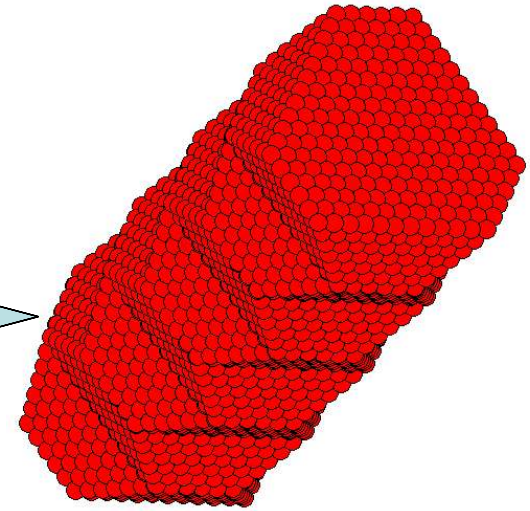




gregations of twin octohedra—the latter rare.

z 2

compare



THE MINERALOGICAL MAGAZINE

AND

JOURNAL

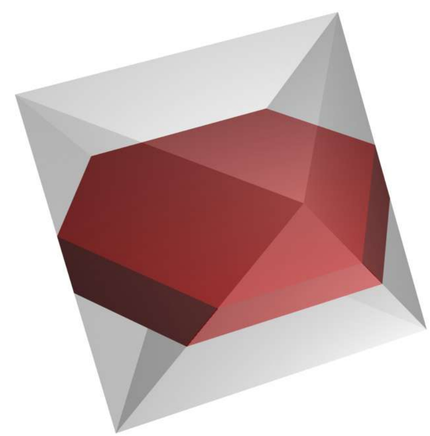
OF THE

MINERALOGICAL SOCIETY OF GREAT BRITAIN AND IRELAND.

No. 26. FEBRUARY 1884. Vol. V.

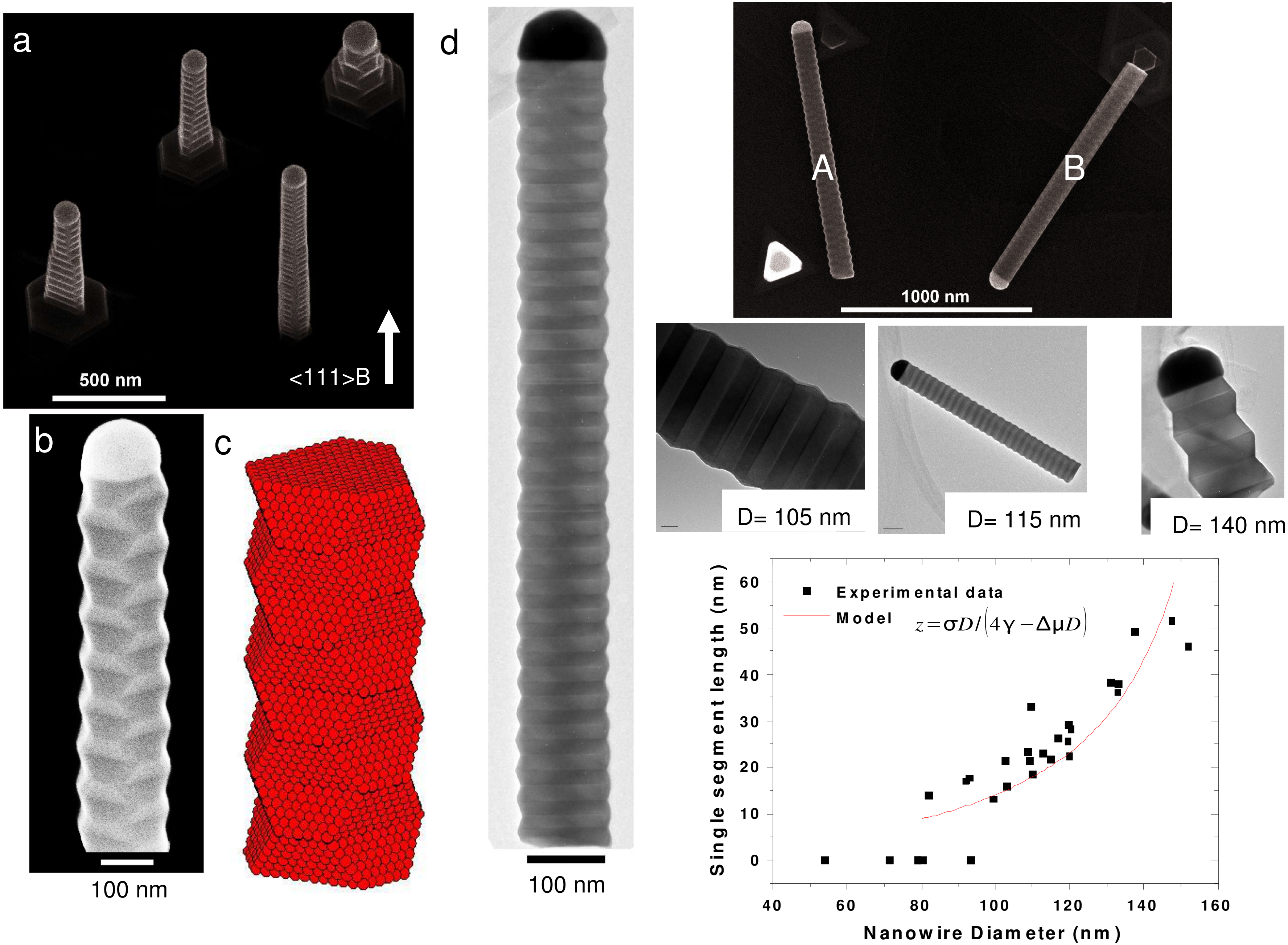
*The Geognosy and Mineralogy of Scotland.*

By Professor Heddle.



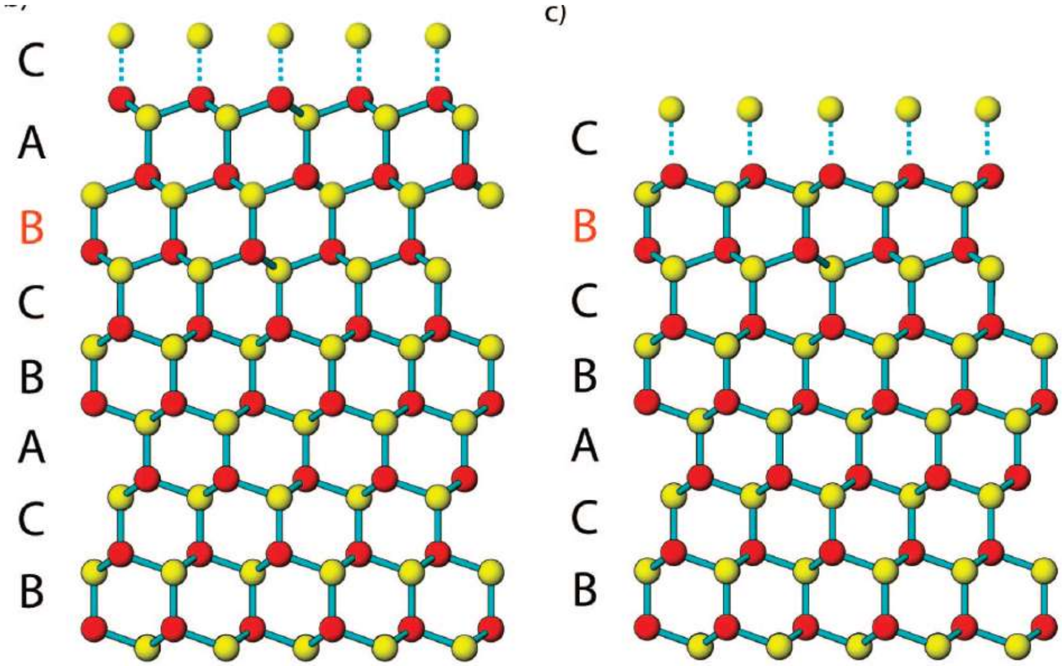
Johansson et al, Nat Mater, **5** (2006) 574

# Our special case: twin plane superlattices (TPS) in InAs



# Extreme case:

- Wurtzite structure formation in nanowires with zinc blende as bulk crystal structure.



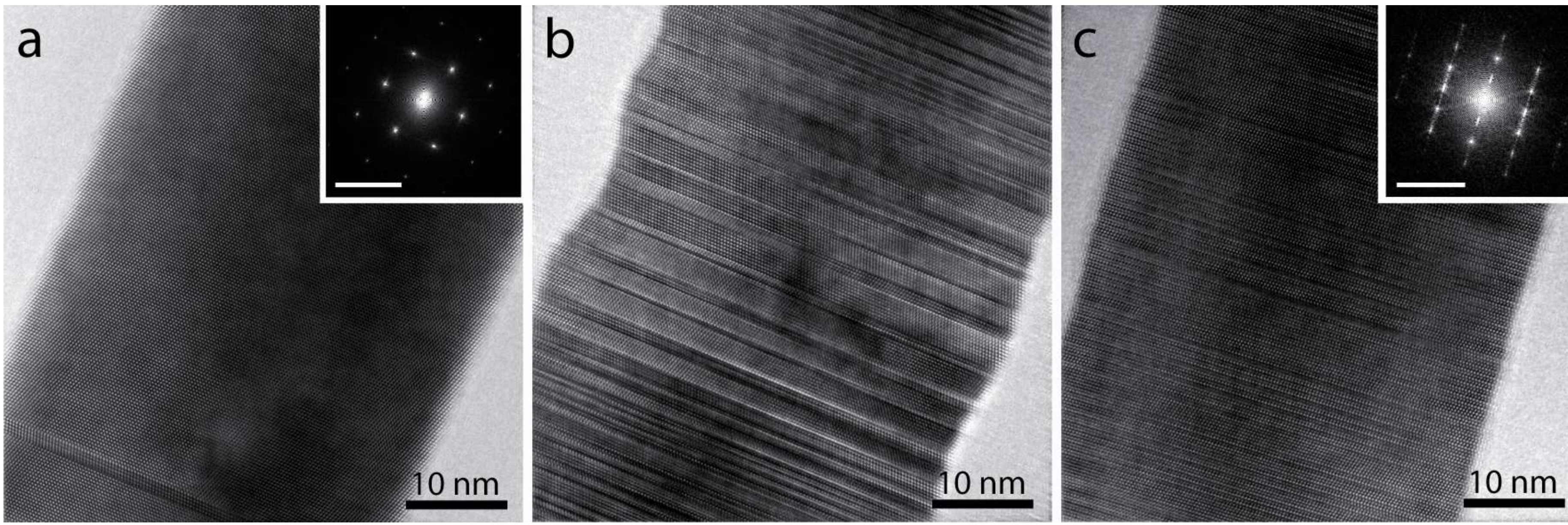

- Wurtzite can be described as an uninterrupted sequence of faulty stacked layers (twin planes)
- Can this behaviour be controlled?
- Yes, to some extent…

# GaP NW growth at different conditions

Pulsed growth
In background

Continuous growth
In background

Continuous growth
In free background




Extended zinc blende (ZB) segments

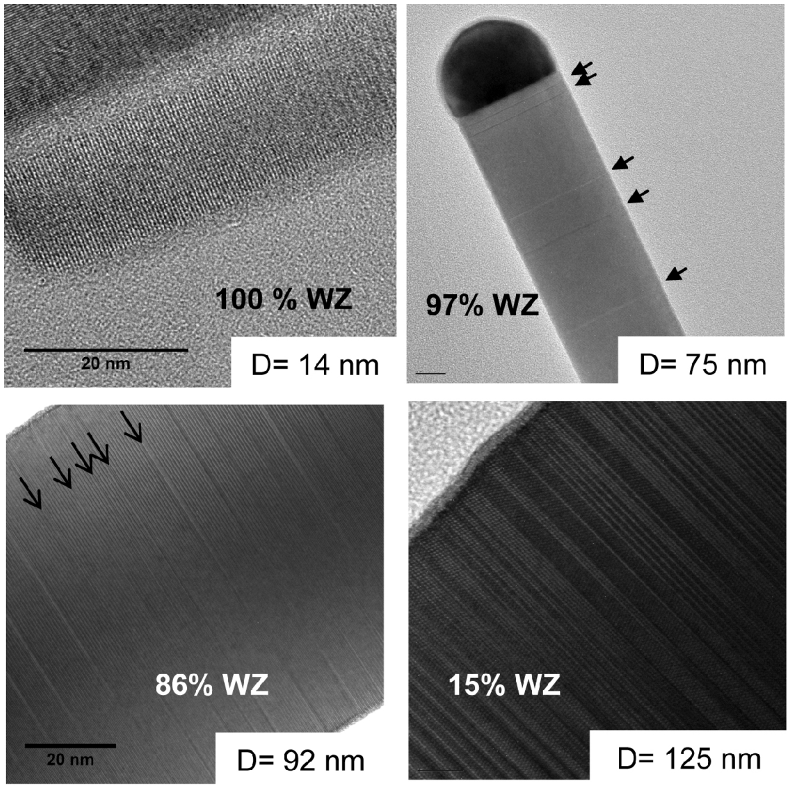
Short ZB segments (lamellar twinning)

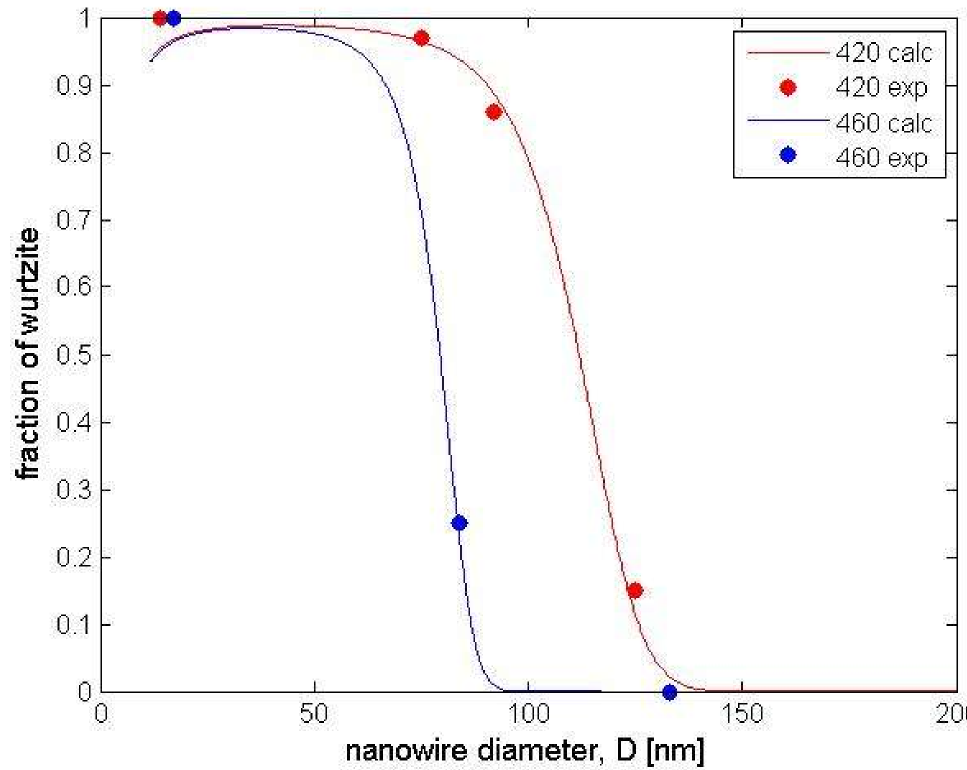
Extended wurtzite (WZ) segments

low **Supersaturation** ($\Delta\mu$, $C/C_{eq}$) high

J Johansson et al., Crystal Growth & Des. 9 (2009) 766

# Fraction of wurtzite in InAs NWs

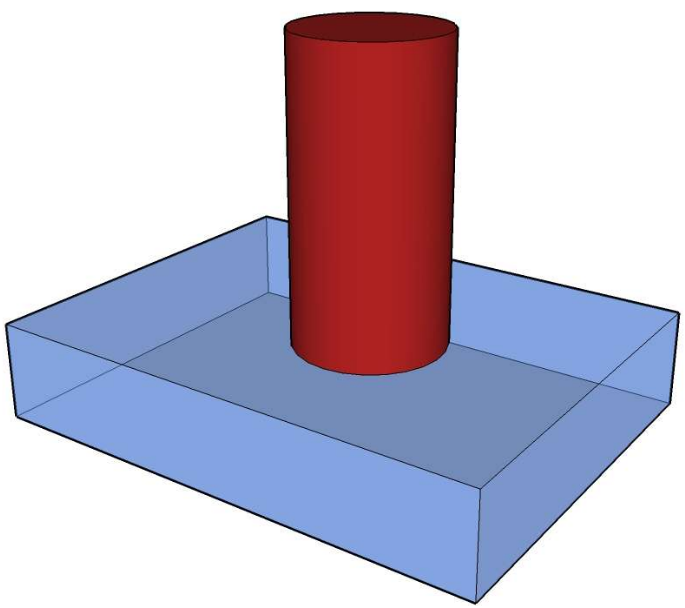



T = 420 °C

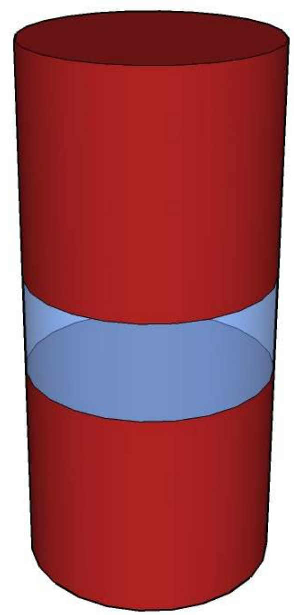
- Thin wires WZ, thick wires ZB
- Cross-over diameter for the WZ to ZB transition

# Nanowires – heterostructures unlimited?



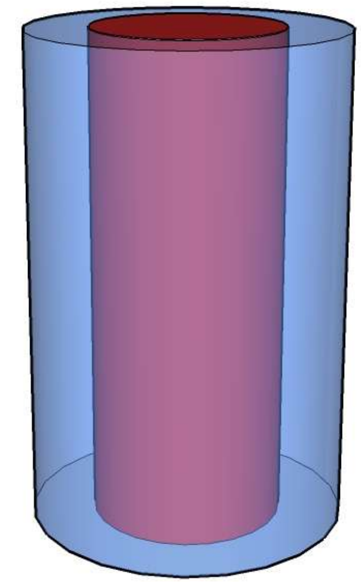
*Substrate–wire*

(III–V on Si)



*Axial*

(QD, barriers)

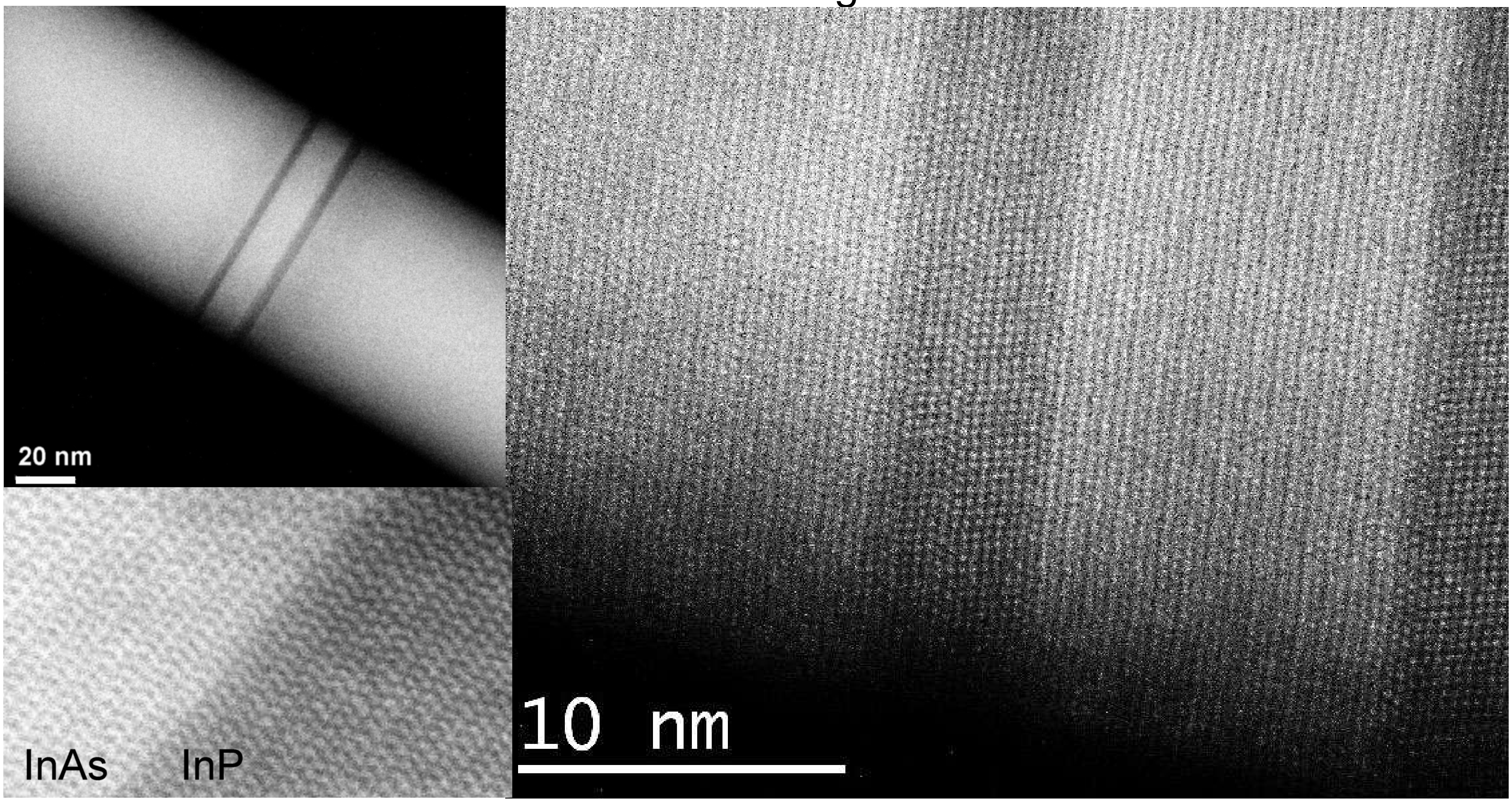


*Radial*

(QW, passivation)

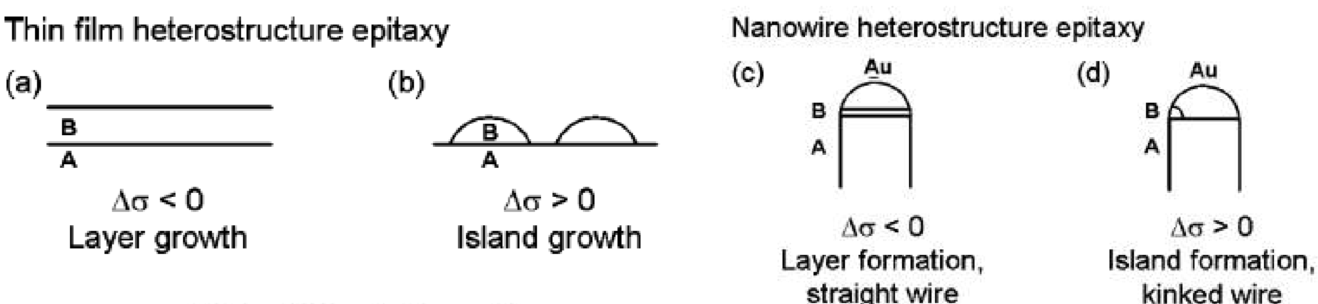
# Atomically flat interfaces

- Example of axial heterostructure: High-angle annular dark field TEM of Double Barrier Resonant Tunneling Diode

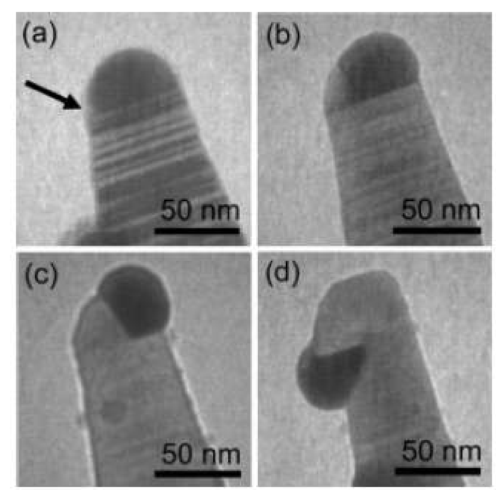


# Combinations

| Material A | Material B | Material A Lattice Constant (Å) | Material B Lattice Constant (Å) | Morphology: B on A[a] | Morphology: A on B | Mismatch[b] (%) |
|---|---|---|---|---|---|---|
| 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 | InAs | 5.6533 | 6.0584 | kinked | straight | 7.17 |
| GaAs | InP | 5.6533 | 5.8686 | kinked | straight | 3.81 |
| GaAs | Si | 5.6533 | 5.4310 | kinked | straight | -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[c] | -3.13 |



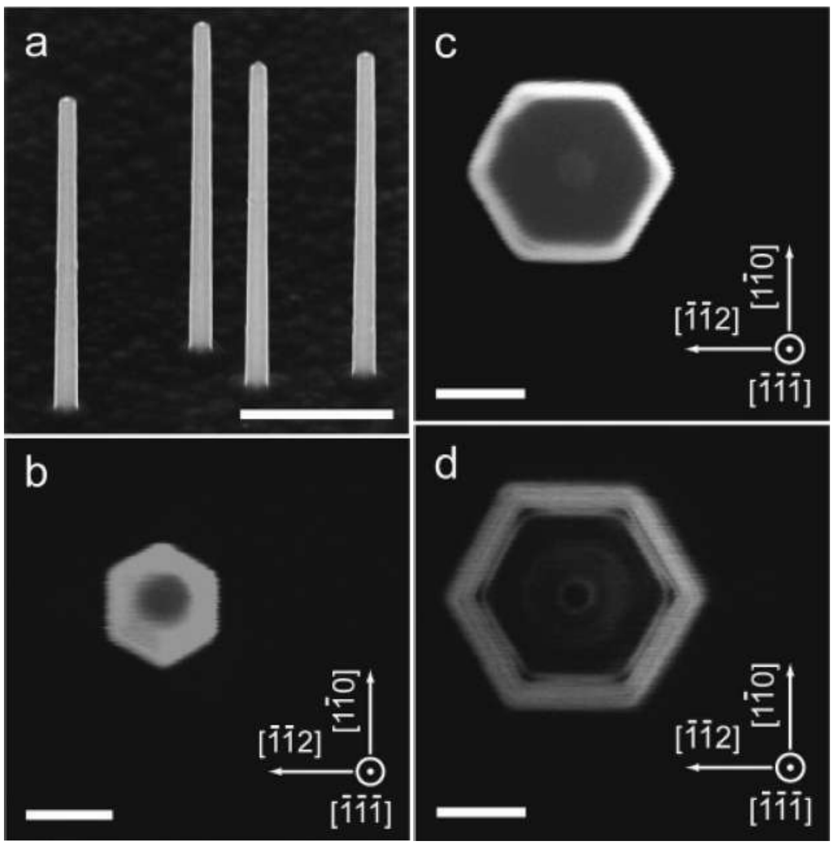

$$\Delta\sigma = \sigma_B + \sigma_i - \sigma_A$$

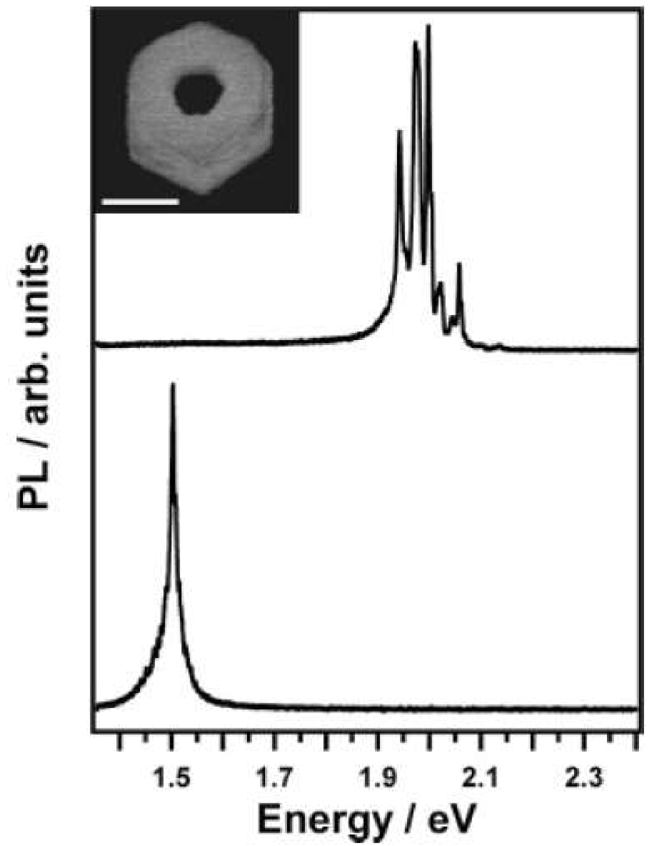



K.A. Dick *et al.*, Nano Lett. 7 (2007) 1817

# Core/shell wires

- Example of radial heterostructure: characterization of AlInP shells on GaAs nanowires




Scale bar = 100 nm

N. Sköld *et al.*, Nano Lett. 6 (2006) 2743

# Band structure calculations

PHYSICAL REVIEW B **78**, 115319 (2008)

**Band structure of core-shell semiconductor nanowires**

M.-E. Pistol*
*Solid State Physics, The Nanometer Structure Consortium, Lund University, P.O. Box 118, SE-221 00 Lund, Sweden*

C. E. Pryor†
*Optical Science and Technology Center and Department of Physics and Astronomy, University of Iowa, Iowa City, Iowa 522*
(Received 21 May 2008; revised manuscript received 19 August 2008; published 23 September 2008)

We have calculated band structures for strained core-shell nanowires involving all combinations of AlN, GaN, and InN, as well as all combinations of AlP, GaP, AlAs, GaAs, InP, InAs, AlSb, GaSb, and InSb, as functions of core and shell radii. This gives 78 combinations, most of which have not been experimentally realized, and provides a quite complete overview of which interesting structures can be realized in core-shell

Phys Rev B accepted

**Band structure of segmented semiconductor nanowires**

M.-E. Pistol*
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*Department of Physics and Astronomy and Optical Science and Technology Center,*
*University of Iowa, Iowa City, Iowa, 52242, USA*
(Dated: June 12, 2009)

We have calculated the band structures for strained segmented nanowires involving all combina tions of AlN, GaN, InN, AlP, GaP, AlAs, GaAs, InP, InAs, AlSb, GaSb, and InSb, as a functio of segment length. This was done for two different growth directions of the wires, [100] and [111

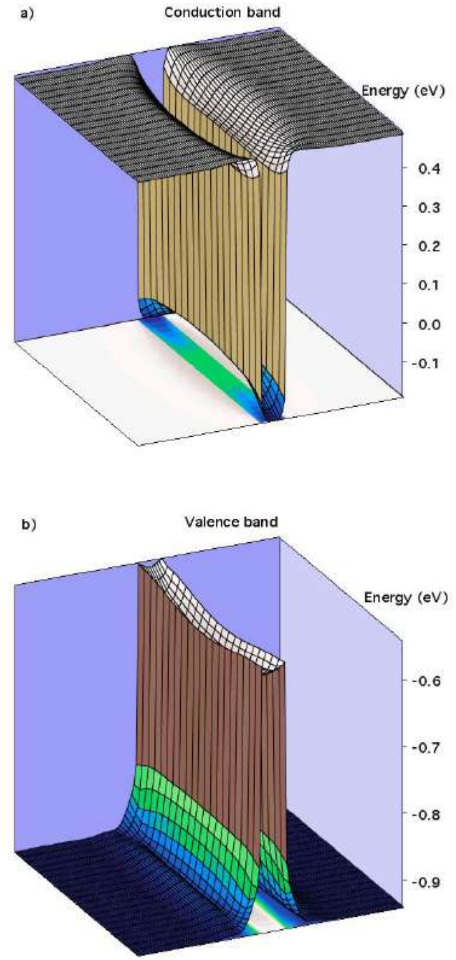
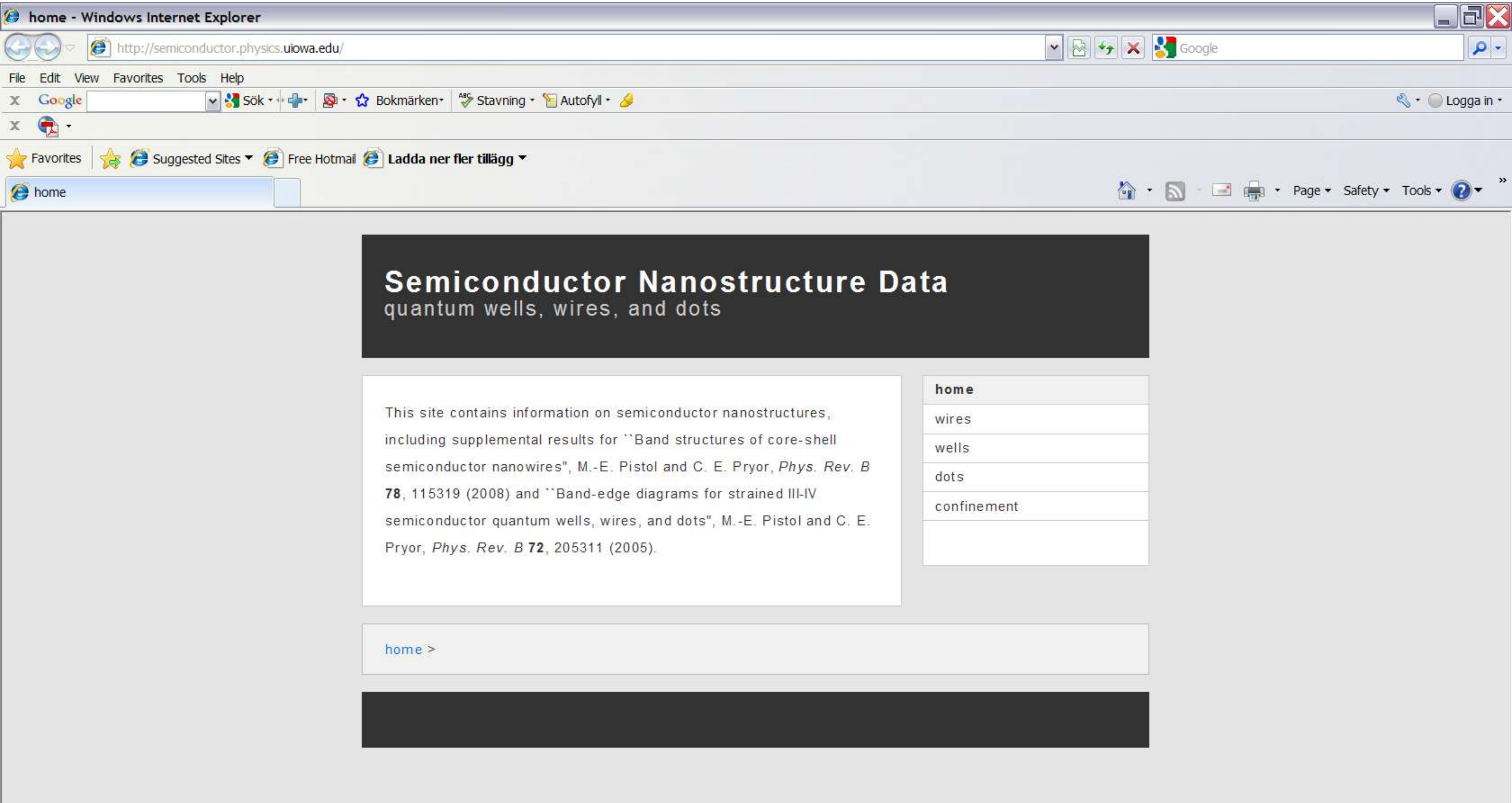



FIG. 3: a) A surface plot of the conduction band minimu for a [001] oriented wire in the yz-plane defined in Fig. 1 a consisting of an InP wire with an InAs segment. The lengt of the InAs segment is 50 and the width of the wire is 10ith a b) A surface plot of the valence band maximum for the sam core wire.

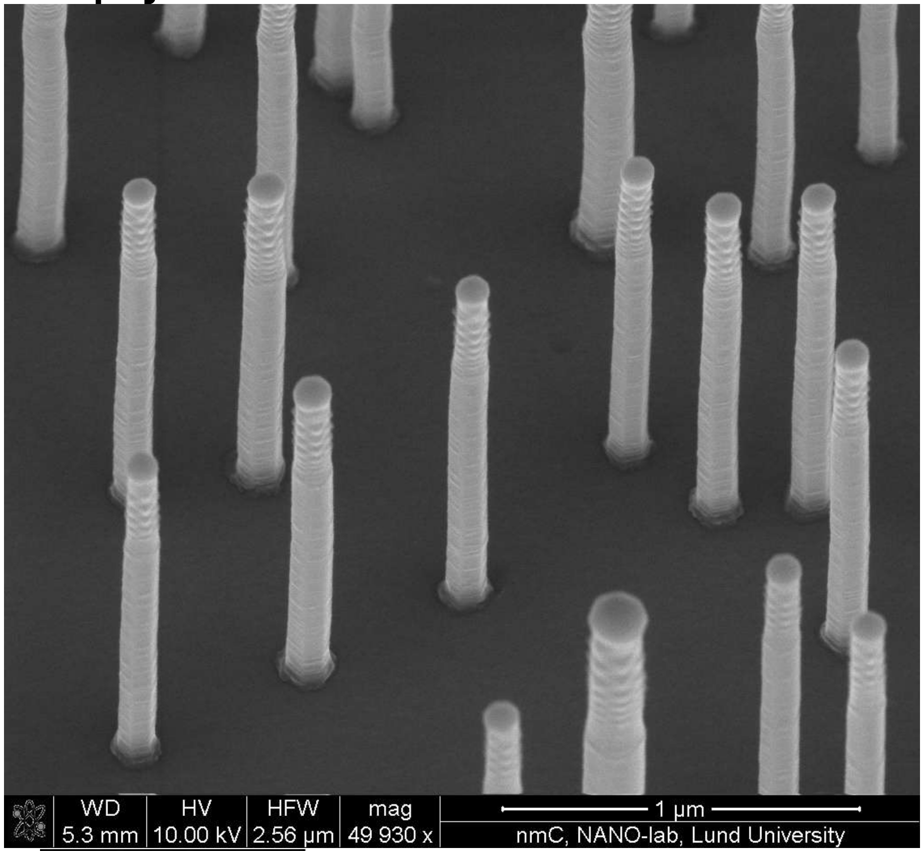
# Band structure calculations




For more information, visit: http://semiconductor.physics.uiowa.edu/

# Nanowire doping

- $n^+p$ junctions in InP nanowires

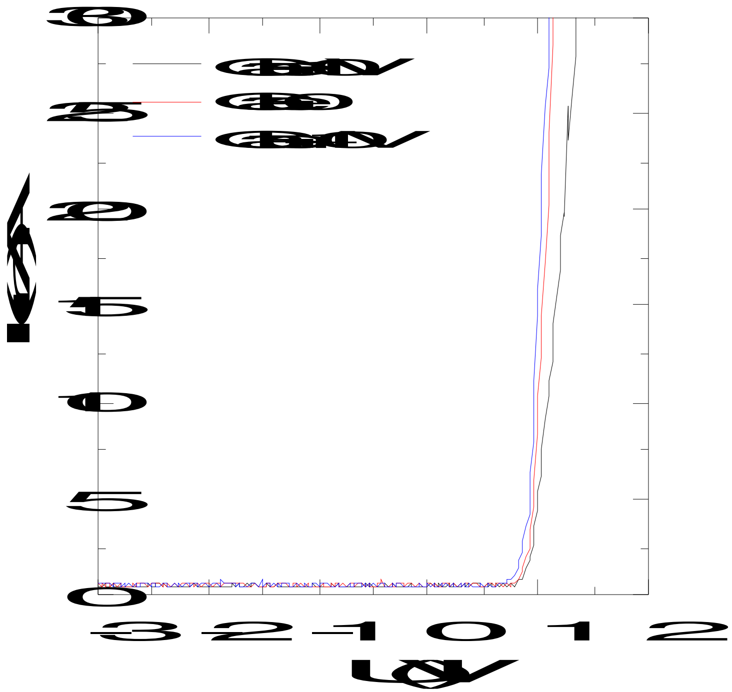


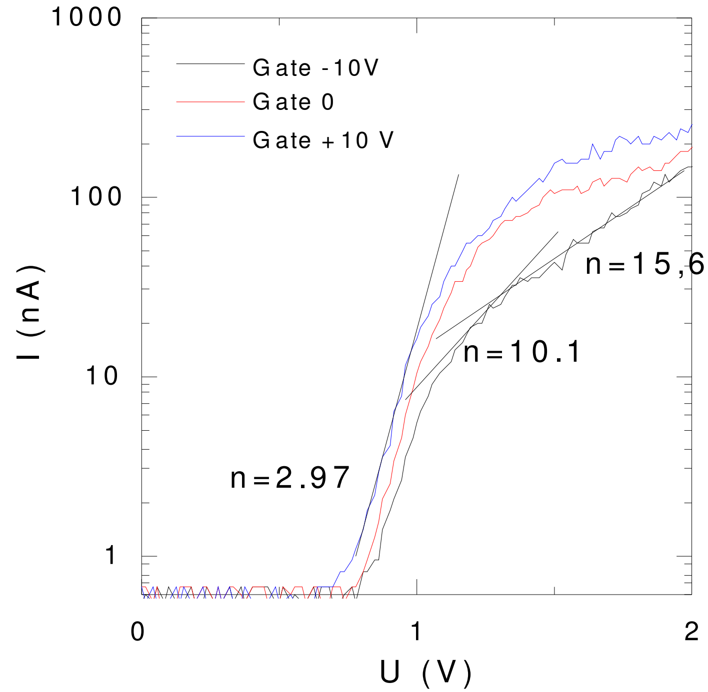


- $X_{TESn}$=1E-5, $X_{DMZn}$=5.5 E-5
- $N_D$=6E18 cm-3, $N_A$= xE17
- 80 nm Au catalyst

order is important

# n⁺p junction I-V characteristics






- *pn junction behaviour*
- *Reverse breakdown voltage about 20V*
- *Ideality factor around 3*

# Optical activity

**Electroluminescence**

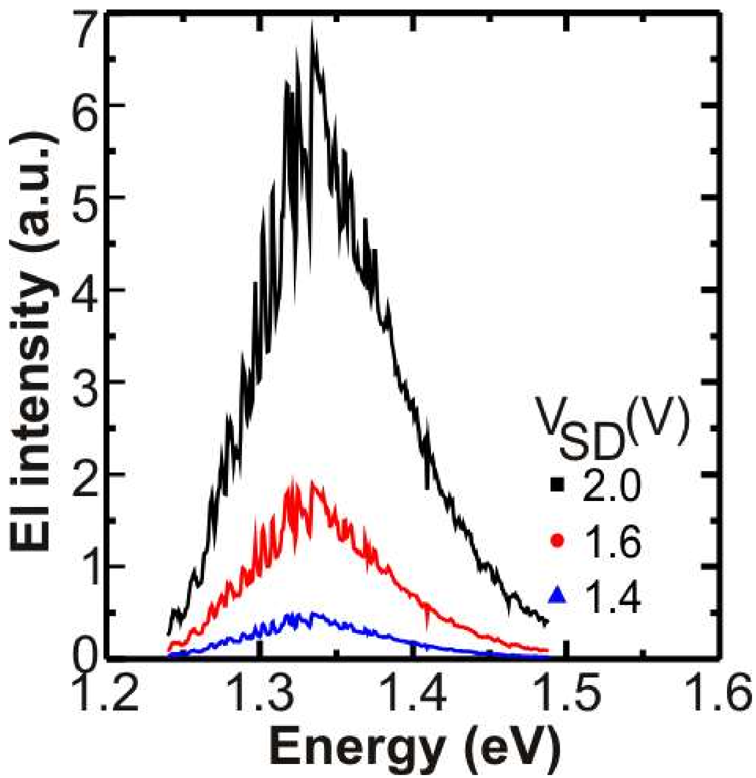
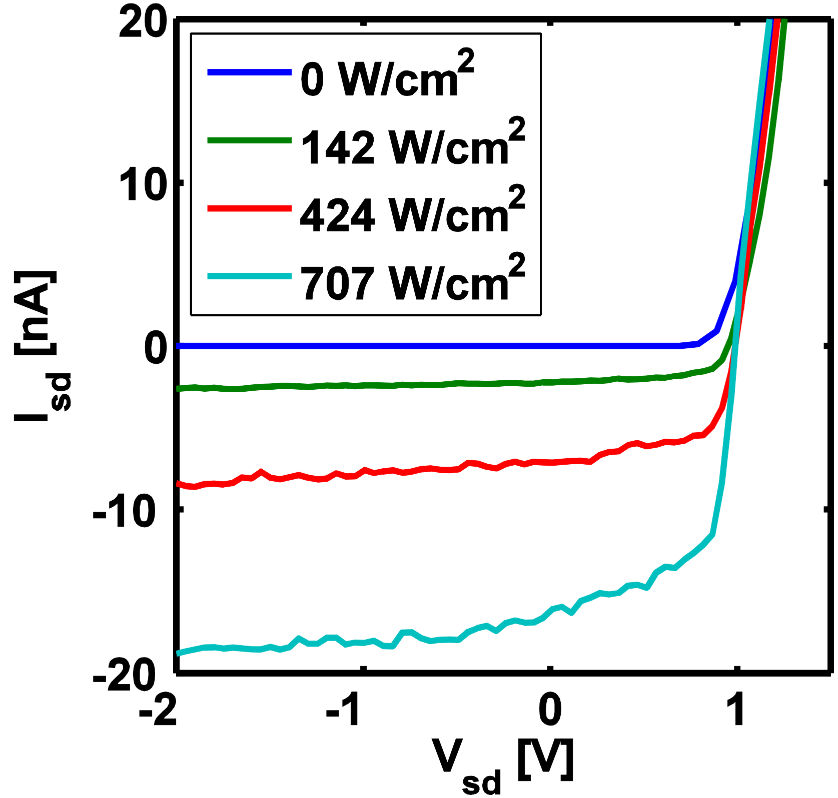


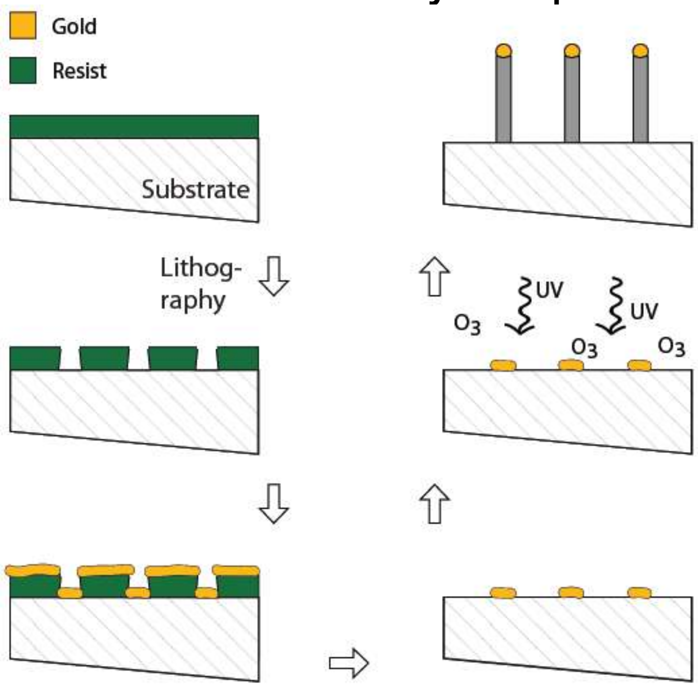

**Photo current**

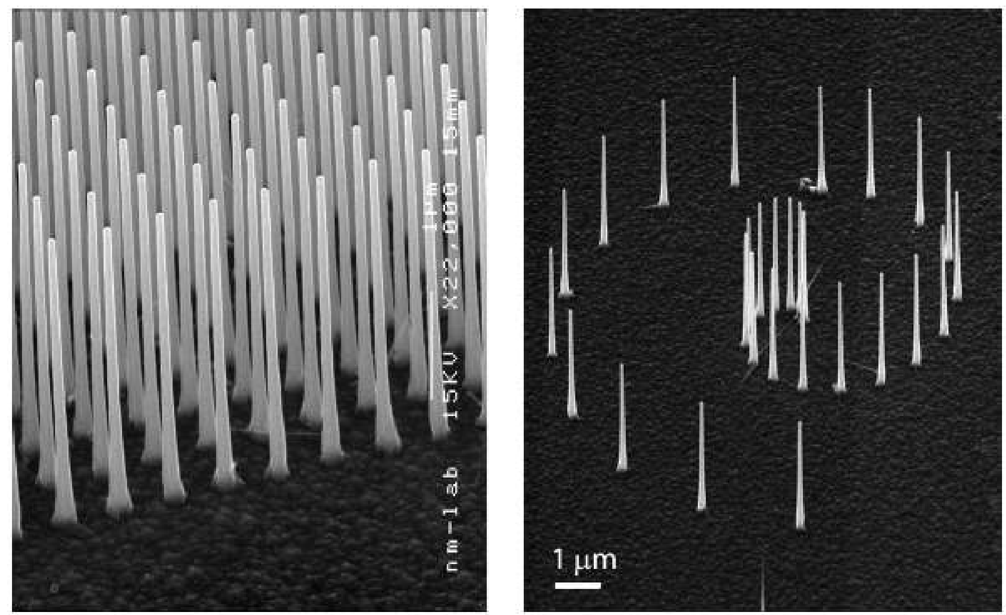



- *Light emitting diode*
- *Quantum efficiency ~$10^{-5}$ at 300K*

# Patterned growth

- Instead of randomly deposited aerosol deposition – use e-beam lithography (ebl) + lift–off to define the gold particles
- Nanowires in any 2D pattern




*InP nanowires on InP(111)B*

- Potential for upscaling: use nanoimprint lithography (NIL) instead of ebl

T. Mårtensson, PhD thesis
T. Mårtensson et al, Nanotechnology 14 (2003) 1255; Nano Letters 4 (2004) 699

# Patterned growth, core/shell, doping

IOP Publishing — Nanotechnology

Nanotechnology **19** (2008) 305201 (6pp) doi:10.1088/0957-4484/19/30/305201

## Monolithic GaAs/InGaP nanowire light emitting diodes on silicon

C Patrik T Svensson[1], Thomas Mårtensson[1,2], Johanna Trägårdh[2], Christina Larsson[1], Michael Rask[3], Dan Hessman[2], Lars Samuelson[2] and Jonas Ohlsson[1]

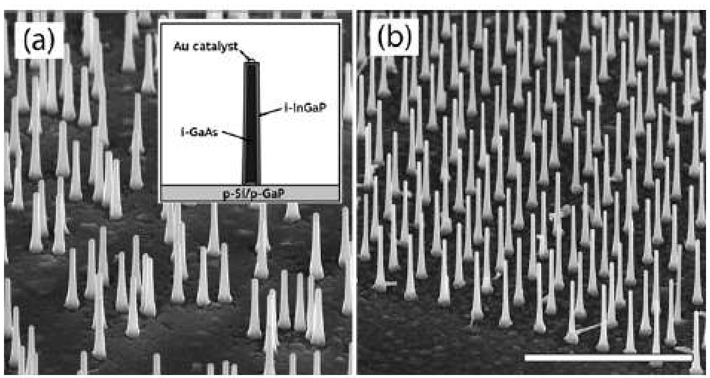
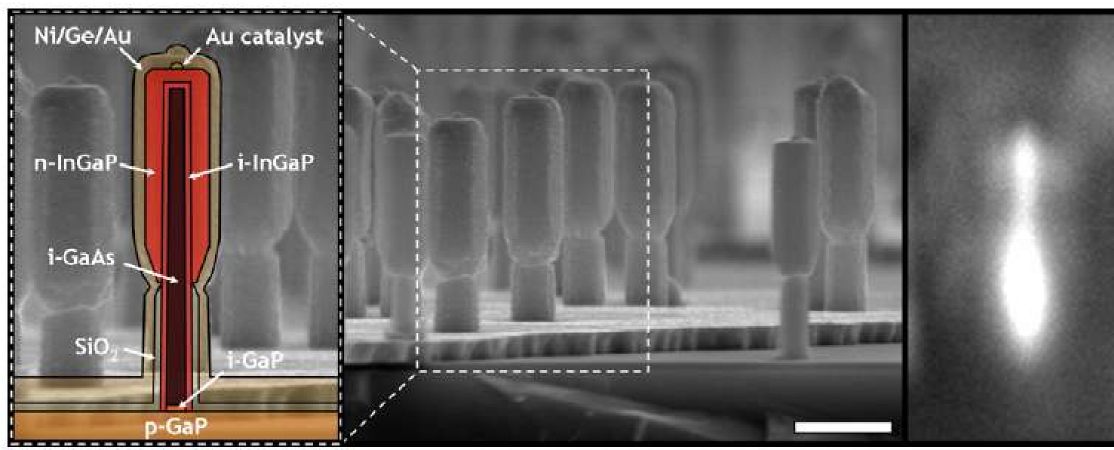



**Figure 2.** (a) Core–shell nanowires grown on Si(111). The epi-structure is shown in the inset. The same nanowires were used for PL measurements. (b) The same epi-structure as panel (a), but lithographically defined in an array with 1 $\mu$m pitch. The scale bar is 5 $\mu$m, and it applies to both panels.




Schematics of the device

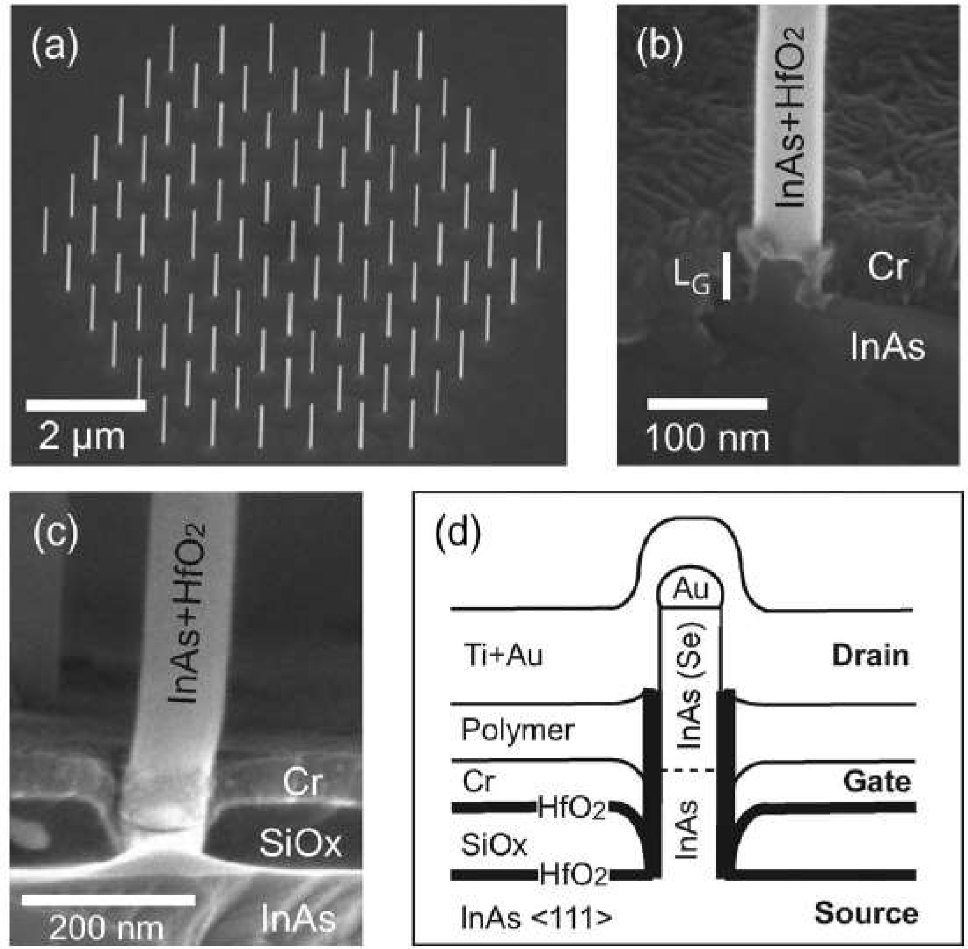
SEM image

CCD image showing EL

C. P. T Svensson et al, Nanotechnology 19 (2008) 305201

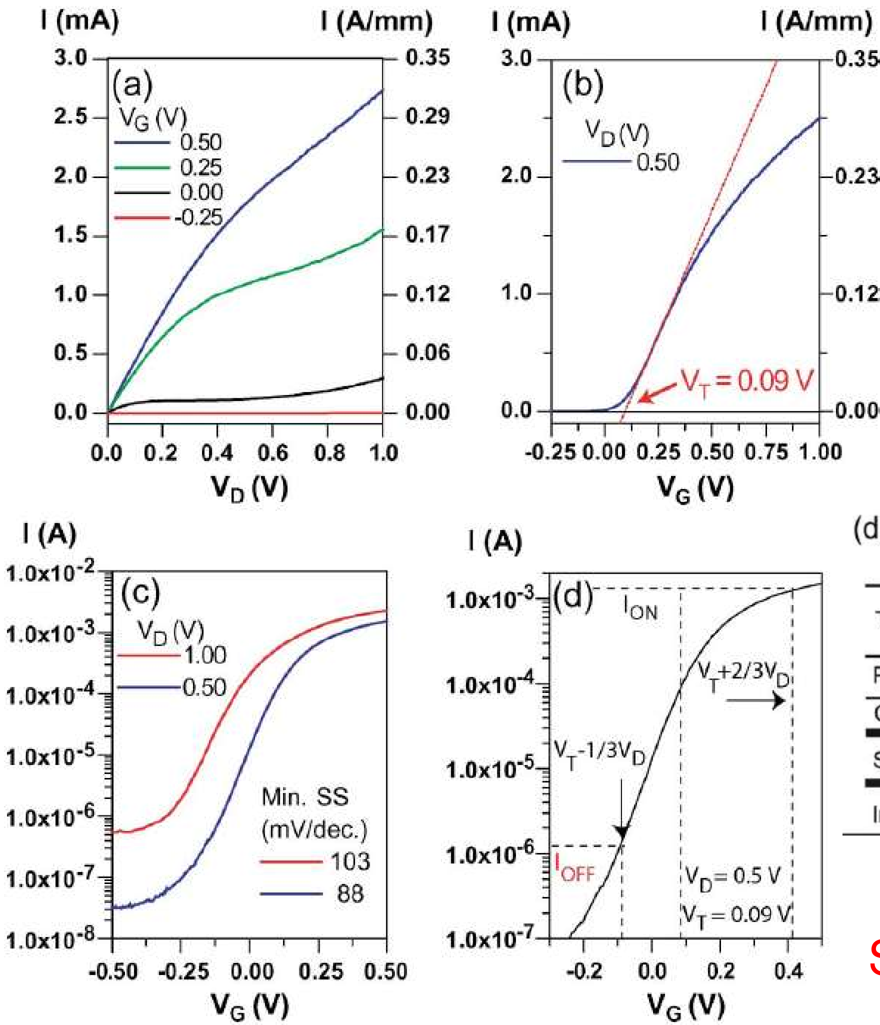
# Nanowire field effect transistor

- Process technology for InAs nanowire wrap-gate FETs:
  - $HfO_2$ by ALD
  - $SiO_x$ by evaporation
  - $HfO_2$ by ALD
  - Cr by evaporation
  - Photoresist as insulator
  - Ti/Au drain contact evaporation



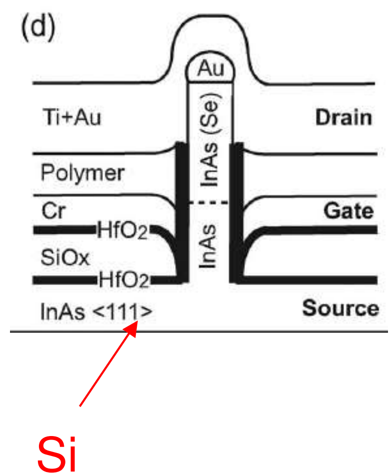

C Thelander et al, IEEE Electron Device Lett., **29** (2008) 206

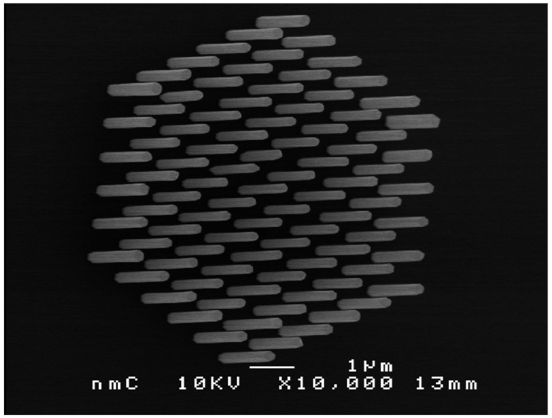
# Electrical characteristics




- High scalability
  - High-k dielectric ($HfO_2$)
  - Wrap gate architecture

- Promising material for integration
  - InAs nanowires can be grown directly on Si (also without gold)*




C Thelander et al, IEEE Electron Device Lett., **29** (2008) 206
*T Mårtensson et al, Adv Mat, **19** (2007) 1801 and B Mandl, unpublished

# Summary

- Good understanding of nanowire growth
- Many possibilities for heterostructures
- Demonstration of pn-junctions in nanowires
- Process technology for nanowire devices

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structures

# Acknowledgements


- Nanowire growth:
  - Kimberly Dick
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  - Reine Wallenberg
  - Lisa Karlsson
- Aerosol fabrication:
  - Knut Deppert
  - Kimberly Dick
  - Maria Messing
- Optical characterization
  - Niklas Sköld
  - Johanna Trägårdh
  - Dan Hessman
  - Mats-Erik Pistol
- Electronics applications
  - Claes Thelander
  - Linus Fröberg
  - Carl Rehnstedt
  - Lars-Erik Wernersson
- Scientific leadership
  - Lars Samuelson


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Thank you for listening!

structures

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Slovenia
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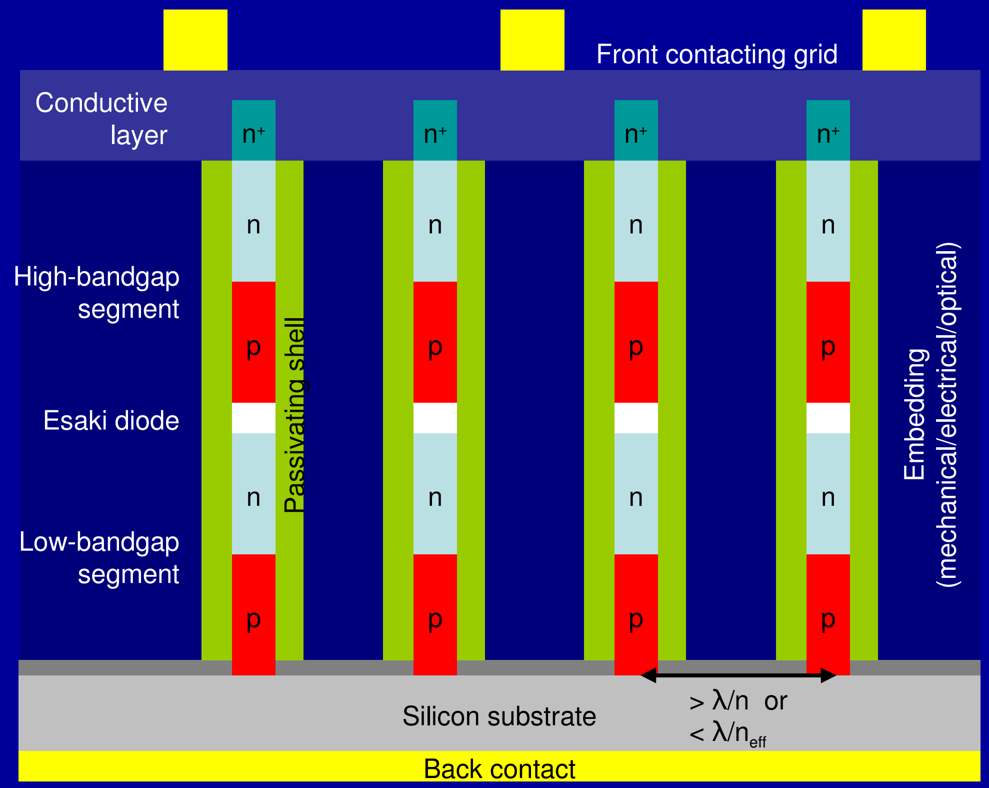
San Marino
Serbia and Montenegro
Andorra
Portugal
Spain
Italy

# New EU-STREP: AMON-RA

- Architectures, Materials and One-dimensional Nanowires for Photovoltaics - Research and Applications

- Partners:
  - ULUND: Development of NW materials, NWPV physics, project coordination
  - ISE: Design of PV architecture, verification, system design
  - ETH: Modeling of NWPV structure
  - QuNano: Development of processing
  - JKU: X-ray and PL characterization of materials
  - DTU: TEM characterization of materials




Schematic of tandem PV cell with embedded Esaki tunneling diode and surrounding light guide