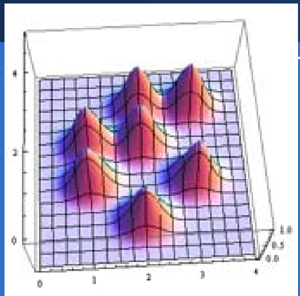
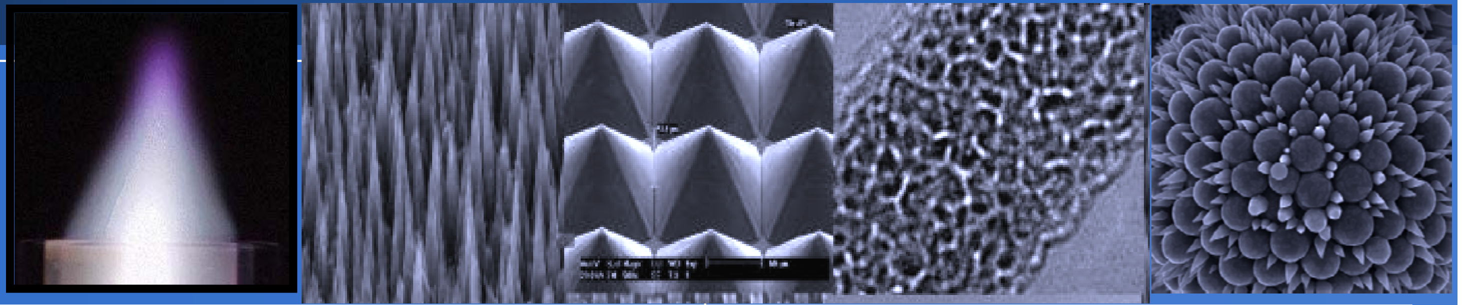


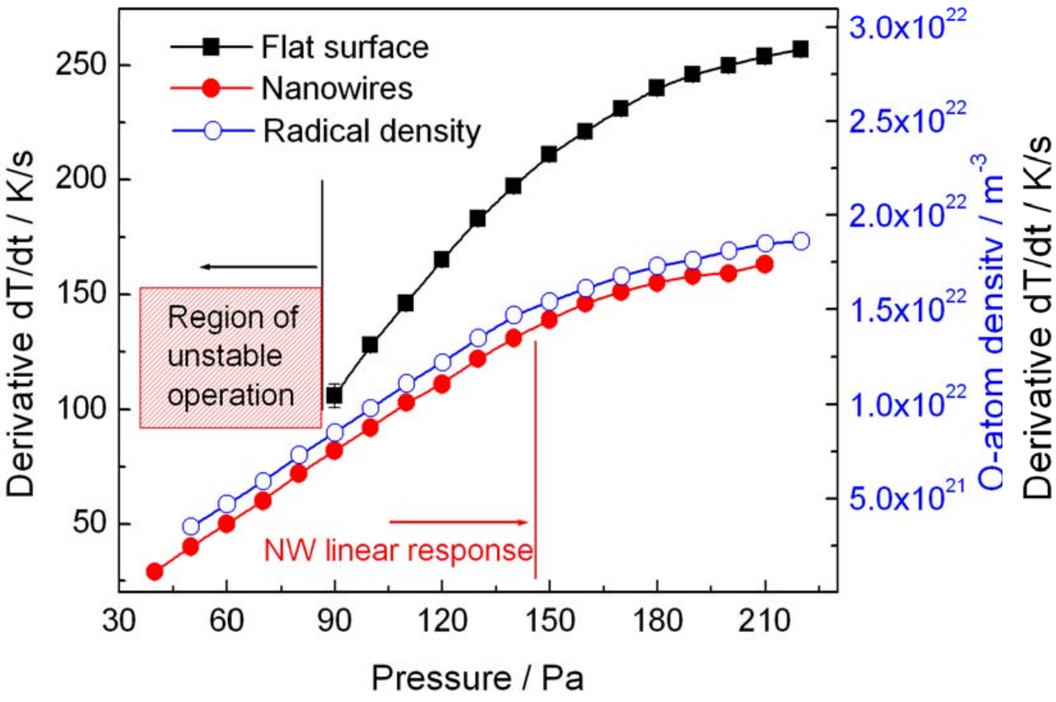


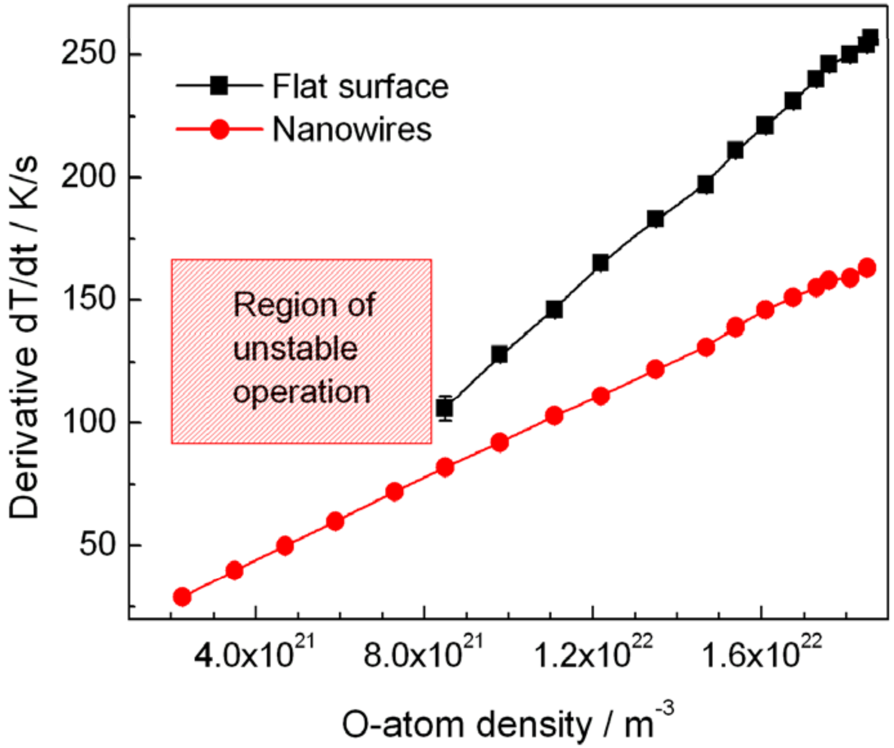
Uros Cvelbar Jozef Stefan Institute, Slovenia

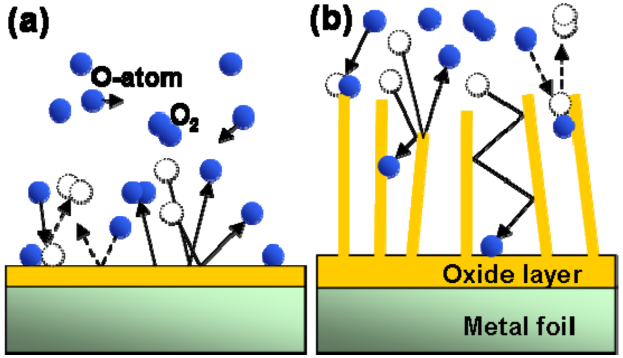
Building new catalytic sensors and devices with plasma nanostructuring and large-scale synthesis of nanowires

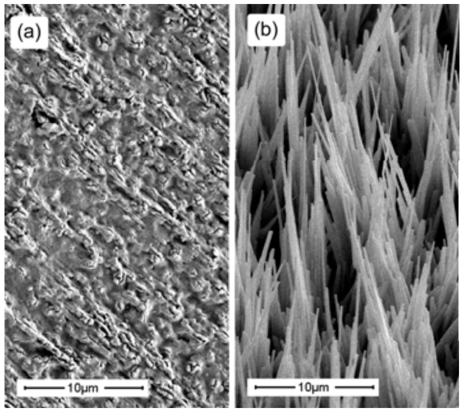
PlasmaLab F4-IJS

Sensors - Measurements of neutrals with nanostructured surfaces







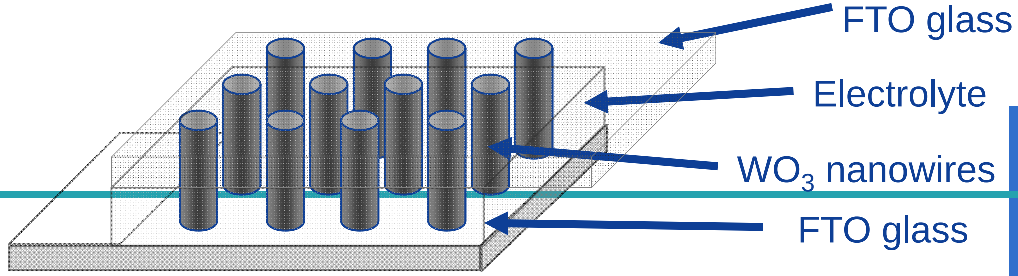


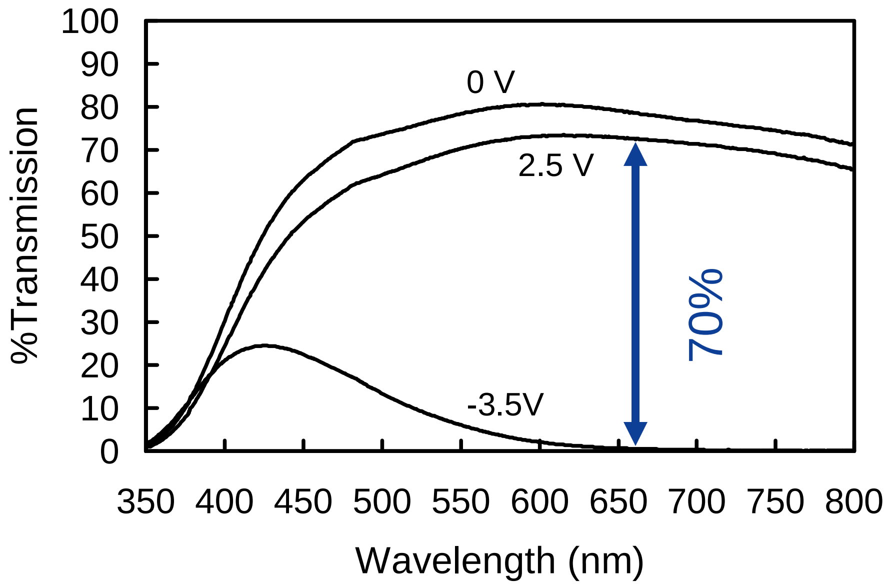
1. Linear response
2. Wider operation range
3. Better correlation with O-atom density

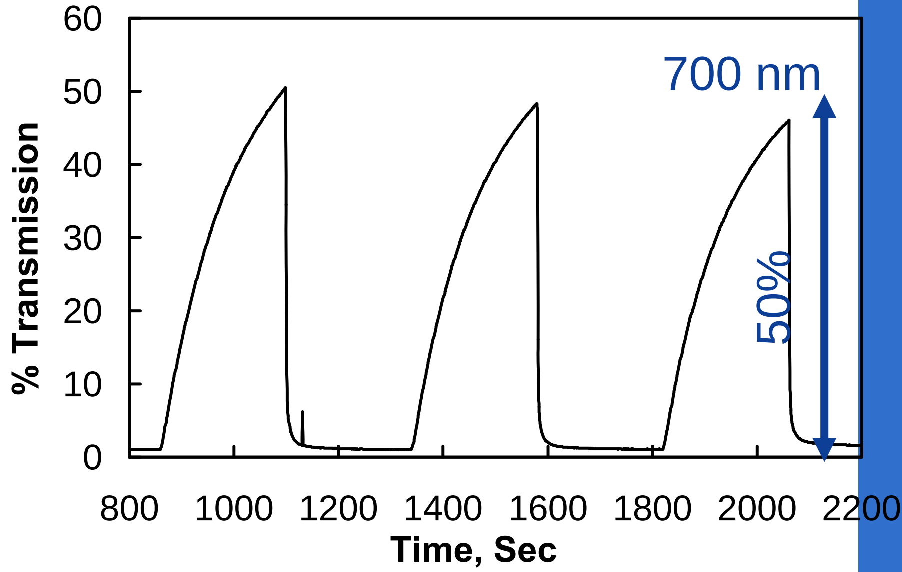
CVELBAR, et al. [also selected as a topical article for the Aril 14, 2008 issue of Virtual journal of nanoscale science & technology]. *Appl. phys. lett.*, 2008, vol. 92, no. 13, str. 133505-1-133505-3

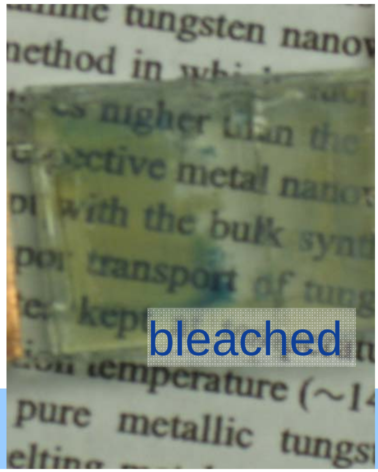
Applications

Nanowire array electrodes for electrochromics



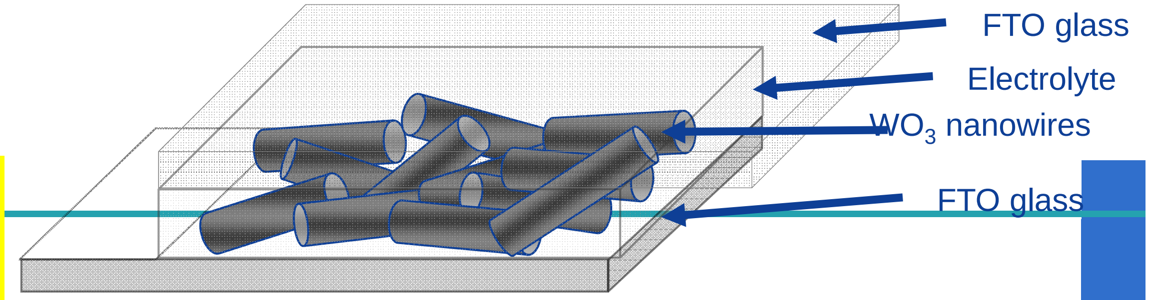


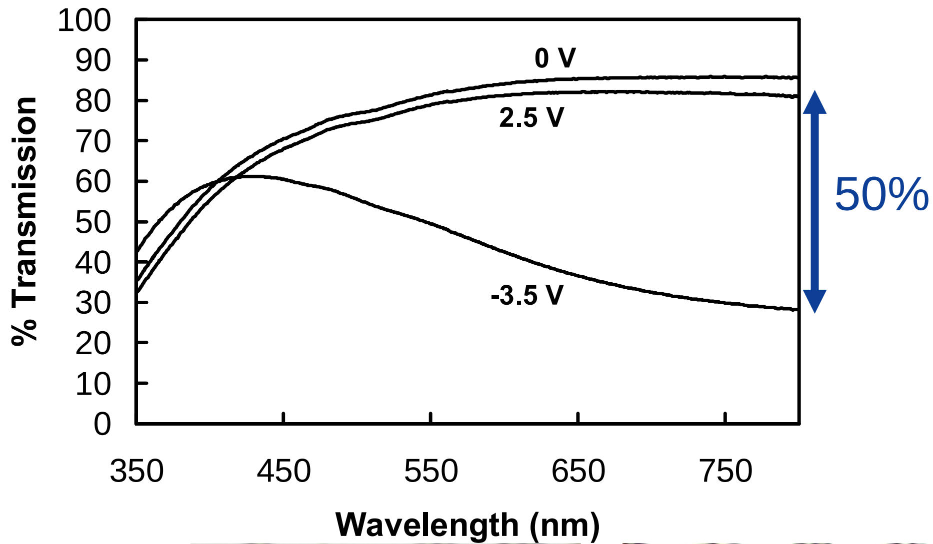


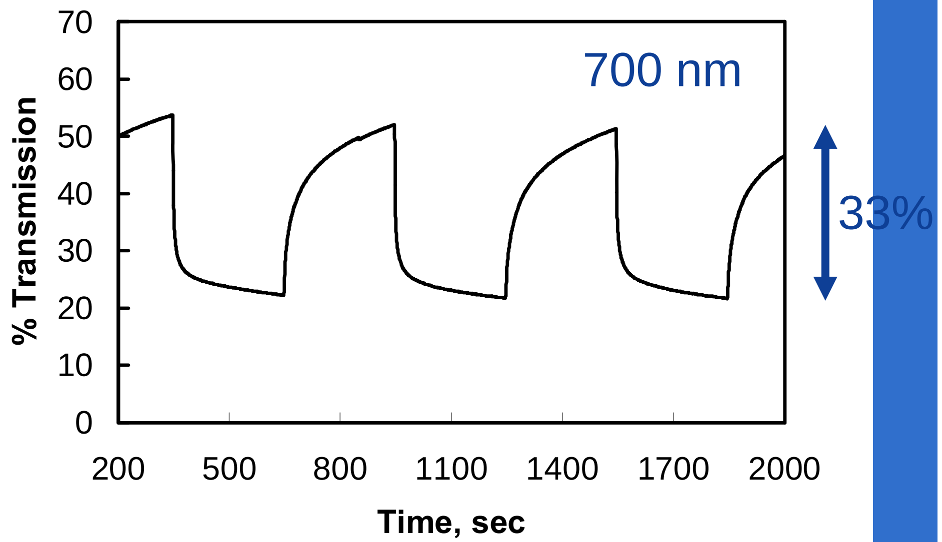


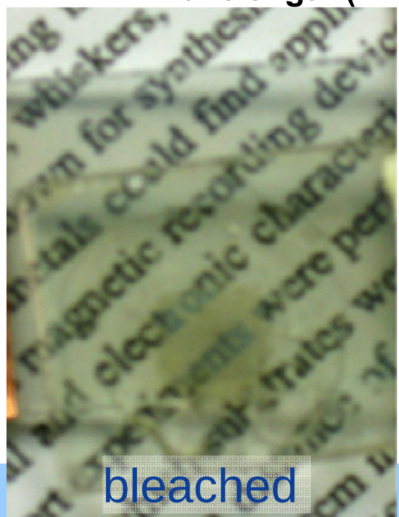
Applications

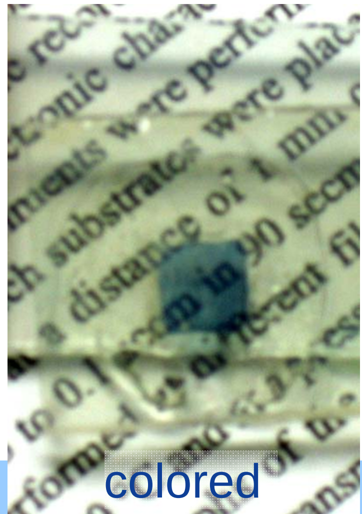
Nanowire mat electrodes for electrochromics











Differences in the timescales of coloration and bleaching

Problem to solve

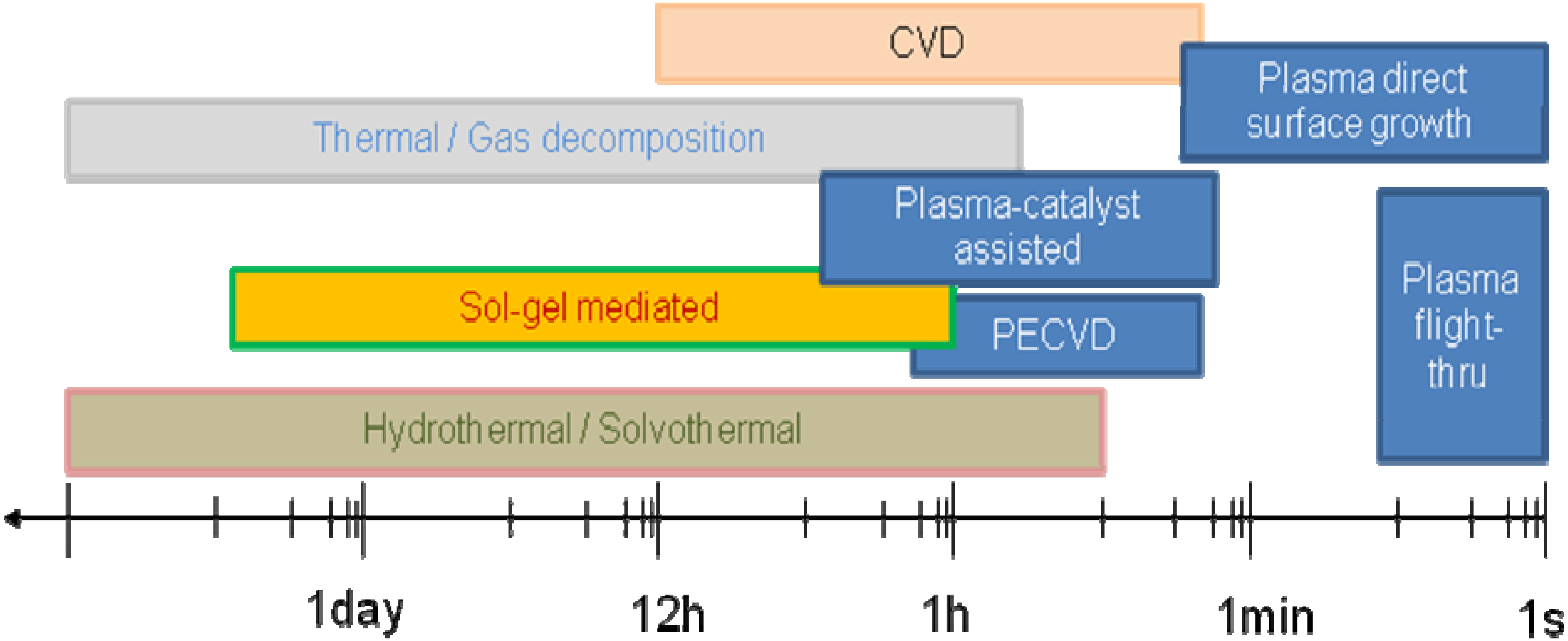
Synthesize large quantities of NW at small costs for satisfy future industrial needs!

Winner processes:

1. Fast process
2. Cheap material in (powders) / out (NW)
3. Yield quantities
4. Efficient (and small) energy consumption
5. Pureness of material and new properties (crystallinity, p/n-type, etc.)
6. No post-processing, purification

3D problem: TIME – QUANTITY- QUALITY

Time consumption for processing



Plasma routes

Different plasma routes for nanostructuring and large – scale synthesis of nanowires

Separate NW –to build in

1. Plasma-Enhanced Chemical Vapor Deposition (PECVD)

3. Plasma flight-thru

Pre-deposited NW - electrodes

2. Plasma-Catalyst assisted

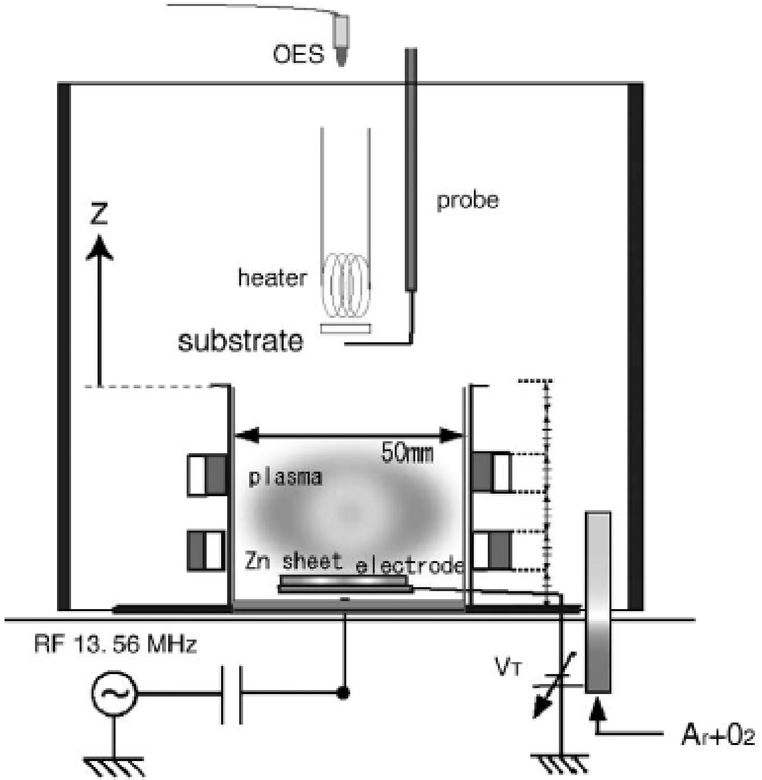
4. Direct Plasma synthesis

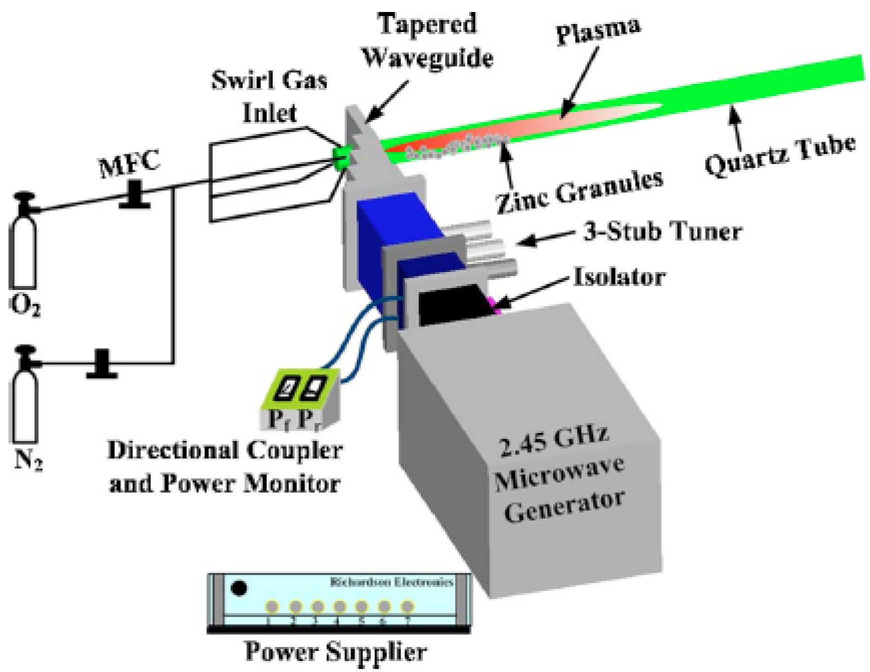
5. Mixed plasma routes

Case of ***IRON OXIDE*** and ***ZINC OXIDE*** – interest in sensors**,** solar cells, batteries or other photochemical and electrochromic applications

1. PECVD

Evaporation/melting-plasma interactions-deposition



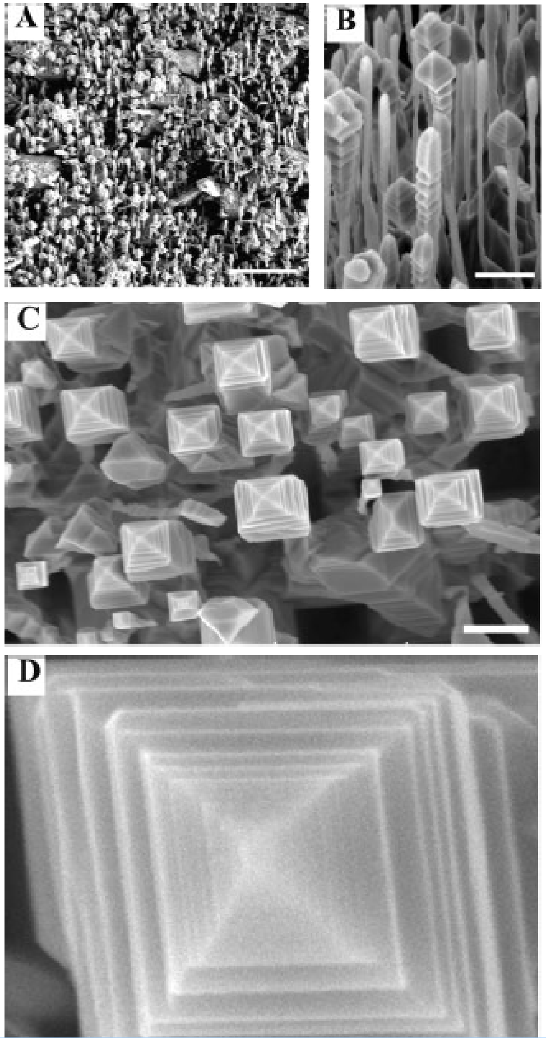


Liu et al. *Adv. Mater.* **2005**, 17, 1893-1897.
Ostrikov et al. 2007 Thin Solid Films 516, 6609-6615.
Liu et al. 2003 J. Appl. Phys. 95, 3141-3147.
Kumeta et al. 2009 Thin Solid Films 518, 3522-3525
Ono H et al. 2009 Thin Solid Films 581, 1016-1019
Baxter et al. 2003 Appl. Phys. Lett. 83, 3797-3799.

Hong et al. 2006 Phys. Plasmas 13, 063506.
Hong et al 2006 Jpn. J. Appl. Phys. 47, 5940-5944.

1.PECVD

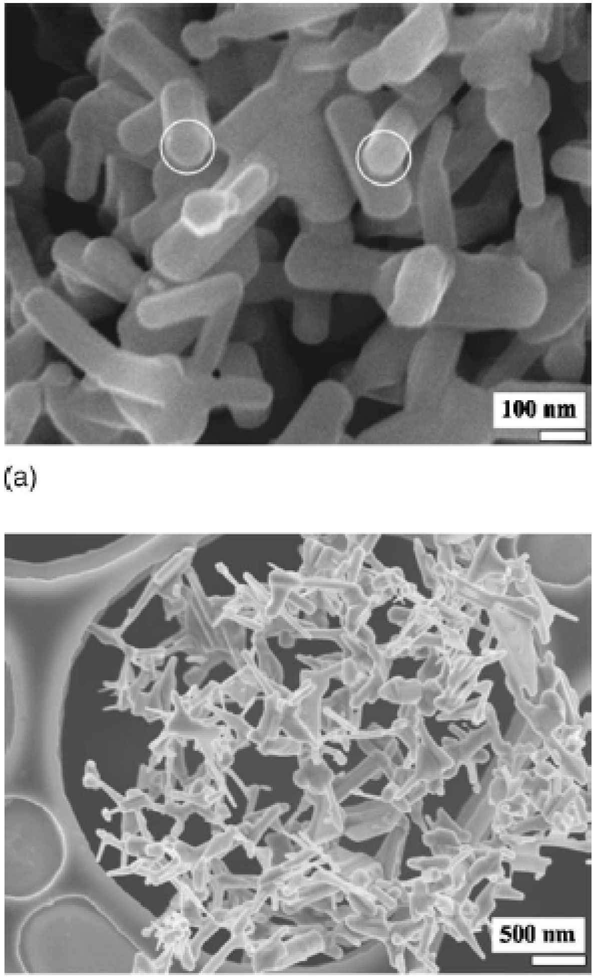
Fe3O4 NW



Liu et al 2005 Adv. Mater., 17, 1893-1897

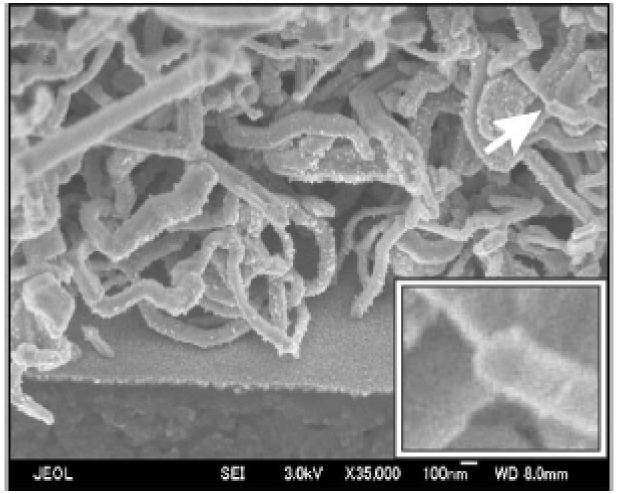
ZnO NW

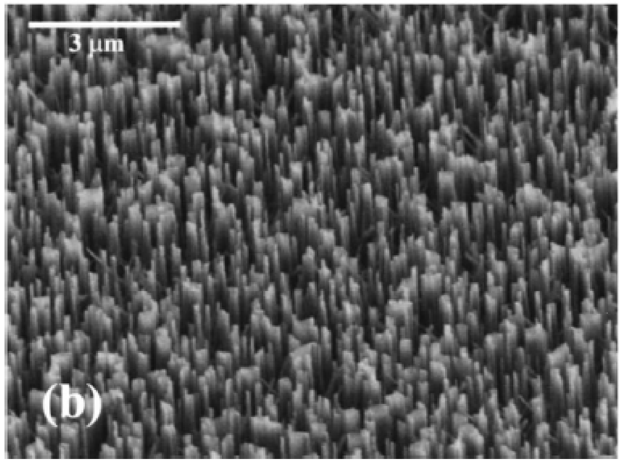
Hong et al. 2006 Phys. Plasmas 13, 063506.



(a)

(b)





Ostrikov et al. 2007 Thin Solid Films 516, 6609-6615.
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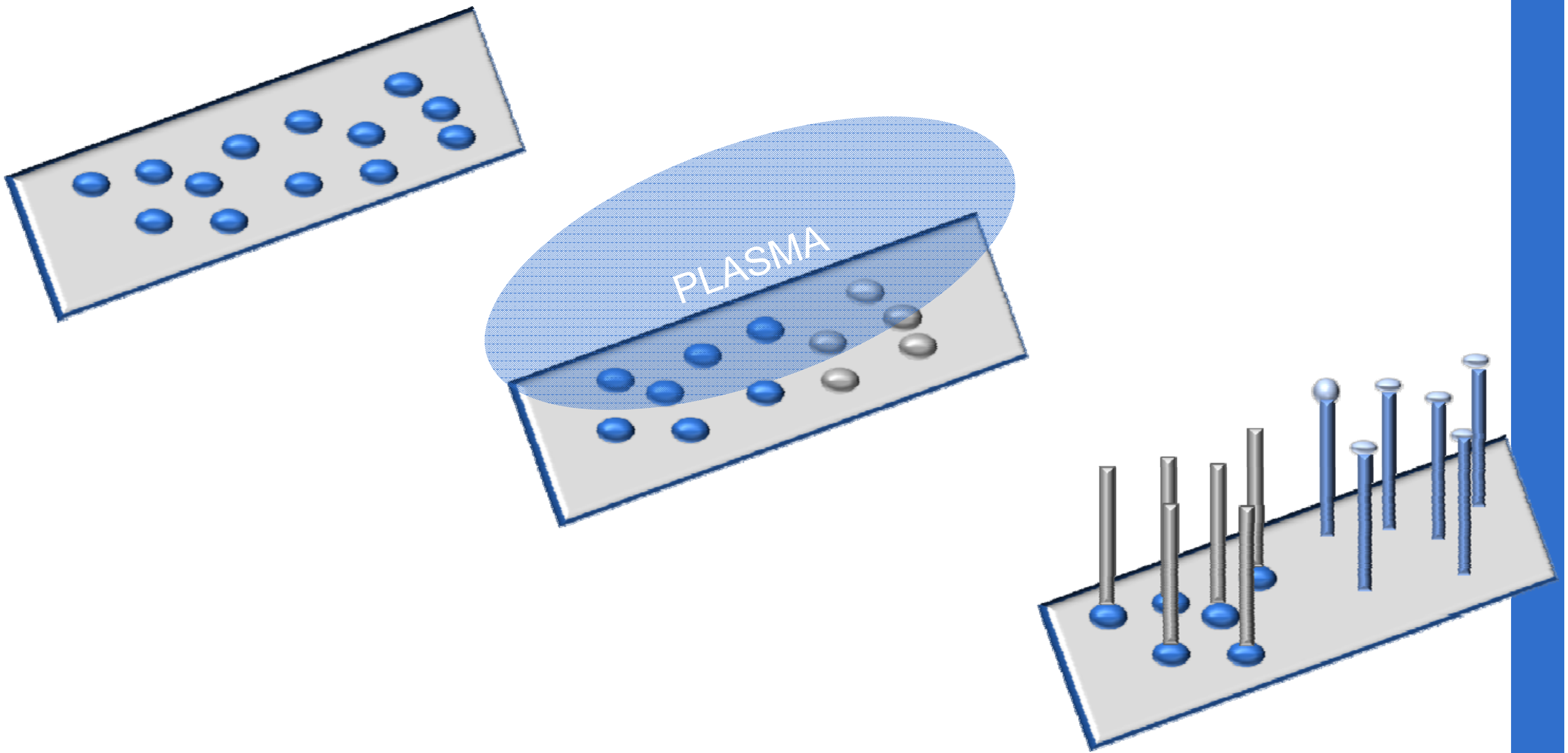
Kumeta et al. 2009 Thin Solid Films 518, 3522-3525
Ono H et al. 2009 Thin Solid Films 581, 1016-1019
Baxter et al. 2003 Appl. Phys. Lett. 83, 3797-3799.

2. Plasma-catalyst assisted

Catalyst deposition – plasma interactions – NW growth

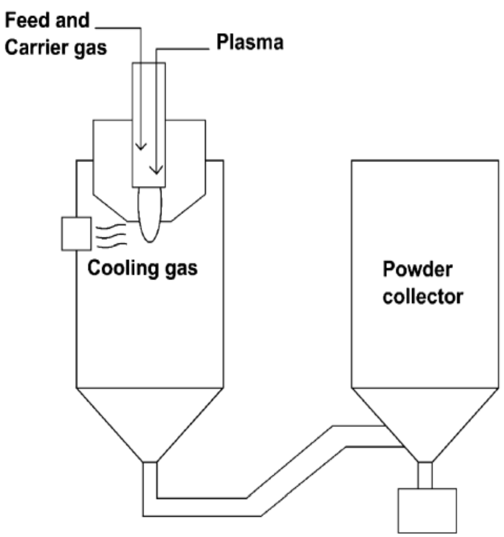


Fe2O3 = O

ZnO = book *Inorganic nanowires and applications* by M. Meyyappan, MK Sunkara

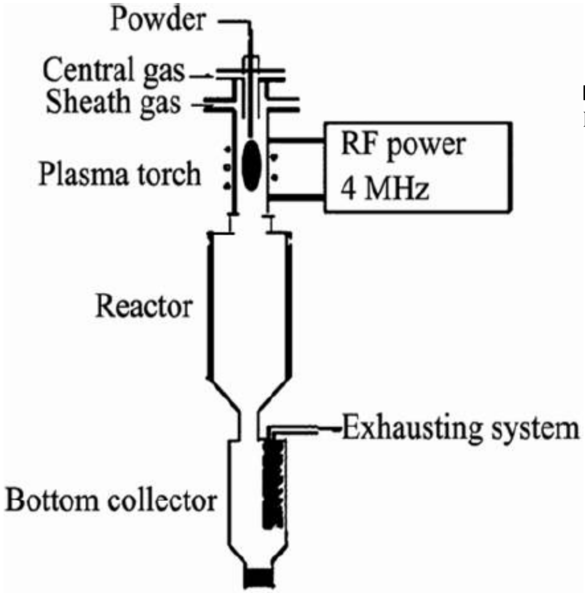
3. Plasma flight-thru

DC



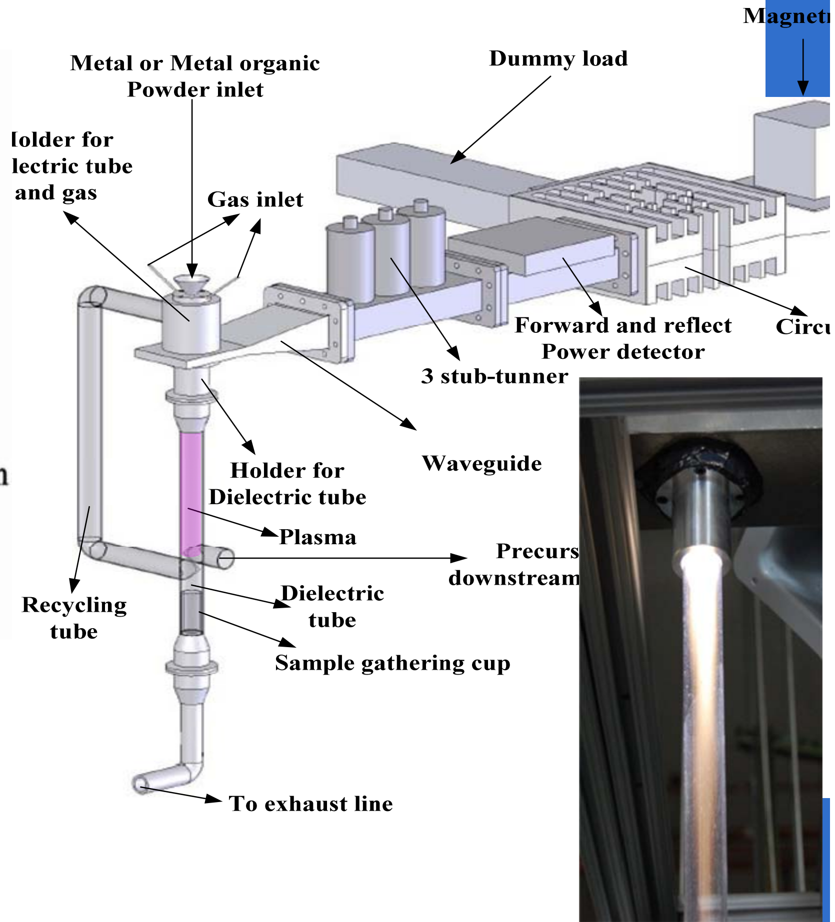
Ko TS et al 2006 Mater. Sci. Eng. B 134, 54-58.
Lin Hf et al 2009 J. Cryst. Grow. 311, 1378-1384.

RF



Peng H et al 2007 J. Phys. Chem. C 111, 194-200.

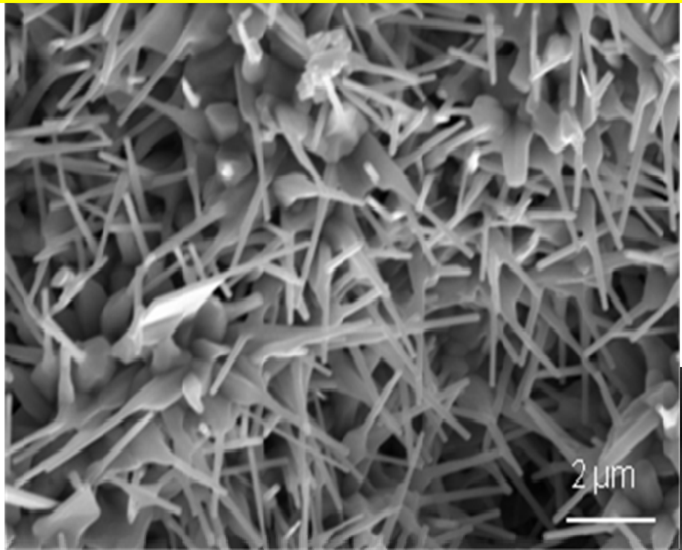
MW

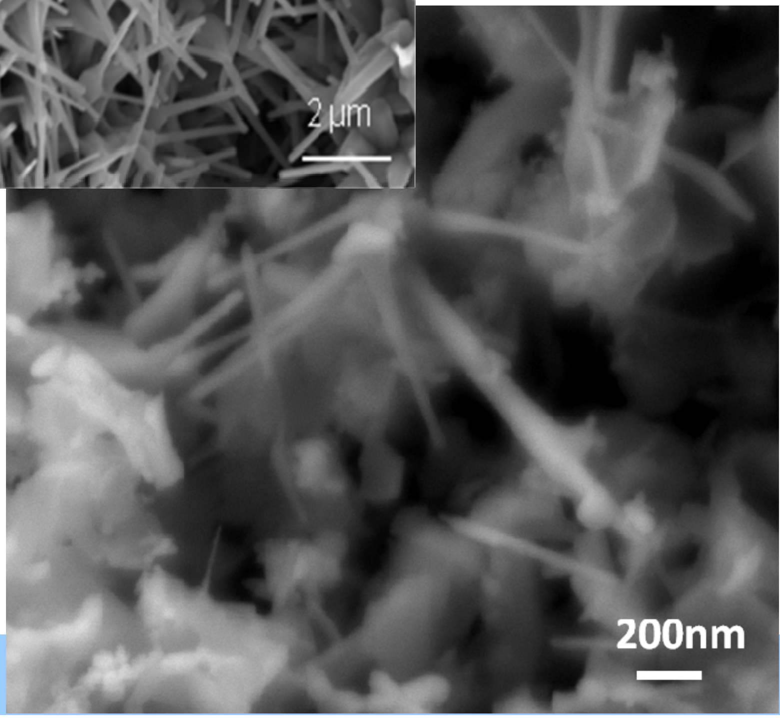


Kumar V et al 2008 J. Phys. Chem. C 112, 17750-17754.
Kim JH et al MK 2008 Informacije Midem 38, 237-243.

3. Plasma flight-thru

ZnO Nanowires

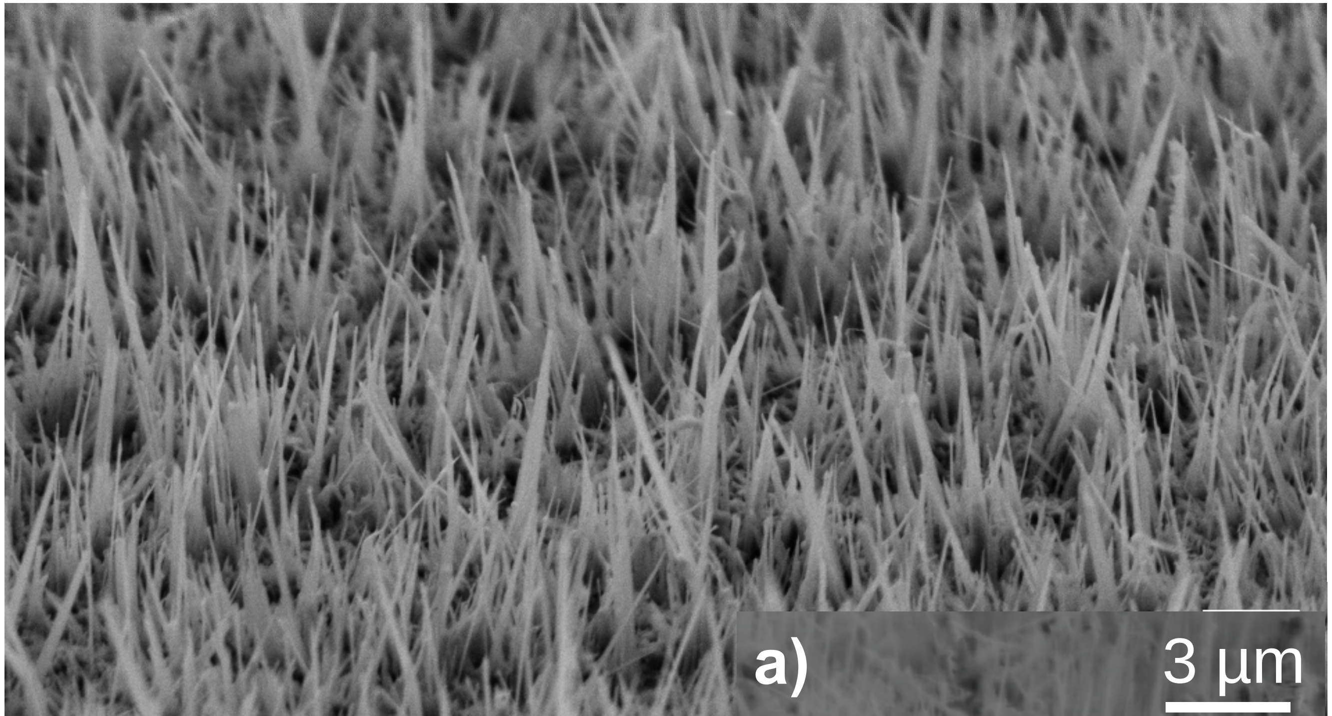


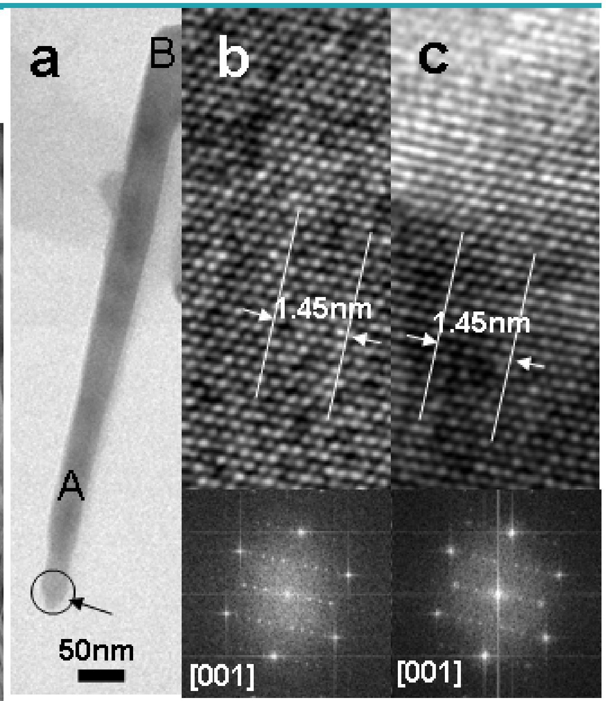


αFe_2O_3 Nanowires

4. Direct plasma growth

αFe2O3 Nanowires



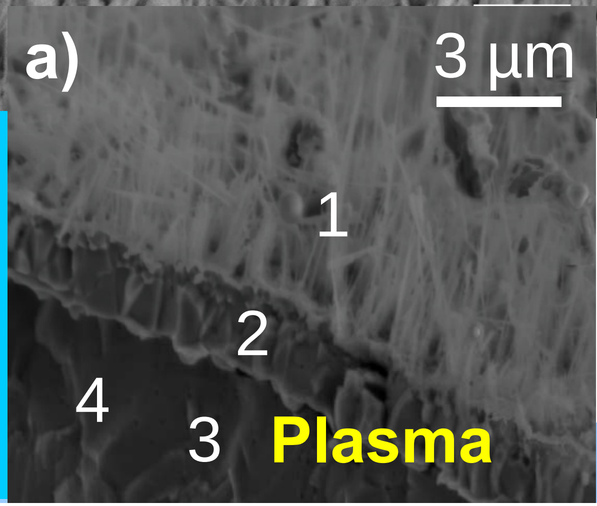


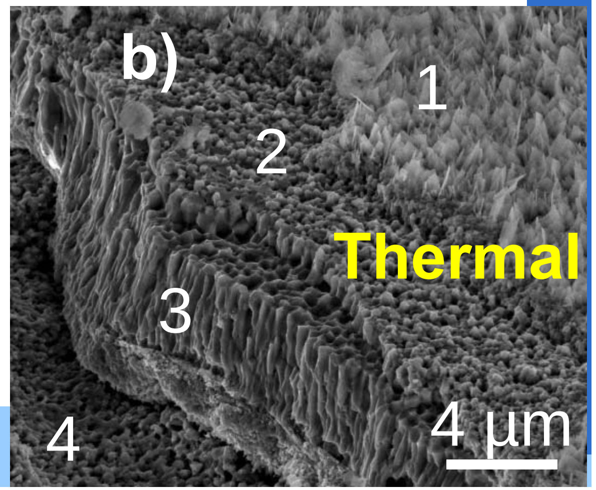
Chen, Cvelbar, Mozetic, Sunkara *Chem. Mater.* (2008) pp 00288y

Cvelbar, Chen, Sunkara, Mozetic, 2008 Small 4, 1610-1614

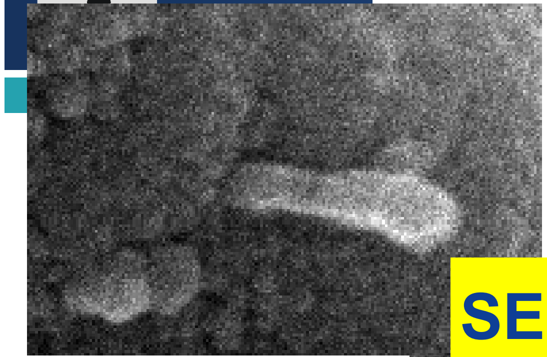
Cvelbar U and Ostrikov K 2008 Cryst. Growth Des. 8, 4347-4349

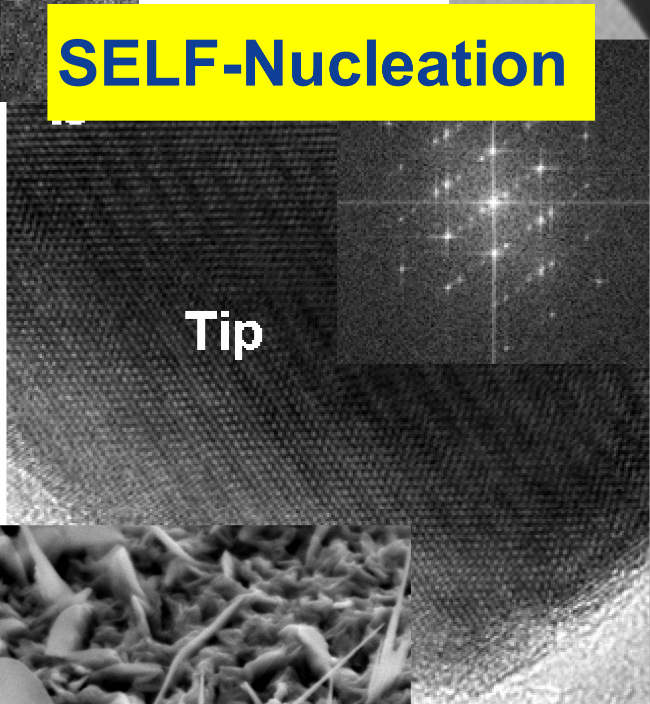
Ostrikov K, Levchenko I, Cvelbar U, Mozetic M and Sunkara MK 2010 Nanoscale 2, 2012-2027

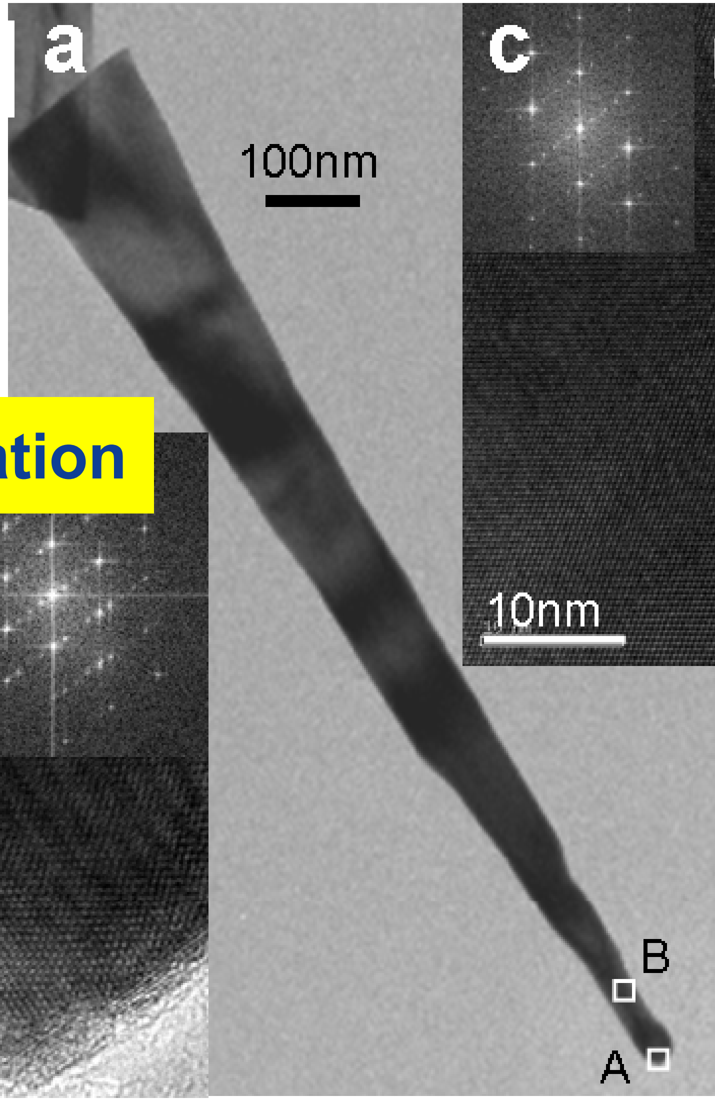


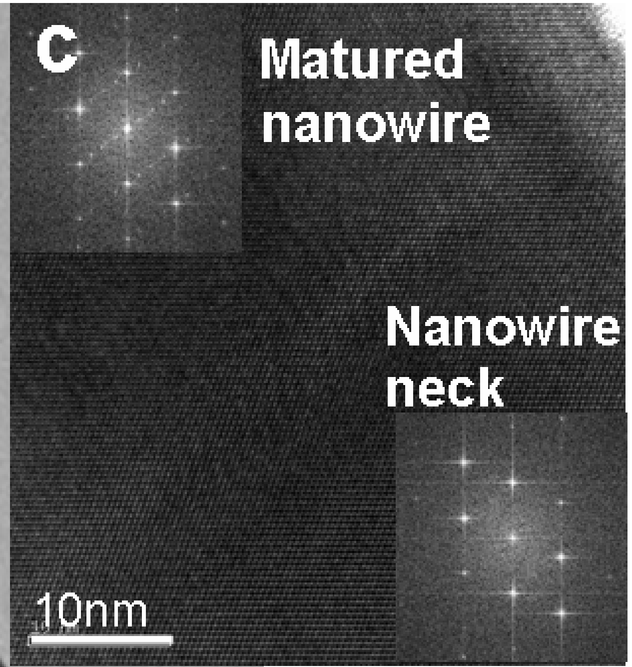


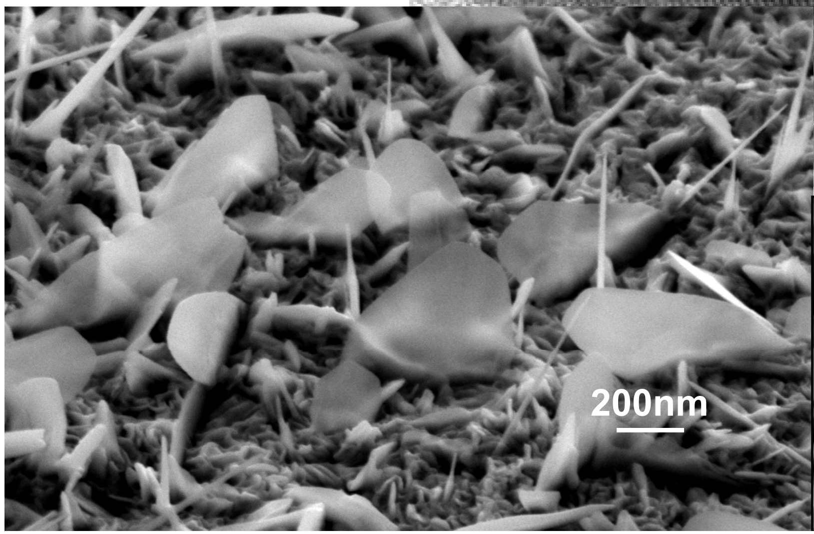
4. Direct plasma growth











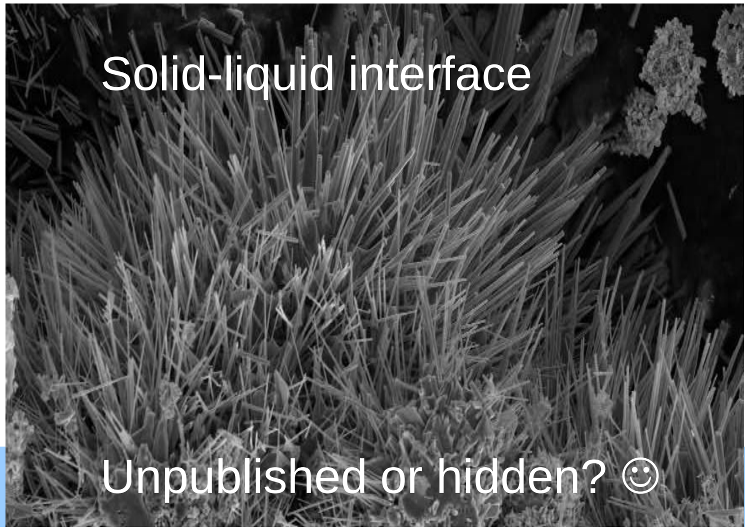
4. Direct plasma growth

ZnO Nanowires

Sunkara

Solid-solid interface

Cvelbar



5. Mixed plasma routes

Plasma-catalyst assisted + flight-thru

Plasma-catalyst assisted + flight-thru + PECVD

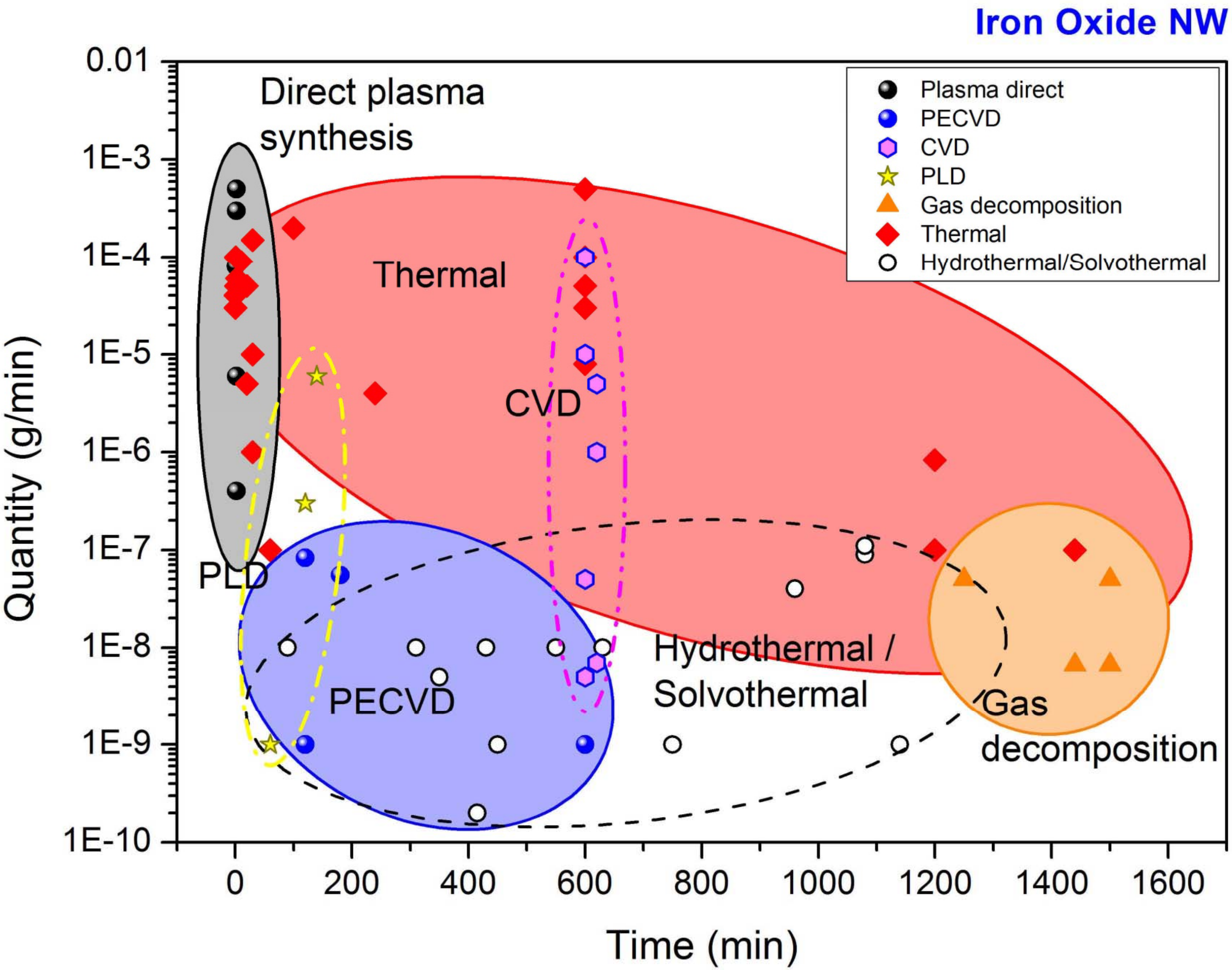
?

Iron oxides

?

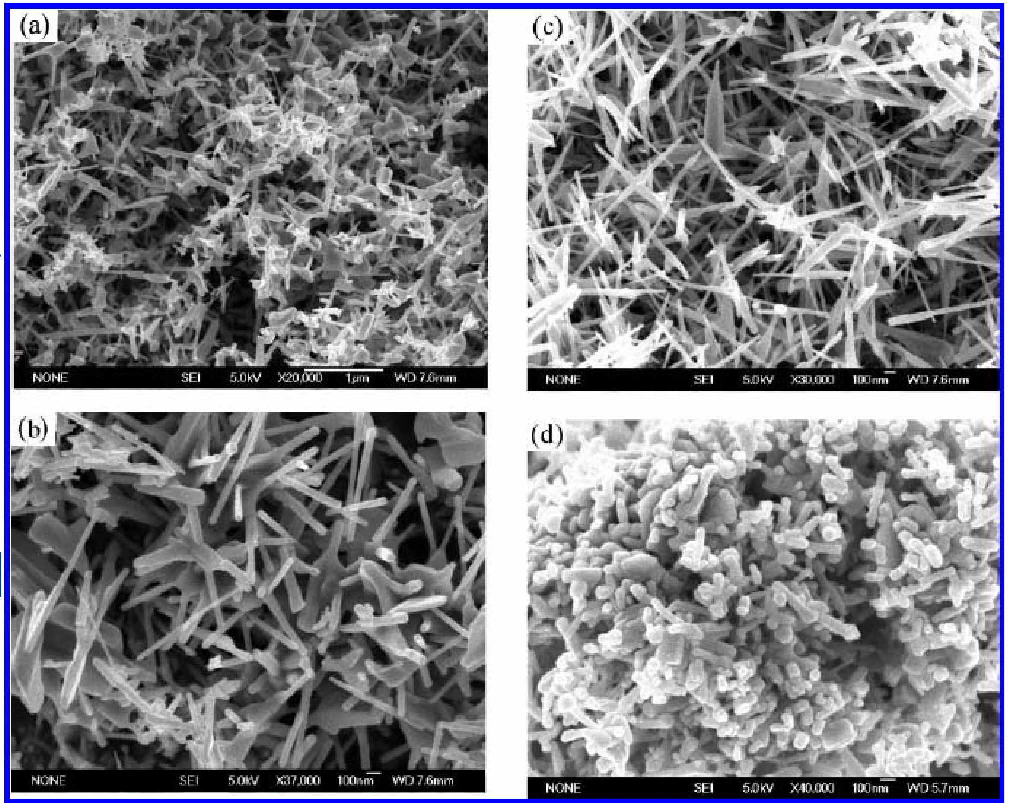
ZnO NW

Time vs. Quantity (Fe oxide)



Time vs. Quantity (ZnO)

1. PECVD
10^{-9} – 10^{-4} g/min



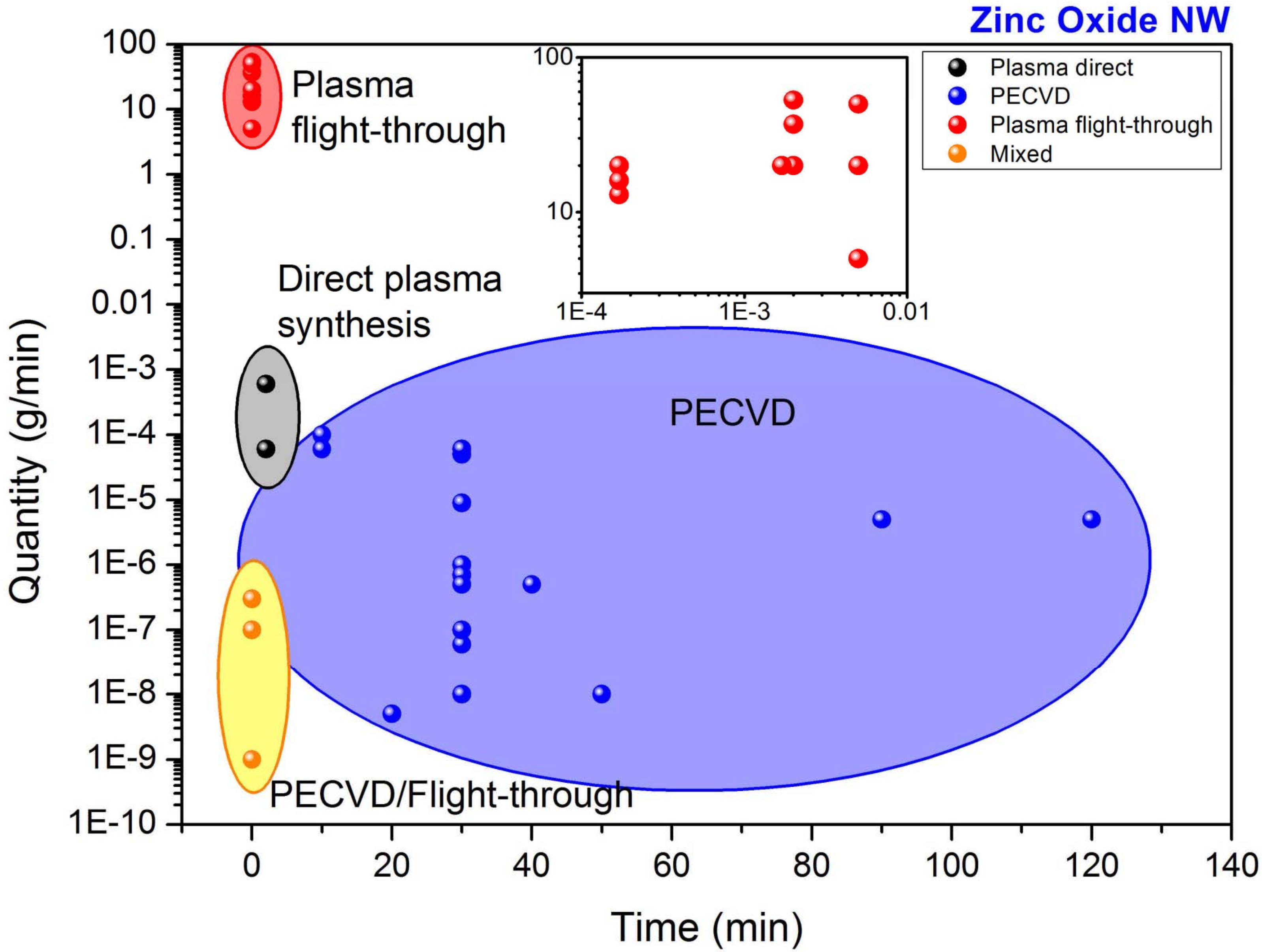
3. Plasma flight-thru

DC → **13 – 20 g/min**
(Mat.Sci. Eng. B 134(2006)

RF → **20 g/min**, ratio l/d=14 [optimal]
37 g/min, ratio l/d=8
53 g/min, ratio l/d=2
(J. Phys. Chem. C 111(2007)

MW → **5g/min**, ration l/d=20 (J.Phys.Chem C (2008))
<20g/min (Midem Info 2008)

Time vs. Quantity (Zn oxide)

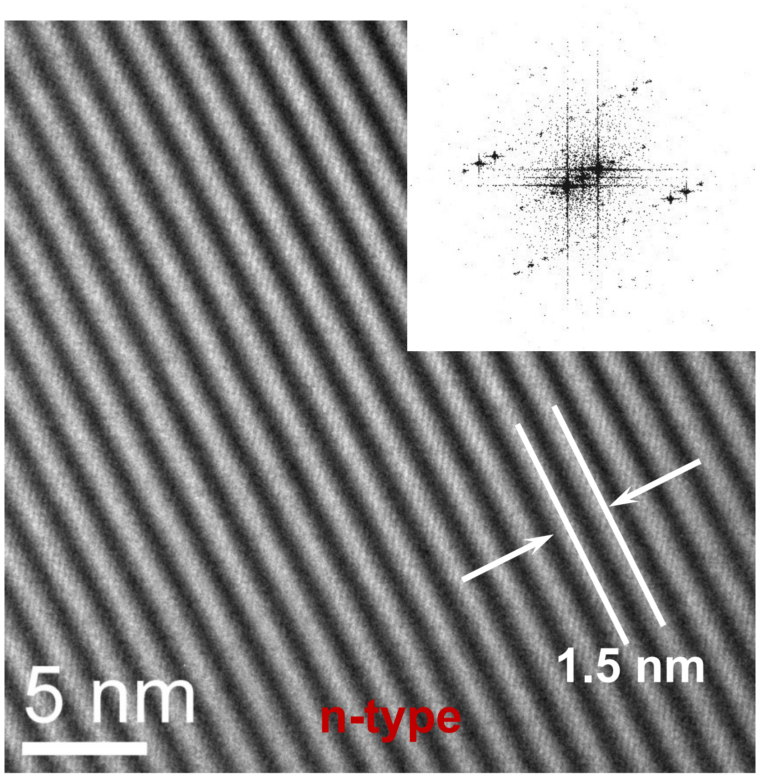


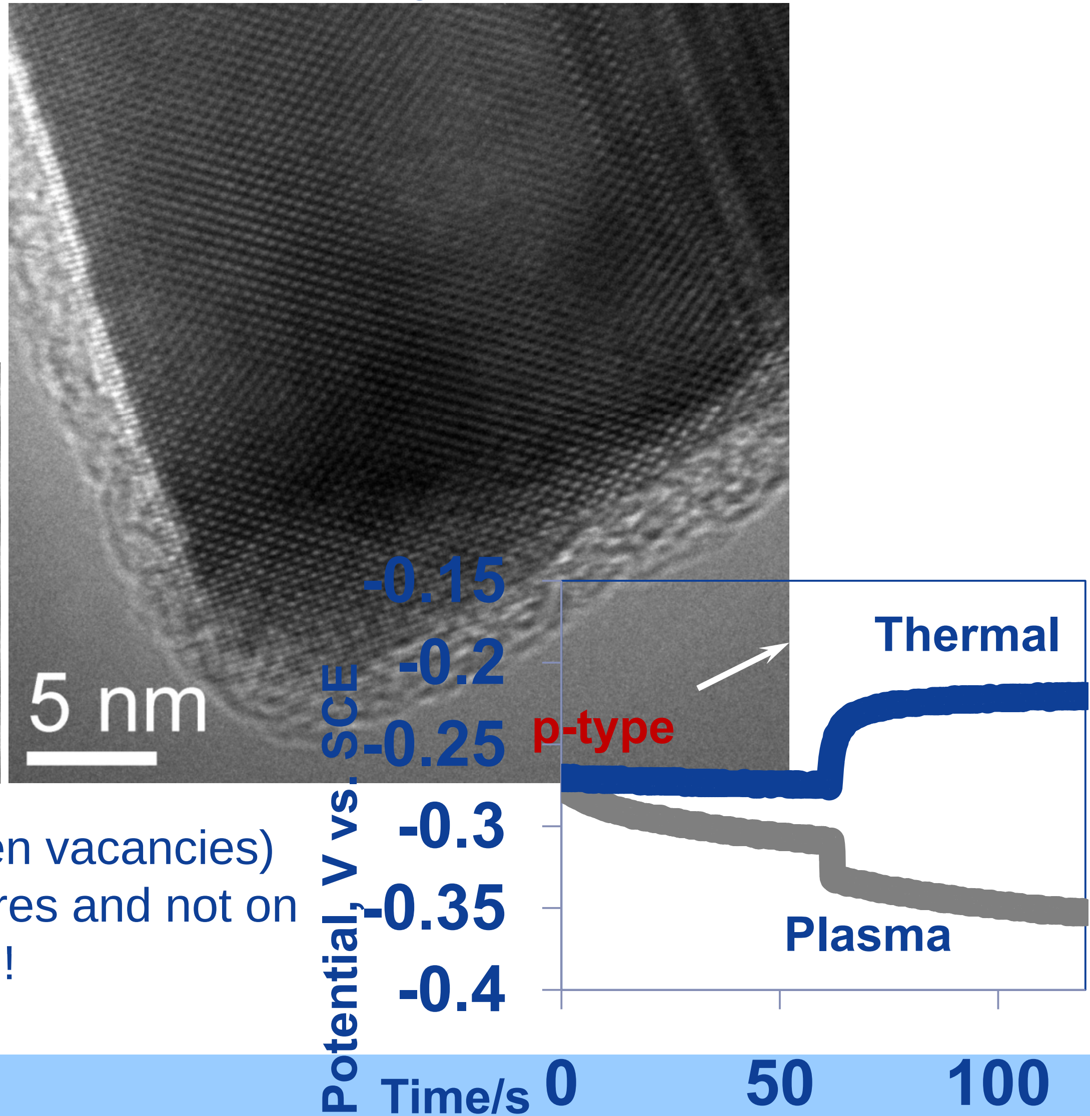
Quality

- Advanced properties of NW
- “Pure” structures / no impurities (in most cases)
- Dimensions, shapes, ratio l/d
- Process control

Advantages of plasma nanostructures

Why is plasma so important for nanostructure or NW growth? - **SUPERSTRUCTURE**





Superstuctured lattices (1/10 oxygen vacancies) grow only on plasma synthesize wires and not on thermal synthesized ones (furnace)!

Prespectives & pros-cons

1. PECVD

1. Polycrystalline / crystalline NW
2. Aligned array growth is difficult to achieve
3. NW growth on substrate depends on the substrate
4. Multiple step procedures
5. Low energy efficiency per synthesized NW

2. Plasma –catalyst assisted

1. Impure NW
2. Multiple step procedures
3. High temperatures needed for dissolvation of metal into catalyst for NW growth (e.g. 925C for Zn vapor dissolved into Au catalyst)
4. High energy consumption / low energy efficiency per synthesized NW
5. Growth limited by supplied catalyst

3. Plasma flight-thru

1. Single-crystalline NW
2. High amount of NW yield
3. Particles mixed with NW – post-purification needed
4. Difficult to control NW shape and ratio length/diameter
5. Difficult to control morphology
6. Synthesis smaller than second
7. Influence of reactor size to feed and efficiency of conversion/syntheis
8. Single-step procedure
9. Good energy efficiency per synthesized NW

4. Direct plasma synthesis

1. Single-crystalline NW
2. Medium amount of NW yield
3. No purification needed
4. Good control of NW shape and ratio length/diameter
5. Difficult to control nucleation
6. Nucleation determines the number of NW
7. Difficult to control aligment of NW
8. Synthesis in order of seconds to minutes
9. Single-step procedure
10. Medium energy efficiency per synthesized NW