NTNU

Norwegian University of Science and Technology

TMT4320 Nanomaterials
November 2nd, 2016

- TNN-Chapter 6-Nanowire fabrication, ZnO and TiO_2 nanoparticles

Wikipedia

Nanowire fabrication

Few methods of nanowire fabrication:

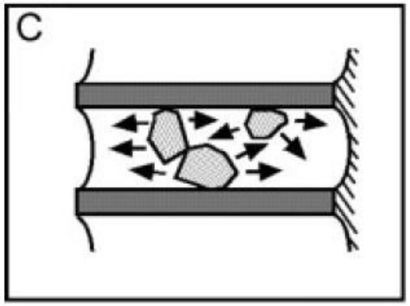
- Template assisted synthesis
- Electrochemical deposition
- High-pressure injection
- Chemical vapour deposition
- Laser assisted techniques
- VLS method

Nanowire fabrication

Few methods of nanowire fabrication:

- Template assisted synthesis
- VLS method

4. Template-directed synthesis

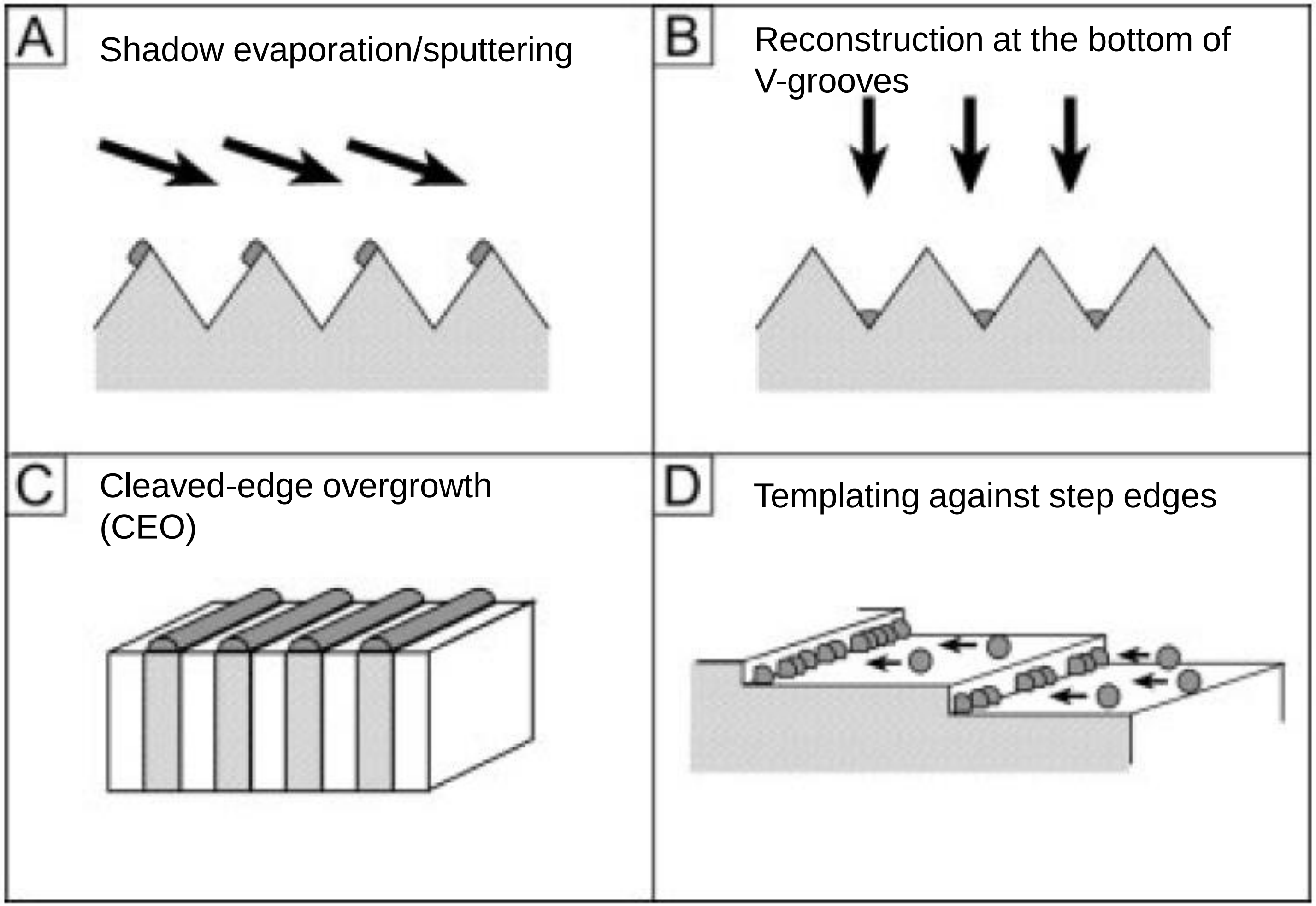


- The template serves as a skeleton or frame. Different materials can be generated within (or around) with shapes that are complementary to that of the template
- Templates:
  - Step edges present on the surfaces of a solid substrate
  - Channels within a porous material
  - Mesoscale structures self-assembled from organic surfactants or block co-polymers
  - Biological macromolecules such as DNA strains or rod-shaped viruses
  - Existing nanostructures synthesized using other approaches

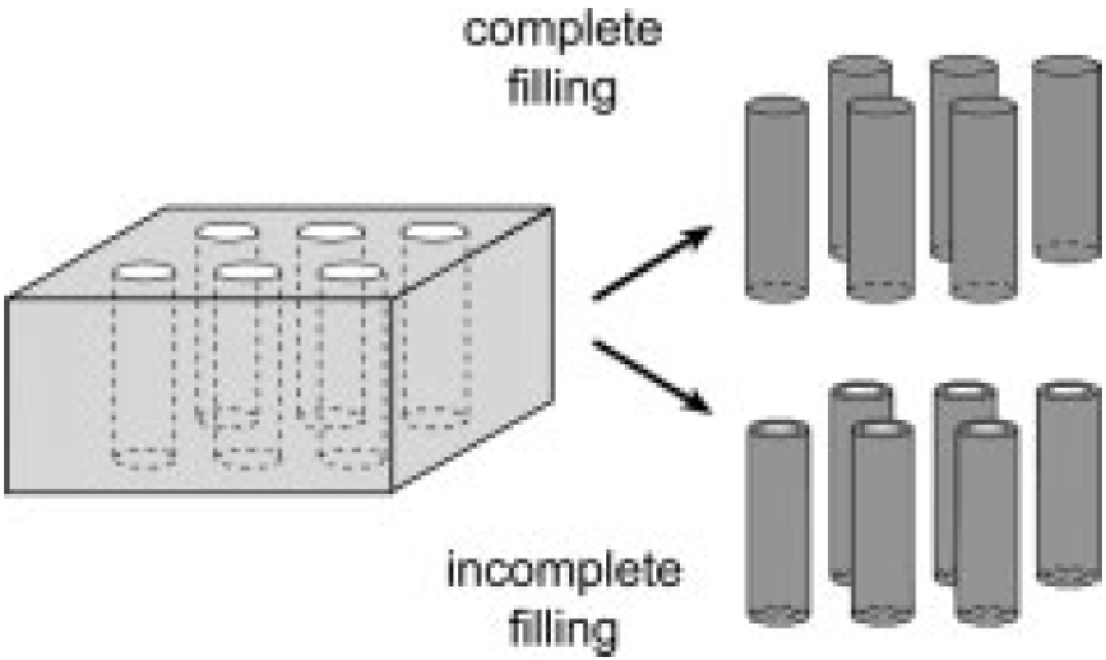
Benefits and limitations of templates

- Often necessary to selectively remove the template using post-synthesis treatment
  - Chemical etching
  - Calcination
- Produced nanostructures are often polycrystalline
- Low quantities for each run of synthesis
- Benefits include:
  - Simple method
  - High throughput
  - Cost-effective
  - Allows the complex topology of the surface of a template to be duplicated in a single step

Templating against features on solid substrates



Channels in porous materials



Types of porous membranes

- Polymer films with track-etched channels
  - Film is irradiated with heavy ions → damaged spots in the surface
  - Amplify spots through chemical etching → uniform, cylindrical pores penetrating the membrane film
  - Randomly scattered pores

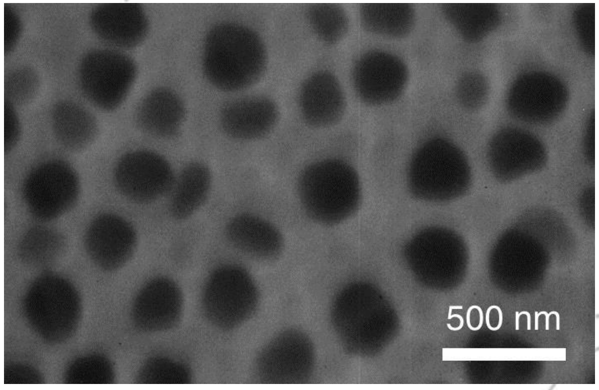
- Alumina films with anodically etched channels
  - Anodization of aluminium foils in acidic medium
  - Hexagonally packed 2D array of cylindrical pores with uniform size
  - Little or no tilting of pores
  - Higher pore density than in track-etched polymer films

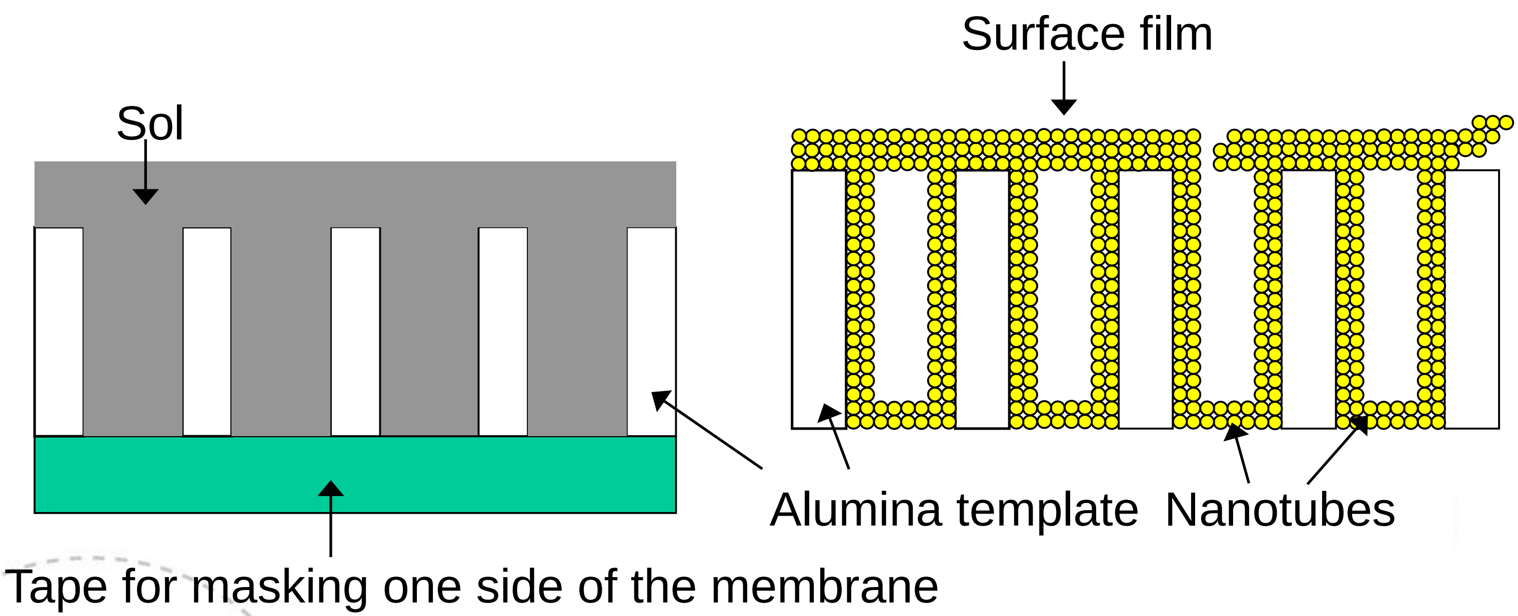
- Mesoporous materials
  - Smaller 1D channels (1.5 - 30 nm in diameter)

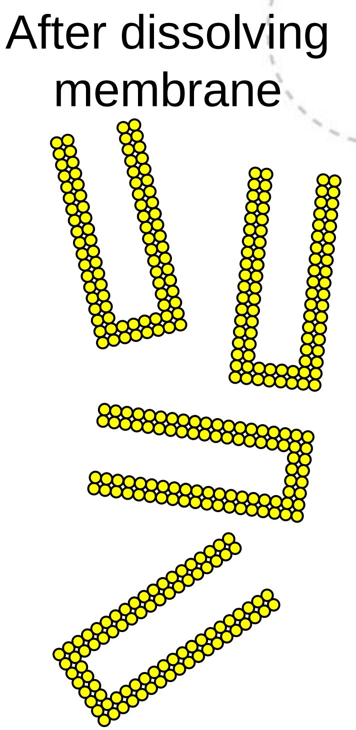
- Variety of materials produced:
  - Metals
  - Semiconductors
  - Ceramics
  - Organic polymers
- Filling of pores:
  - Vapor-phase sputtering
  - Liquid-phase injection
  - Solution-phase chemical or electrochemical deposition
- Crystallization by drying or annealing
- Removal of templates:
  - Etching of alumina membranes by NaOH solution
  - Polymer membranes are burned off at high temperatures

NTNU research: $PbTiO_3$ nanotubes

- Porous Al_2O_3 membranes as template
  - Commercial Whatman Anodisc membranes
  - Precursors: lead acetate and titanium tetrabutoxidel
  - Infiltration of Pb-Ti sol
  - Heat treated at 700 °C

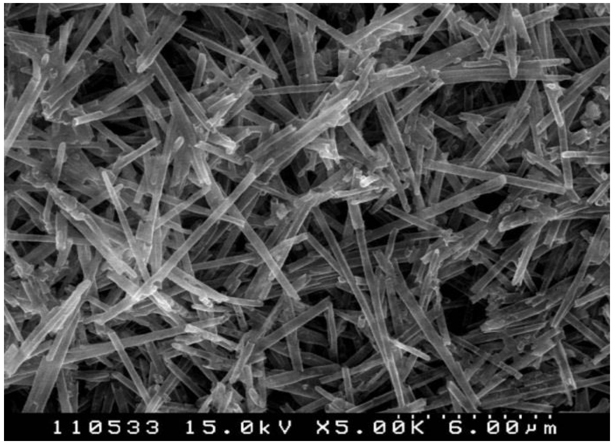




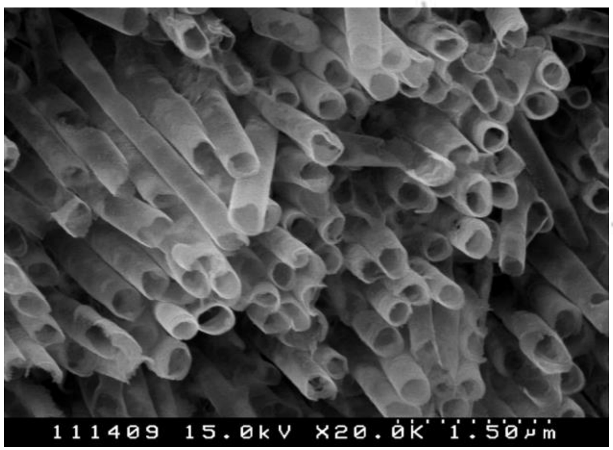


Rørvik *et al.*, *J. Eur. Ceram. Soc.*, 2009

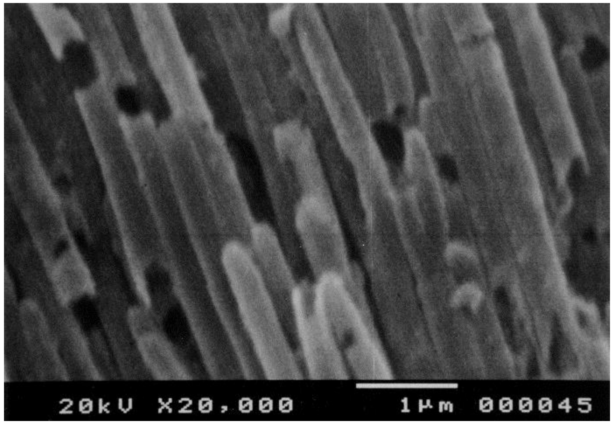
Morphology of nanotubes



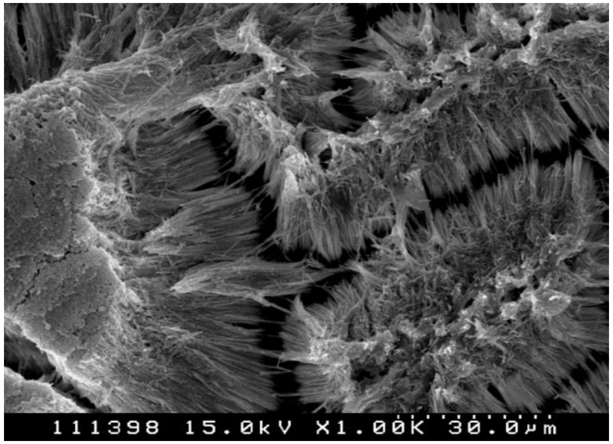
Individual nanotubes after sonication



Nanotube ends – diameters 200-400 nm



Side view revealing growth inhomogeneities

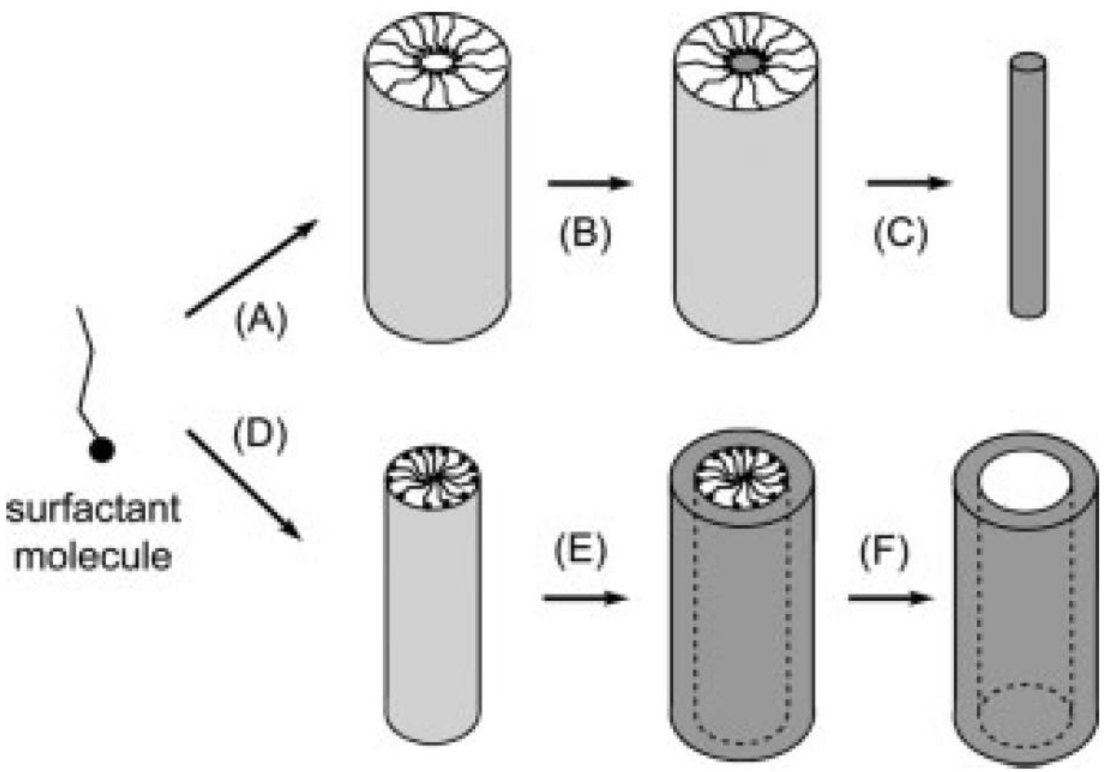


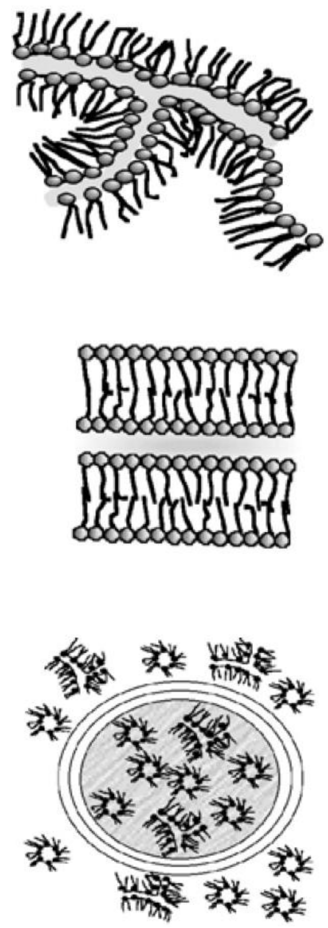
The nanotubes bundle during drying

Rørvik *et al.*, *J. Eur. Ceram. Soc.*, 2009

Templating against self-assembled molecular structures

- Mesophase structures self-assembled from surfactants





Templating against existing nanostructures

- Especially useful for materials which are difficult to synthesize directly
- Can make more advanced nanostructures
  - Core-shell nanowires
- Formation of a shell around an existing nanowire
  - Selective removal of the core will produce a nanotube
- Chemical transformation of a nanowire of a material into a nanowire of a different material
  - Metal → metal oxide
  - Use carbon nanotubes to form metal carbides
  - Galvanic displacement reactions

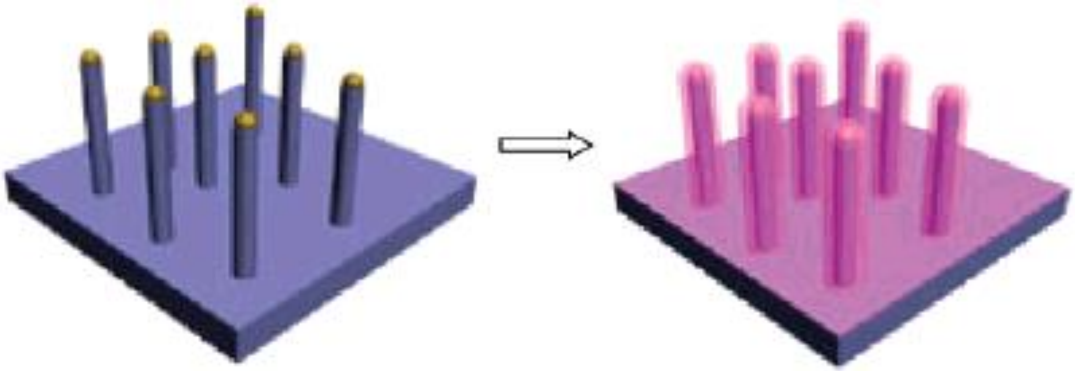
Chemical transformation of template

- Some nanostructures can be converted to other materials without changing their morphology when they react with appropriate reagents under carefully controlled conditions

- Example 1
  - Thermal oxidation of silicon nanostructures
  - Silicon can be transformed into various silicon oxides
- Example 2
  - Boron nanowires have been used as templates to form highly crystalline MgB_2 nanowires

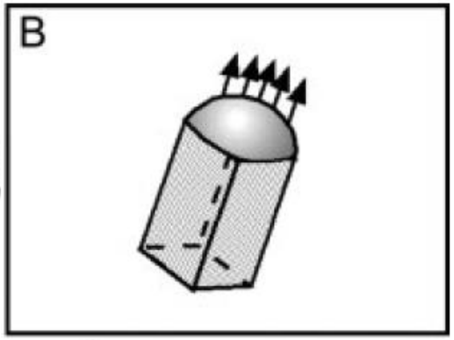
Simplifying complex nanowires

- Complex oxides with superconducting, ferroelectric, and ferromagnetic properties can not easily be made as nanowires by “conventional” methods
- Solution → use single crystal MgO (or similar material) nanowires as templates
- Example: $La_{0.67}Ca_{0.33}MnO_3$ (the metal-insulator transition and giant magnetoresistance properties were retained at the nm scale)



S. Han *et al.*, *Nano Lett.*, 2004

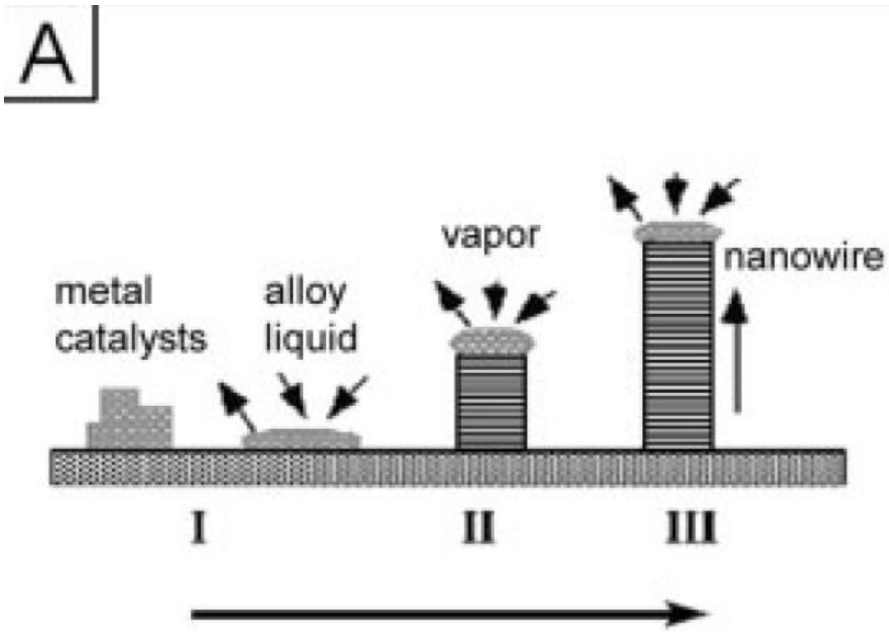
5. Generic methods suitable for all solid materials: VLS and related growth

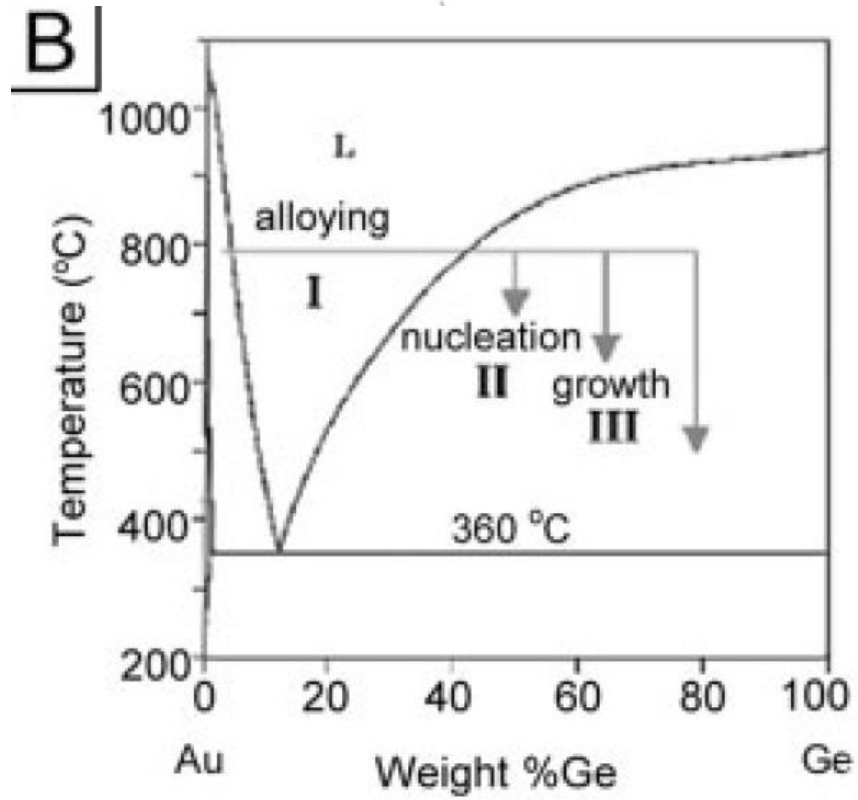


- Vapor-solid growth (VS)
  - Much studied
  - Heating powders and collecting 1D nanostructures in a colder region of the reaction chamber
  - Not fully understood mechanism (may involve intermediate phases)
  - Typically oxide semiconductors
- Vapor-liquid-solid growth (VLS)
- Solution-liquid-solid growth (SLS)

VLS growth

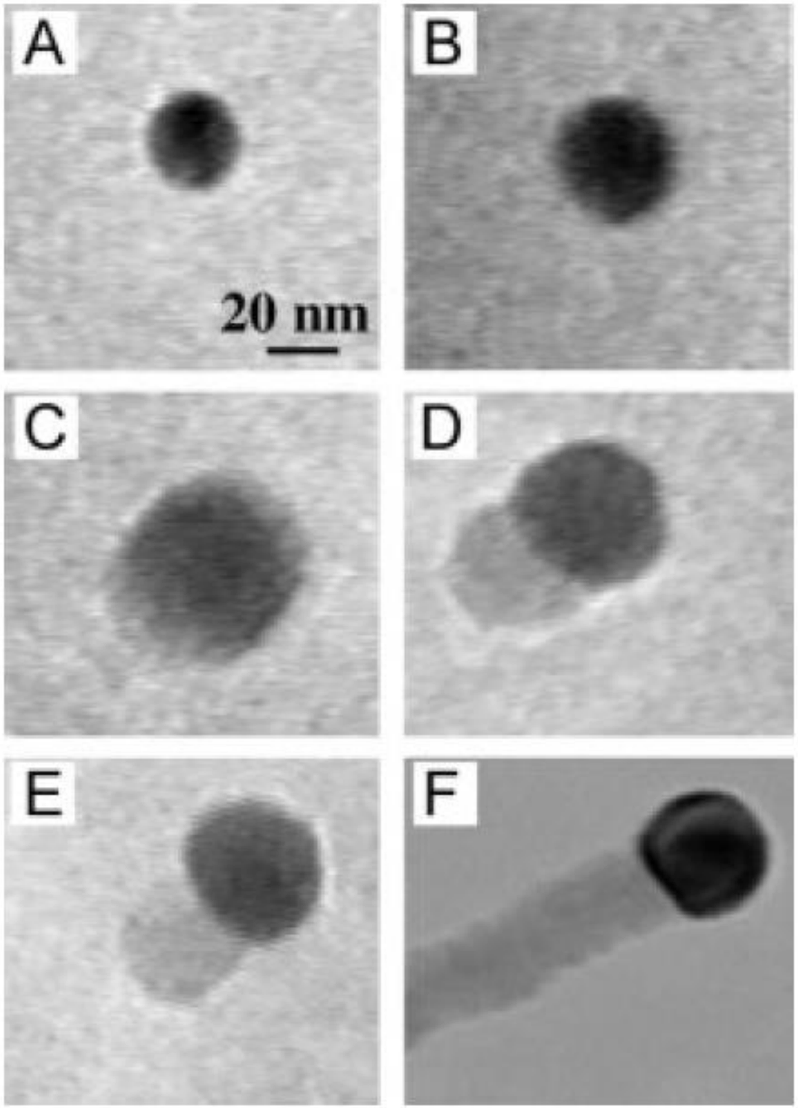
- VLS process:
  - Dissolution of gaseous reactants into nanosized liquid droplets of a catalyst metal
  - Nucleation and growth of single-crystalline rods and wires
- 1D growth is induced and dictated by the liquid droplets
  - Sized of droplet remain essentially unchanged during the entire process of wire growth
  - Each liquid droplet serves as a soft template to strictly limit the lateral growth of an individual wire
- Major requirement:
  - There should exist a good solvent capable of forming liquid alloy with the target material





The binary phase diagram between Au and Ge

- Ge nanorods
  - GeI_2 as vapour source
  - Au as catalyst
  - In situ TEM



- Examples of 1D nanostructured materials produced using the VLS:
  - Elemental semiconducors (Si, Ge, and B)
  - III-V semiconductors (GaN, GaAs, GaP, InP, InAs)
  - II-VI semiconductors (ZnS, ZnSe, CdS, CdSe), and
  - Binary oxides (ZnO, MgO, SiO_2)

- Main challenge in the VLS process:
  - Selection of catalyst that will work with the solid material to be processed into 1D nanostructures

- It seems to be impossible to apply the VLS method to metals and ternary oxides

ZnO nanoparticles

Adequate optical and electrical properties (wide band gap (3.3 eV) and large excitation binding energy (60 meV)) → semiconducting, piezoelectric, and optoelectronic devices → high temperature and hostile environments

ZnO advantage over GaN for various applications such as thin film transistors which need to be protected from light exposure → ZnO overcomes this problem because it is insensitive to visible light → Transparent electrodes

ZnO nanoparticles

Crystal structure and properties of ZnO

ZnO exists over a range of crystal structures: hexagonal (wurtzite), zinc blende and rocksalt.

Wurtzite thermodynamically stable at ambient conditions.

High pressures stabilize cubic rocksalt structure whereas zinc blende stabilizes when it is grown on cubic structures.

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ZnO nanoparticles

Synthesis of bulk-structures and nanostructure

BULK SINGLE CRYSTAL GROWTH

Lower supertaruation favours *hydrothermal reaction* → ZnO seeds and sintered ZnO together in aqueous solution of KOH and LiOH at 300–400°C and 70–100 MPa in a platinum crucible placed inside a two-zone vertical furnace.

Melt growth. Melt the ZnO in the crucible and after it is taken out to allow to crystallize.

ZnO nanoparticles

Synthesis of bulk-structures and nanostructure

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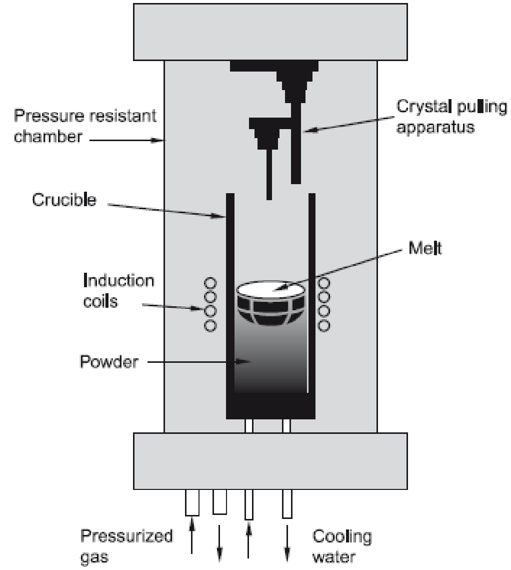

Fig. 6.15 Schematic diagram of the melt growth system.

ZnO nanoparticles

Synthesis of bulk-structures and nanostructure

BULK SINGLE CRYSTAL GROWTH

Thin films. Transparent electrodes in new-generation opto-electronic devices.

Techniques such as pulsed laser deposition, RF (radio frequency) magnetron sputtering, chemical vapour deposition and molecular beam epitaxy.

Magnetron sputtering. DC, RF and reactive sputtering. Low temperatures and cost.

ZnO nanoparticles

Synthesis of bulk-structures and nanostructure

MOLECULAR BEAM EPITAXY

ZnO thin films by evaporating highly pure Zn metal from an effusion cell in oxygen plasma generated by and RF/ECR source. Good control on the deposition conditions.

PULSED LASER DEPOSITION (PLD)

Grow ZnO thin films by ablating a highly pure ZnO target in the presence of O_2 gas. Advantage: preserving stoichiometry and high quality films at lower temperatures

METAL ORGANIC CHEMICAL VAPOUR DEPOSITION (MOCVD)

ZnO nanoparticles

Synthesis of bulk-structures and nanostructure

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Grow ZnO thin films by ablating a highly pure ZnO target in the presence of O_2 gas. Advantage: preserving stoichiometry and high quality films at lower temperatures

METAL ORGANIC CHEMICAL VAPOUR DEPOSITION (MOCVD)

Metal organic precursors ((CH3)2Zn, (C2H5)2Zn) used to deposit thin films. Films with better optical and structural properties with high growth rates.

ZnO nanoparticles

Synthesis of bulk-structures and nanostructure

GROWTH OF ZnO NANOSTRUCTURES

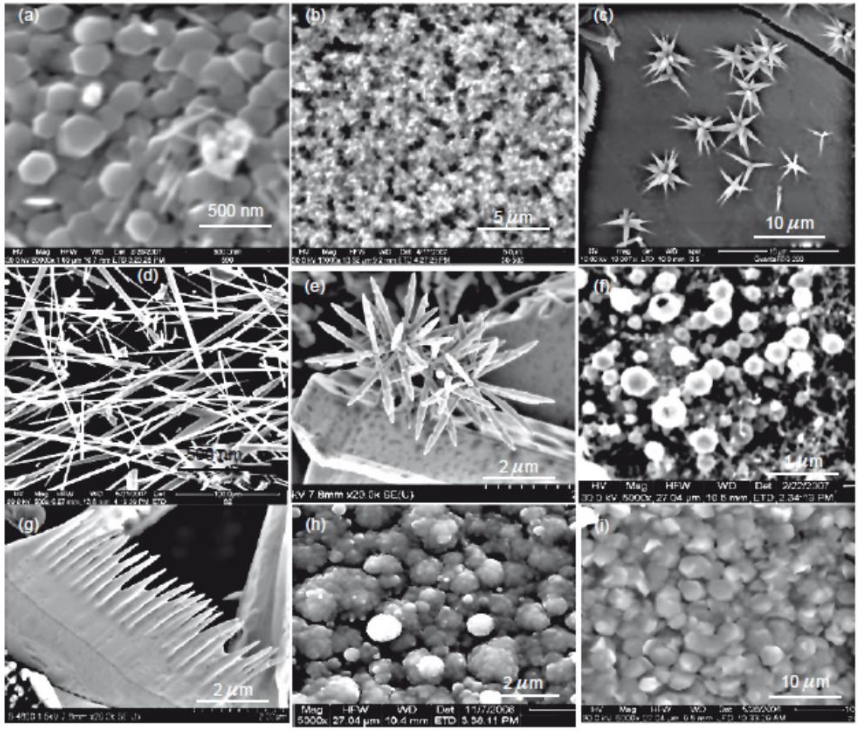

Fig. 6.16 SEM images of ZnO nanostructures synthesized using different techniques. ZnO (a) hexagons, (b) wires and (c) tetrapods by chemical synthesis route (d) ZnO wires, (e) tetrapods, (f) spheres, (g) brush grown by thermal evaporation technique and (h) ZnO spheres and (i) hexagons grown by pulsed laser deposition technique. (*Source:* MS Ramachandra Rao, IIT Madras).

ZnO nanoparticles

Applications of ZnO nanostructures

PIEZOELECTRIC SENSORS

BIOSENSORS

SOLAR CELLS

GAS SENSORS

TiO_2 nanoparticles-Next lecture