Introduction to Nanotechnology

- Textbook：
  Nanophysics and Nanotechnology
  by:
  Edward L. Wolf

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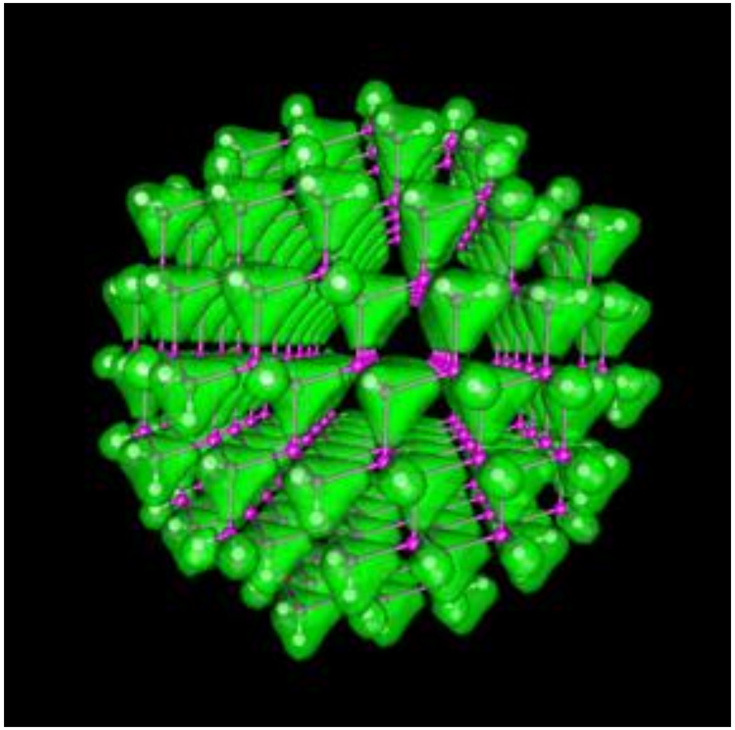
Classroom: A209
Time: Thursday; 13:40-16:30 PM
Office hour: Thur., 10:00-11:30 AM or by appointment

Self-Assembled Nano-Structure in Nature and Industry-II

Subjects: Today class

1. Self-assembly Systems
2. Carbon atom
3. Nano-tube
4. **Quantum Dot**
5. **Nano-crystal**
6. **Nano-wire**
7. Nano-particles in Bacterial life
8. Smooth Surface

Quantum Dots



Quantum Dots

- Synthetic “droplets” containing anything from a single electron to thousands of atoms but behave like a single huge atom.
- Size: nanometers to microns
- These are nanocrystals with extraordinary optical properties
  - The light emitted can be tuned to desired wavelength by altering the particle size
  - QDs absorb light and quickly re-emit but in a different color
  - Colors from blue to IR
- Common QDs: CdS, CdSe, PbS, PbSe, PbTd, CuCl…
- Manufacturing
  - Wet chemistry
  - Template synthesis (zeolites, alumina template)

Introduction

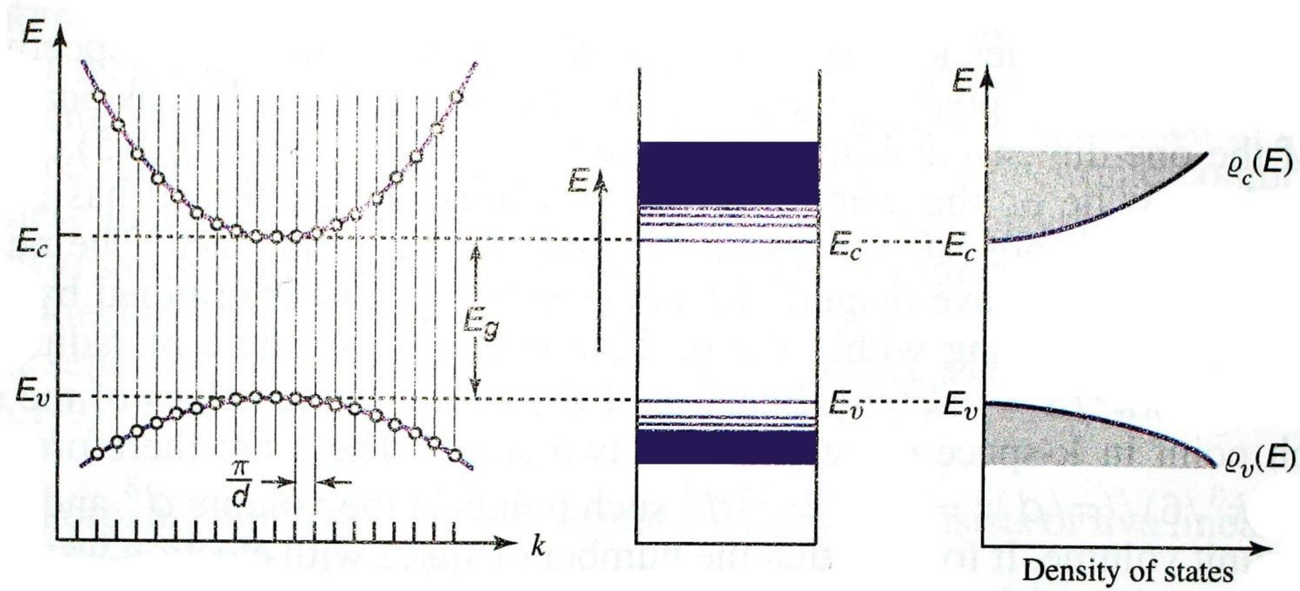
- Quantum dots are semiconductors whose excitons are confined in all three dimensions of space.
- Quantum dots have properties combined between
  - Those of bulk semiconductors
  - Those of atoms
- Different methods to create quantum dots.
- Multiple applications.

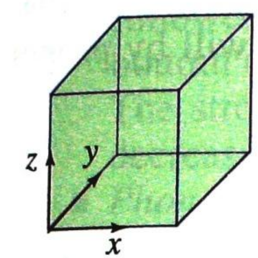
Outline

1. Quantum Confinement and Quantum Dots
2. Fabrication of Quantum Dots
3. Quantum Dot Applications

Bulk Semiconductors

- Electrons in conduction band (and holes in the valence band) are free to move in all three dimensions of space.

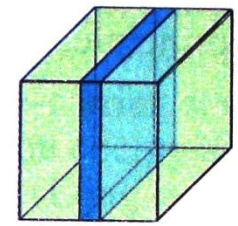


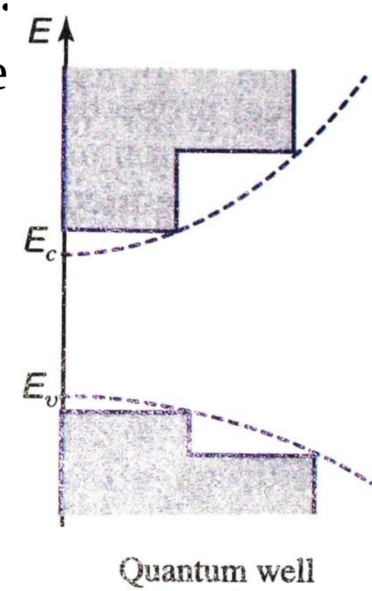


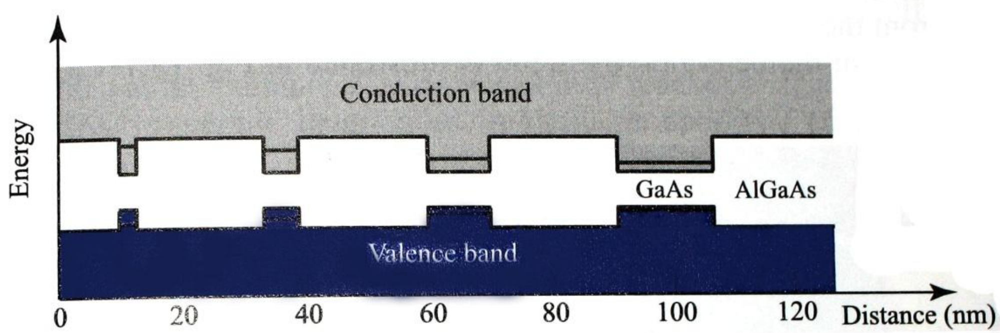
B.E.A. Saleh, M.C. Teich. <u>Fundamentals of Photonics</u>. fig. 16.1-10 and 16.1-29.

Thin Film Semiconductors

- Electrons in conduction band (and holes in the band) are free to move in two dimensions.
- Confined in one dimension by a potential well.
  - Potential well created due to a larger bandgap of the semiconductors on either side of the thin film.
  - Thinner films lead to higher energy levels.



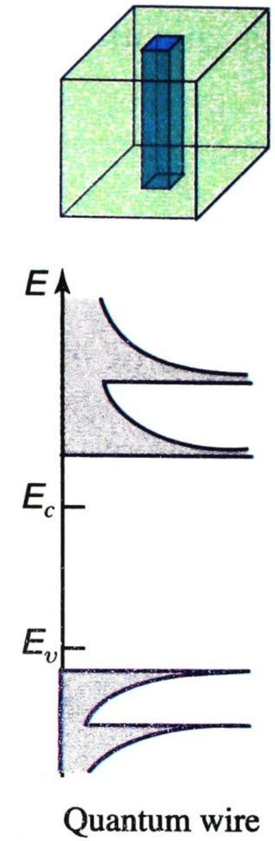




B.E.A. Saleh, M.C. Teich. Fundamentals of Photonics. fig. 13.1-11 and 16.1-29.

Quantum Wire

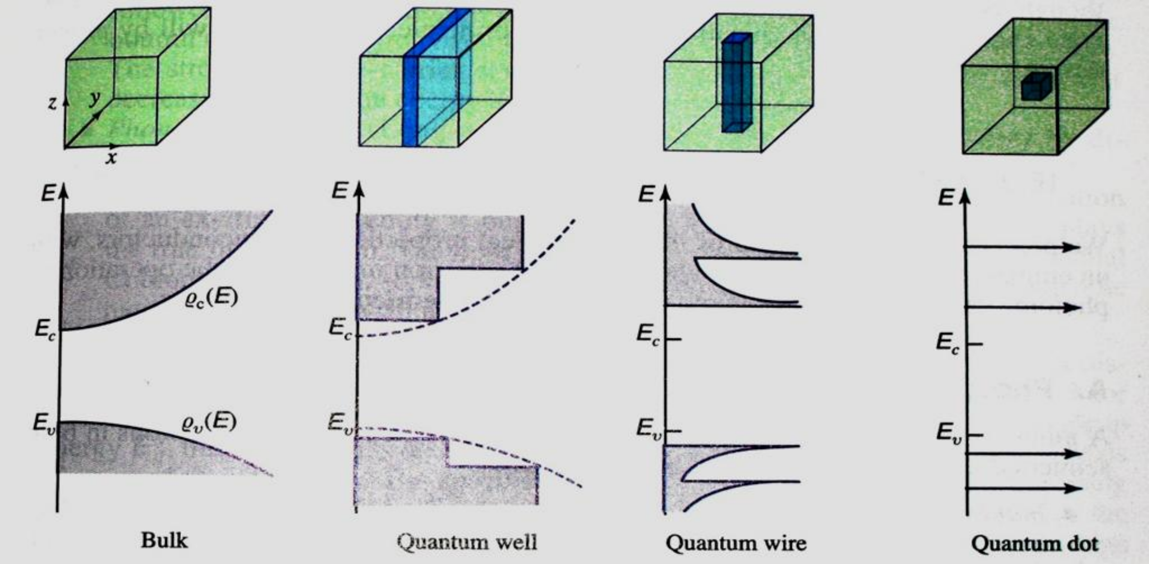
- Thin semiconductor wire surrounded by a mat
  larger bandgap.
  - Surrounding material confines electrons and holes i
    dimensions (carriers can only move in one dimensi
    larger bandgap.
    - Quantum wire acts as a potential well.



B.E.A. Saleh, M.C. Teich. Fundamentals of Photonics. fig. 16.1-29.

Quantum Dot

- Electrons and holes are confined in all three dimensions of space by a surrounding material with a larger bandgap.
- Discrete energy levels (artificial atom).
- A quantum dot has a larger bandgap.
- Like bulk semiconductor, electrons tend to make transitions near the edges of the bandgap in quantum dots.



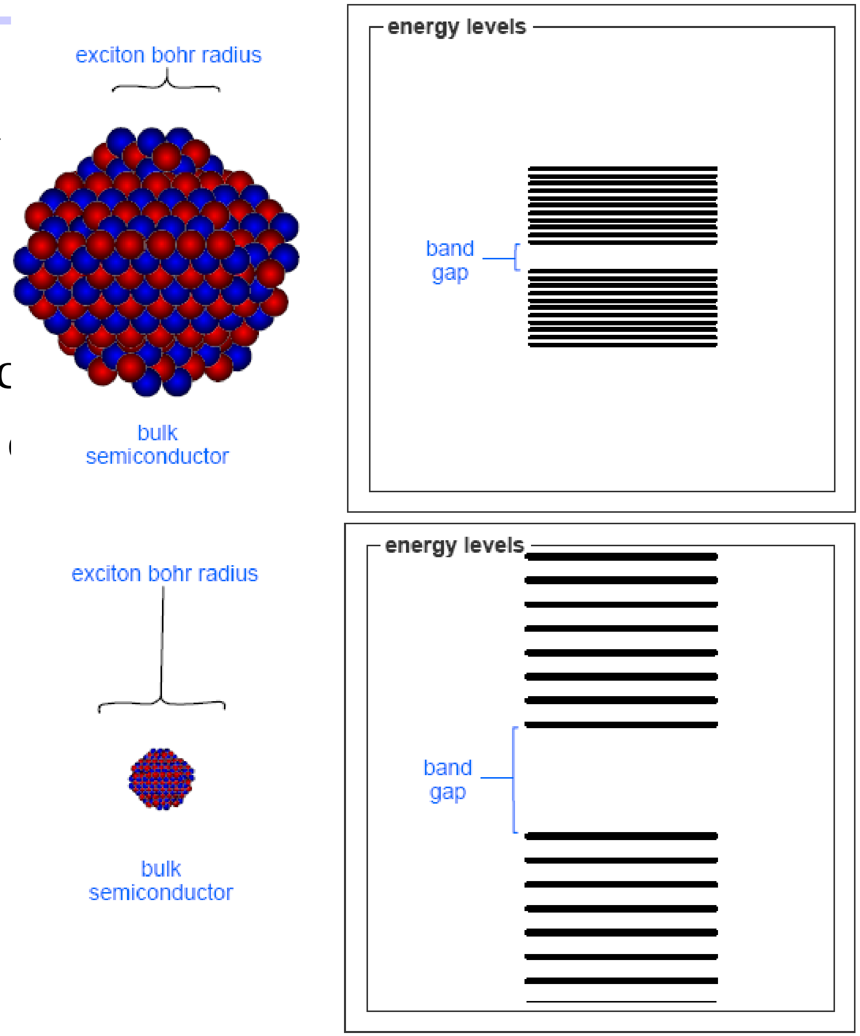
B.E.A. Saleh, M.C. Teich. Fundamentals of Photonics. fig. 16.1-29.

Quantum Dot

- Very small semiconductor particles with a size comparable to the Bohr radius of the excitons (separation of electron and hole).
  - Typical dimensions: 1 – 10 nm
  - Can be as large as several μm.
  - Different shapes (cubes, spheres, pyramids, etc.)

Discrete Energy Levels

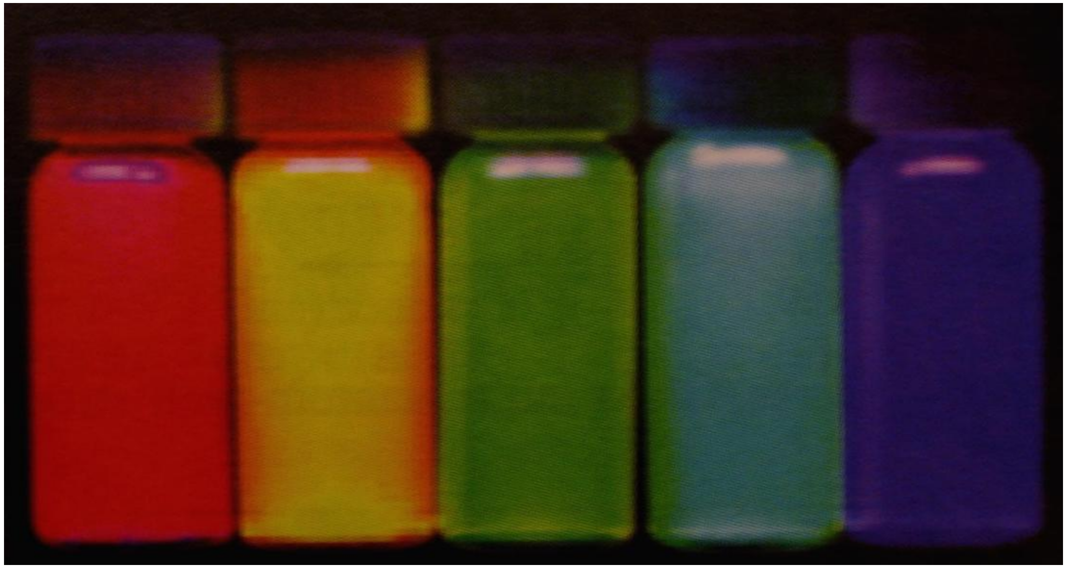
- The energy levels depend of the quantum dot.
- Smaller quantum dot:
  - Higher energy required to c
    - Energy levels increase in
    - Higher band gap energy.



Figures are from "Quantum Dots Explained." Evident Technologies. 2008.

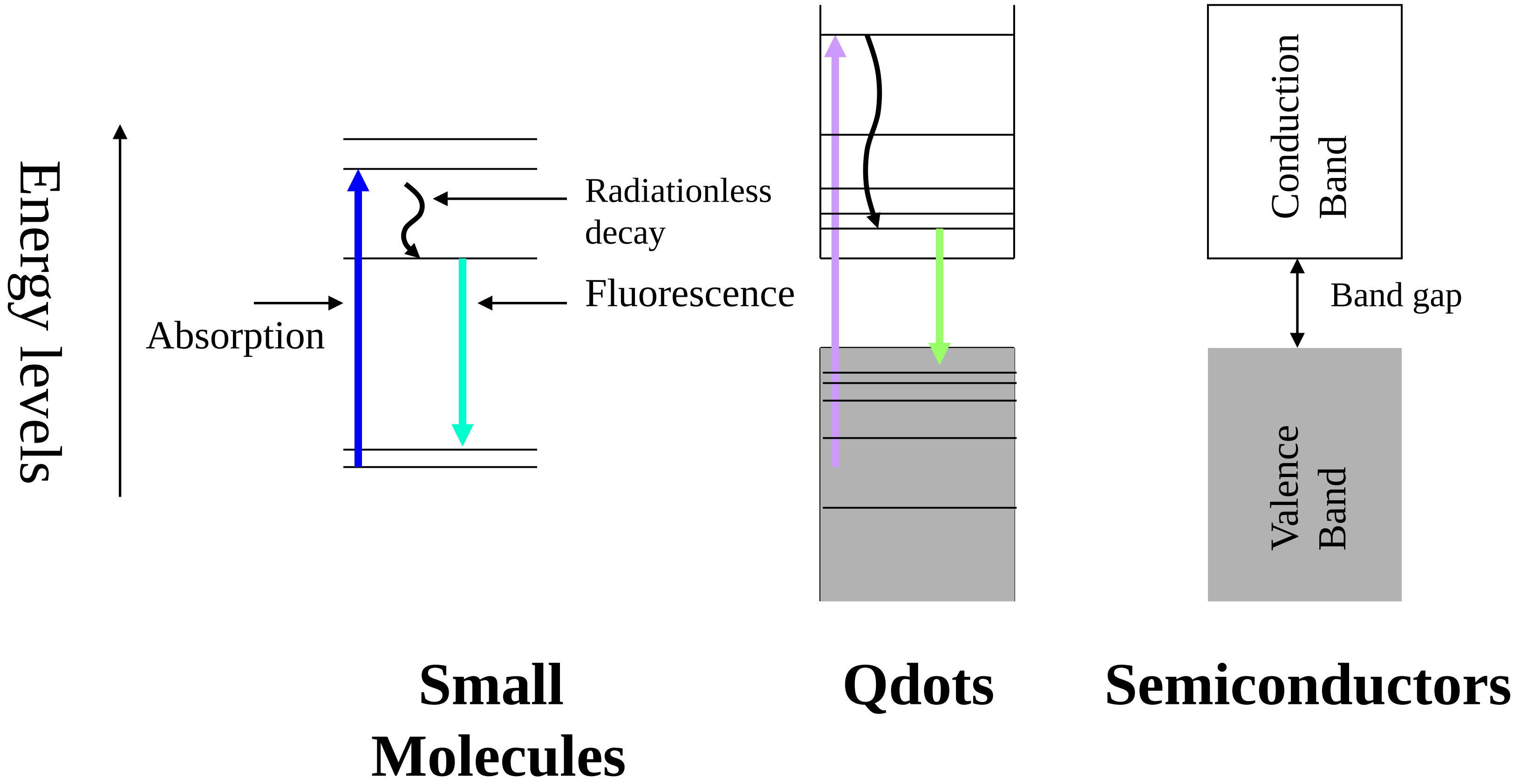
CdSe Quantum Dot

- 5 nm dots: red
- 1.5 nm dots: violet



B.E.A. Saleh, M.C. Teich. Fundamentals of Photonics. fig. 13.1-12.

Qdots® Have a Unique Electronic Structure



Source: Bala Manian, Quantum Dot Corp.

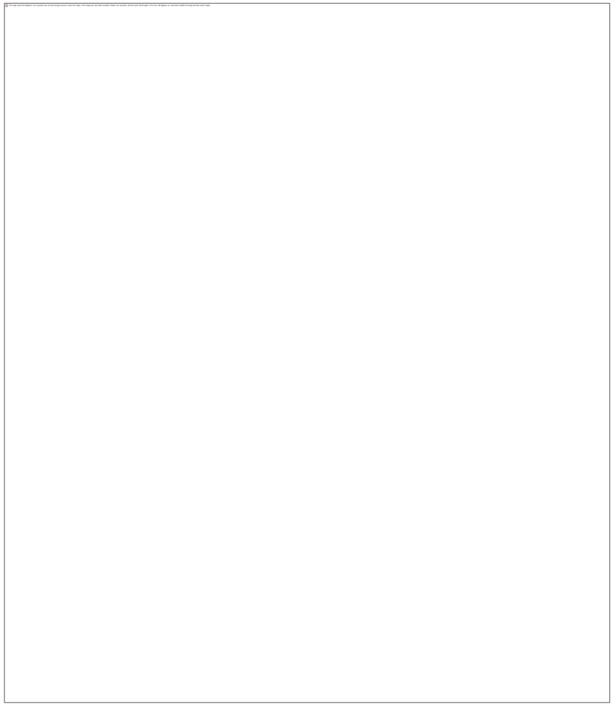
How to Make Quantum Dots

- There are three main ways to confine excitons in semiconductors:
  - Lithography
  - Colloidal synthesis
  - Epitaxy:
    - » Patterned Growth
    - » Self-Organized Growth

Lithography

- Quantum wells are covered with a polymer mask and exposed to an electron or ion beam.
- The surface is covered with a thin layer of metal, then cleaned and only the exposed areas keep the metal layer.
- Pillars are etched into the entire surface.

- Multiple layers are applied this way to build up the properties and size wanted.
- Disadvantages: slow, contamination, low density, defect formation.



Resulting quantum dot etched in GaAs/AlGaAs superlattice.
L. Jacak, P. Hawrylak, A. Wojs. Quantum dots fig. 2.2.

Colloidal Synthesis

- Immersion of semiconductor microcrystals in glass dielectric matrices.
- Taking a silicate glass with 1% semiconducting phase (CdS, CuCl, CdSe, or CuBr).
- Heating for several hours at high temperature.

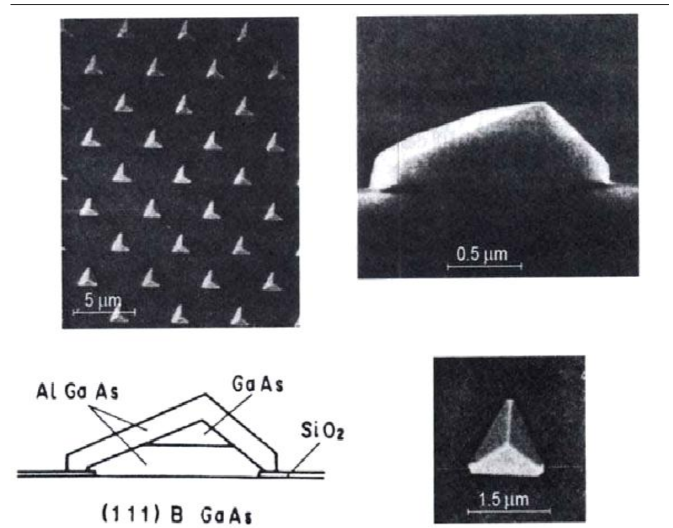
⇒ Formation of microcrystals of nearly equal size.

- Typically group II-VI materials (e.g. CdS, CdSe)
- Size variations (“size dispersion”).

Epitaxy: Patterned Growth

- Semiconducting compounds with a smaller bandgap (GaAs) are grown on the surface of a compoundwith a larger bandgap (AlGaAs).
- Growth is restricted by coating it with a masking compound (SiO_2) and etching that mask with the shape of the required crystal cell wall shape.

- Disadvantage: density of quantum dots limited by mask pattern.

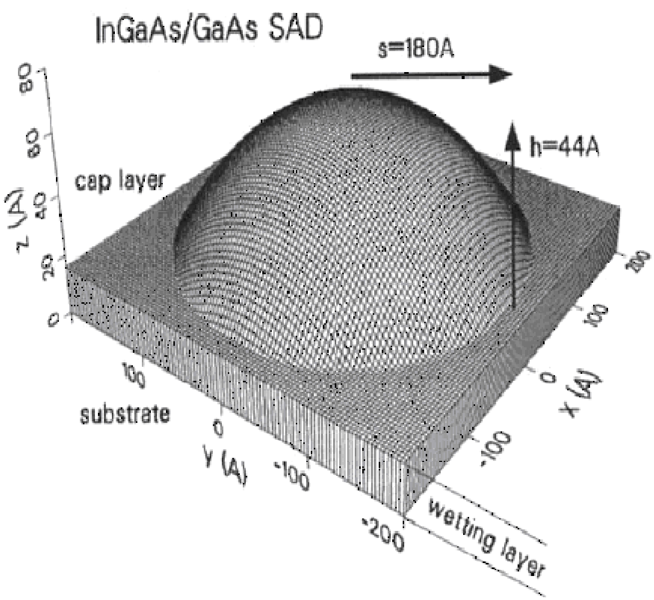


L. Jacak, P. Hawrylak, A. Wojs. Quantum dots fig 2.7.

Epitaxy: Self-Organized Growth

- Uses a large difference in the lattice constants of the substrate and the crystallizing material.
- When the crystallized layer is thicker than the critical thickness, there is a strong strain on the layers.
- The breakdown results in randomly distributed islets of regular shape and size.

- Disadvantages: size and shape fluctuations, ordering.

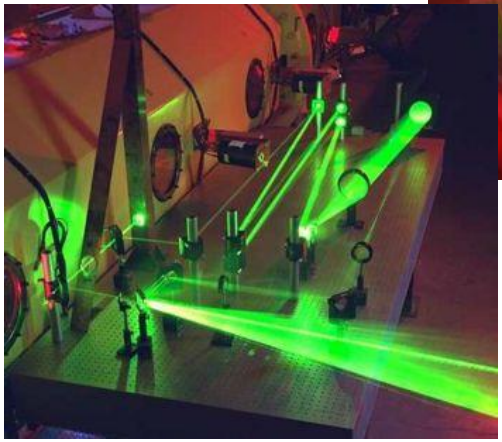


Schematic drawing of lens-shaped self-organized quantum dot.

L. Jacak,
P. Hawrylak,
A. Wojs. Quantum dots
fig 8.1.

Applications

- Photovoltaic devices: solar cells
- Biology : biosensors, imaging
- Light emitting diodes: LEDs
- Quantum computation
- Flat-panel displays
- Memory elements
- Photodetectors
- Lasers



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Applications

- LEDs, solar cells, solid state lighting
- Biomedical
  - Bioindicators
  - Lateral flow assays
  - DNA/gene identification, gene chips
  - Cancer diagnostics
- Biological Labeling Agent

Organic Dye

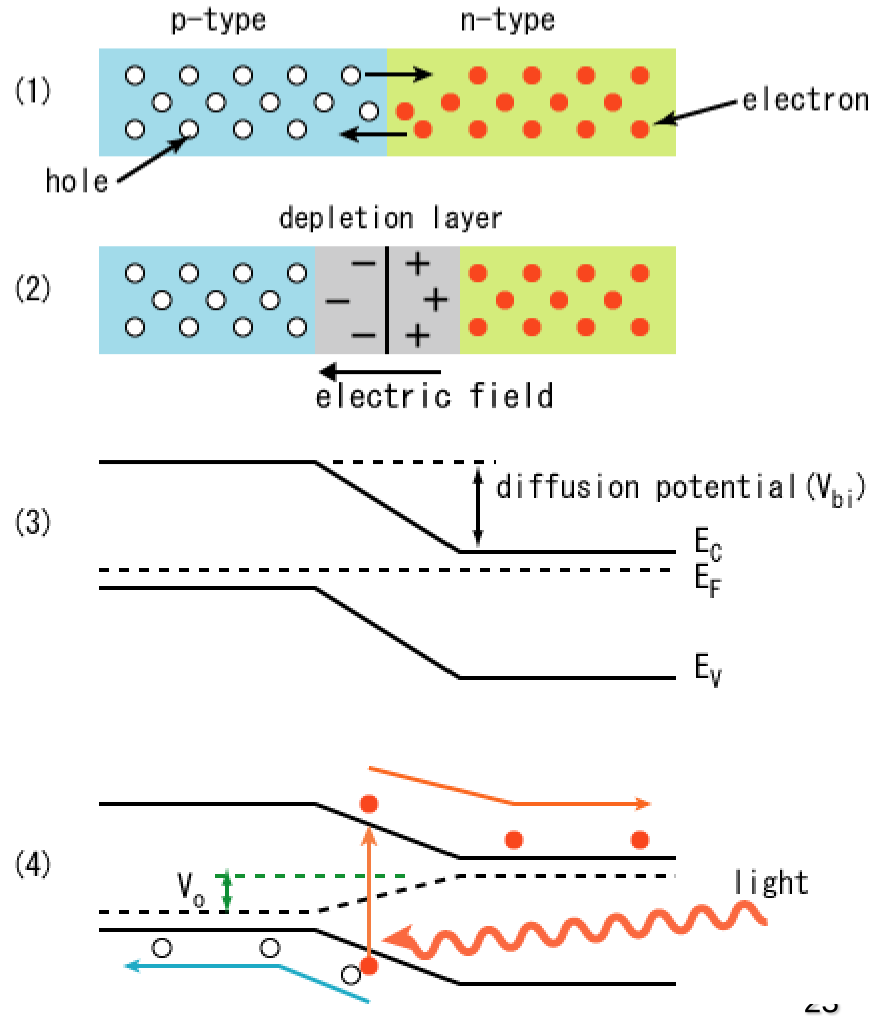
- Broad output spectrum
- Fades quickly ~ 100 ps
- Unstable
- One dye excited at a time

Quantum Dot

- Sharper spectrum
- 5-40 ns
- Stable output over time
- Multicolor imaging, multiple dyes excited simultaneously

Solar Cells

- Photovoltaic effect:
  - p-n junction.
  - Sunlight excites electrons and creates electron-hole pairs.
  - Electrons concentrate on one side of the cell and holes on the other side.
  - Connecting the 2 sides creates electricity.



Different Generations of Solar Cells

- First generation:
  - Single crystal silicon wafer.
  - Advantages: high carrier mobility.
  - Disadvantages: most of photon energy is wasted as heat, expensive.
- Second generation:
  - Thin-film technology.
  - Advantages: less expensive.
  - Disadvantages: efficiency lower compared with silicon solar cells.
- Third generation:
  - Nanocrystal solar cells.
  - Enhance electrical performances of the second generation while maintaining low production costs.

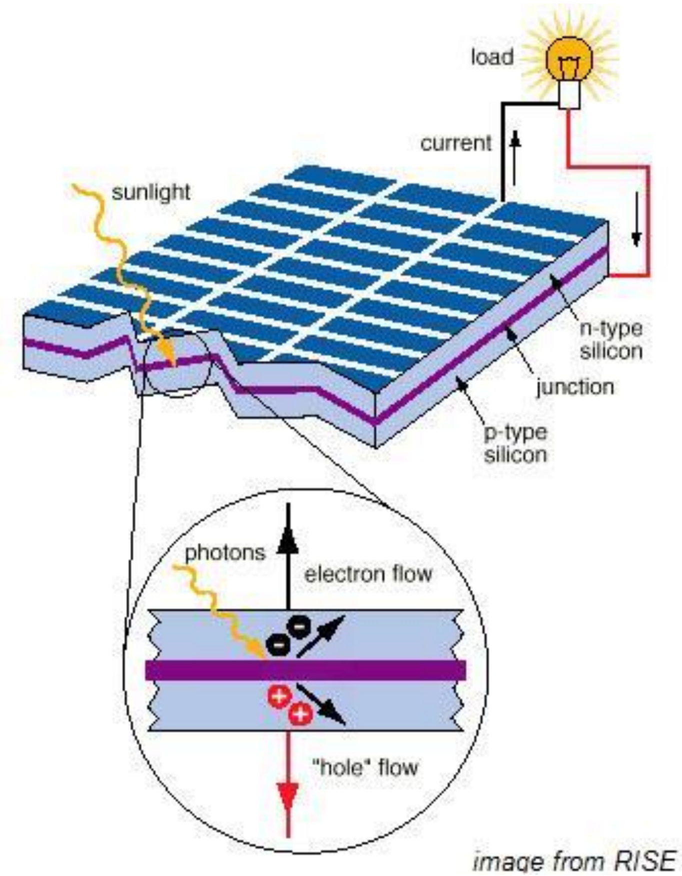


image from RISE

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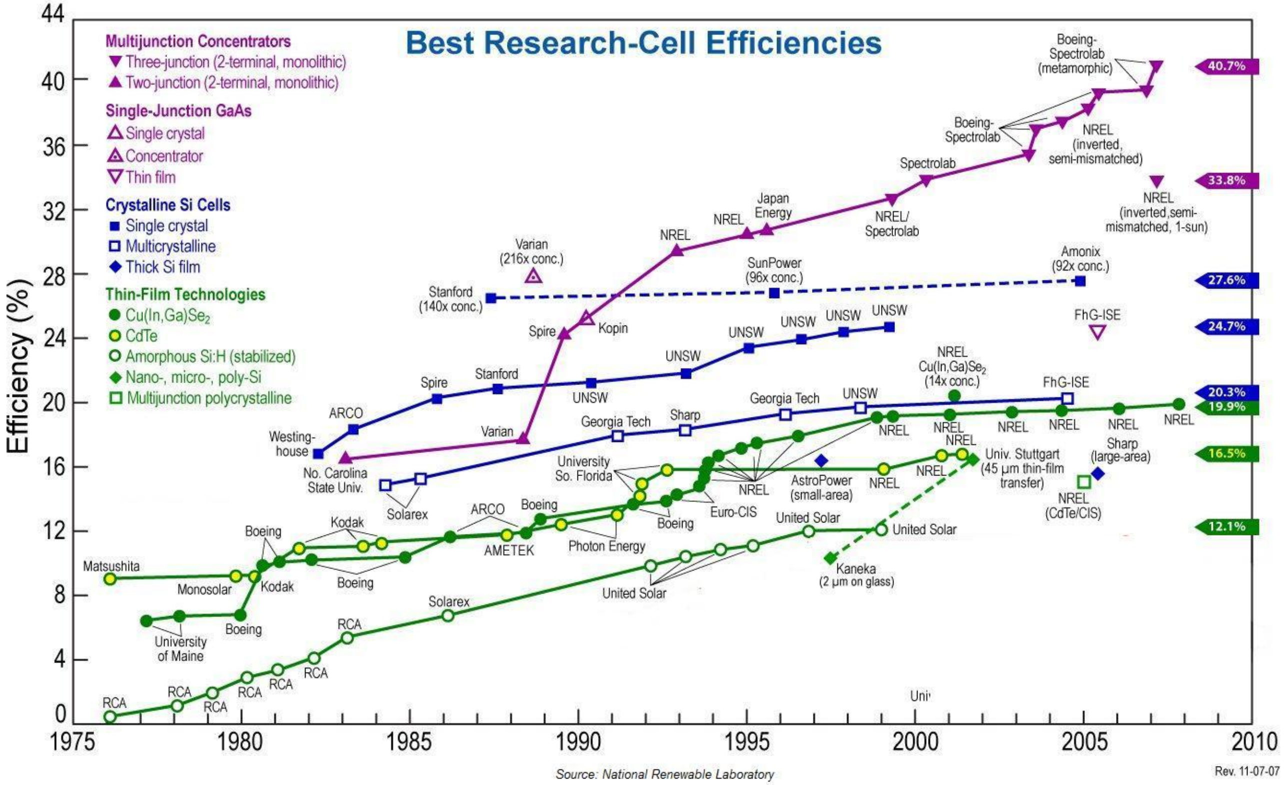
Solar Cells Efficiency



- What limits the efficiency:
  - Photons with lower energy than the band gap are not absorbed.
  - Photons with greater energy than the band gap are absorbed but the excess energy is lost as heat.

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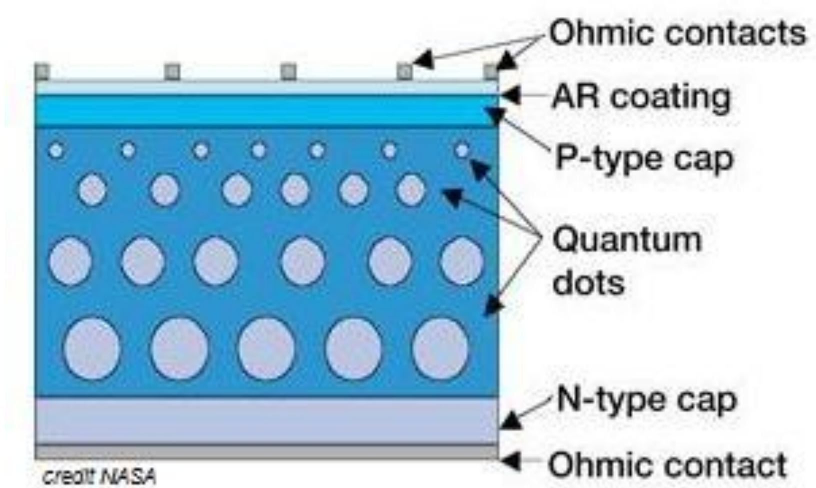
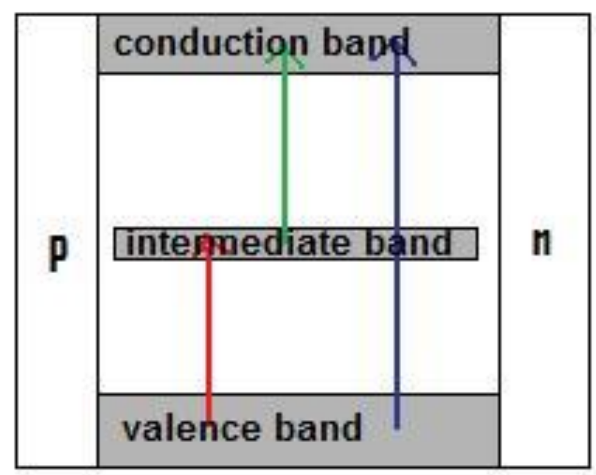
How Can Quantum Dots Improve the Efficiency?

- The quantum dot band gap is tunable and can be used to create intermediate bandgaps. The maximum theoretical efficiency of the solar cell is as high as 63.2% with this method.





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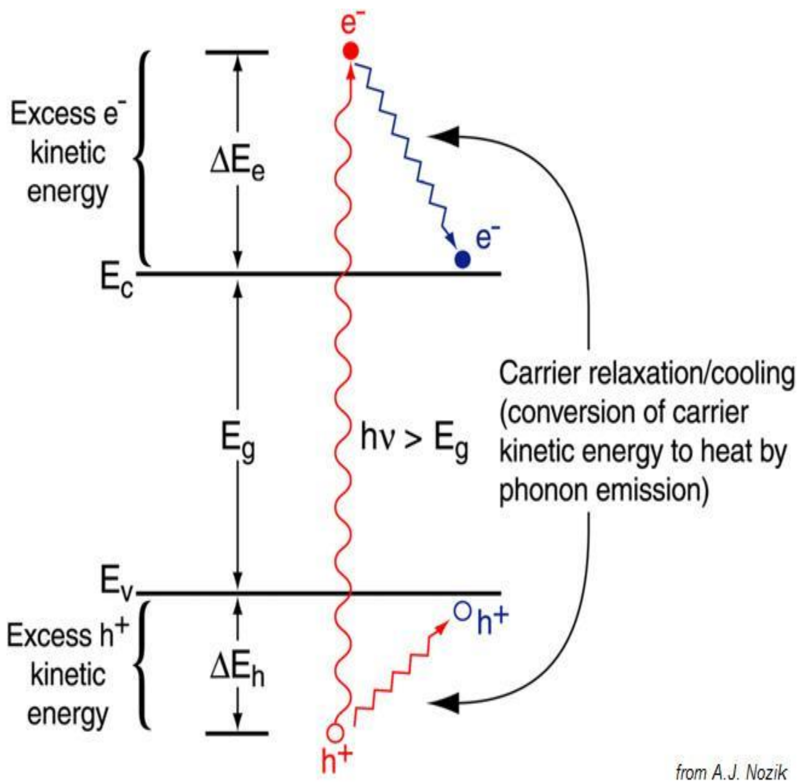
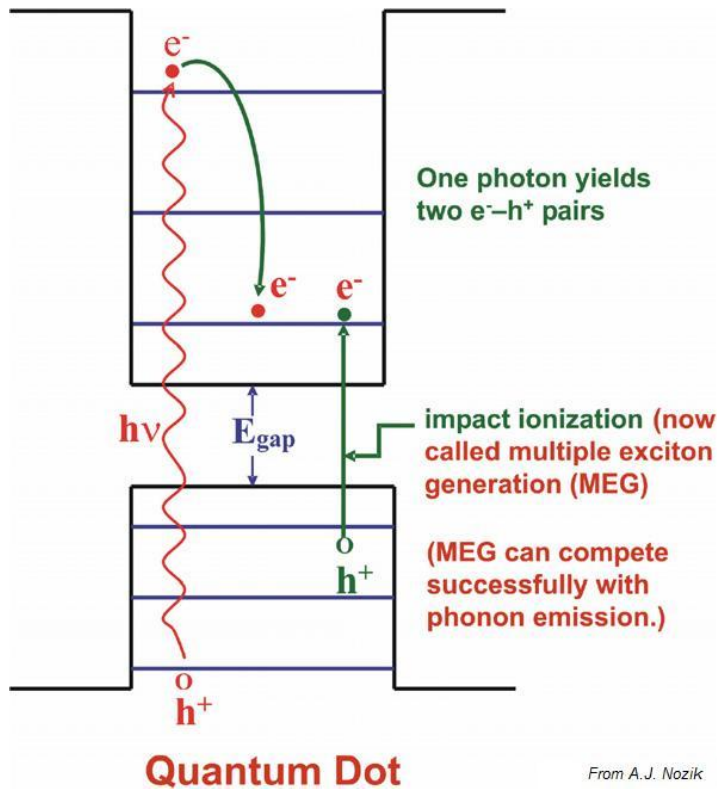
How Can Quantum Dots Improve the Efficiency?

- Quantum dots can generate multiple exciton (electron-hole pairs) after collision with one photon.





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Conclusion

- Quantum dot:
  - Semiconductor particle with a size in the order of the Bohr radius of the excitons.
  - Energy levels depend on the size of the dot.
- Different methods for fabricating quantum dots.
  - Lithography
  - Colloidal synthesis
  - Epitaxy
- Multiple applications.

Extra Study:

- L. Jacak, P. Hawrylak, A. Wojs. Quantum dots. Springer-Verlag, Berlin, 1998.
- B.E.A. Saleh, M.C. Teich. Fundamentals of Photonics. 2nd ed. Hoboken, New Jersey, John Wiley & Sons, Inc. 2007.
- "Quantum Dots Explained." Evident Technologies. 2008. <http://www.evidenttech.com/quantum-dots-explained.html>.
- M.Y. Levy et al. "Quantum dot intermediate band solar cell material systems with negligible valence band offsets." Presented at the 31st IEEE Photovoltaics Specialist Conference, Orlando, Florida, January 2005.
- Antonio Luque and Antonio Martı. "Increasing the Efficiency of Ideal Solar Cells by Photon Induced Transitions at Intermediate Levels." Phy. Rev. Letters. 78, 26, June 1997.
- Arthur J. Nozik. "Multiple exciton generation in semiconductor quantum dots." Chemical Physics Letters 457 (2008) 3–11.

Nanowires

- Growth mechanism and methods
- Examples of device applications

- One dimensional nanostructures obtained by higly anisotropic growth
- Single crystal
- “bottom up” approache
- Not embedded in a matrix

  (≠ QWs, T-wires, self assembled Qdots)

- Nanodevices
- Interconnection in nano-optoelectronics
- Photonic crystal
- ....

Volume 4, Number 5 APPLIED PHYSICS LETTERS 1 March 1964

VAPOR-LIQUID-SOLID MECHANISM OF SINGLE CRYSTAL GROWTH

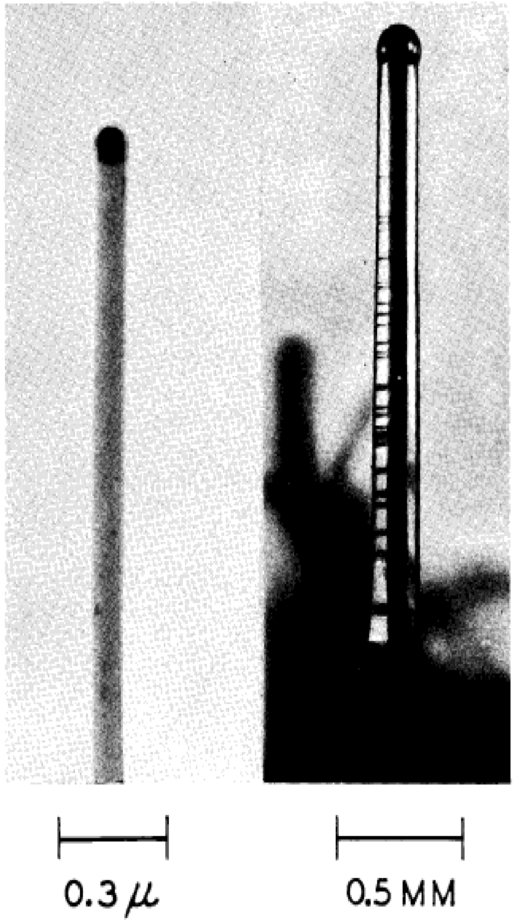
R. S. Wagner and W. C. Ellis
Bell Telephone Laboratories, Inc.
Murray Hill, New Jersey
(Received 4 February 1964)

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

(111) oriented Si "whiskers":

- a small Au particle on a Si(111) surface
- heated at 950°
- exposed to a flow of $SiCl_4$ and H_2

similar results obtained with:
Pt, Ag, Pd, Cu and Ni



Experimental evidences:

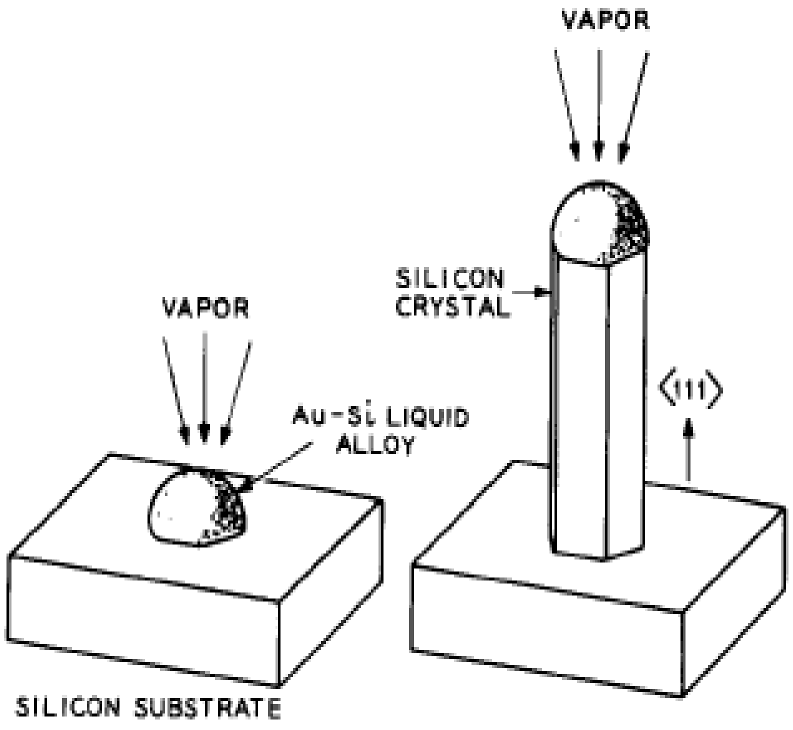
- no axial screw dislocation
- an "impurity" is essential
- a small "globule" is present at the tip of the whiskers during the growth

The role of the impurity is to form a liquid alloy droplet at relatively low T.

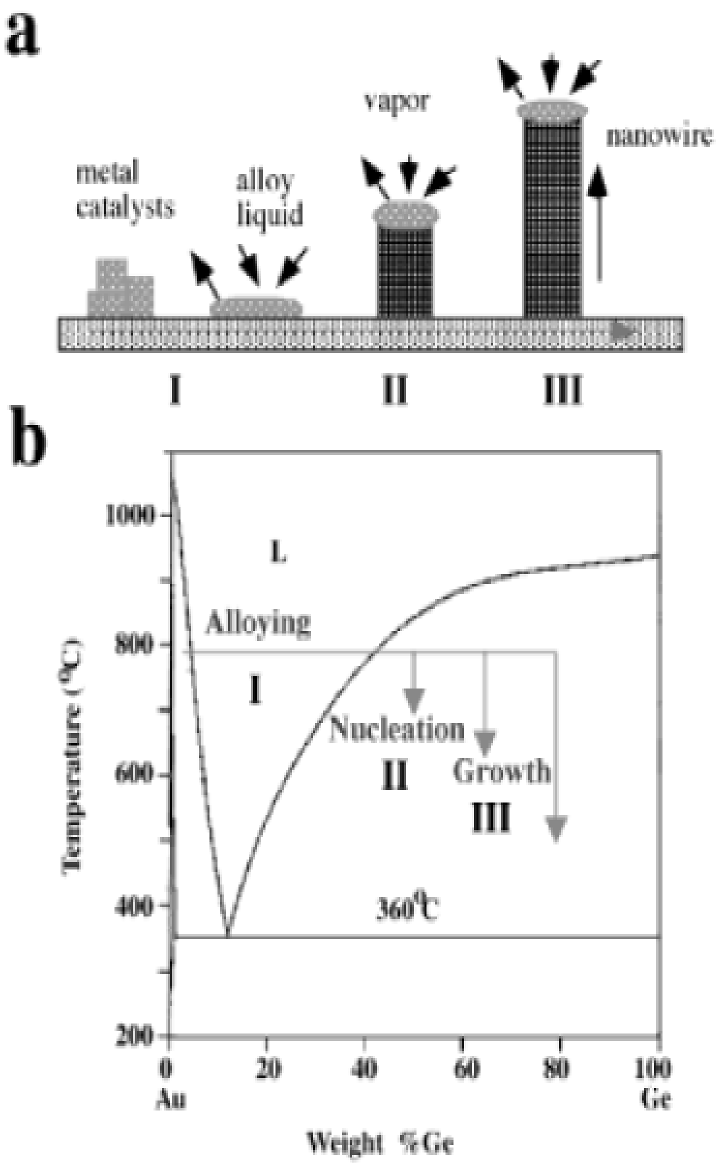
The selection of the impurity is important.

The VLS model:

- The impurity melt at the surface making an alloy
- The liquid droplet is the preferred site for deposition and become supersaturated
- The whiskers grow by precipitation of Si from the droplet

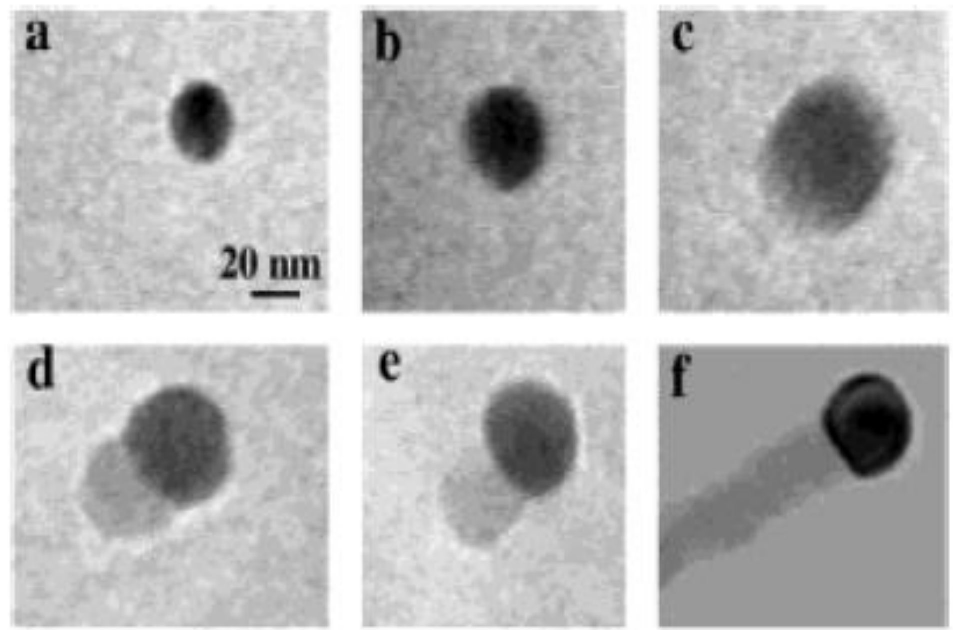


VLS growth of Ge nanowires with Au catalyst



Ge particles+ Au nanoparticles on a TEM grid, heated in the TEM

T= 500° C T=800 ° C



Wu et al, *J. Am. Chem. Soc.* 123, 3165 (01)

Different growth methods:

laser ablation, thermal evaporation, MOCVD, MOVPE, CBE, MBE

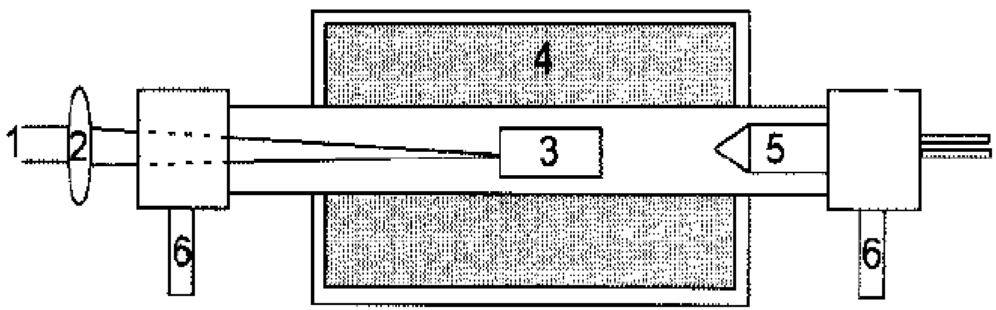
Different catalyst shape and processing:

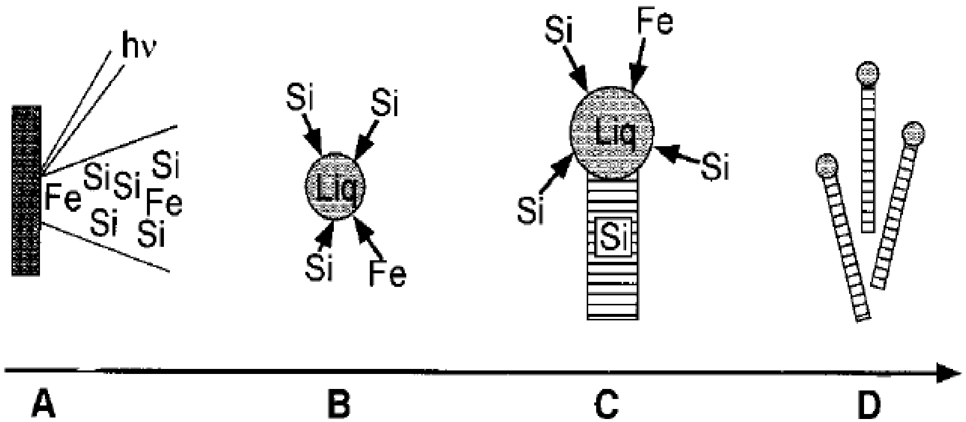
uniform layer, nanoparticle, patterned layer

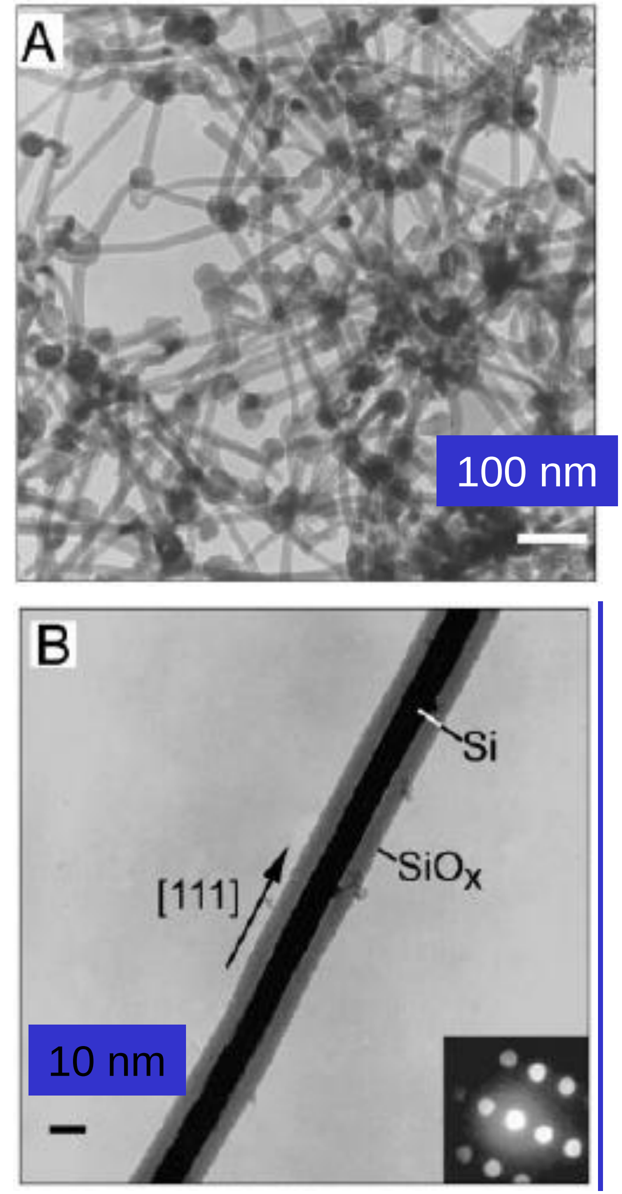
Different substrates:

no substrate, oxide, oriented wafer, looking for oriented NWs

Laser catalytic growth of Si NW with the $Si_{0.9}Fe_{0.1}$ target T_F=1200°C



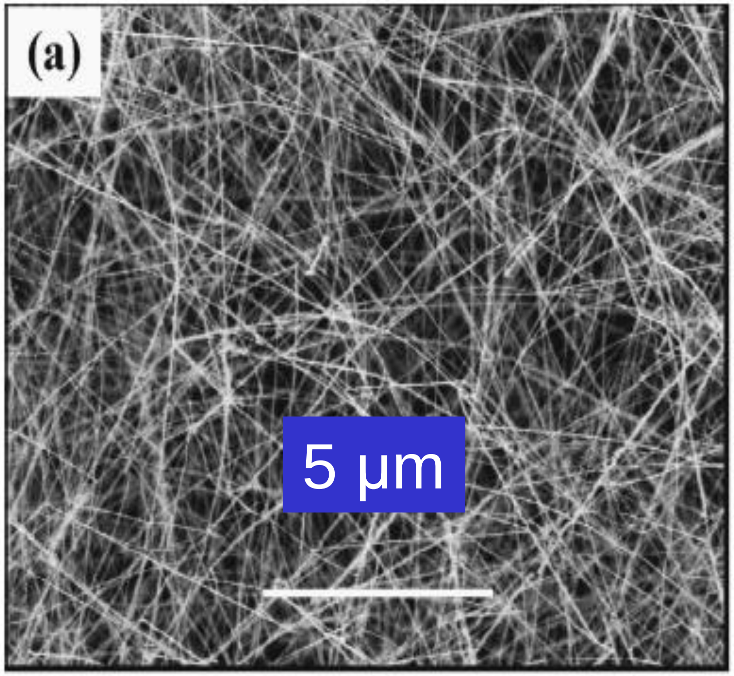




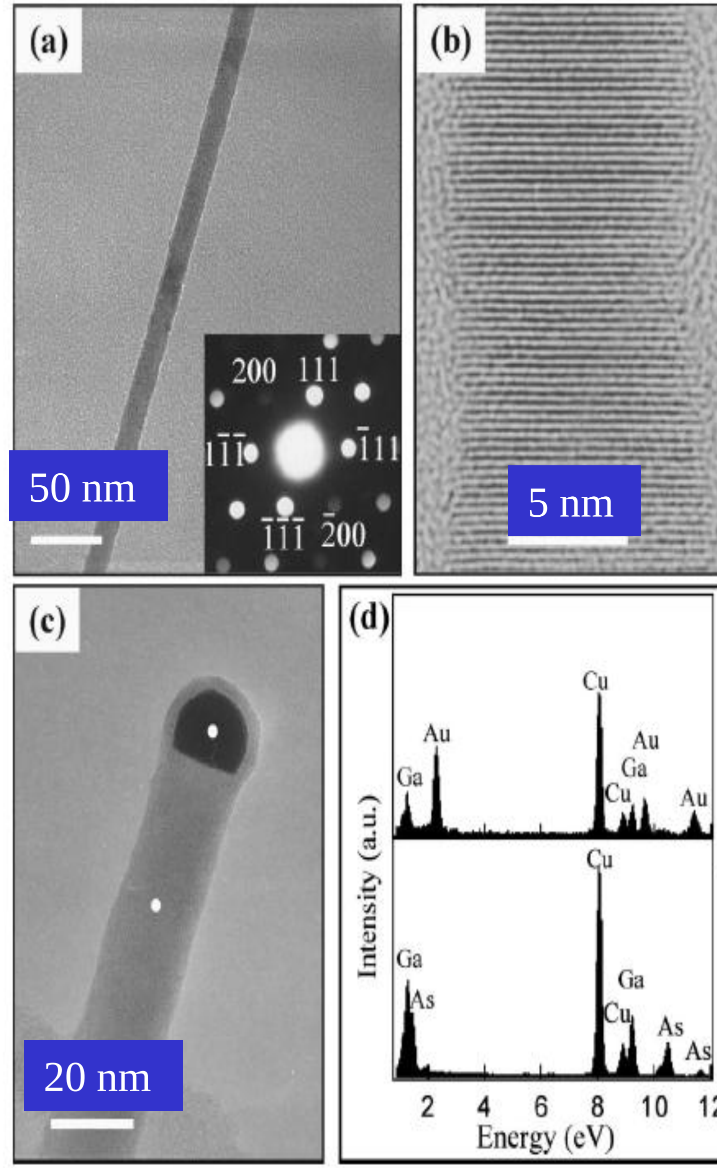
Morales *et al*, Science 279, 208 (98)

Laser catalitic growth of GaAs NWs using $(GaAs)_{0.95}M_{0.05}$ target (M=Au, Ag, Cu)

T_F=800-1030°C



single cristal (111) GaAs nanowires
Au is present at the tip.



Duan *et al* APL 76, 1116 (2000)

Self catalitic growth of GaN NWs

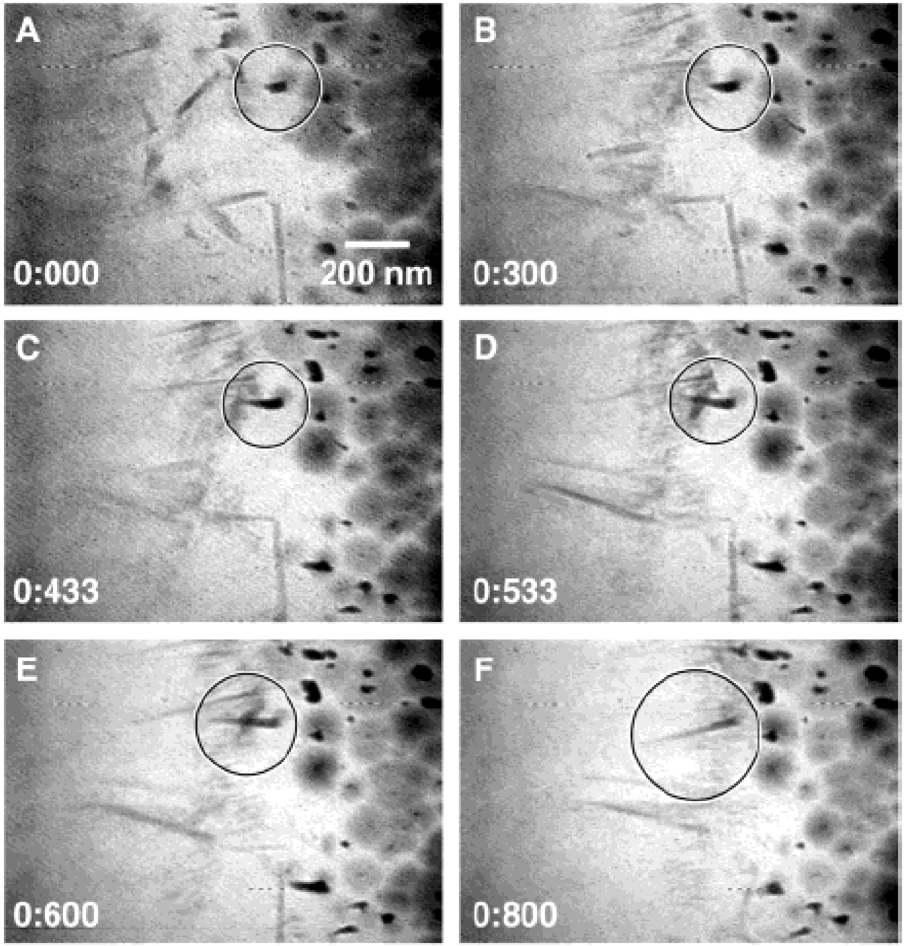
- self standing GaN layer
- thinned for TEM (≤ 300 nm)
- heated at 1050° C in a TEM

Above 850 in high vacuum

GaN(s) —›
Ga (l) + 0.5 N (g) + 0.25 N_2 (g)

GaN(s) —›
GaN (g) or $[GaN]_x$ (g)

in-situ study of the decomposition and resulting nanostructure evolution

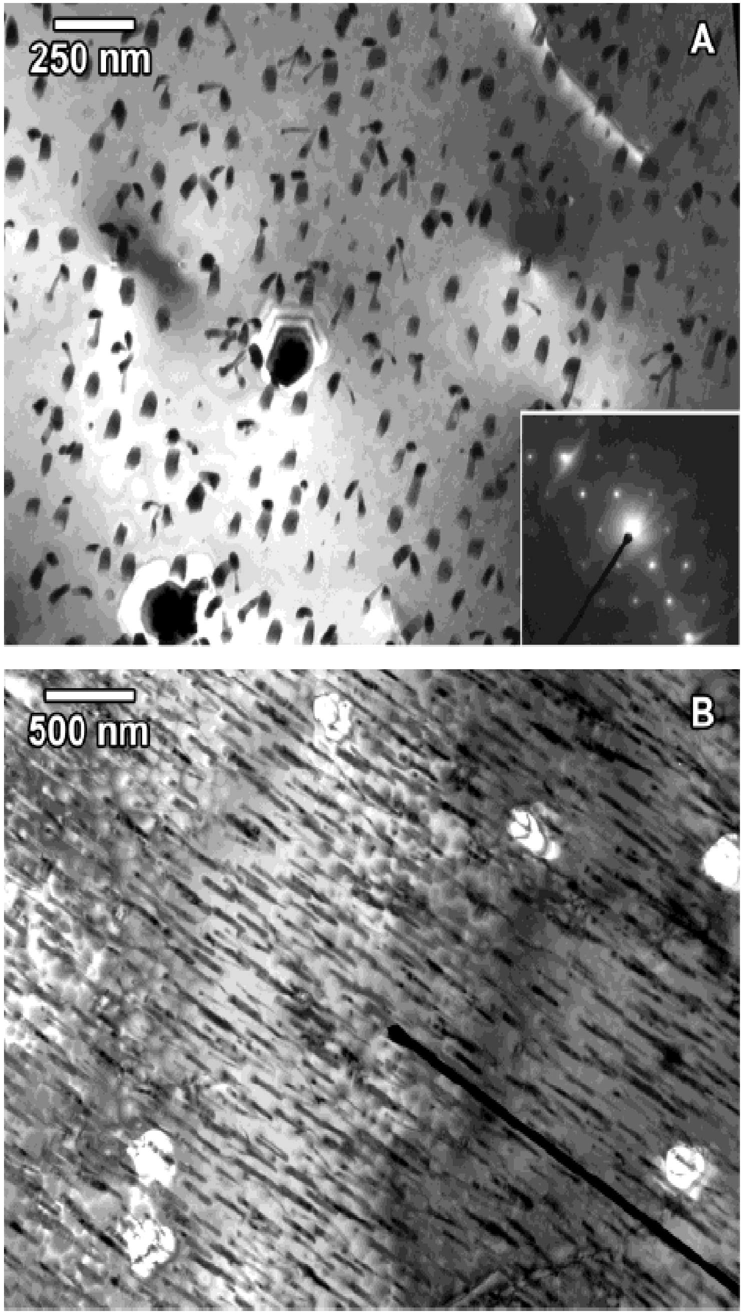


Stach *et al*, Nano Lett. 3, 867 (2003)

room temperature analysis
of the nanostructures:

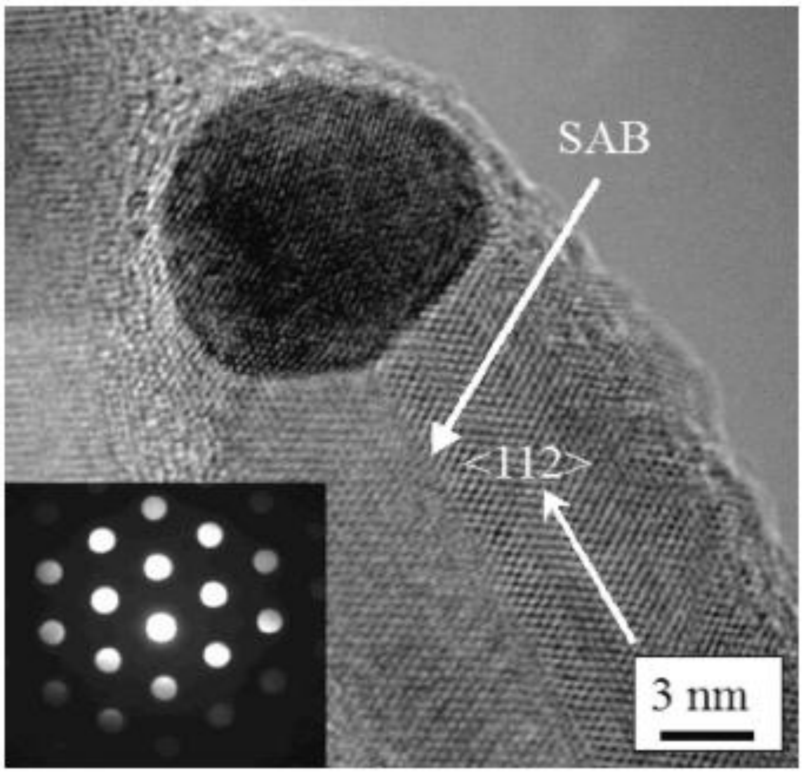
•single crystal GaN NWs
•[0001] oriented
•av diameter 50 nm
•gr rate 300 nm/s

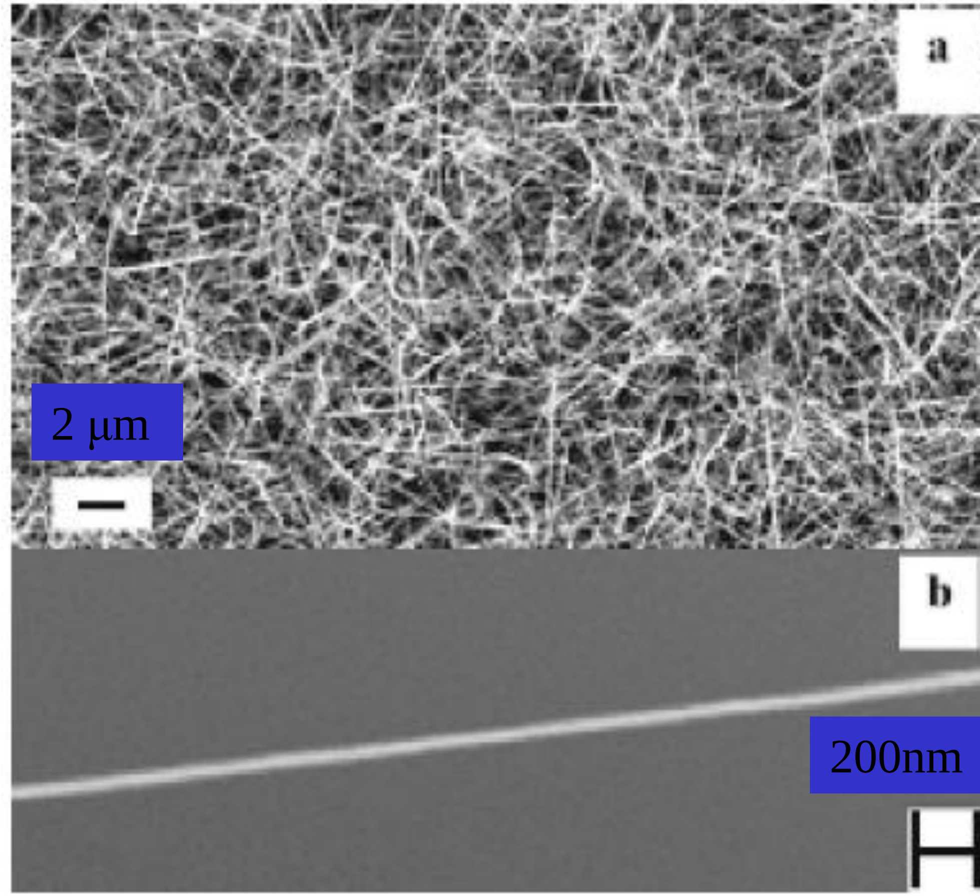
self catalytic process could be important to avoid undesired contamination from foreign metal atom (catalyst)



MOCVD grown ZnSe NWs on Si(100)

uniform 1 nm Au catalyst

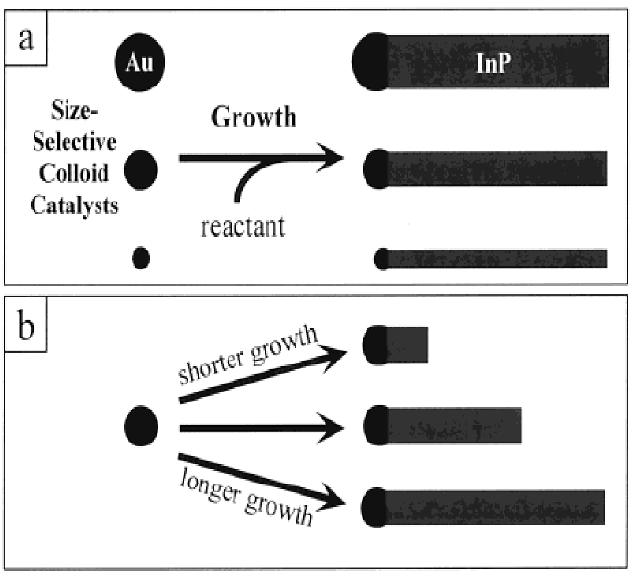




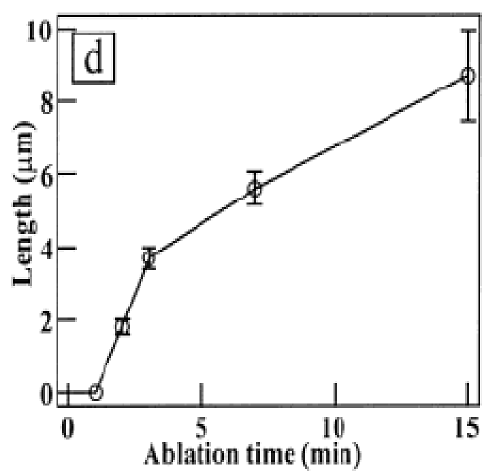
Zhang *et al* APL 84, 2641 (2004)

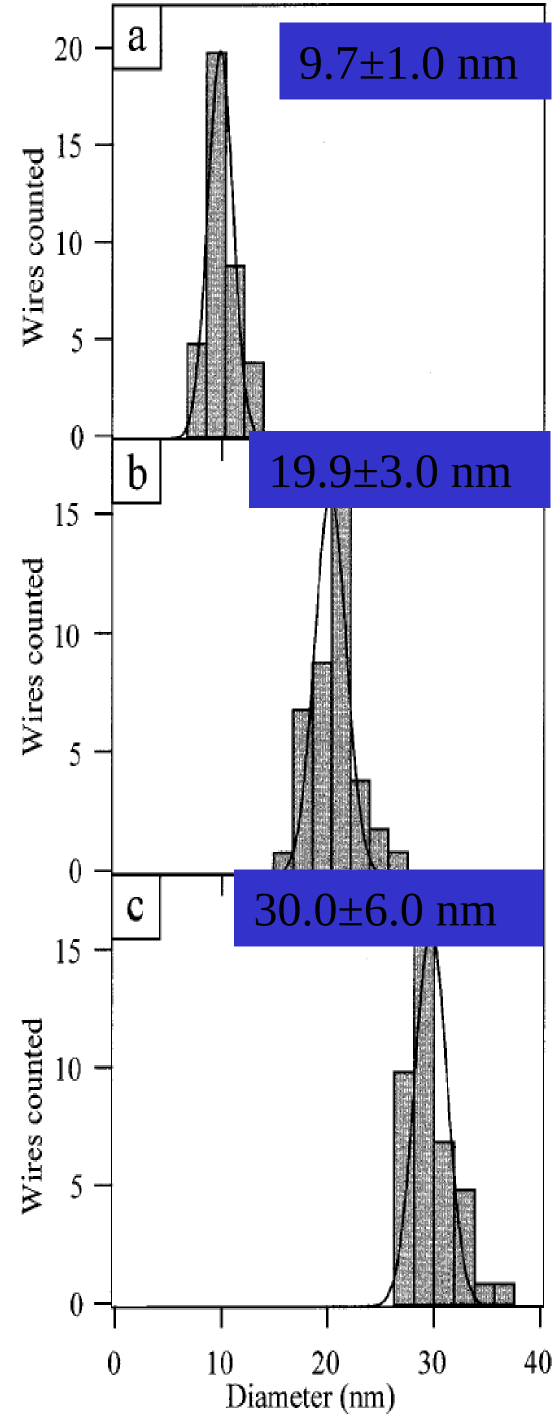
Control of Diameter and lenght of NW

- InP NW grown by laser ablation
- Si/SiO_2 substrate
- size selected Au nanocluster solution



≠0 nucleation time

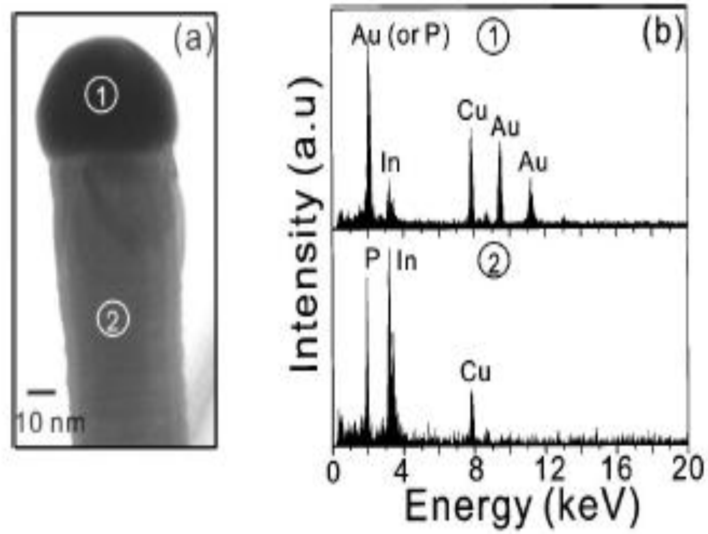


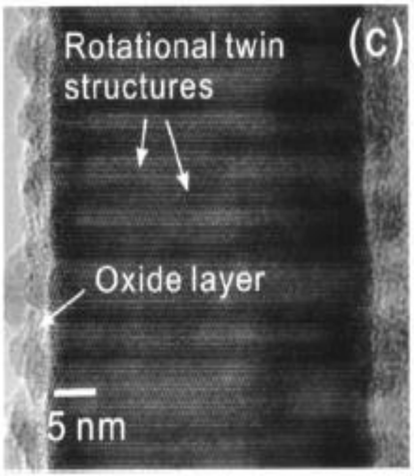


Gudiksen et al, J. Phys. Chem. B 105, 4062 (2001)

In group IV and III-V mainly [111] NW.
On (111)B substrates, vertical NW!

- Colloidal solution of 20 nm Au particles
- MOVPE growth of InP NWs on (111)B InP wafer





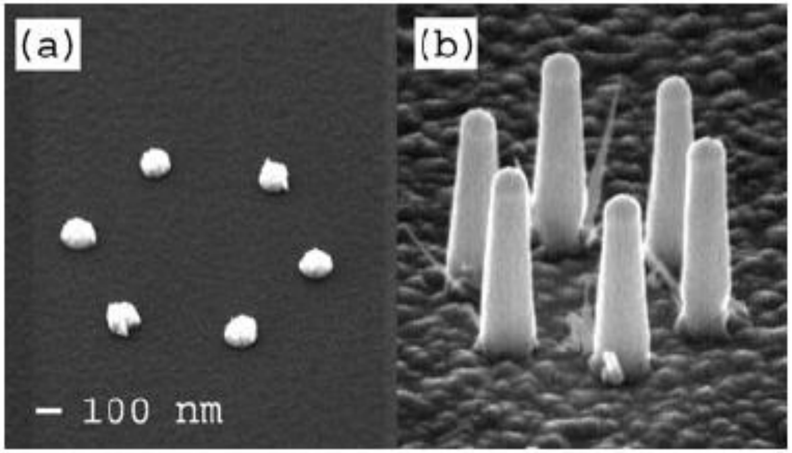
- vertical NW
- uniform diameter
- ZB structure
- [111] oriented

but high density of rotational twins

Bhunia *et al*, APL 83, 3371 (2003)

vertical NWs array:
photonic crystal?

•EBL + metal lift-off → Au discs
•annealing
•growth



l= 1 µm, top Ø 140 nm

l= 3 µm, top Ø 50 nm

Mårtensson *et al*,
Nanotechnology 14, 1255 (2003)

Oriented NW could be usefull for “multi-wire” devices applications

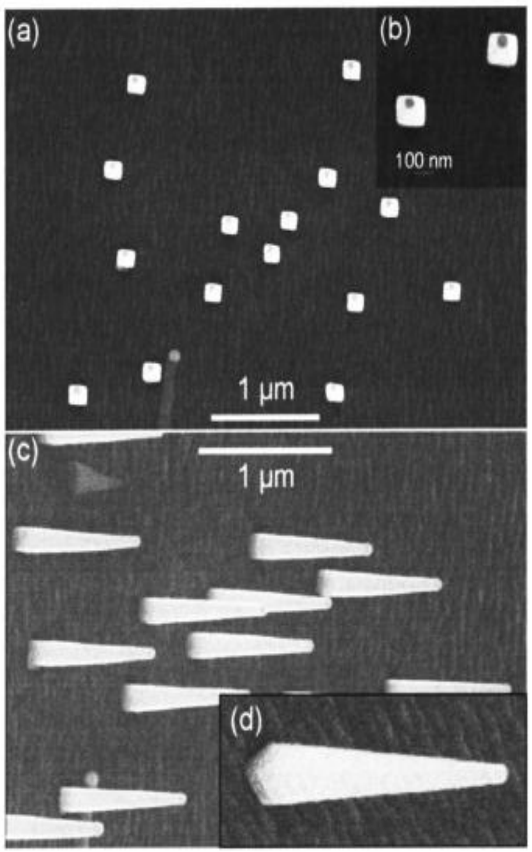
However, the “easy” growth direction [111] has two important drawbacks:

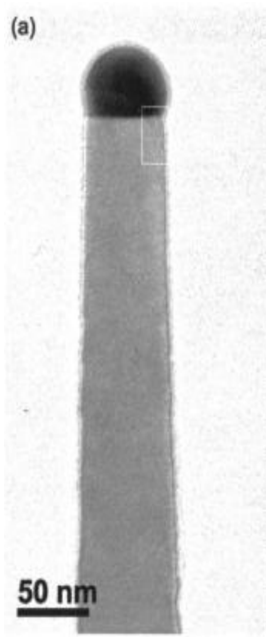
- it is the preferable direction for forming stacking faults
- one needs to use the technologically unfavourable (111)B substrate orientation instead of the widely used (001)

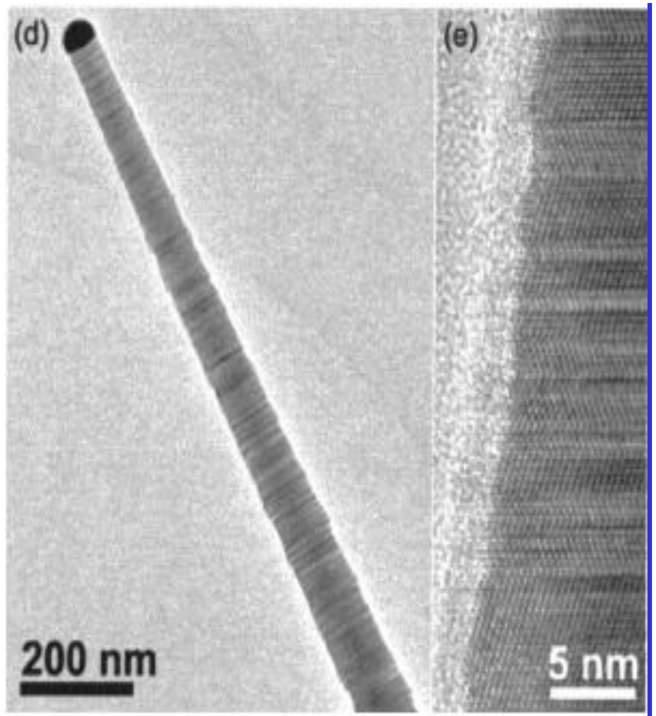
InP (001) surface
Au nanoparticles +
MOVPE

[001] NW
defect free

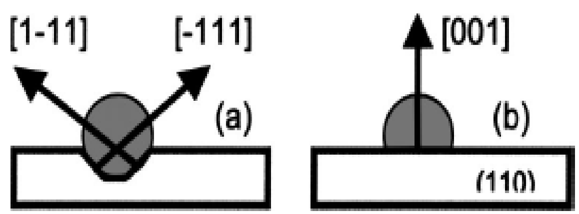
[111] NW
twinned





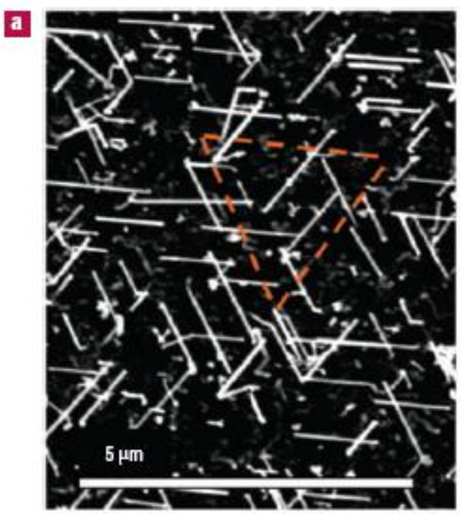


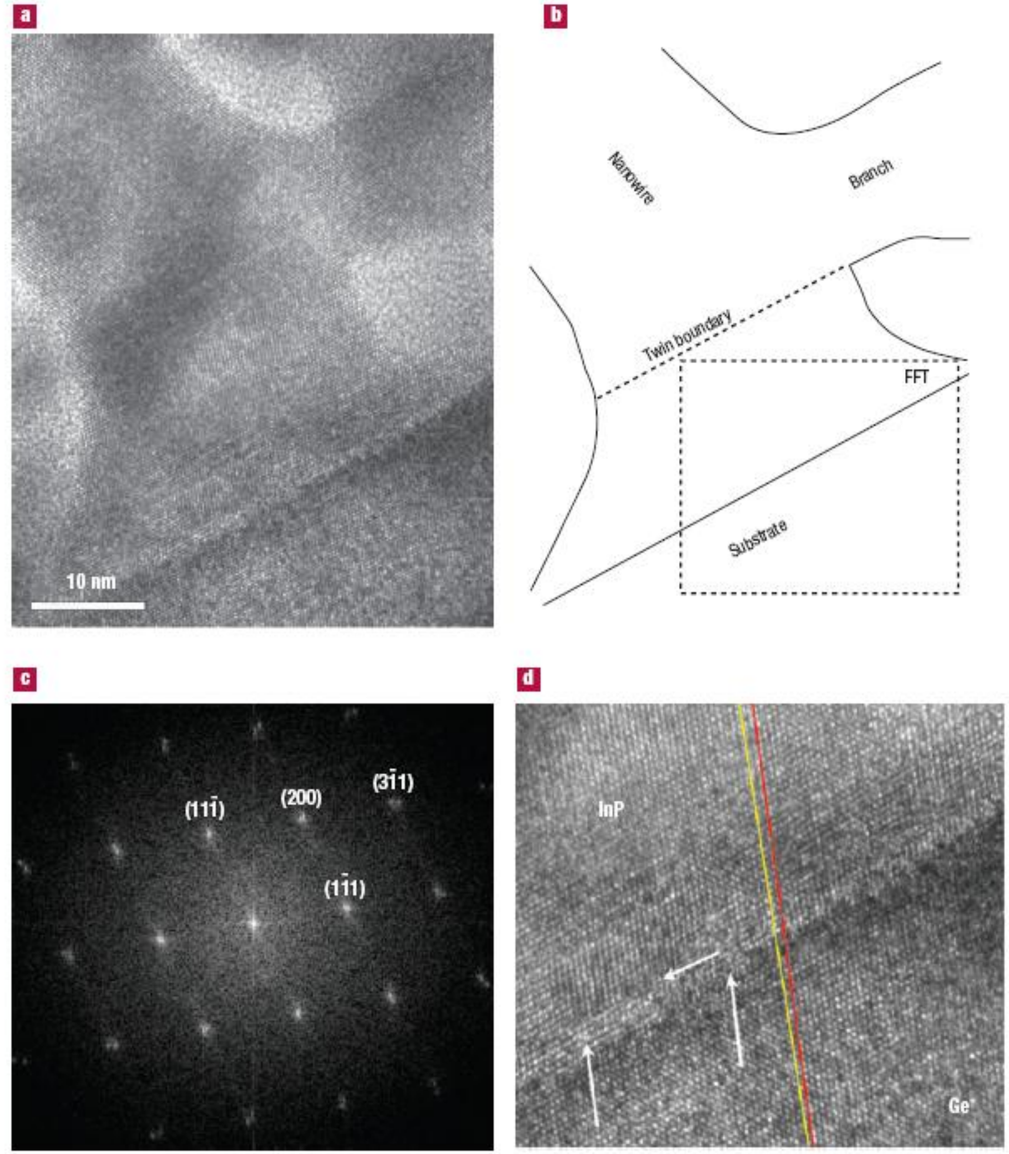
preferential orientation depend on the annealing



Krishnamchari et al, APL 85 2077 (04)

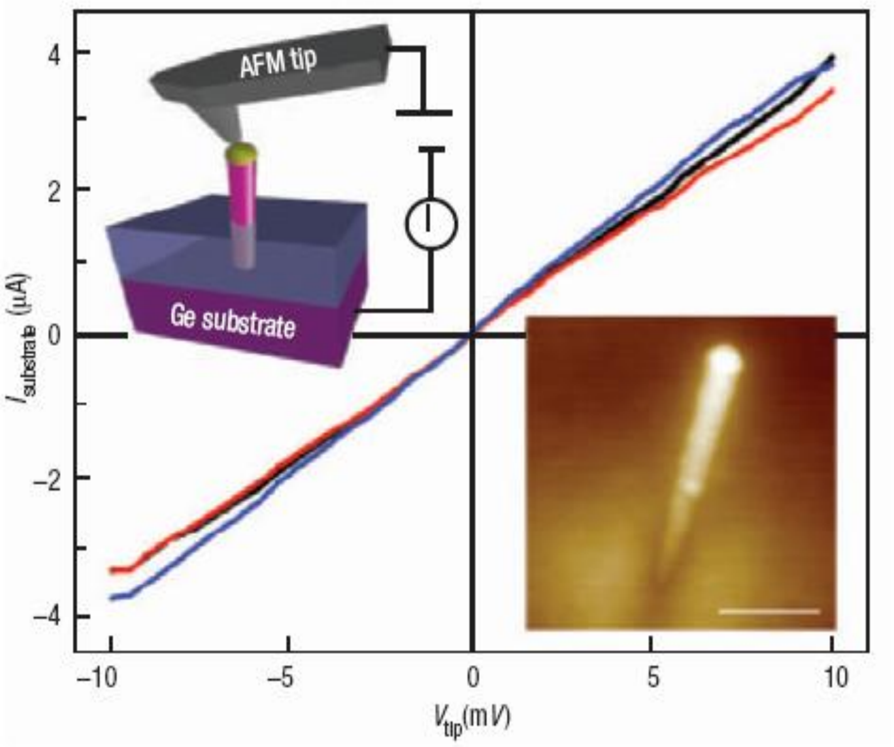
NWs can grow epitaxially and defect free on highly mismatched substrate: (111) InP wires on Ge(111) (3.7 % mismatch)





Bakkers et al,
Nat Mat 3,769 (2004)

n-type InP NW on n-type Ge substrate



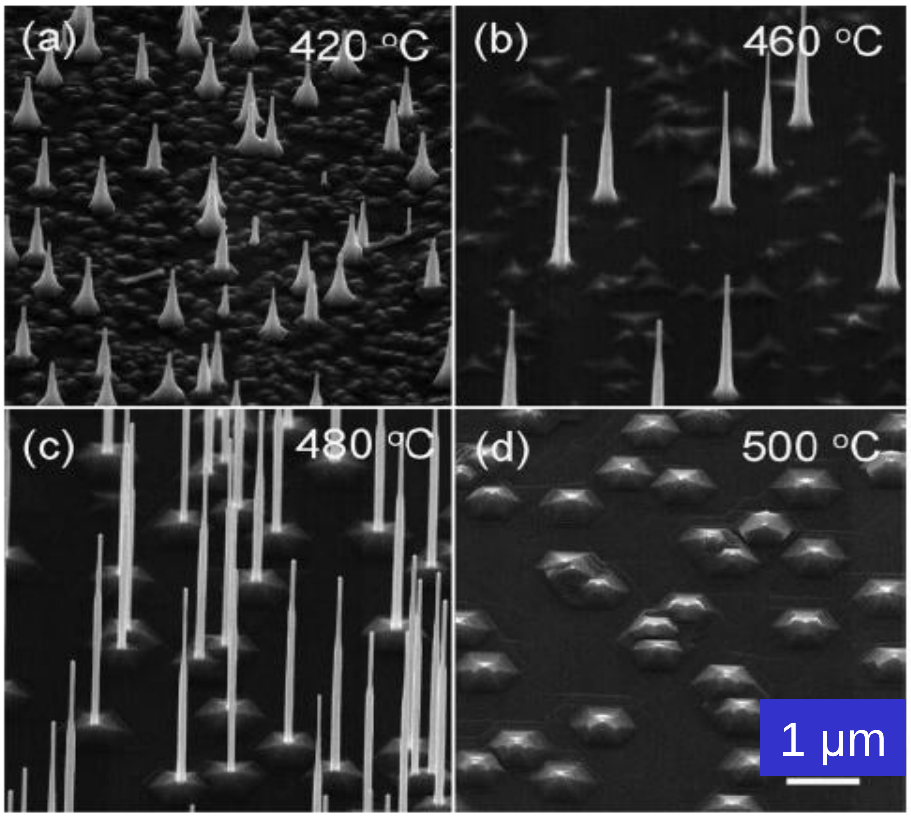
I-V measurement between the NW tip and the substrate by using a AFM with conducting tip.

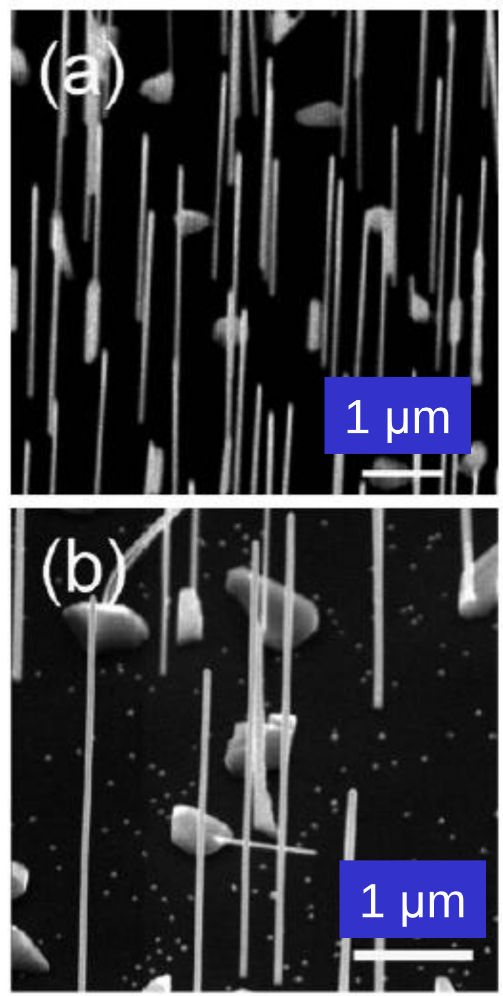
Low resistance ohmic behavior → Low resistance heterointerface

Can VLS always explain NW's growth?

InAs NW growth by MOVPE on InAs(111)B

Au nanoparticles

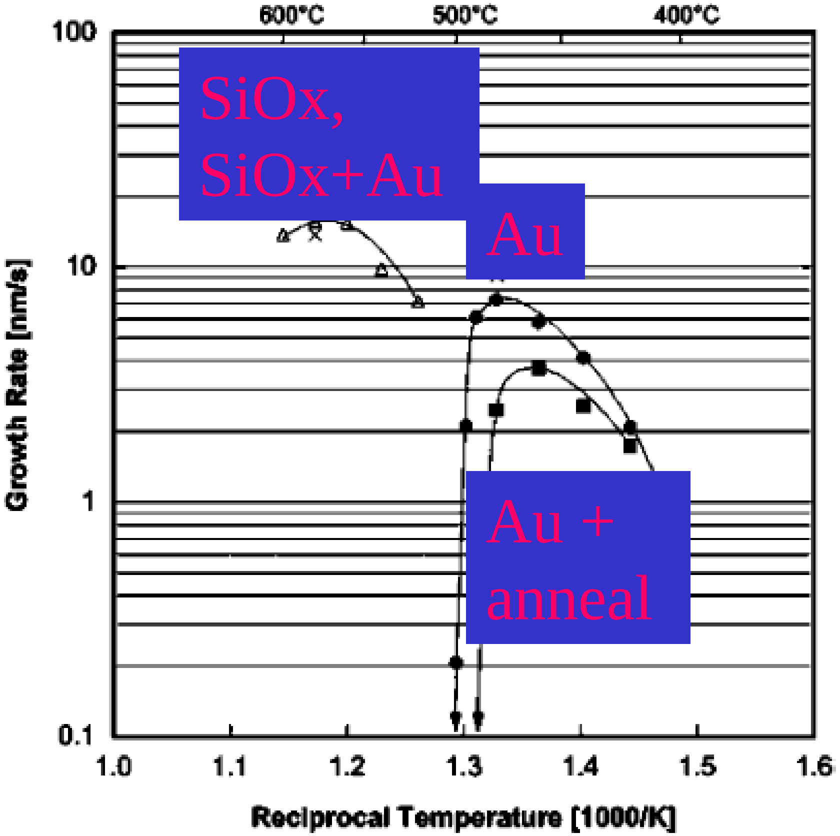




1.3 nm SiOx, 580° C

1.3 nm SiOx + Au nanop. , 580° C

Dick *et al*, Nano Lett. 5, 762 (2005)



from Au-In phase diagram:

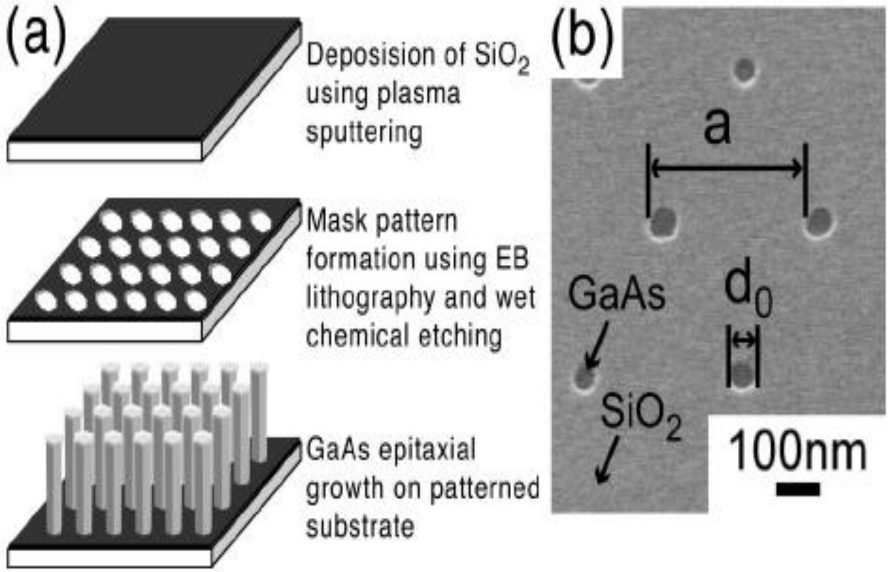
T_m= 490° 24.5-25.0% In
T_m= 490° 28.8-31.5 % In
T_m= 460° 35.4-39.5% In

EDS on the NW's tip:
25-30% In in Au.

growth stops when the particle melts!

Growth rate drop is not a matter of InAs decomposition.
The oxide layer reduces In incorporation in Au, and prevents melting.
Au is not a catalyst, but provide a low energy interface where material is collected, yealding higher growth rate.

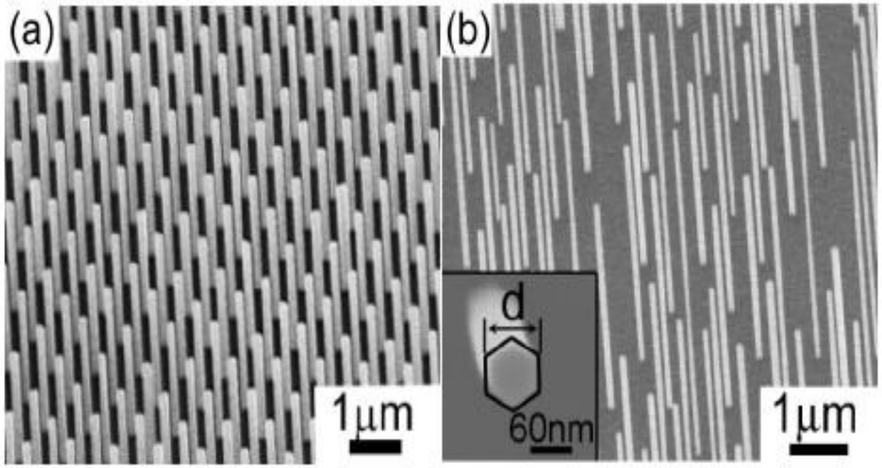
But also catalyst free growth of GaAs NWs!



Selective Area MOVPE

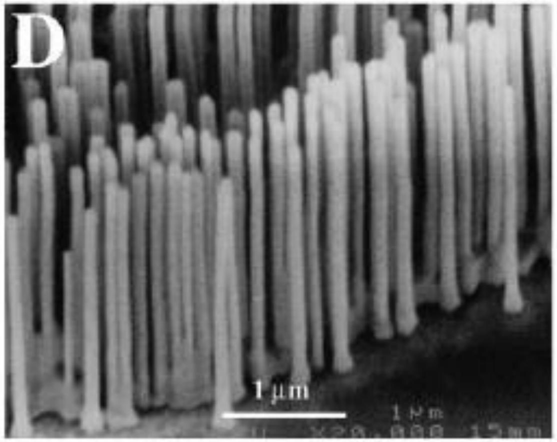
on GaAs (111)B

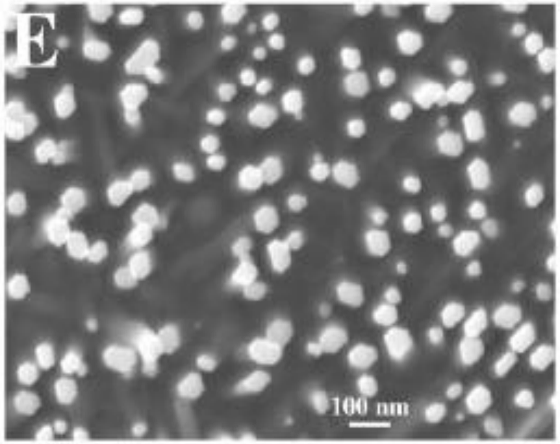
d_0=200 nm d_0=50 nm



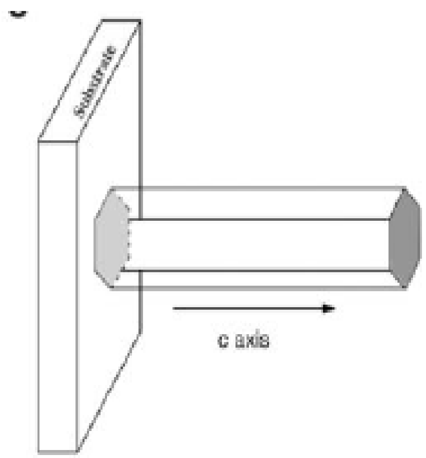
Noborisaka *et al*, APL 86, 213102 (05)

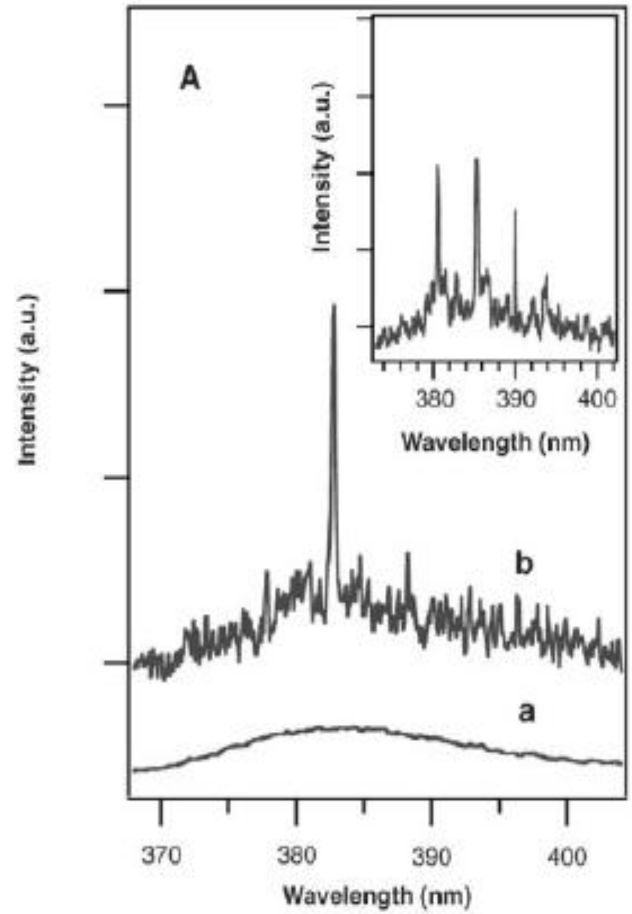
Optically pumped NW laser





ZnO on sapphire,
Au catalysed
[1000] growth,
exagonal facets.
Optical pumping
at 10° from the axis,
light collection in axis





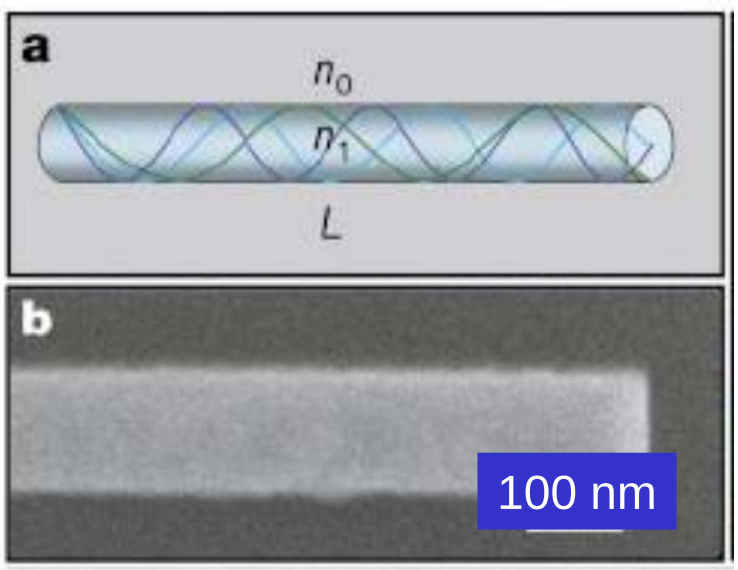
Huang *et al*, Science 292, 1897 (2001)

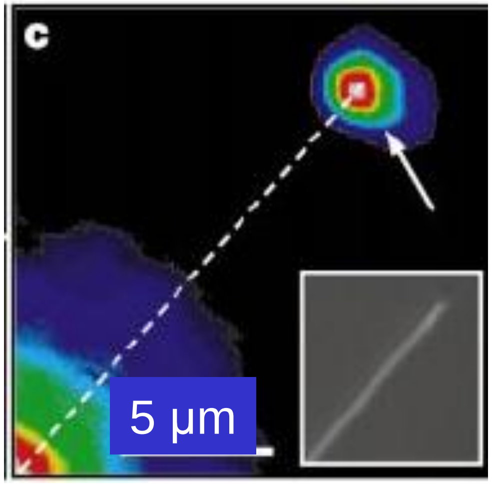
Single NW electrically driven laser

Duan *et al*, Nature 421, 241 (2003)

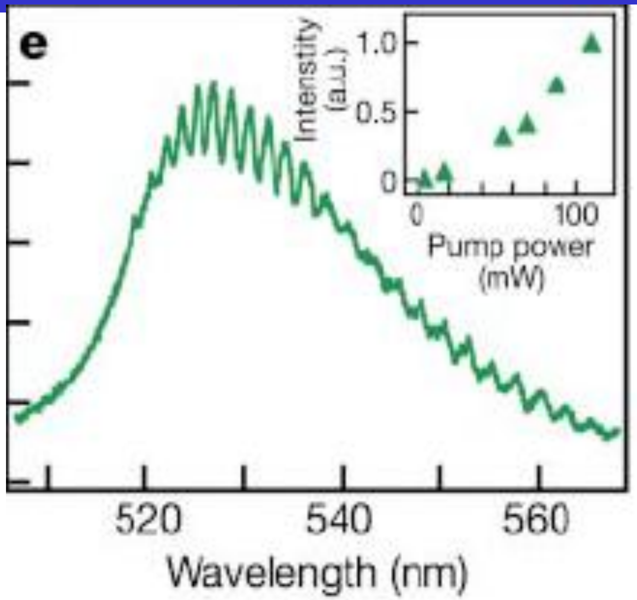
[0001] wurzite Au cat. CdS NW

NW as single mode optical cavity when $1 \approx (\pi D/\lambda)(n_1^2 - n_0^2)^{0.5} < 2.4$ for CdS $D \geq 70$ nm



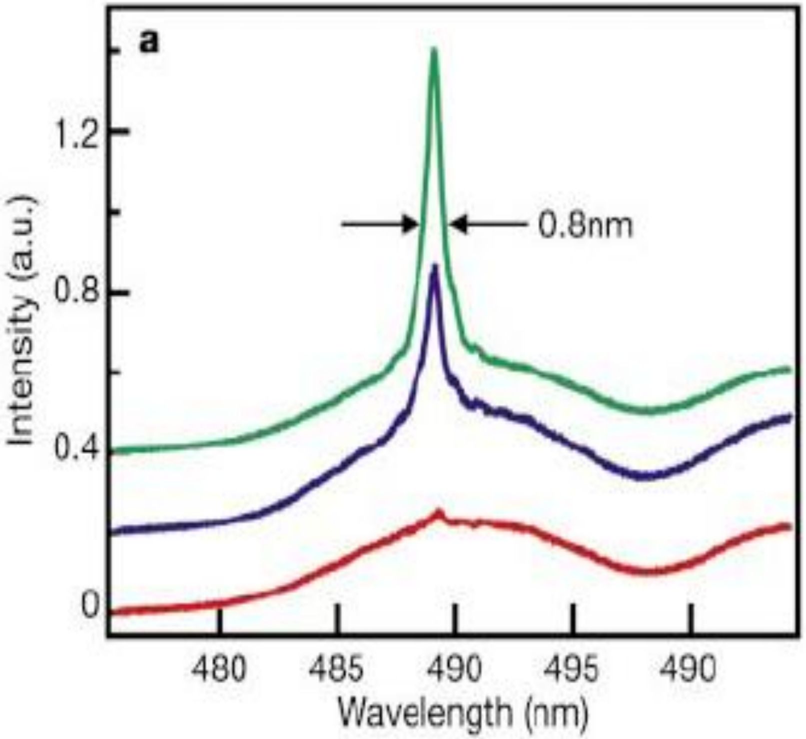


PL excited on the NW, emission at the tip!



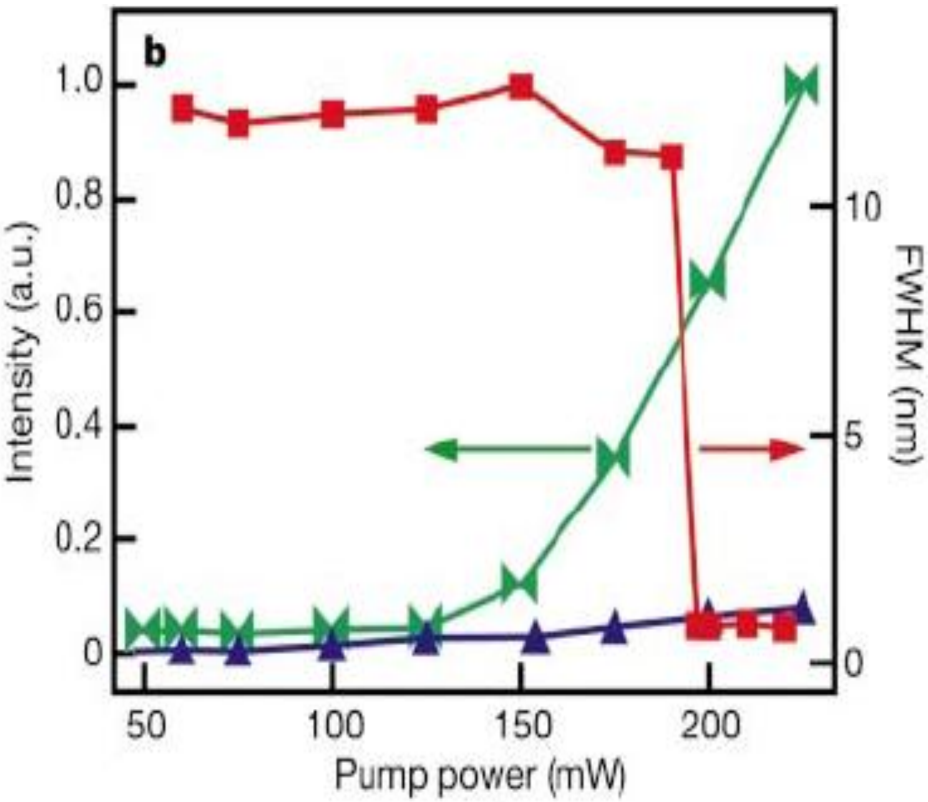
PL collected at the NW tip: Fabry-Perot cavity!

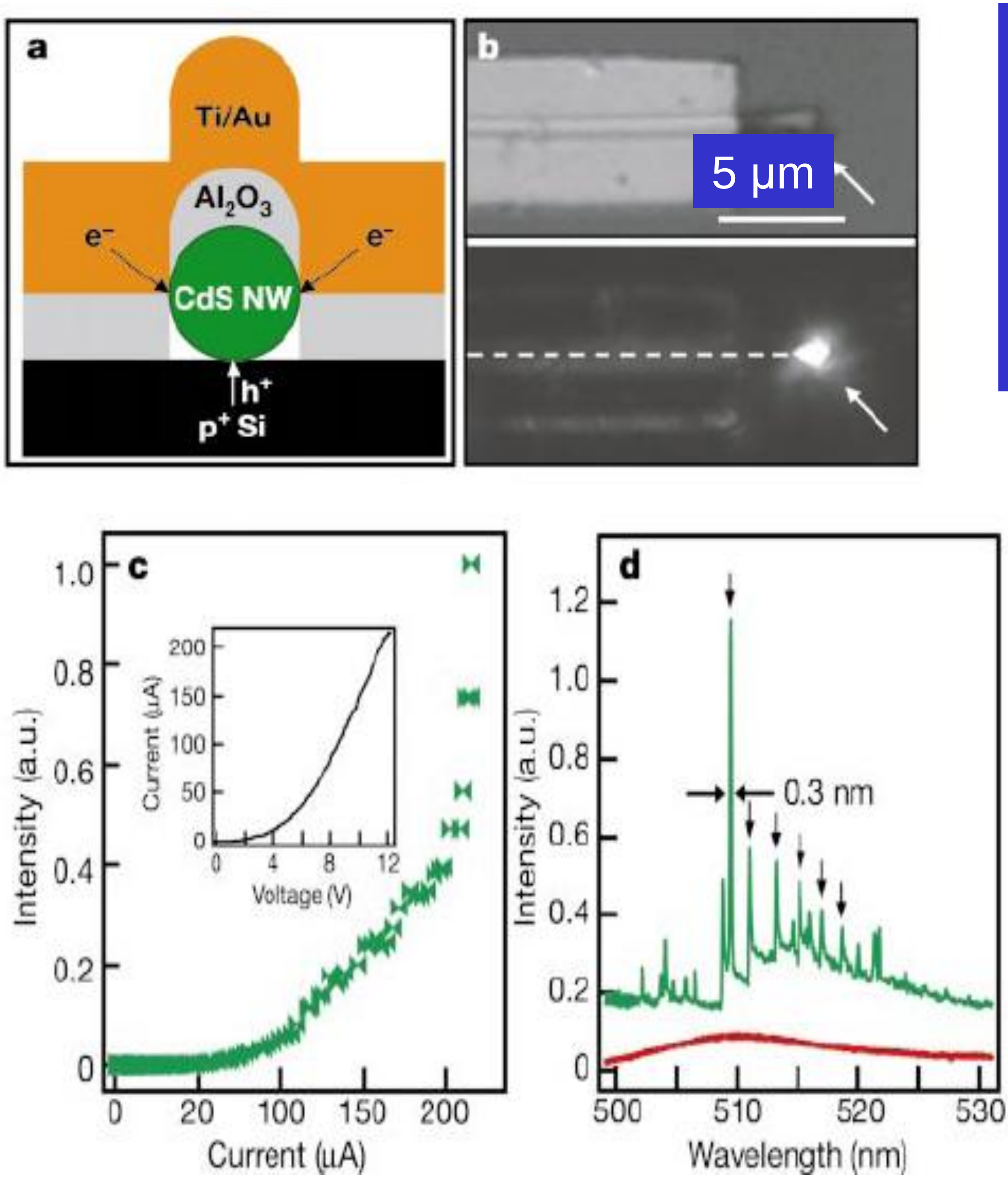
$m(\lambda/2n_1) = L$



Optically pumped single mode lasing of single NW!

emission from the NW end



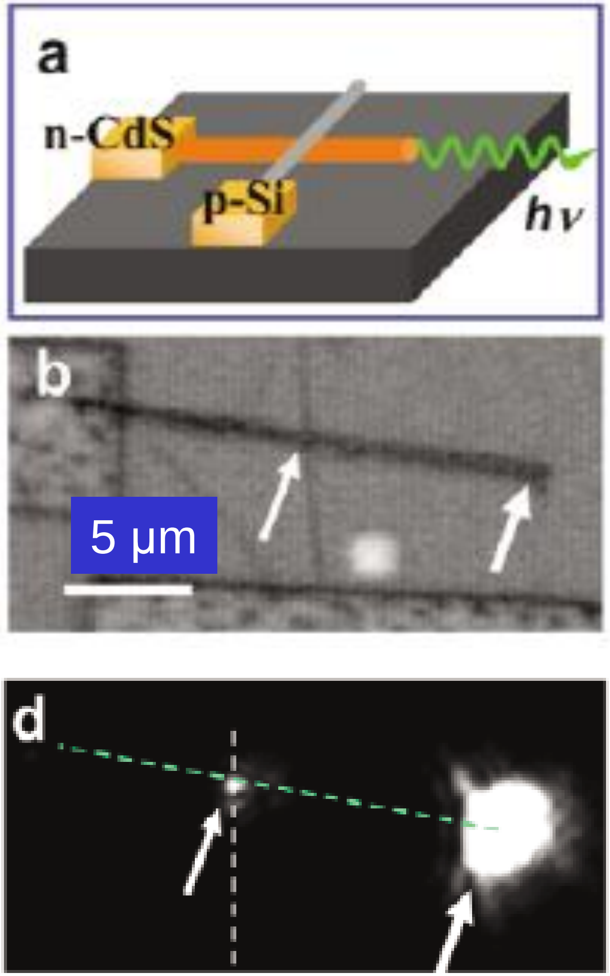


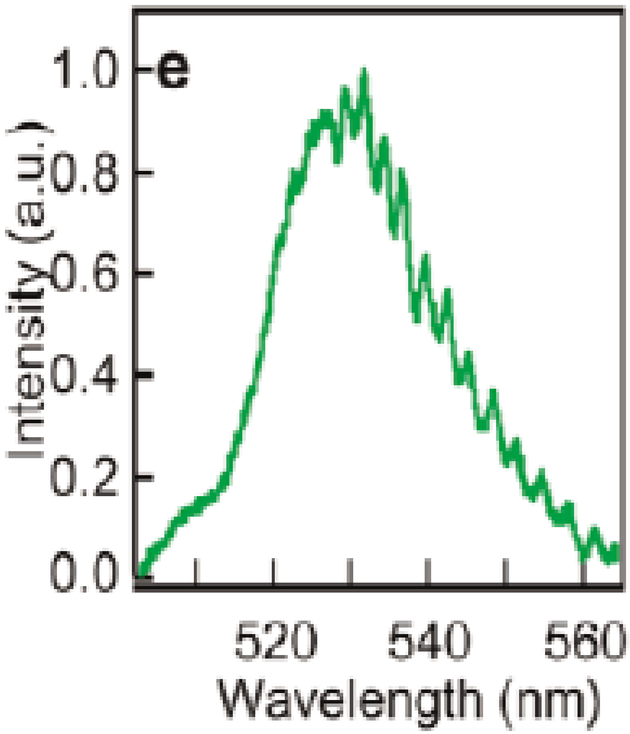
n-type CdS wire
on p+ Si wafer
+ EBL and contact
deposition=
distributed p-n junction

RT electrically driven
single NW lasing!!

p-n junction by crossing
p- and n-type NWs

electroluminescence from the
NW end is modulated: optical cavity





Huang *et al*, Pure Appl. Chem, 76,2051 (2004)

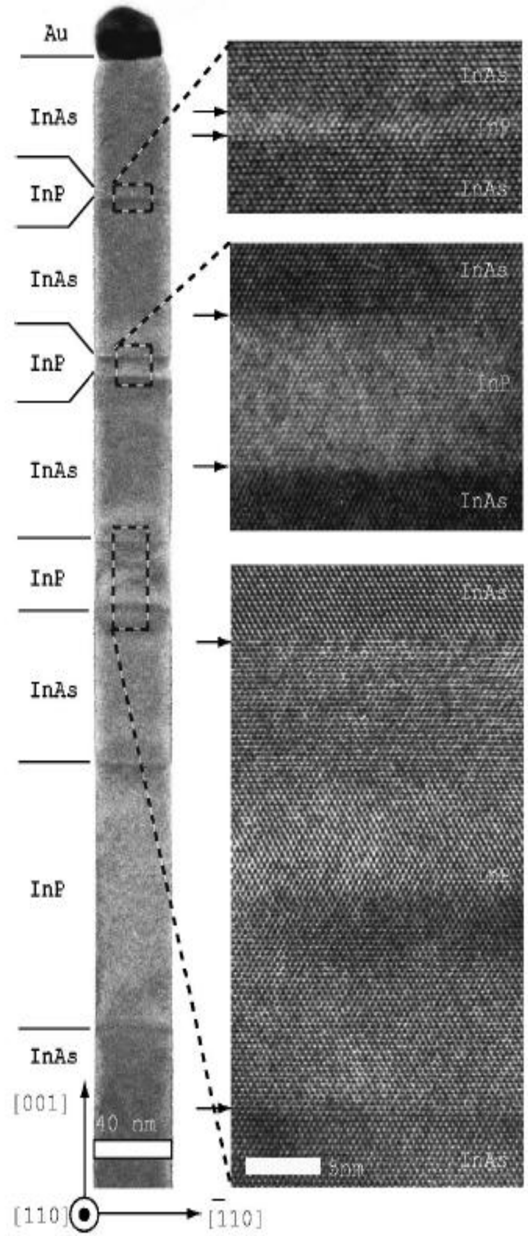
Heterostructures technolgy + nanowhisker growth = one dimensional heterostructures

•small cross section,
•efficient lateral lattice relaxation
→ one can combine different materials despite their bulk lattice mismatch

CBE on GaAs(111)B

40 nm Au nanoparticles

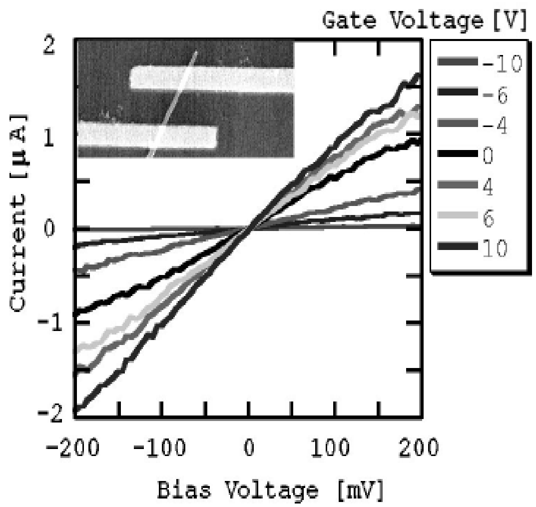
[100] oriented due to the GaAs/InAs misfit at the interface



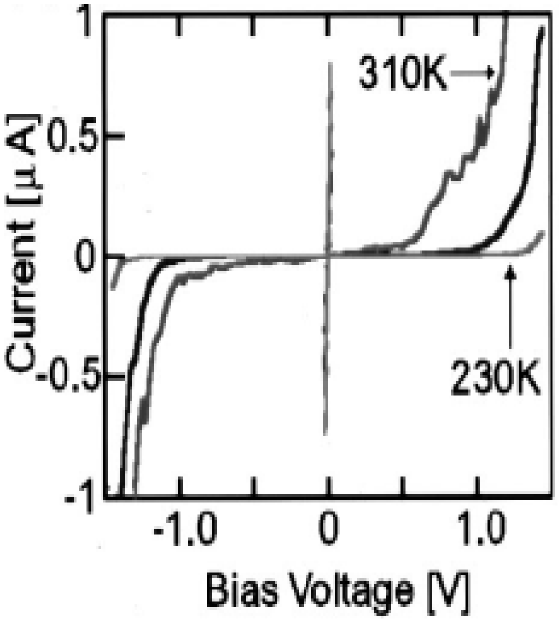
Björk *et al*, APL 80, 1058 (2002)

single wire transport measurement:

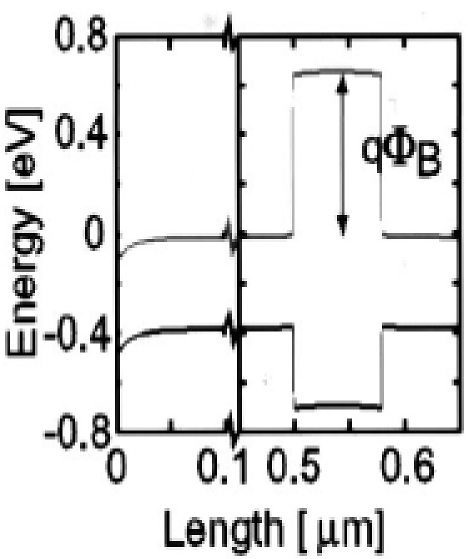
reference InAsNW



InAs/InP/InAs NW

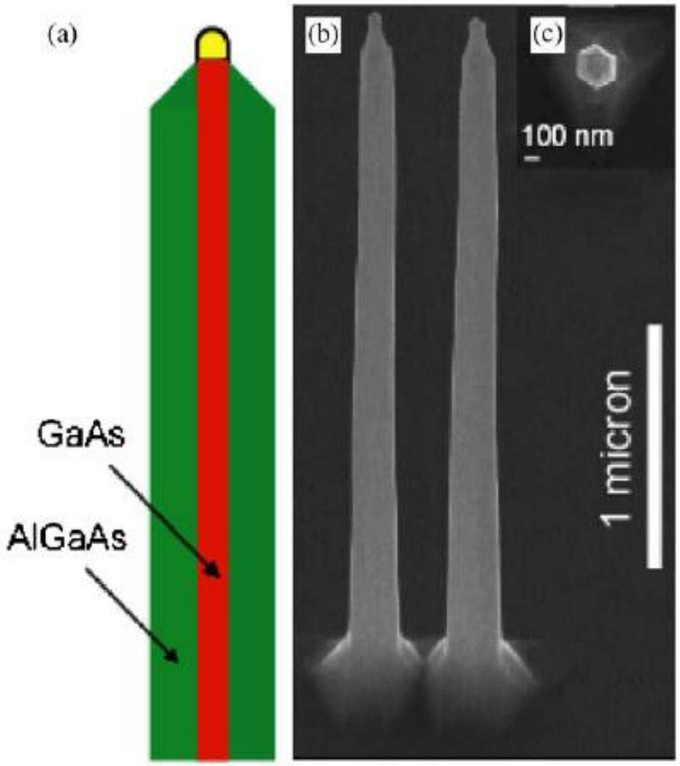


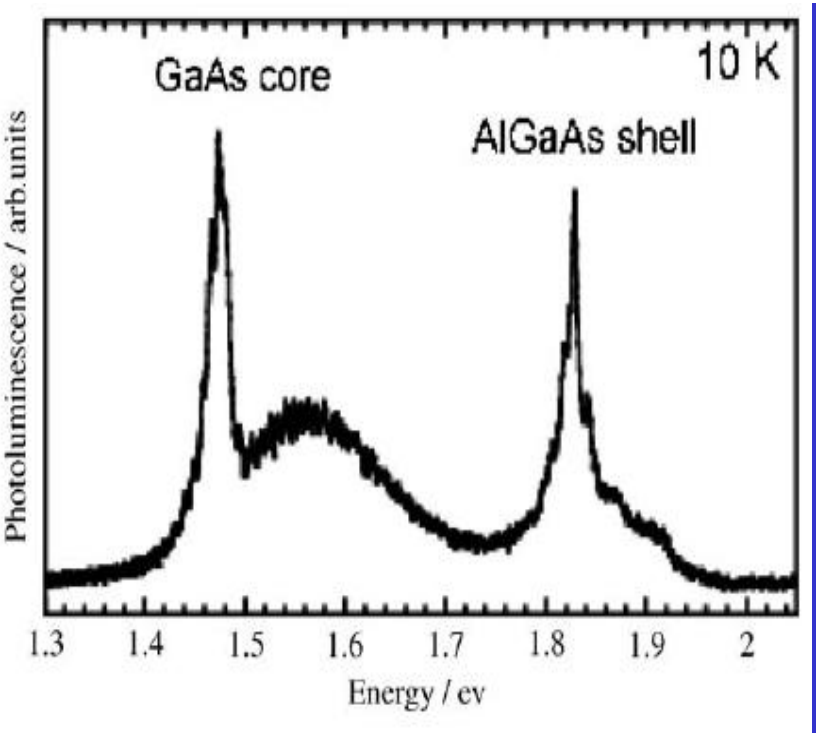
barrier height qΦB=0.6 eV



Core-shell heterostructures

strong GaAs core PL



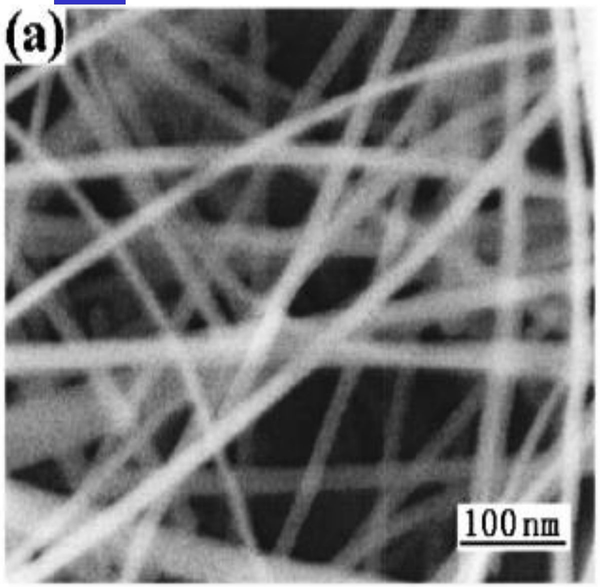


MOVPE growth:
GaAs first at 450°C, then AlGaAs at 630°C.
enhanced lateral growth (non VLS)

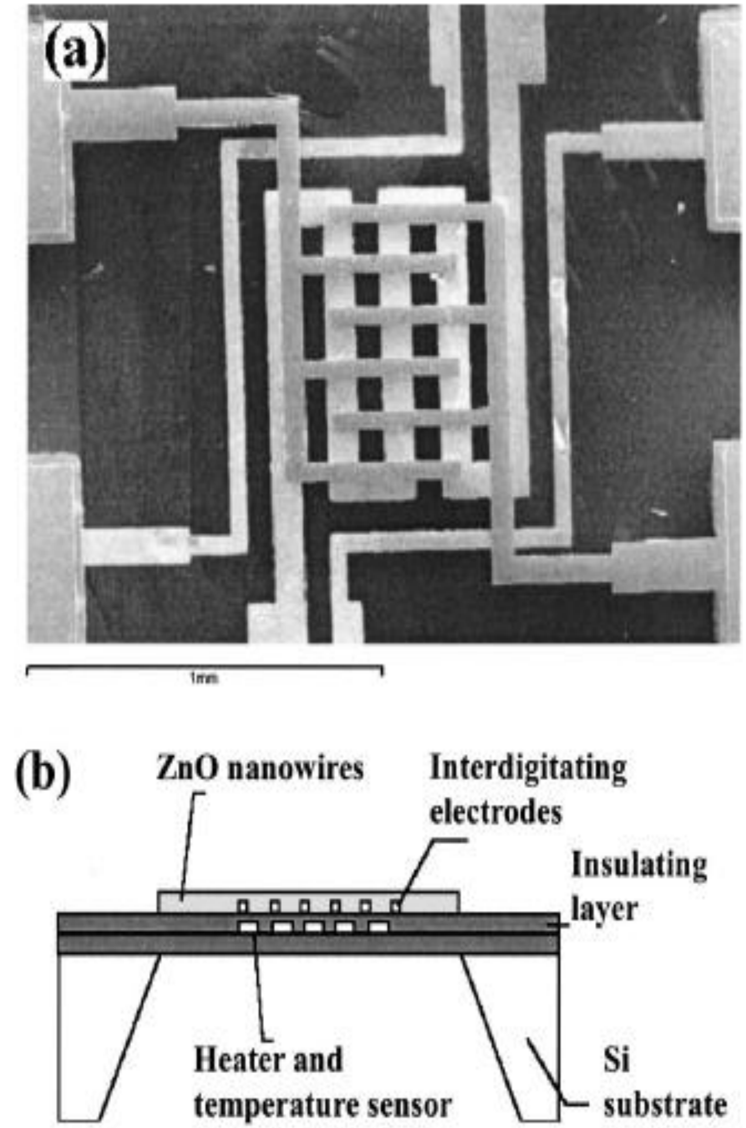
in combination with modulation doping promising canditates for 1D electron gas structures

Seifert *et al*, JCG 272, 211 (2004)

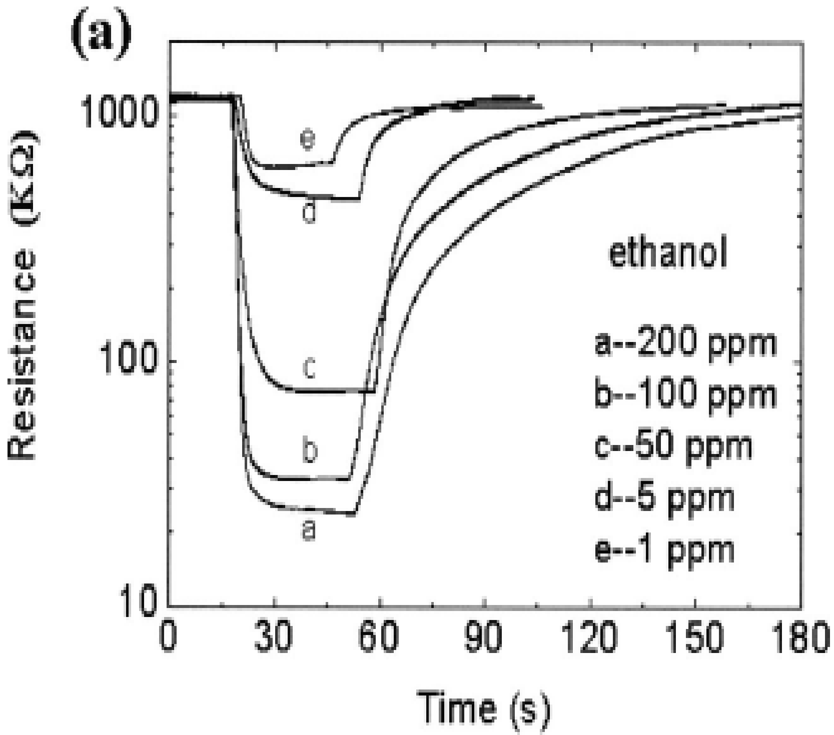
Ethanol sensing ZnO NW-based device

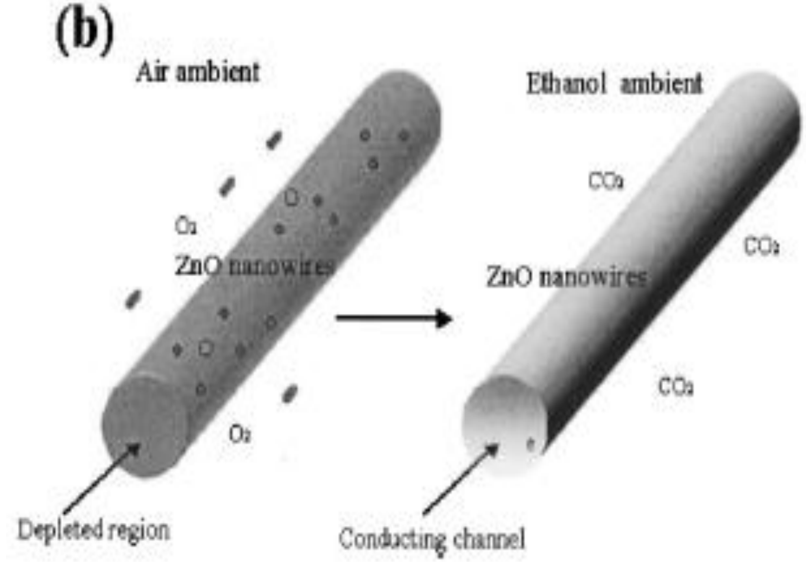


NW ultrasonically dispersed in ethanol, dried, deposited on interdigitated Pt contacts by spin coating.



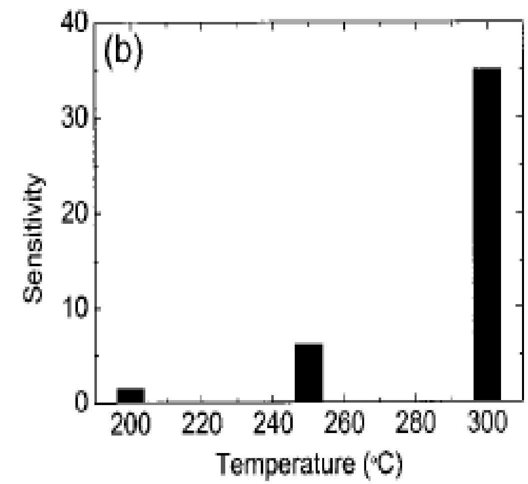
Wan et al, APL 84, 3654 (2004)



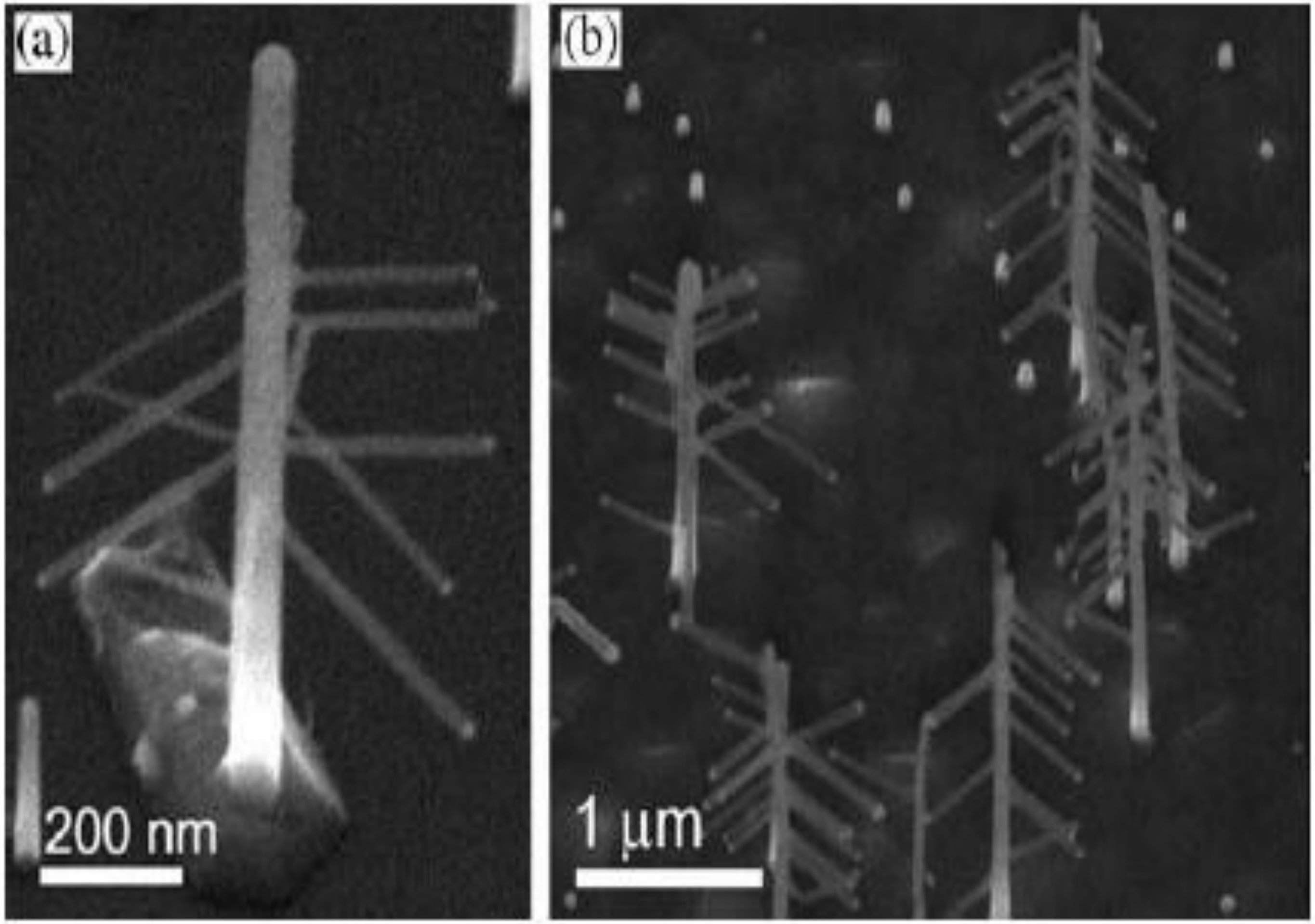


In air high R due to O_2^- adsorbed at the surface capturing electrons.

Ethanol reduces the density of O_2^- ions and increase the electron density.Transport properties of the entire NW change



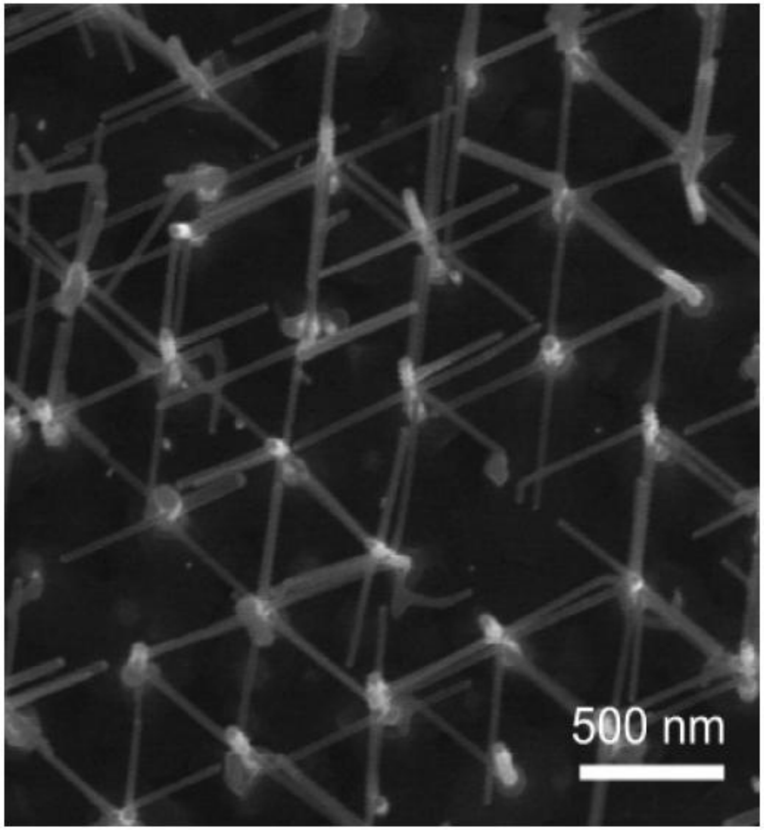
enhanced sensitivity at 300°C



Nanotrees by multistep seeding with Au nanoparticles

GaP on GaP (111) by MOVPE

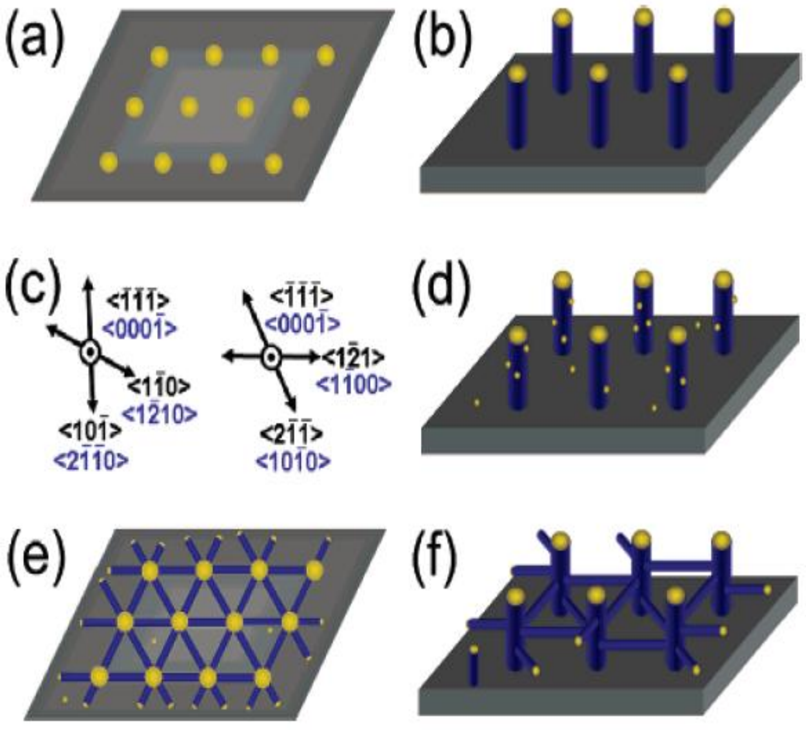
Position-controlled Inteconnected InAs Nanowire Networks



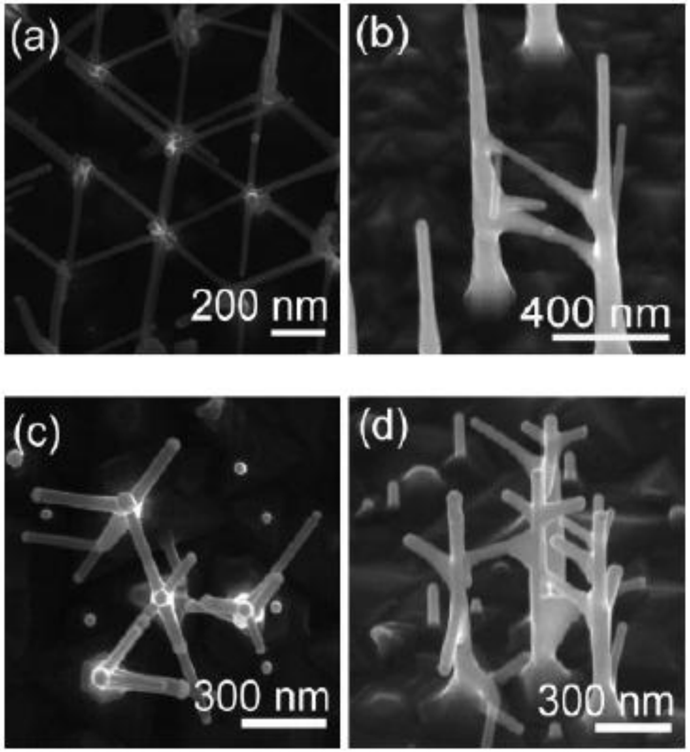
InAs on InP (111) by MOVPE

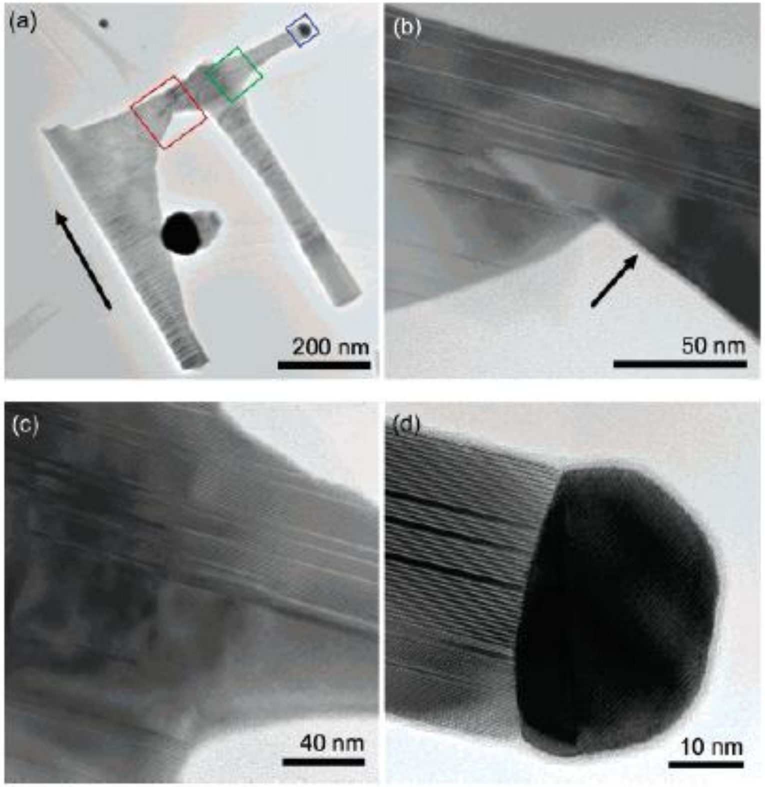
Au and Au-In assisted

Dick *et al*, Nano Letters (2006)



- Litographycally defined Au seeds to form a nework in the <211> directions
- growth of the “trunks” in the wurtzite <0001> direction
- branches seeded by aerosol Au-In particles
- Growth of the branches in the six equivalent <1100> direction
- merge of the btranches with the neighboring trunks





Branches grows epitaxially on the trunks and merge as single crystal to the neighboring trunks

Dick *et al*, Nano Letters 2006

Sensor

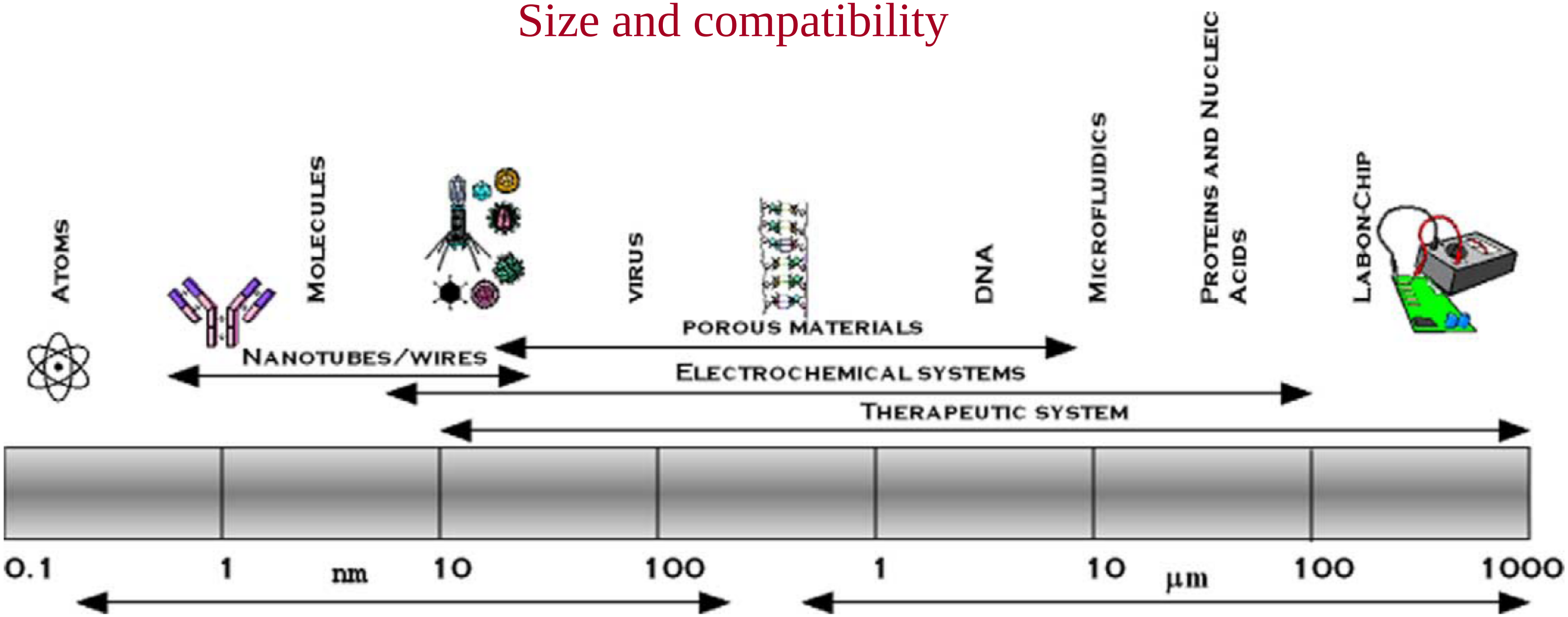
- A sensor is an instrument that responds to a physical stimulus (such as heat, light, sound, pressure, magnetism, or motion)

- It collects and measures data regarding some property of a phenomenon, object, or material

- Sensors are an important part to any measurement and automation application

- The sensor is responsible for converting some type of physical phenomenon into a quantity measurable by a data acquisition (DAQ) system

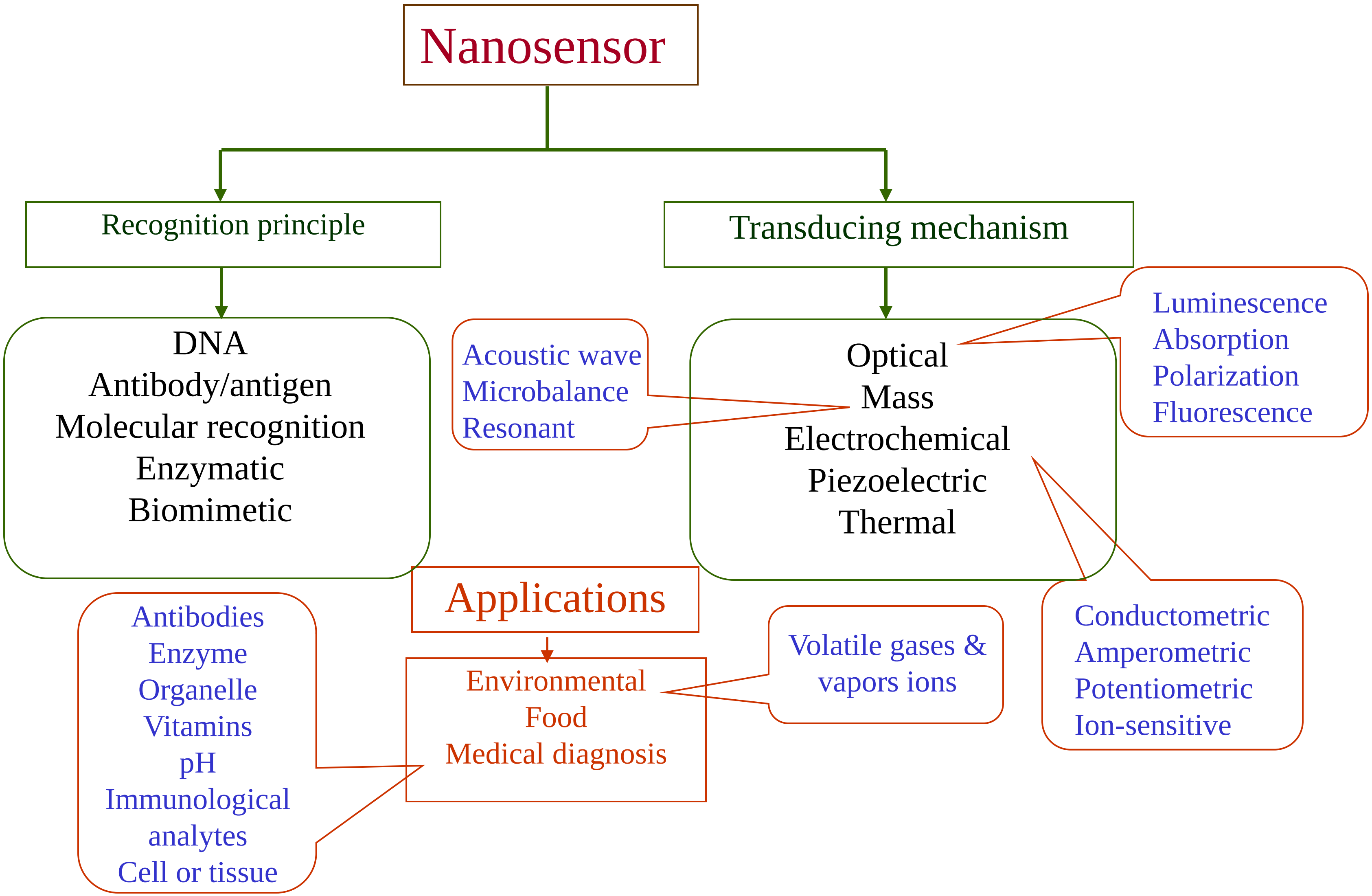
Size and compatibility



Nano sensors deliver real-time information about the antibodies to antigens, cell receptors to their glands, and DNA and RNA to nucleic acid with a complimentary sequence

Sensitivity of the conventional biosensors is in the range between 10^3 and 10^4 colony forming units (CFU)/ml. The dimensional compatibility of nanostructured materials renders nanotechnology as an obvious choice derived from its ability to detect ~ 1 CFU/ml sensitivity

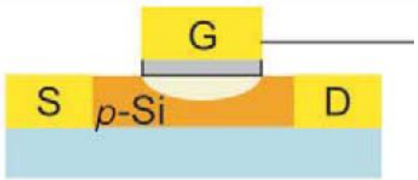
Reduced detection time than conventional methods



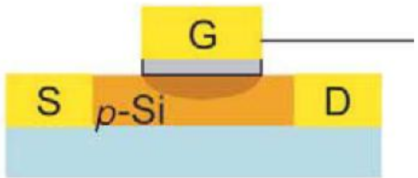
Scheme 1. Representation of recognition process and application of Nanosensor

Field-Effect Sensors (FET)

Si nanowire sensor device

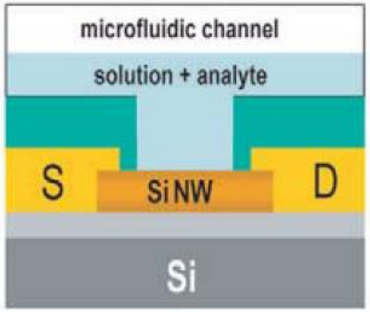


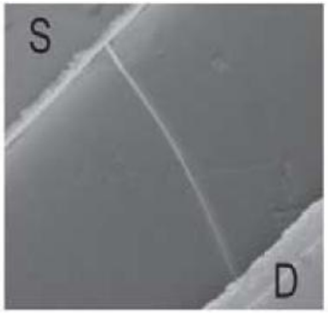
$V_G > 0$ depletion of carriers conductance decreases

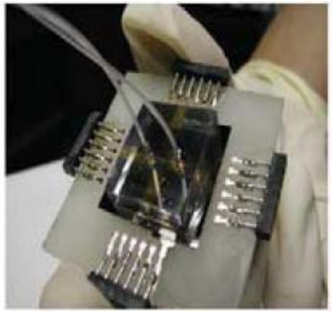


$V_G < 0$ accumulation of carriers conductance increases

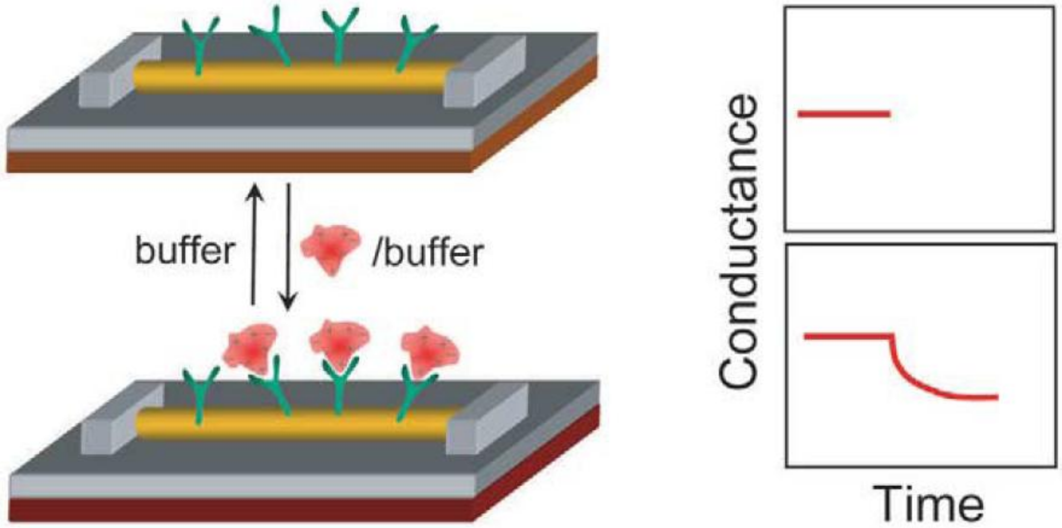
Schematic of a regular planar FET device, where S, D, & G correspond to source, drain, and gate, respectively







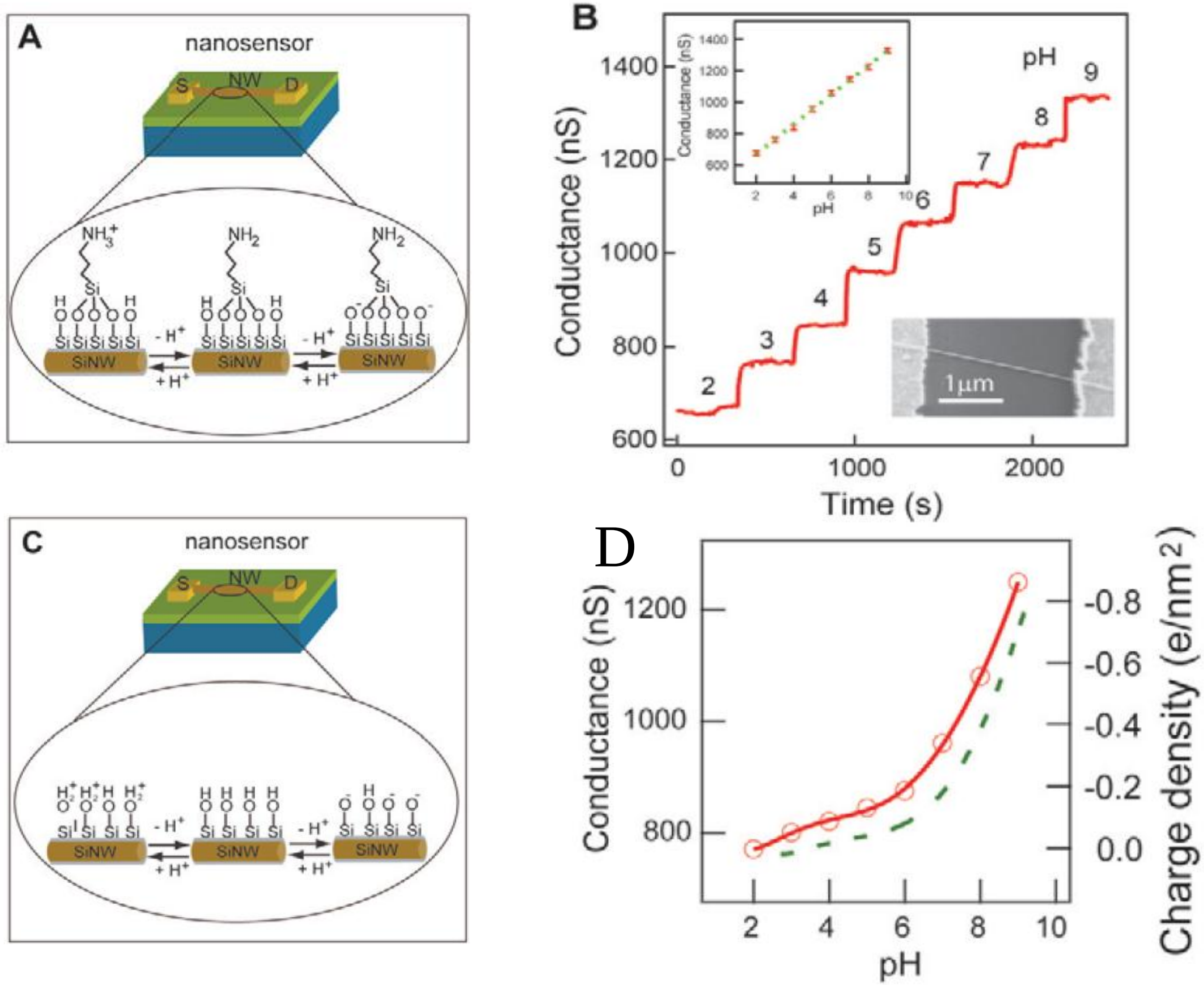
Cross-sectional diagram and scanning electron microscopy image of a single Si nanowire sensor device, and a photograph of a prototype nanowire sensor biochip with integrated microfluidic sample delivery.



Schematic of a Si nanowire-based FET device configured as a sensor with antibody receptors (green), where binding of a protein with net positive charge (red) yields a decrease in the conductance

- A general sensing device can be configured as illustrated in Fig. 1C, where specific sensing is achieved by linking a recognition group to the surface of the nanowire
- Si nanowires with their natural oxide coating make this receptor linkage straightforward
- When the sensor device with surface receptor is exposed to a solution containing a macromolecule like a protein that has a net positive charge in aqueous solution, specific binding will lead to an increase in the surface positive charge and a decrease in conductance for a p-type nanowire device

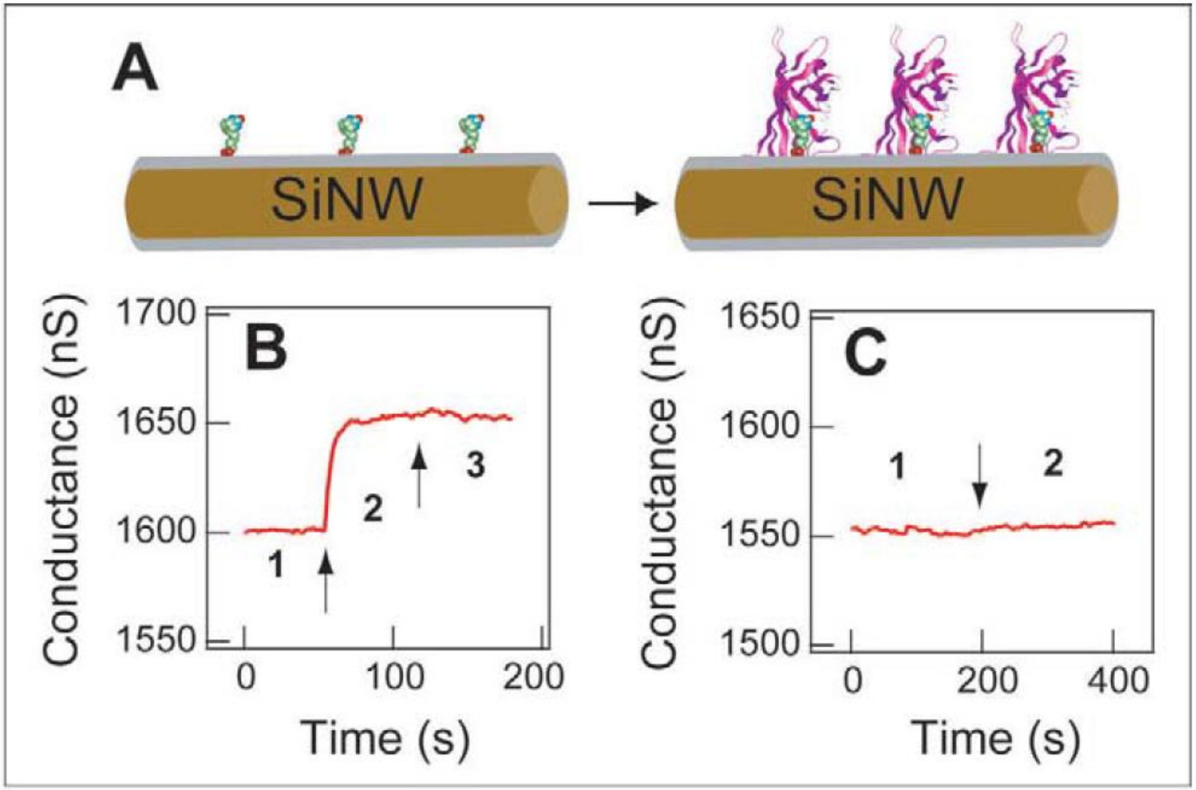
Nanowire pH sensors



(A) Schematic of an amino-functionalized nanowire device. (B) Changes in nanowire conductance as the pH of solutions delivered to the sensor is varied from 2 to 9; inset is a plot of conductance data versus pH. (C) Schematic of an unmodified nanowire sensor containing silanol groups. (D) Conductance of an unmodified Si nanowire device (red) versus pH.

Real-time detection of proteins and DNA

Detection of Proteins



(A) Schematic of a biotin-modified Si nanowire and subsequent binding of streptavidin to the modified surface. (B) Plot of conductance versus time for a biotin-modified Si nanowire, where region 1 corresponds to the buffer solution, region 2 corresponds to the addition of 250 nM streptavidin, and region 3 corresponds to pure buffer solution. (C) Conductance versus time for an unmodified Si nanowire, where regions 1 and 2 are the same as in (B).

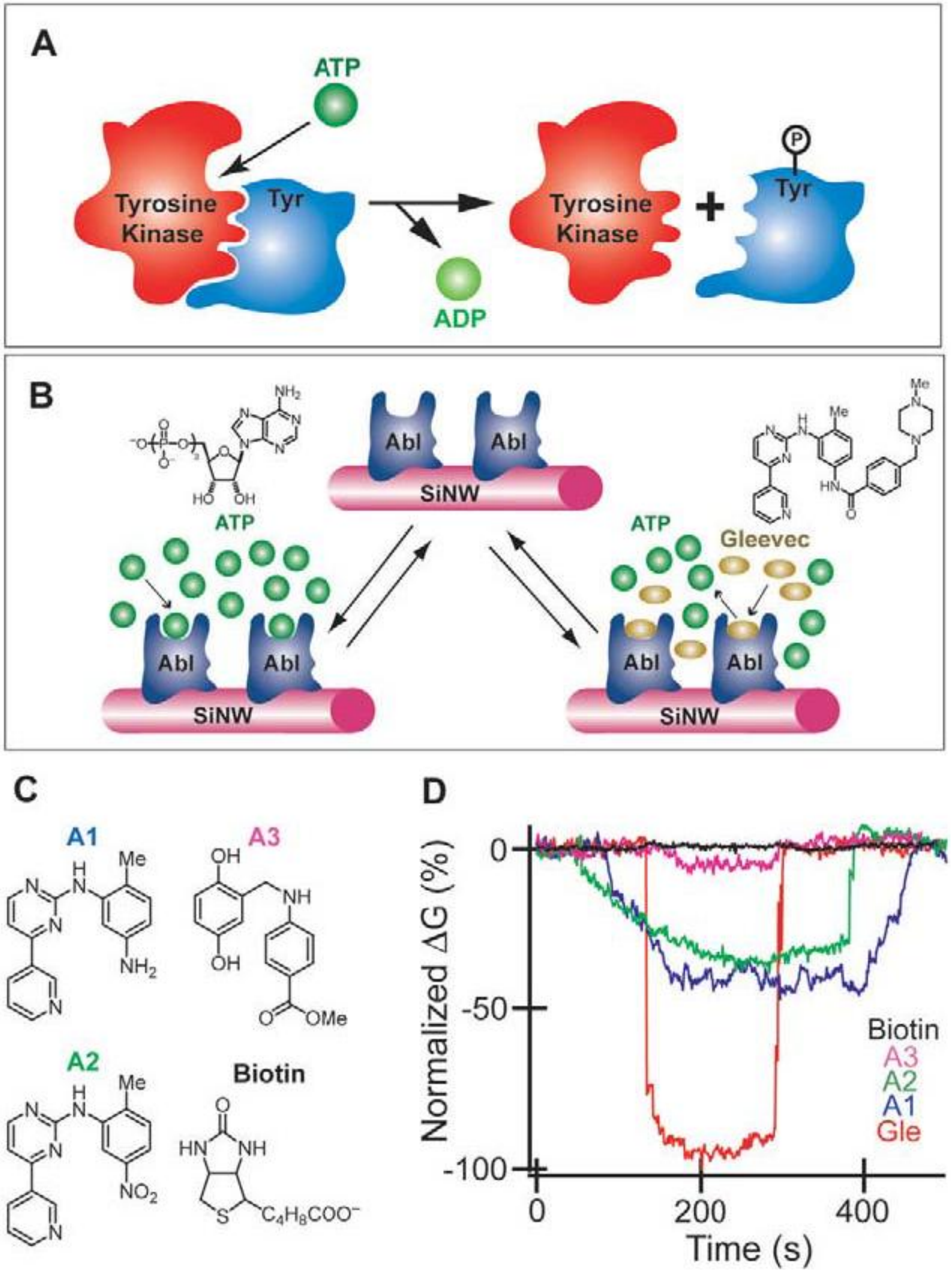
Nanosensors for drug discovery

(A) Illustration of tyrosine kinase function, where ATP binds to the kinase active site and then phosphate is transferred to a tyrosine (Tyr) residue of the substrate protein.

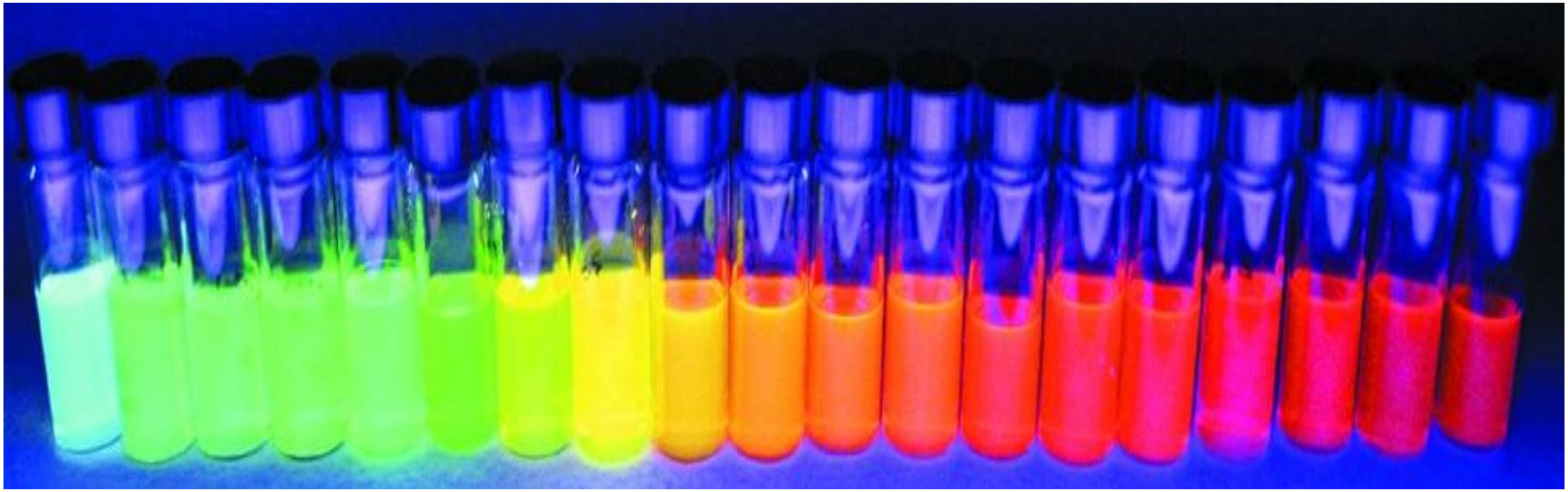
(B) Detection of ATP binding and small-molecule inhibition using a Si nanowire sensor device functionalized with the tyrosine kinase Abl.

(C) Structures of small molecules investigated for the inhibition of ATP binding to Abl.

(D) Normalized conductance versus time data recorded from Ablmodified Si nanowire devices using solutions containing 100 nM ATP and 50 nM small molecule Gleevec (red), A1 (blue), A2 (green), A3 (pink), and biotin (black).



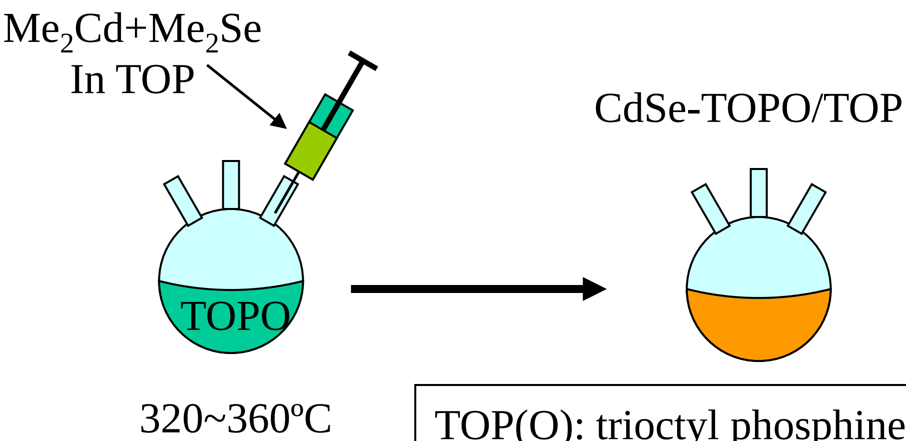
Nano-crystals



Outline

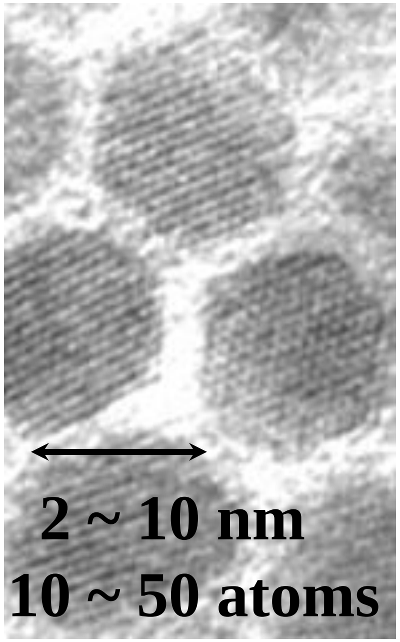
- What are Nanocrystal Quantum Dots
- What are they useful for in Solar Cell technology

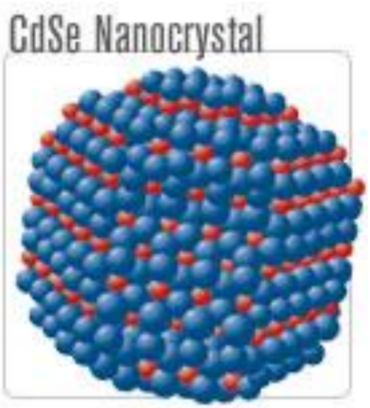
What are Nanocrystals?

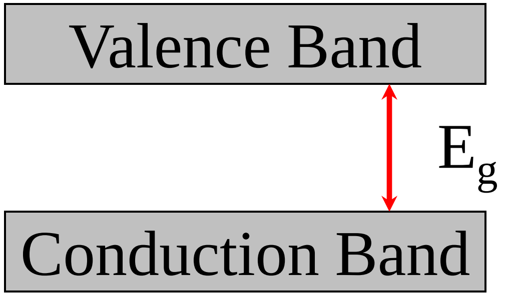


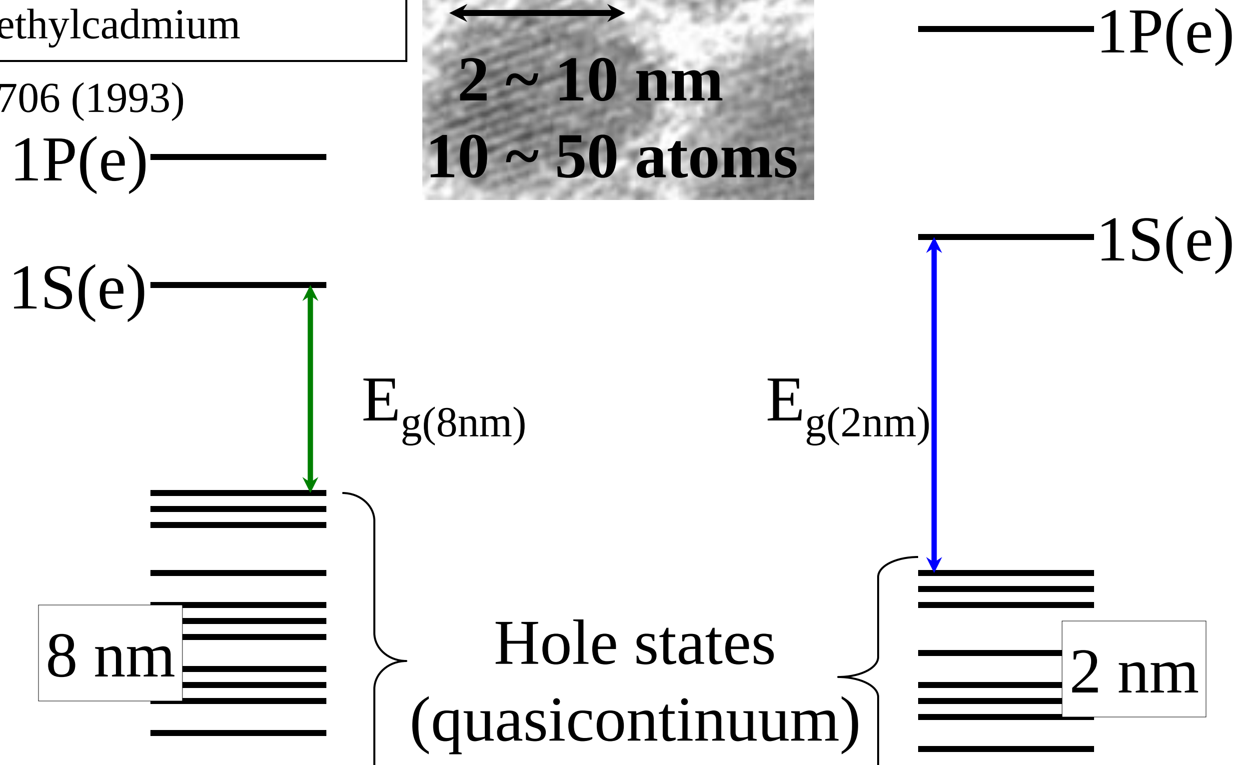
TOP(O): trioctyl phosphine (oxide)
Me_2Cd: dimethylcadmium

Murray et al., J. Am. Chem. Soc. **15**, 8706 (1993)

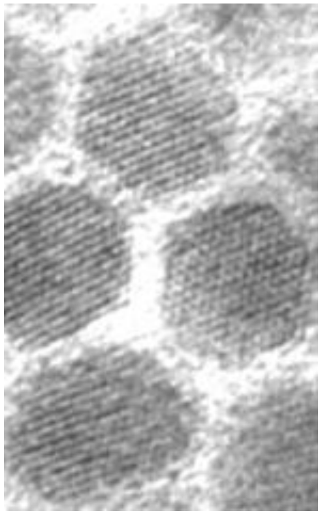


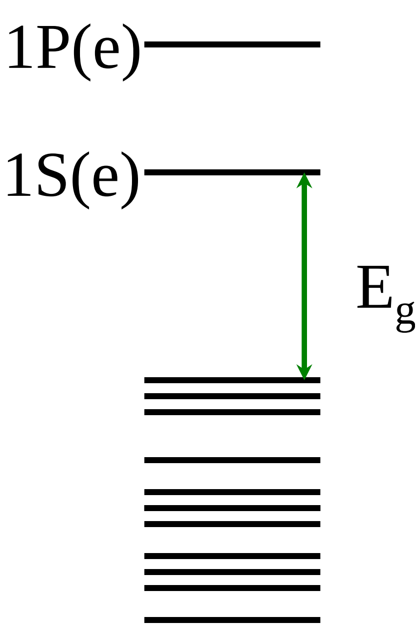


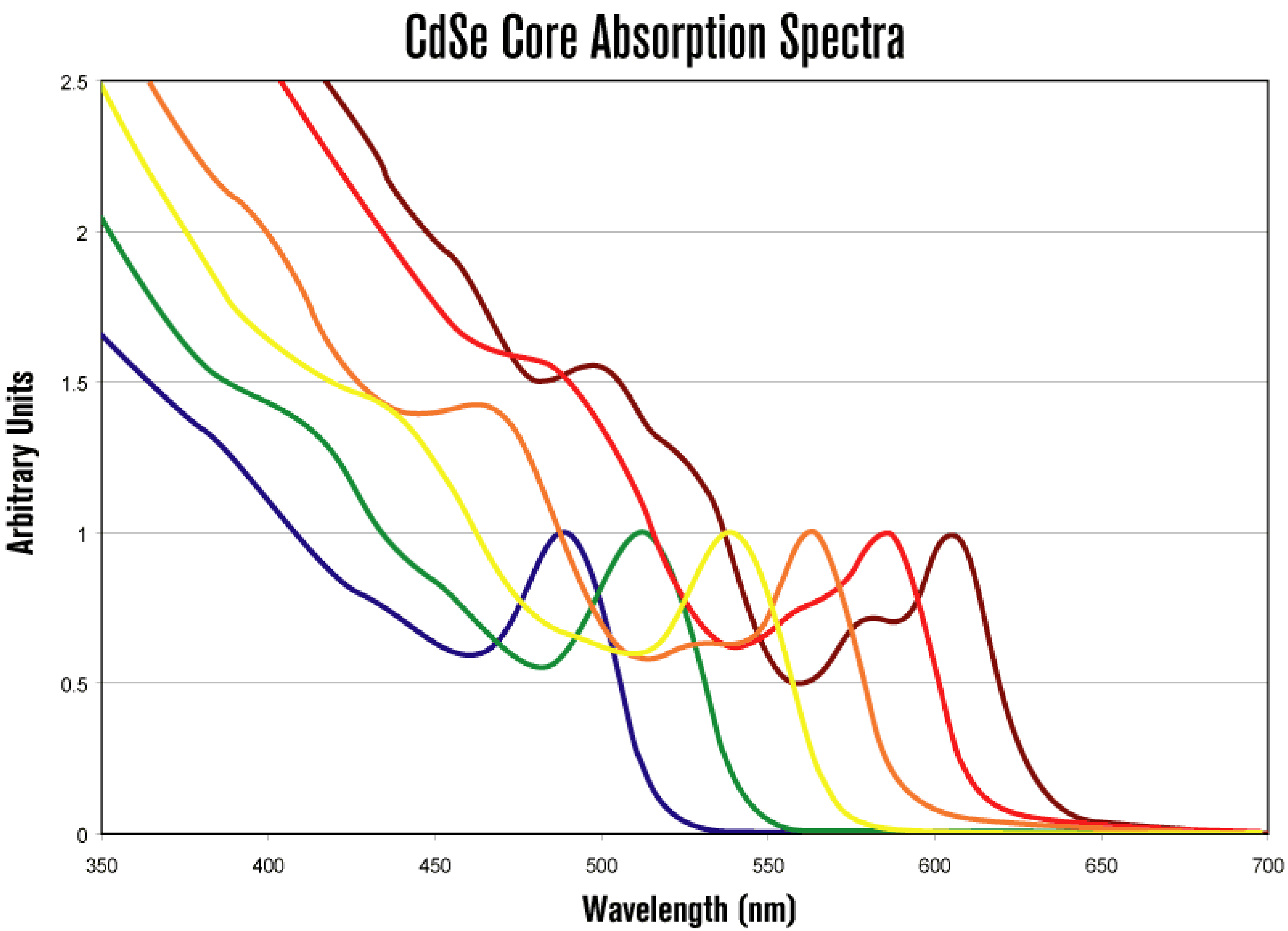




What are Nanocrystals?







Nano Crystal as Storing Bit

- Nano Crystal Technology has been studied extensively to replace traditional floating gate as charge storage media.
- Advantages:
  - Scalability with Channel Tunneling and Erase
  - Compatible with Traditional CMOS Platform
  - Improved Charge Retention and Endurance
  - Potential Multi Bit usage
- Challenges:
  - Strictly control the size and distribution of nano crystals
  - Still Litho node limited
  - Much work to be done for a integrated reliable and high yield process

Silicon Nano Crystal as Storing Media

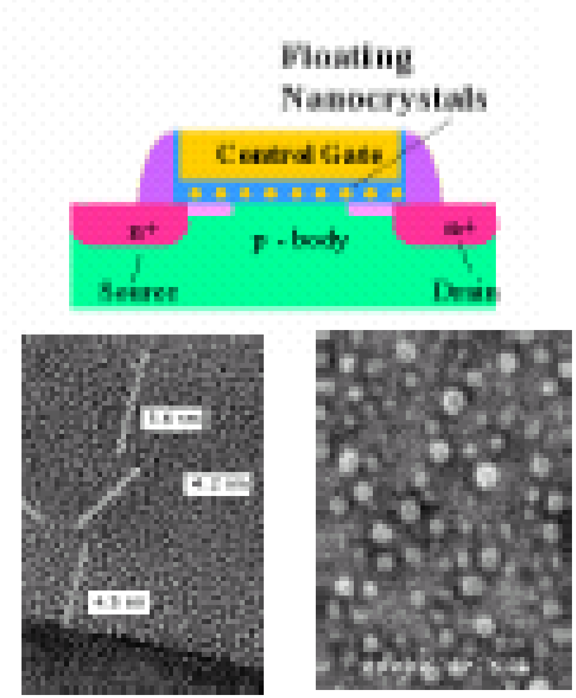


Figure 1 Silicon nanocrystal nonvolatile memory bitcell showing the floating silicon nanocrystals used for isolated charge storage.

R. Muralidhar et al. IDEM, 2003

- Reduce SILC and thus improve data retention and endurance
- Decrease gate coupling and thus improve leakage and erase saturation
- Possible multi-bit storage as particle size goes down to discrete energy state of electrons

Metal Dots as Storage Media

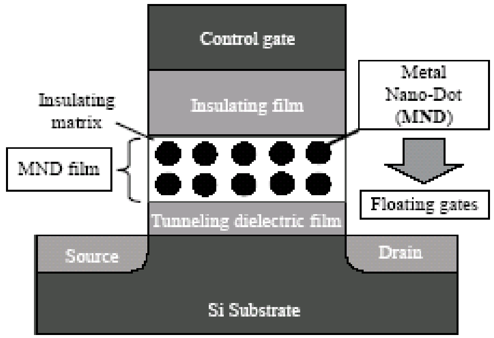
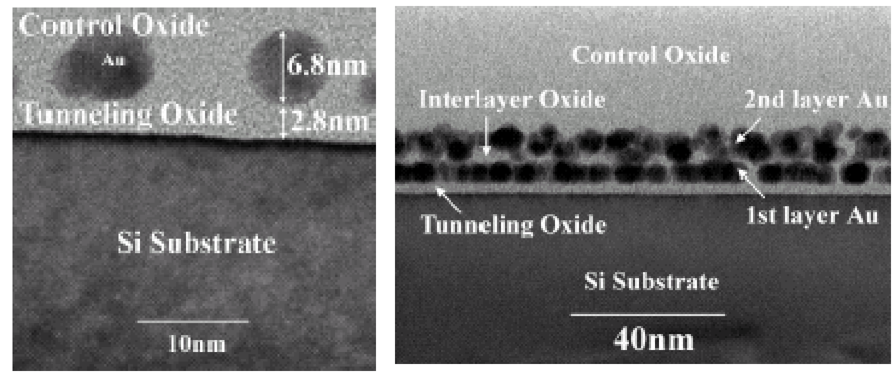


Fig.1 Cross sectional structure of an MND memory cell.



C. Lee, et al, IDEM, 2003

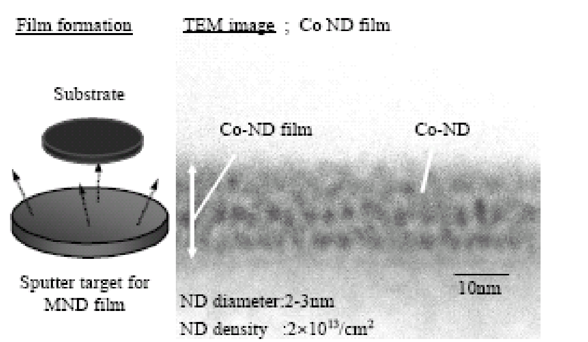
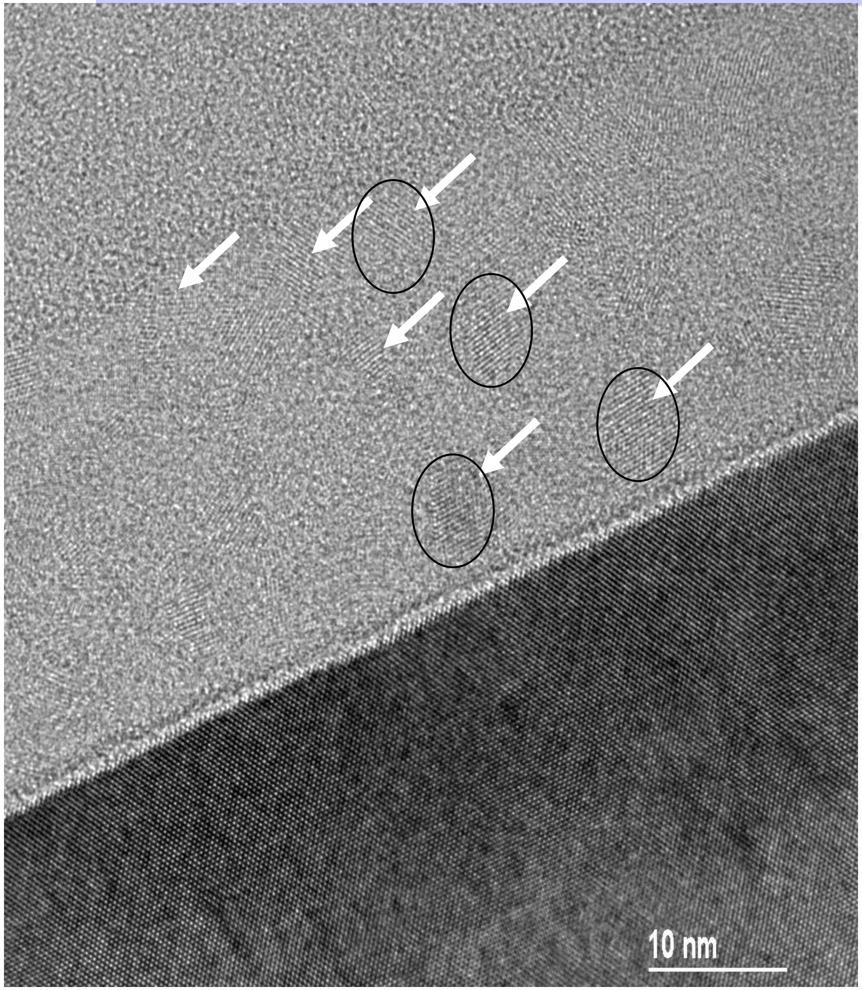


Fig.2 Method of MND film formation and a cross-sectional TEM image of Co-ND (Co-ND/SiO_2-matrix) film on a non-alkali glass substrate.

M. Takata, et al, IDEM, 2003

- Metal dots can be Co, W or Au
- Suppose to be better than Si as work function is higher (more attractive to electrons)
- Multilayer can improve retention and endurance

Silicon Nano Crystals Produced by CVD Methods (I)



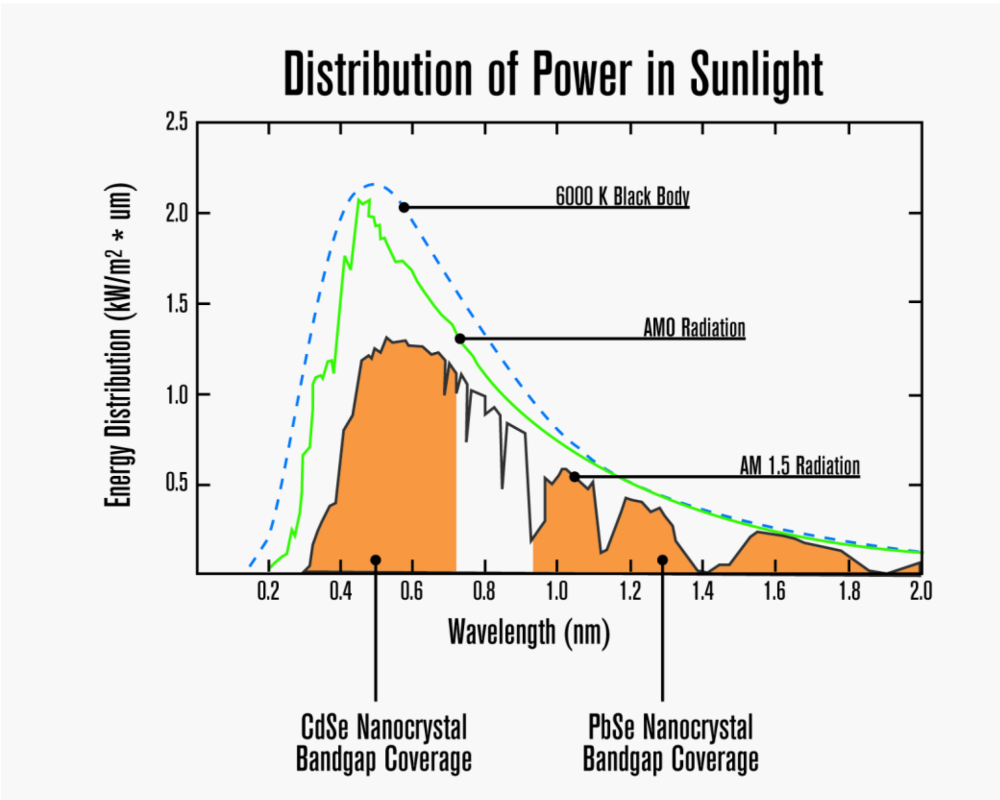
• A Si-rich SiOx thin film is deposited on Si surface by PECVD method. The non-stoichemetry are controlled by gas flow ratios.

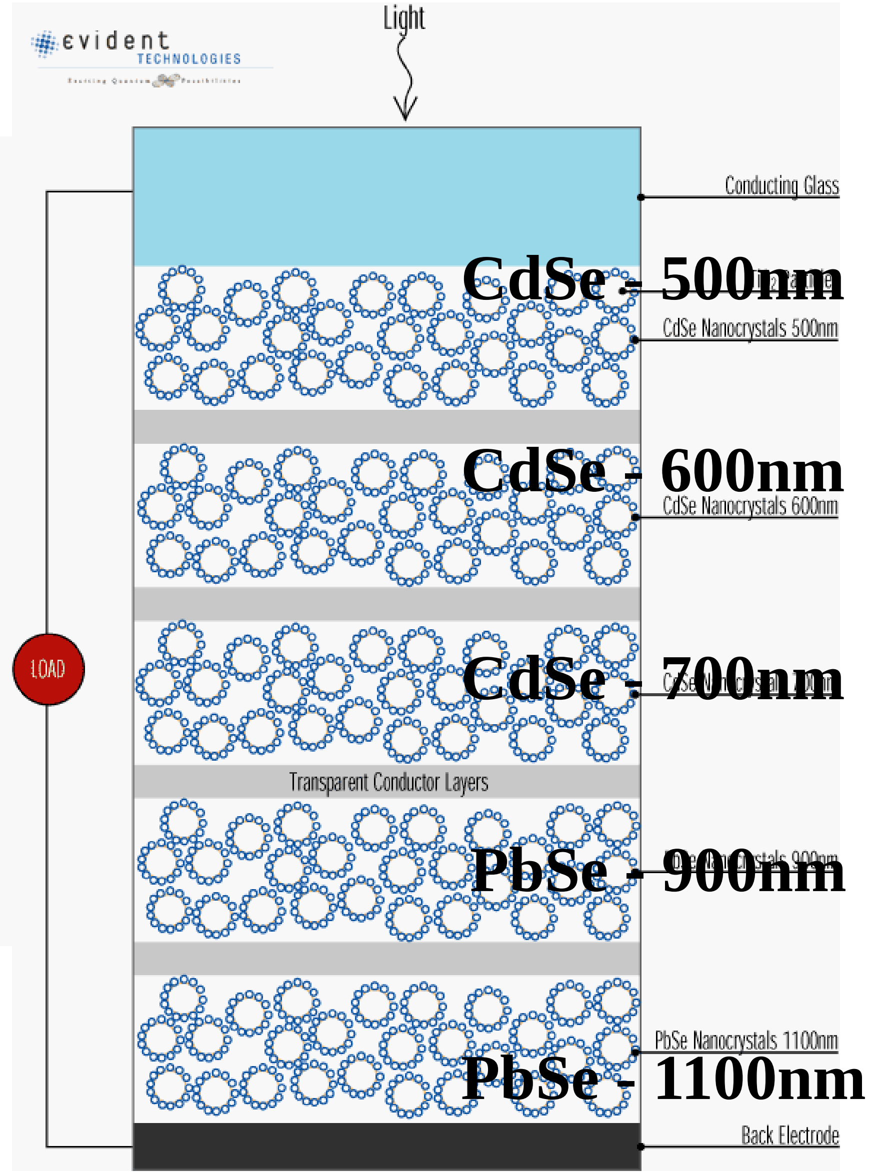
• An furnace annealing were performed on this film at 1000C in N2 atmosphere to precipitate Si Nano crystals out of supersaturated film.

-- U.S. Pattern Pending
Z. Guo, et al.

Why use Nanocrystals?

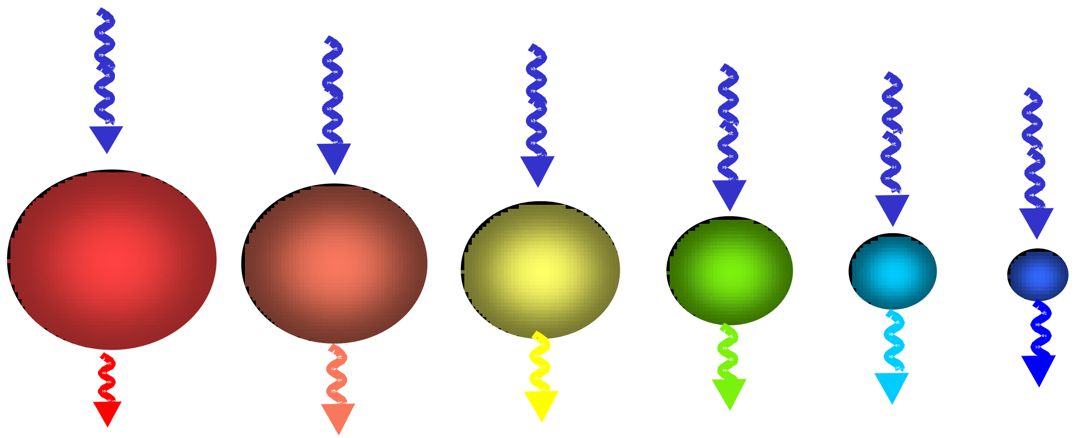
Tunable bandgap



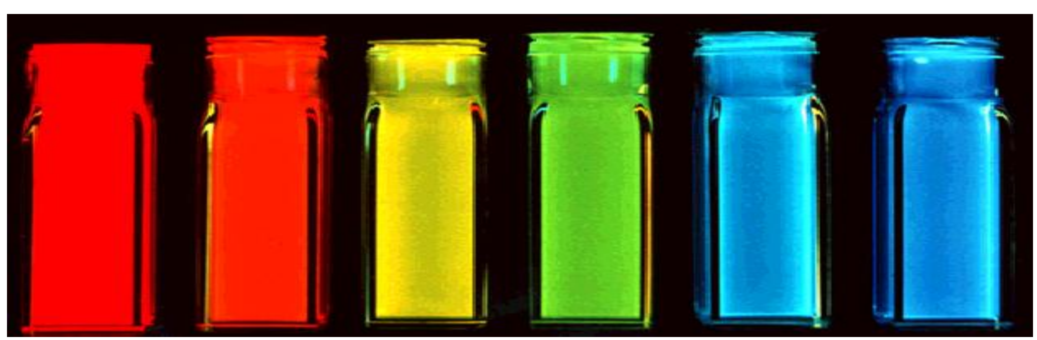


Optical Properties of Nanocrystals

Ordinary light excites all color quantum dots.
(*Any* light source "bluer" than the dot of interest works.)



Quantum dots change color with size because additional energy is required to "confine" the semiconductor excitation to a smaller volume.



Source: Bala Manian, Quantum Dot Corp.