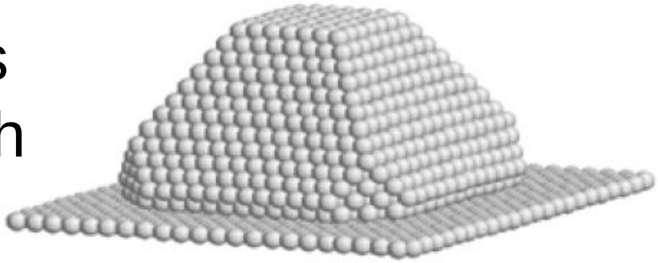
NTNU

Norwegian University of Science and Technology

TMT4320 Nanomaterials
Septemeber 12th, 2016

- Synthesis of nanomaterials
  - NN3. Top-down approach
  - Bottom-up approach
    - Cushing et al. Supercritical fluids



Last lecture

- Physical properties: size effects
  - Magnetic properties
  - Optical properties
  - Thermal properties
  - Mechanical properties
  - Examples
    - $BaTiO_3$
    - Garnets for Li-ion batteries
    - $BaZrO_3$ for PC-FC

Unique properties-Learning objectives

- Defects in nanocrystalline materials
- Effect of grain size on physical properties (melting point, lattice parameter, diffusivity, magnetic, electrical, optical and thermal properties)
- Effect of grain size on mechanical properties (hardness, yield strength, ductility, toughness and creep)
- Grain growth behaviour in nanomaterials

Microstructure and defects

Defects in Crystalline materials

How are defects classified?

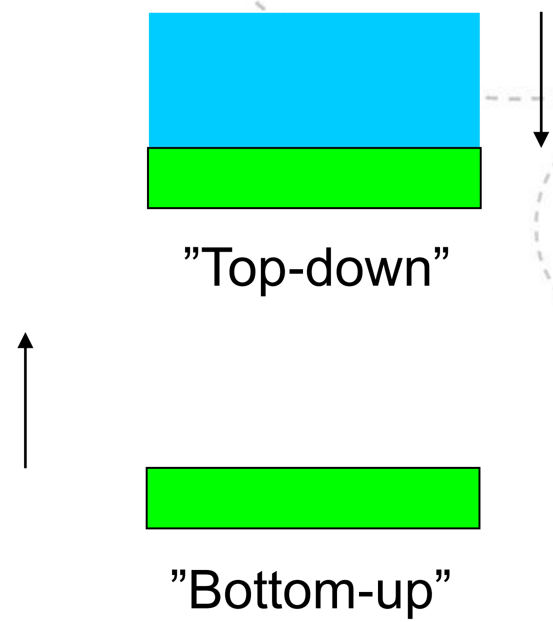
- Point defects (0D)
  - Metal and alloys → Vacancies, substitutional and interstitial
  - Ionic solids → Schottky (anion-cation vacancy pairs) and Frenkel (vacancy-interstitial pairs) defects
- Line defects (1D)
  - Dislocations: missing plane of atoms
- Surface defects (2D)
  - Grain boundaries, twins, stacking faults and free surfaces.
- Volume defects (3D)
  - Voids and microcracks.

Physical properties:size effects

- Fraction of surface atoms (surface energy)
- Lattice constant and melting point
- Diffusivity
- Enhanced solid solubility
- Optical properties
- Thermal properties
- Mechanical properties

Today

- Synthesis of nanomaterials
  - Top-down approach
    - High energy ball milling
    - Nanolithography
  - Bottom-up approach
    - Hydrothermal/Solvothermal: Supercritical fluids
    - Invited guess: Antoine Dalod



Synthesis-Learning objectives

- Different routes for the synthesis of nanoparticles and nanocrystalline materials

  – Bottom-up approach
  – Top-down approach

- Different routes for the consolidation of nanoparticles and nanocrystalline materials

Synthesis of nanomaterials

- Top-down approach
  - A microcrystalline material is fragmented to yield a nanocrystalline material. Ex. Solid state routes.
  - Produce bulk nanostructured materials
  - Be easily scaled up

- Bottom-up approach
  - Individual atoms and molecules are brought together or self-assembled to form nanostructured materials in at least one dimension.
  - Fine nanostructures of individual nanoparticles with narrow size distributions
  - Difficult to scale up

Synthesis of nanomaterials

– Bottom-up approach

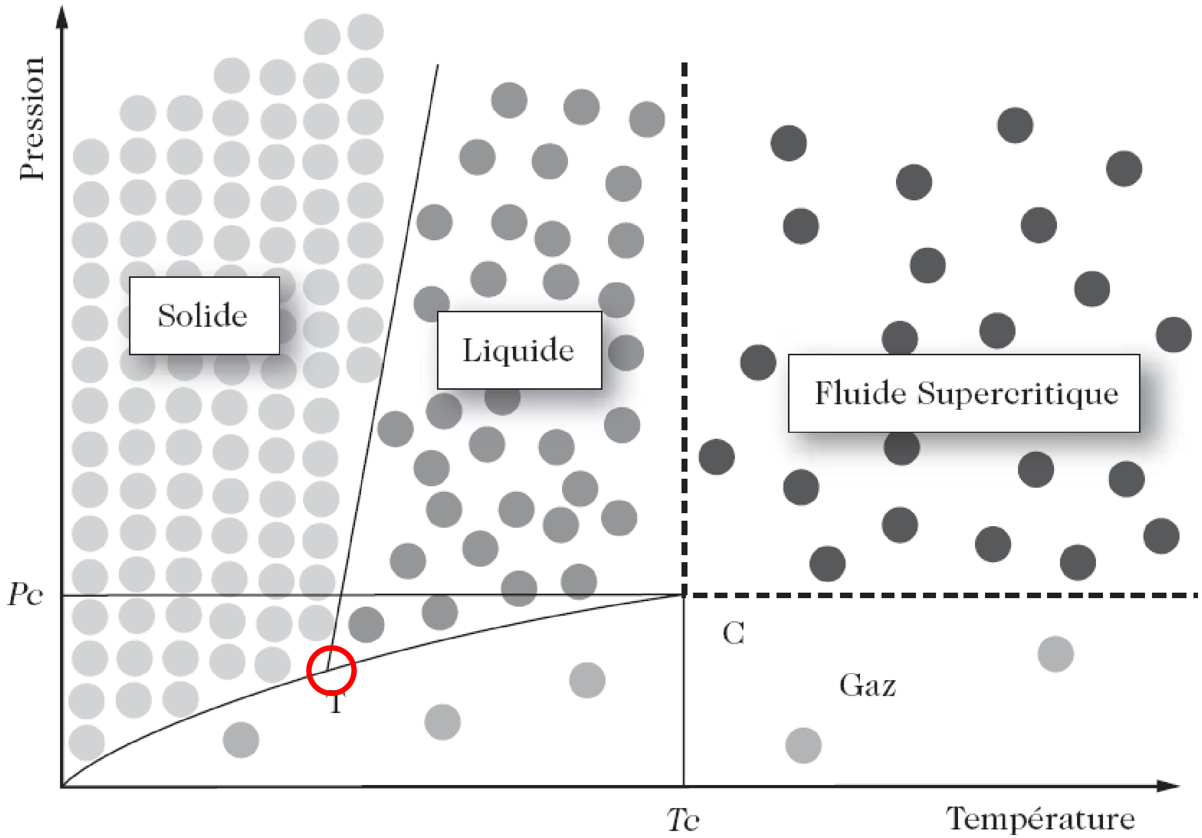
- Supercritical fluids: Hydrothermal/Solvothermal
- Colloidal methods (next day)
- Vapor phase methods (Maria)
- Consolidation of Nanopowders (sintering)

Supercritical fluid

- Intermediate state between liquid and gas
- Critical point
  - End point of the liquid-vapour coexistence curve in a phase diagram
  - Beyond the fluid is both liquid and gas at the same time, i.e., as dense as the liquid while conserving certain properties of the gas
- Temperature/pressure beyond the critical point

- Phase diagram (S, L, G)
  - Triple point
  - Critical point
  - Changes in density

Supercritical fluid (SF)



Pressure vs. temperature phase diagram of a pure substance. T=triple point, C=critical point.

SCF illustration

Table 20.1. Critical coordinates (T_c, P_c) of a few fluids

Compound	T_c [°C]	P_c [bar]	ρ_c [kg/m^3]
CO_2	31.2	73.8	468
NO_2	36.4	72.4	457
NH_3	132.4	112.9	235
H_2O	374.1	22.1	317
C_2H_4	9.5	50.6	220
C_2H_6	32.5	49.1	212
C_3H_8	96.8	42.6	225
C_5H_{12}	196.6	33.7	232
C_6H_{12}	279.9	40.3	270
C_6H_6	289.5	49.2	304
C_7H_8	320.8	40.5	290
CH_4O	240	79.5	275
C_2H_6O	243.1	63.9	280
C_3H_8O	235.6	53.7	274
C_3H_6O	235	47.6	273

Physiochemical properties of SF

- Density
- Solubility
- Viscosity
- Diffusion

Solubility

- What determines the ability of a fluid to solubilize a given substance?
- Dissolving power
  - Depends on the physical and chemical state of the fluid

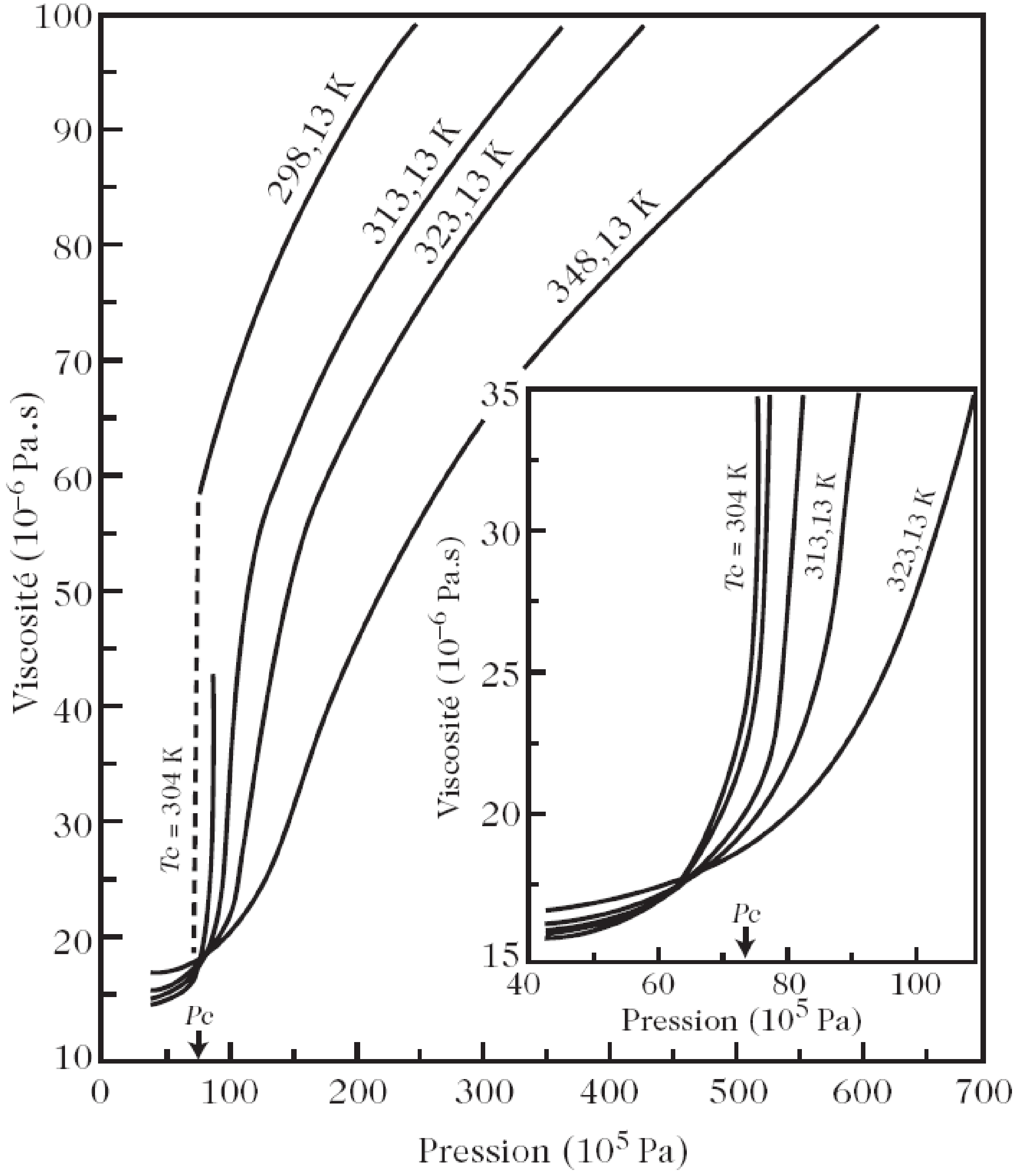
$$\delta_{\mathrm{f}} = 1.25 P_{\mathrm{c}}^{1/2} \frac{\rho(T, P)}{\rho_{\mathrm{liq}}}$$

- where P_c is the pressure of the supercritical fluid, ρ is the density of the fluid in g/ml, and ρ_{liq} is the density of the fluid in the standard liquid state, also in g/ml

Viscosity

- Resistance of fluids to flow
- Reflects the extent to which the molecule is able to move around in an environment containing other molecules
- Supercritical fluid: in the range 10^{-4} to 10^{-3} Pa·s
  - Higher than the value for gases
  - 10 to 100 times lower than the value for liquids
  - The coefficient of diffusion of a solute is higher in a supercritical fluid than in a liquid

- Pressure dependence of the viscosity of CO_2 at different temperatures
- Near the critical point, it can be observed that the viscosity varies rapidly with changes in pressure



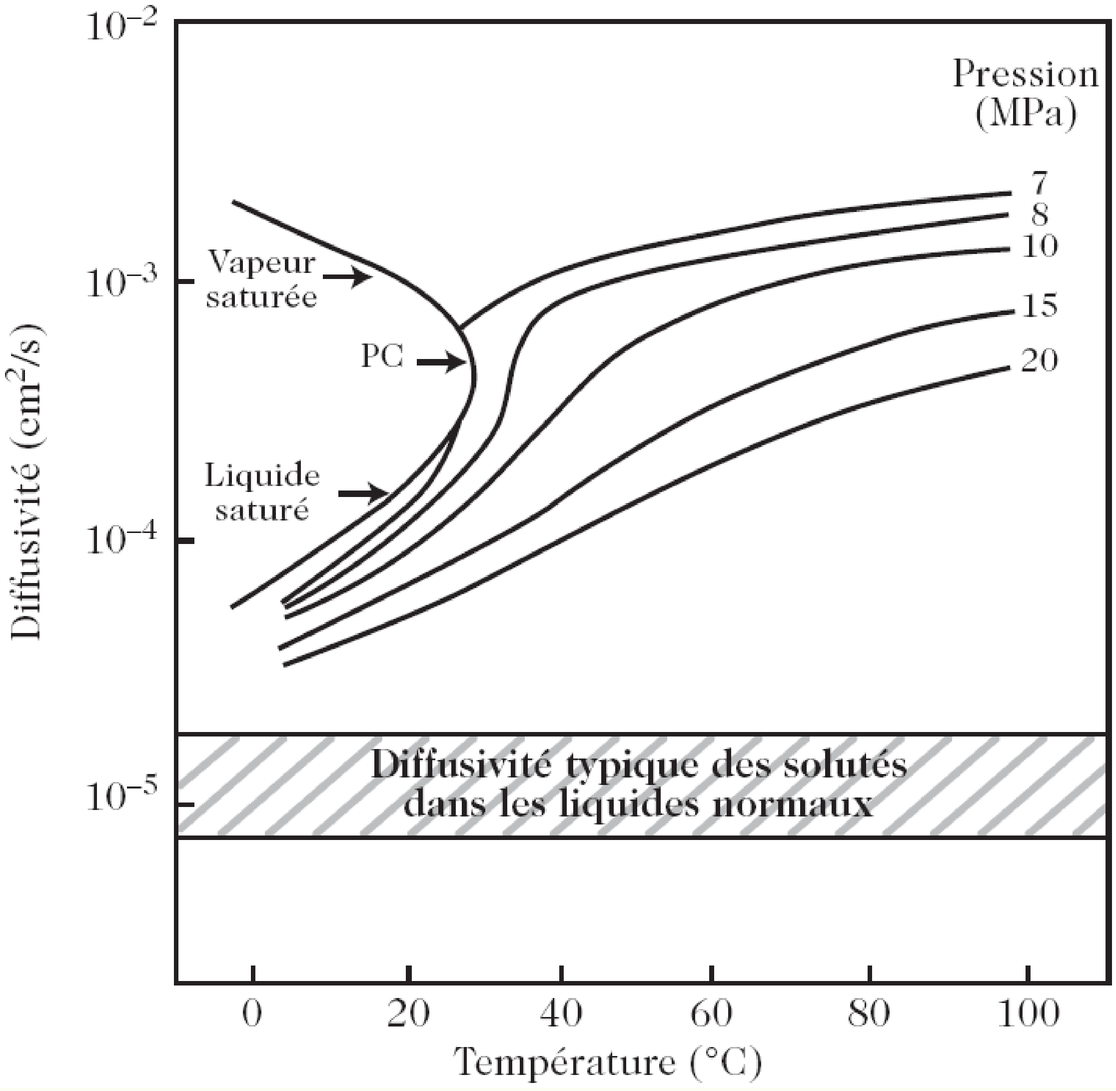
Diffusion

- Higher diffusion in supercritical fluid than in “normal” fluid

Table 20.3. Orders of magnitude of diffusion coefficients in supercritical fluids

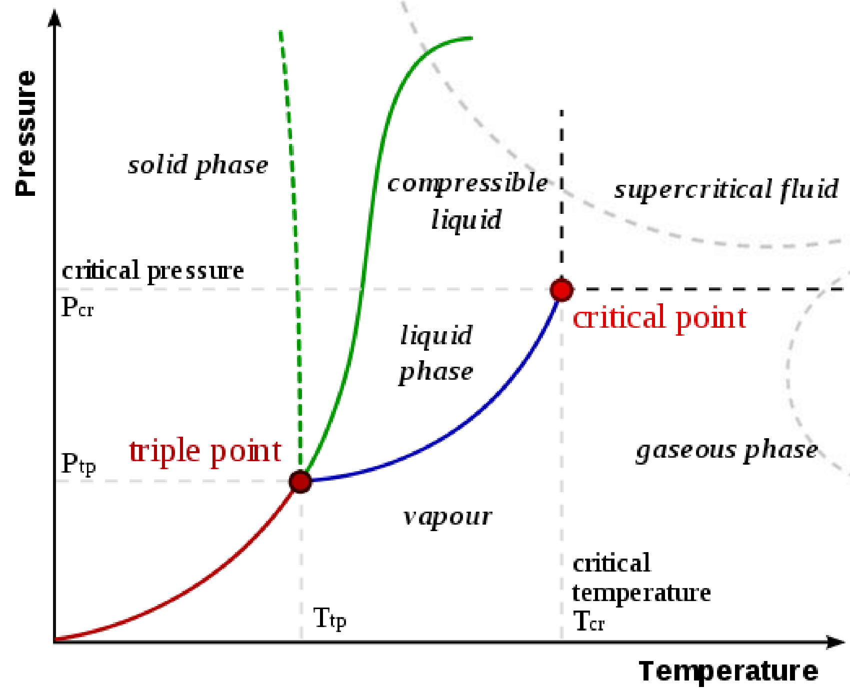
	Gas	Supercritical fluid	Liquid
Diffusion coefficient D [$cm^2 s^{-1}$]	$1–4 \times 10^{-1}$	$10^{-4}–10^{-3}$	$0.2–2 \times 10^{-5}$

- Temperature dependence of the diffusivity at different pressures for a solute in CO_2



Hydrothermal synthesis

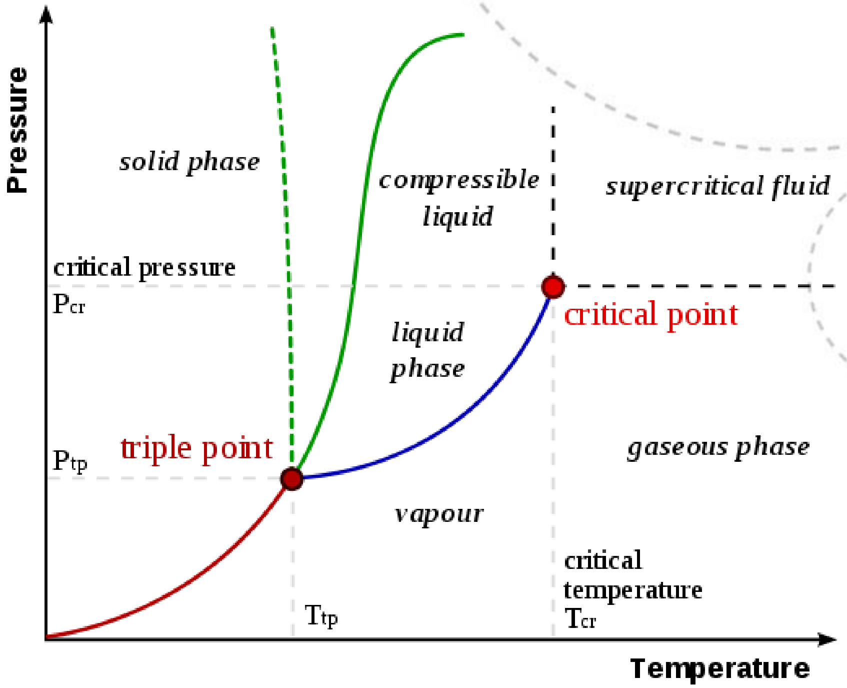
- A product is crystallized in aqueous environment at temperatures above 100 °C and at pressures from 1-200 bar, approaching the supercritical fluid stage.
- Advantages
  - Increased solubility with temperature and pressure.
  - Enables synthesis of materials that are unstable at higher temperatures.
  - Can control phase, particle shape and particle size.



Other solvents than water
→ solvothermal synthesis

Hydrothermal/solvothermal processing

- Approaches supercritical conditions
- Reaction takes place in a sealed vessel (bomb, autoclave, etc.)
  - Temperature well above boiling point of liquid
- Solvothermal processing → non-aqueous solvent
- Hydrothermal processing → water as solvent



Advantages and disadvantages

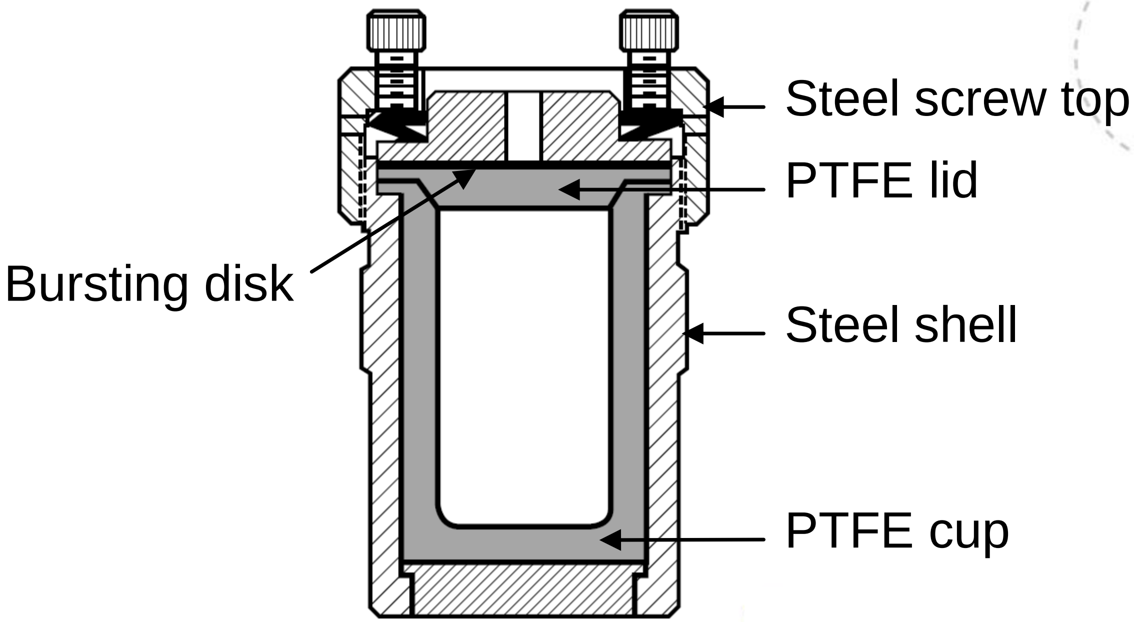
☺ • Temperatures are substantially lower than those required for traditional solid-state reactions

☺ • Products of solvothermal reactions are usually crystalline and do not require post-annealing treatments

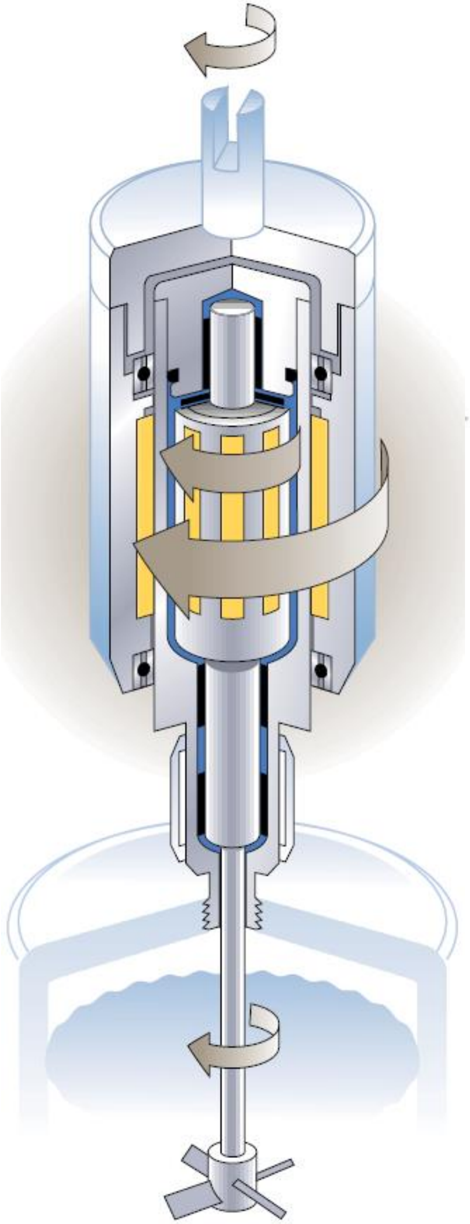
☺ • Many types of materials can be made

☹ • Safety issues
  - High pressures
  - Don’t open hot reaction vessels!

Autoclaves

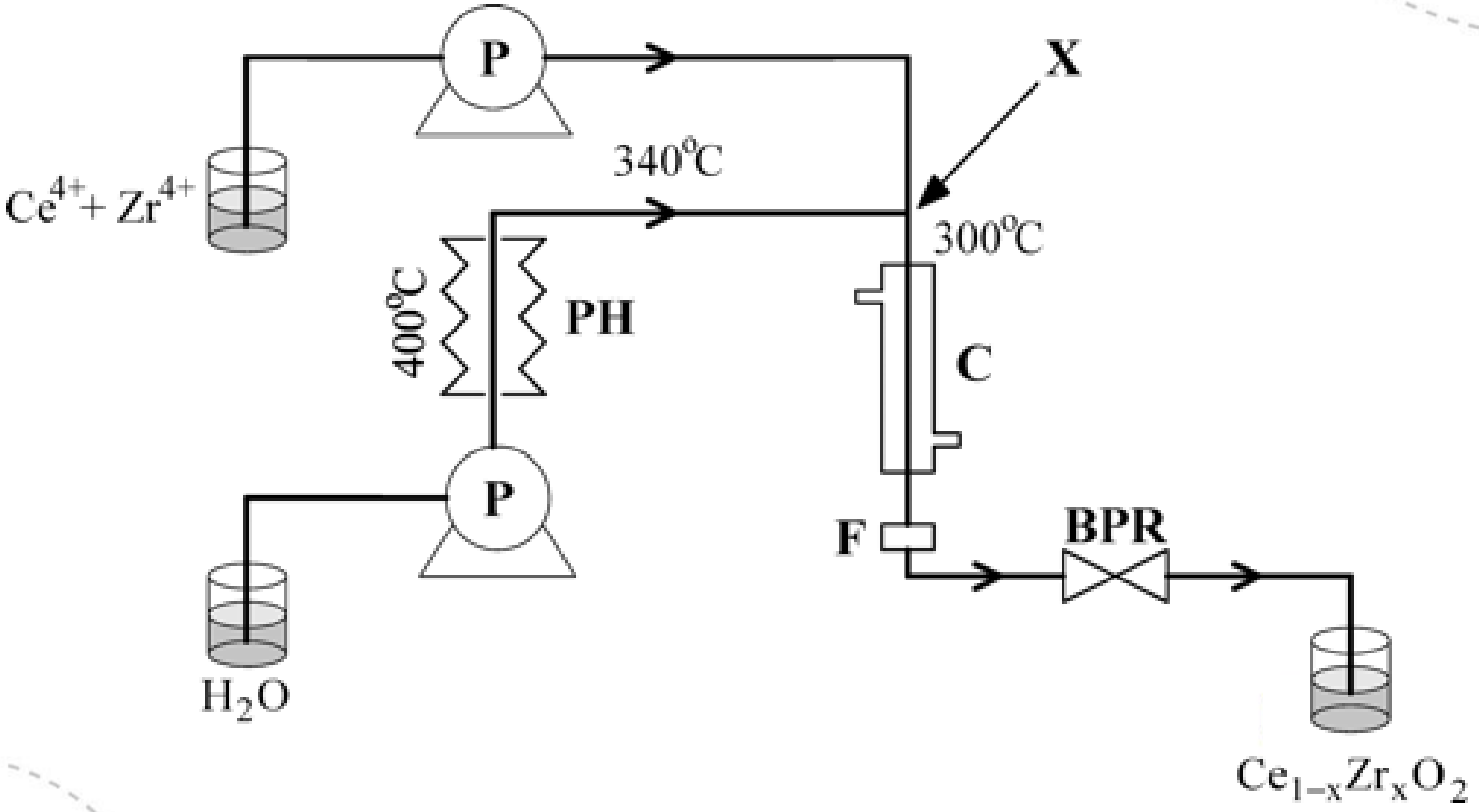


Autoclave with stirring



Continuous-flow hydrothermal reactor

- Particularly relevant given their suitability to large-scale production



NTNU equipment

- NTNU NanoLab
  - 3 × 125 mL autoclaves (Tmax = 250 °C, Pmax = 1900 psi)
  - 2 x 45 mL autoclaves (Tmax = 250 °C, Pmax = 1800 psi)
  - 2 x 23 mL autoclaves (Tmax = 275 °C, Pmax = 5000 psi)
  - 1 autoclave with stirring bar (Tmax = 350 °C, Pmax = 3000 psi)
- Inorganic Materials and Ceramics Research Group
  - 3 × 125 mL autoclaves
  - 3 × 50 mL autoclaves

NTNU research

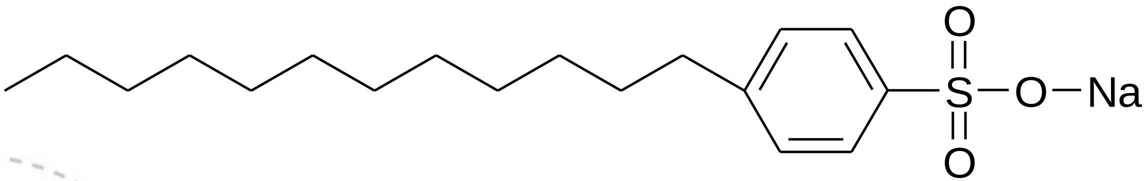
- $PbTiO_3$ nanorods and microspheres
- $KNbO_3$ nanorods
- CeO_2 clusters
- CeO_2@Ca-ZrO_2 core-shell nanospheres
- $CuGaS_2$ powder and thin films
- Zeolites

$PbTiO_3$ nanorods

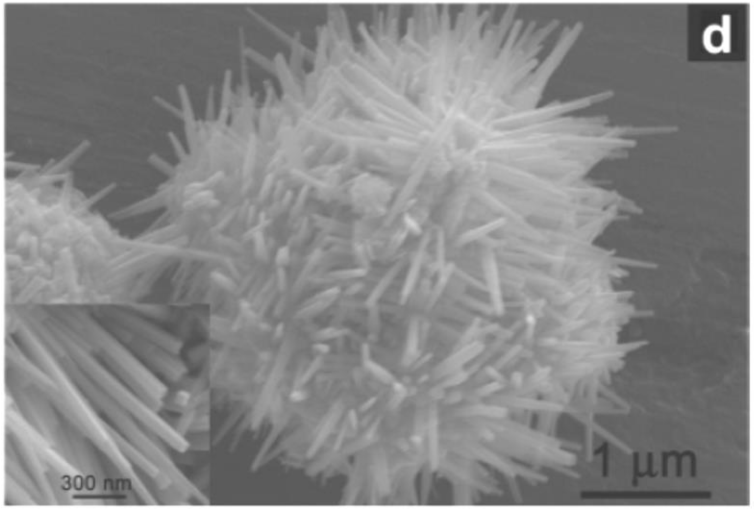
Amorphous $PbTiO_{3-x}(OH)_{2x}$
SDBS surfactant
KOH solution
$SrTiO_3$ substrate

Autoclave
180 °C, 0-48 h, ~14 bar

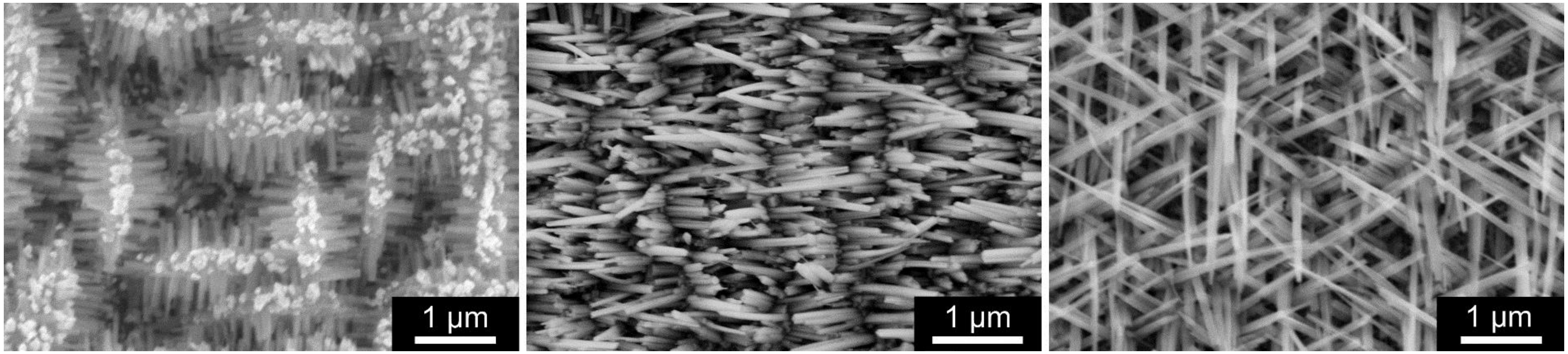
$PbTiO_3$
nanostructures



- $PbTiO_3$ bur-like microspheres



- $PbTiO_3$ nanorods on $SrTiO_3$ substrates

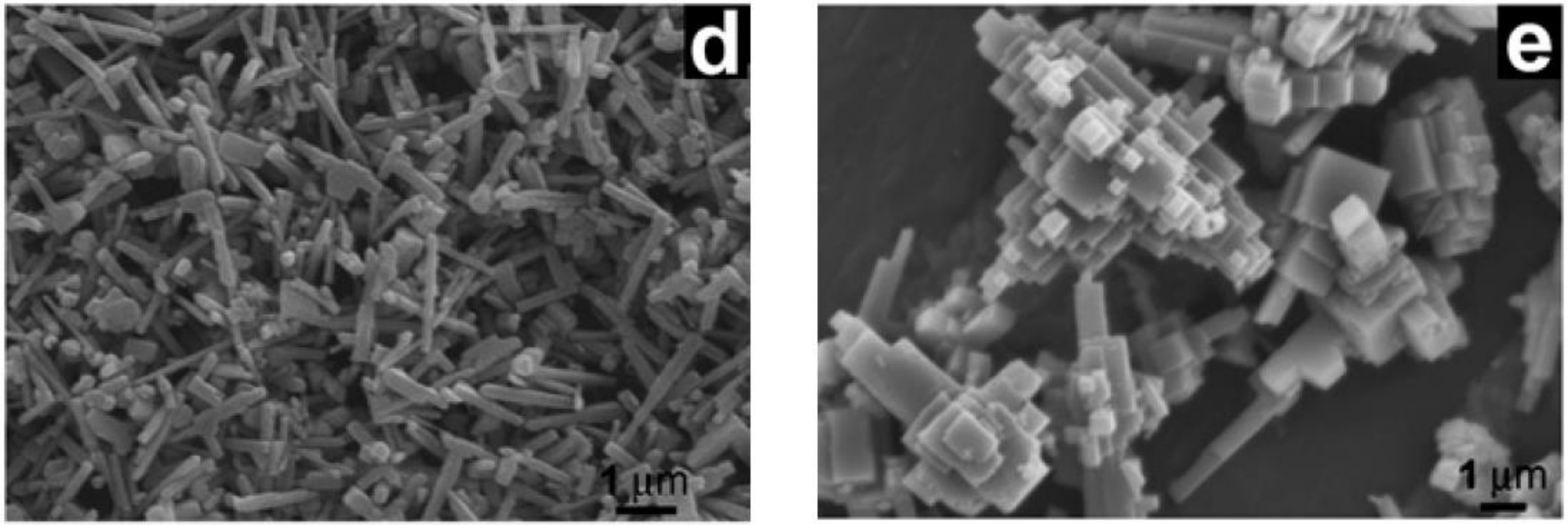


(100) $SrTiO_3$ substrate (110) (111)

G. Wang *et al.*, *J. Nanosci. Nanotechnol.*, 2007
G. Wang *et al.*, *Chem. Mater.*, 2007
P. M. Rørvik *et al.*, *Nanotechnology*, 2008
P. M. Rørvik *et al.*, *Cryst. Growth Des.*, 2009

$KNbO_3$ nanorods

- Nb_2O_5, KOH, sodium dodecyl sulfate, water
- 125 mL autoclave
- 180 °C, 48 h

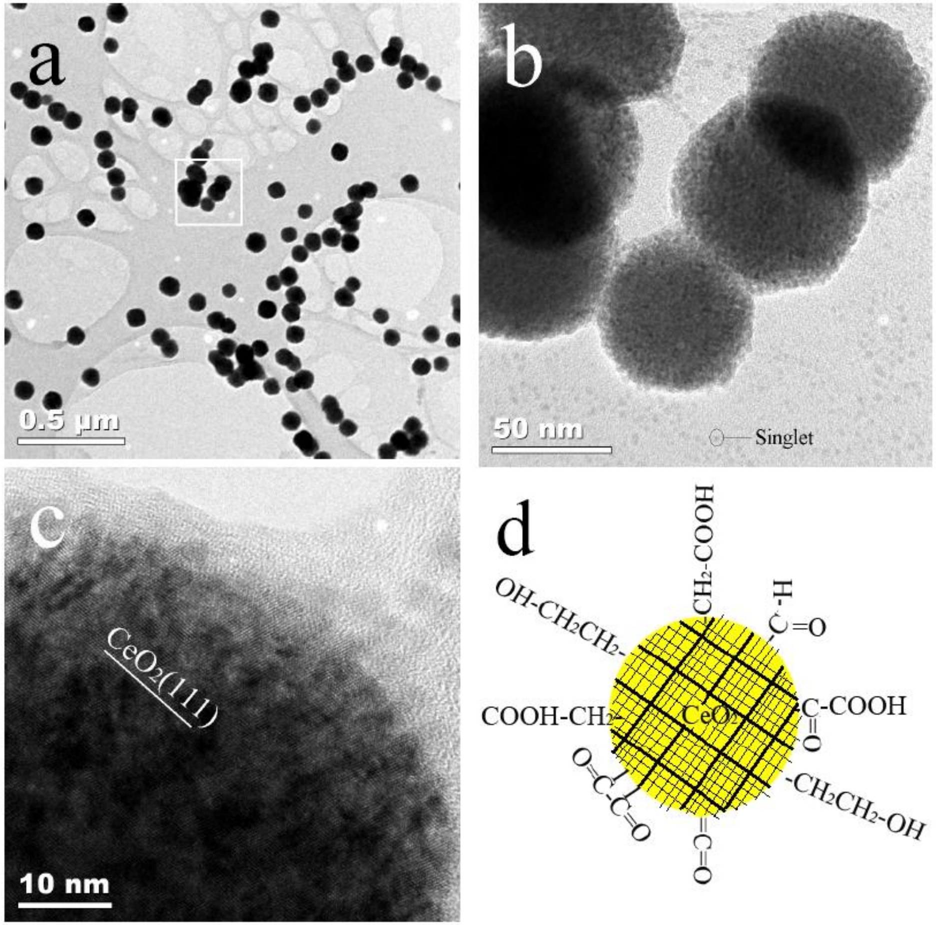


SEM images of $KNbO_3$ products prepared by hydrothermal synthesis at 180 °C for 48 h with increasing amount of SDS: (d) 0.005, (e) 0.01 mol.

G. Wang *et al.*, *Cryst. Eng. Comm.*, 2009

Monodisperse CeO_2 nanoclusters

- $Ce(NO_3)_3$, H_2O_2, ethylene glycol
- 180 °C, 8 h

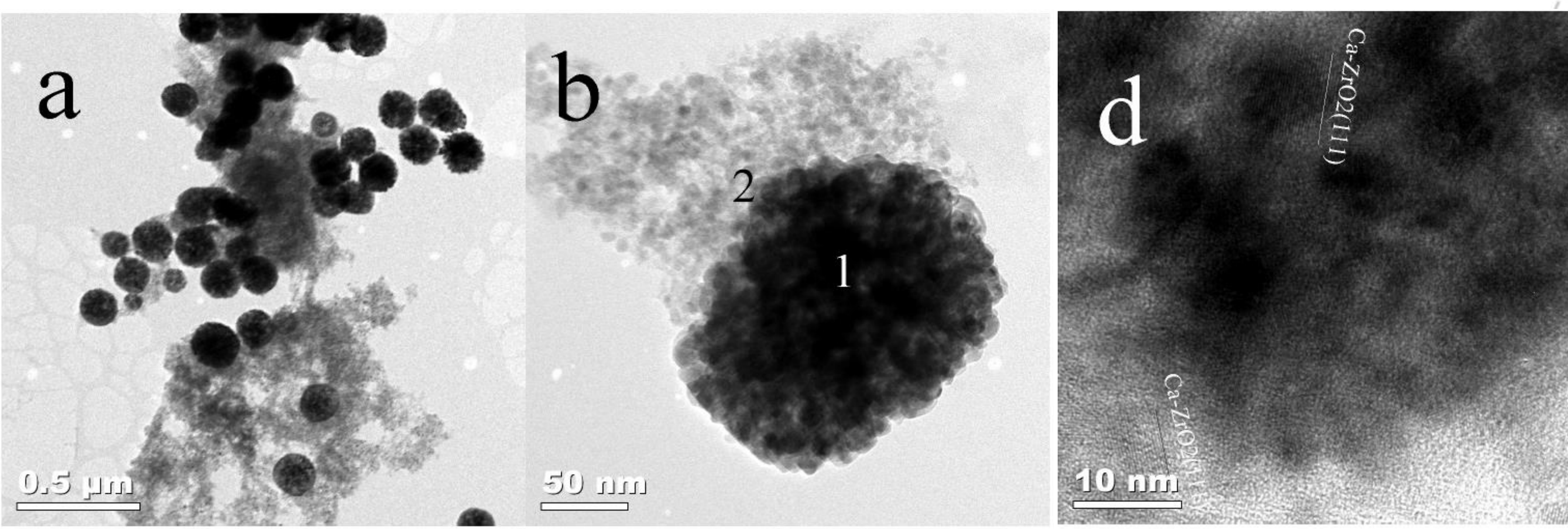


(a)-(c) TEM images of the CeO_2 nanoclusters. (c) HRTEM image. (d) A sketch of the surface modified CeO_2 nanocluster.

Haitao Zhou, Department of Materials Science and Engineering, NTNU, 2009

CeO_2@CSZ core-shell nanospheres

- CSZ = Ca-stabilized ZrO_2 (shell)
- Second hydrothermal step after treatment with $ZrO(NO_3)_3$ and $Ca(NO_3)_2$



TEM images of the CeO_2@CSZ nanoclusters. The HRTEM image in (C) shows the distances between the adjacent two parallel planes are 2.92 nm, which is the $Zr_{0.85}Ca_{0.15}O_{1.85}$ (111) plane.

Haitao Zhou, Department of Materials Science and Engineering, NTNU, 2009

Invited guess: Antoine Dalod

- Hydrothermal synthesis of surface functionalized TiO_2 nanoparticles

Synthesis of nanomaterials

- Top-down approach
  - A microcrystalline material is fragmented to yield a nanocrystalline material. Ex. Solid state routes.
  - Produce bulk nanostructured materials
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Top-down approach

- Mechanical alloying
- Equal channel angular pressing (ECAP)
- High-pressure torsion
- Accumulative roll bonding
- Nanolithography

Top-down approach

– Mechanical alloying

- High energy ball mills: vibratory mills, planetary mills and attritor mills.

- Used grinding vials and balls of different materials (agate, silicon nitride, zirconia, chrome steel, tungsten carbide)

Mechanical alloying: high energy milling

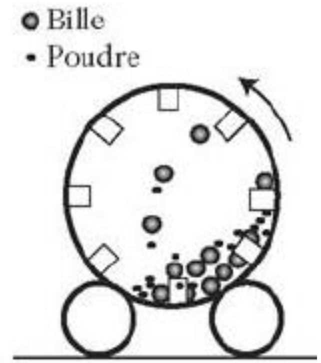
Vibratory ball mill

Mechanical alloying: high energy milling

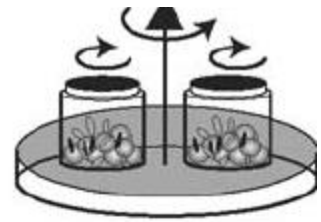
Planetary ball mill

Mechanical alloying: high energy milling

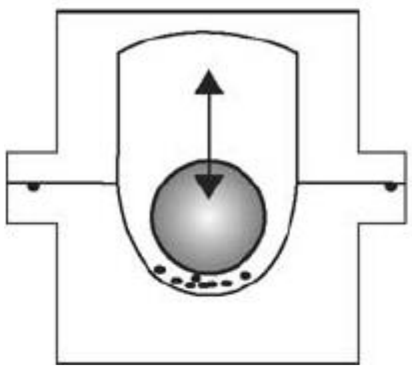
Attritor



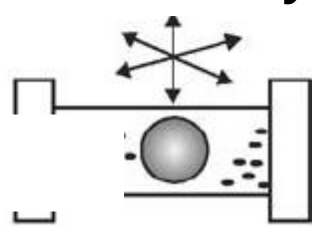
Horizontal mill



Planetary



1D vibratory



3D vibratory

High energy milling: examples

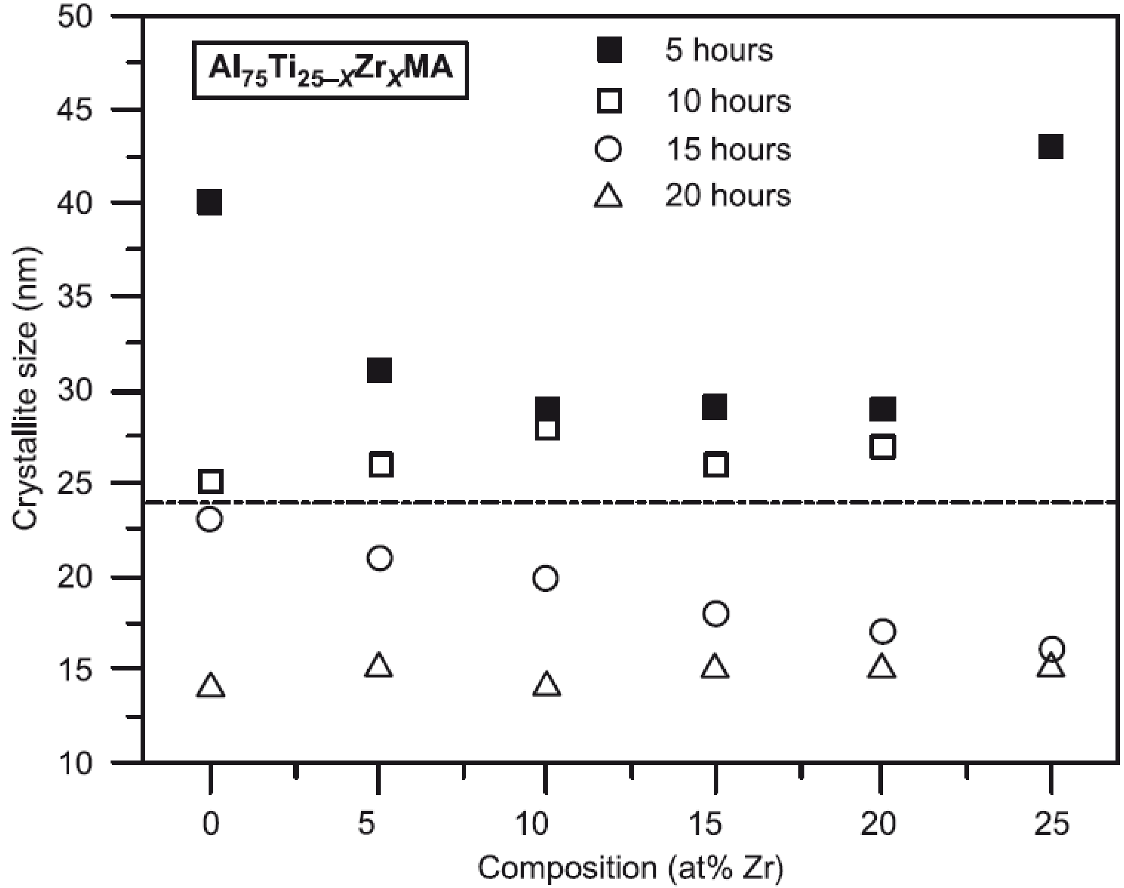


Fig. 3.11 Crystallite size of Al and intermetallic as a function of composition. Nanocrystalline intermetallic compound formation was observed when the crystallite size of Al was below 24 nm. The dotted line demarcates the phase field of mixture of elements and intermetallic compound. (*Source:* BS Murty, IIT Madras).

Top-down approach

Nanolithography

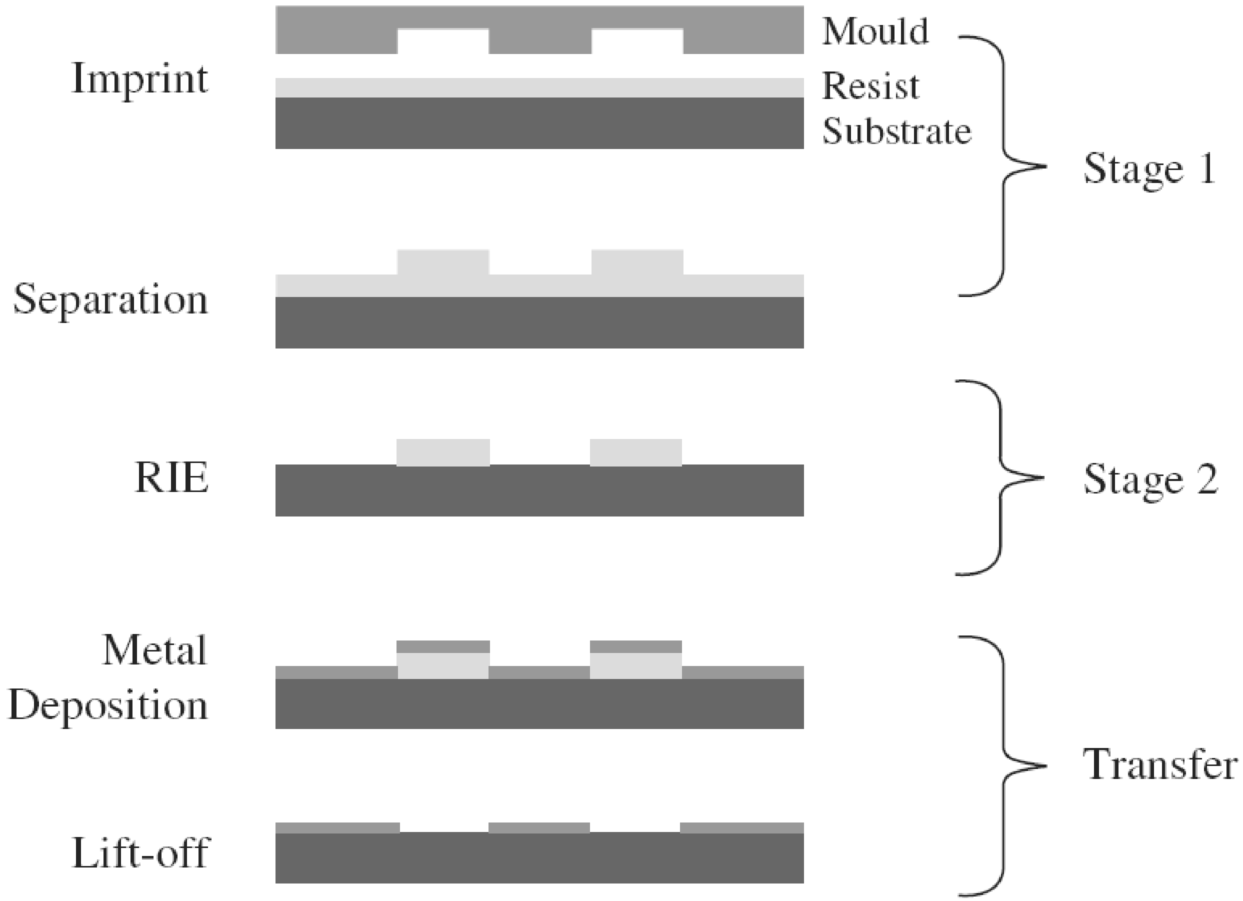
- Nanolithography plays a key part in fundamental research and many areas of industry
  - Methods developed by the electronics industry are often inaccessible to research and development teams
- Want cheaper and more flexible methods
  - Want to avoid diffraction or scattering problems encountered with photons, electrons or ions
- Use moulding or casting → high resolution surface patterns

Nanoimprint lithography

- Two-step process:
  - Patterns are stamped using a mould on a polymer (resist) layer deposited on the substrate;
  - The resist relief pattern stamped onto the polymer is treated by reactive ion etching (RIE) until its recessed areas are all removed

- The final profile is comparable with results obtained by other lithographic methods

Thermoplastic nanoimprint lithography



Thermoplastic nanoimprint lithography

- Advantages
  - Very high resolution
  - High throughput production
  - Simple and cheap method
  - Easy to implement
  - Accessible and applicable in a wide range of situations
- Disadvantages
  - Potentially time consuming heating/cooling stages
  - Mould is necessary
- Mould
  - Typically produced by electron beam lithography on a silicon oxide substrate, followed by reactive ion etching (RIE) or electrodeposition
  - Anti-adhesive treatment may be necessary

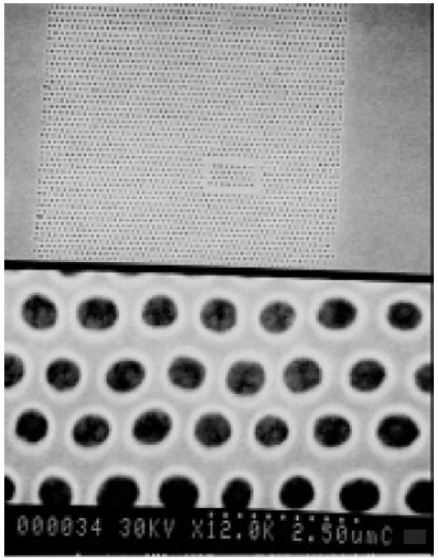
For higher aspect ratios

- The thickness of imprinted features is very limited when high resolution is required
- In order to obtain a high aspect ratio nanostructure, a new process has been developed involving three layers
- Ge acts as a mask during RIE

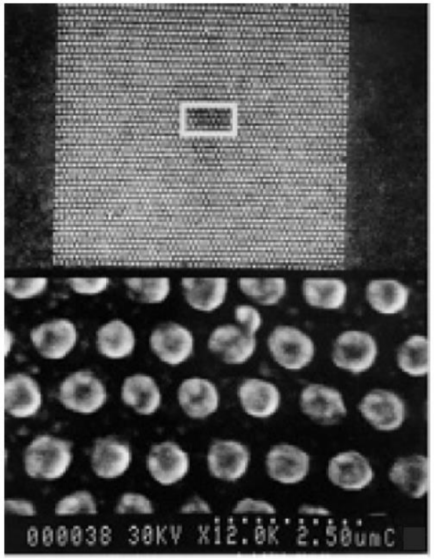
Examples of the trilayer process

- Routine fabrication of dot arrays with period 100 nm
- Critical size control close to 10 nm
- Lines etched in silicon (Si) with widths below 10 nm
- Imprinting at room temperature and/or at low pressure
- Pattern transfer for a variety of applications

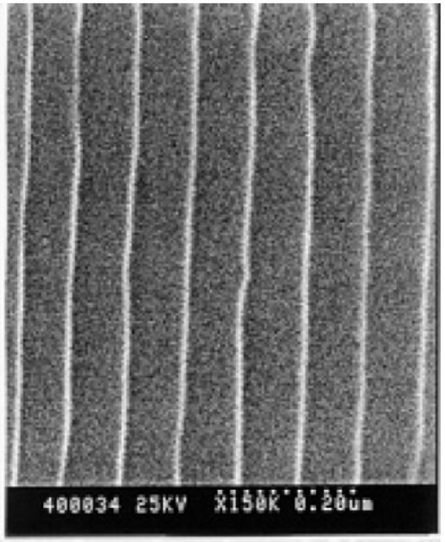
a.



b.



Dot array with period 100 nm, obtained by trilayer nanoimprint before (**a**) and after (**b**) the metal (Ni) lift-off stage.

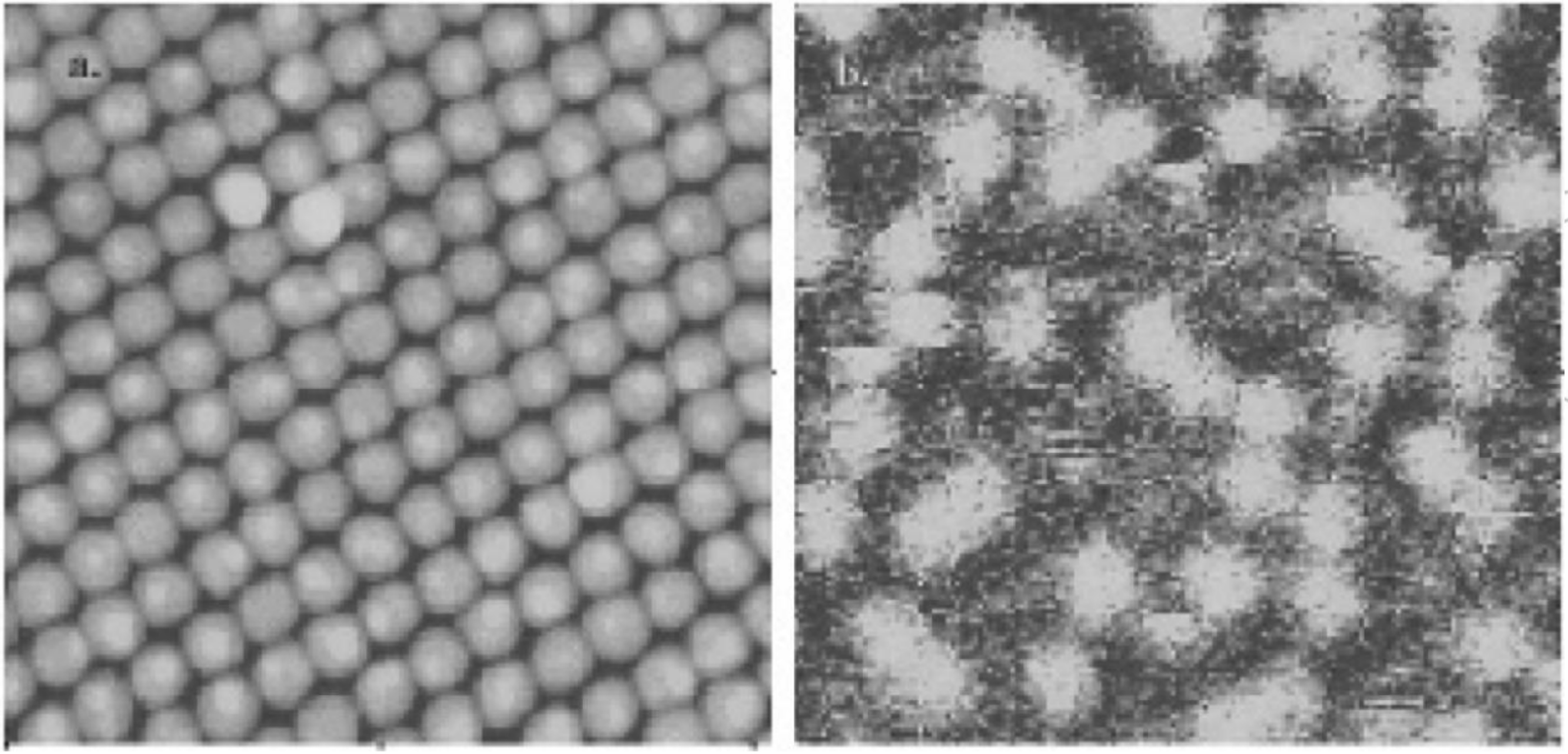


Array of silicon lines with width less than 10 nm, obtained by nanoimprint lithography and RIE of a silicon-on-insulator substrate.

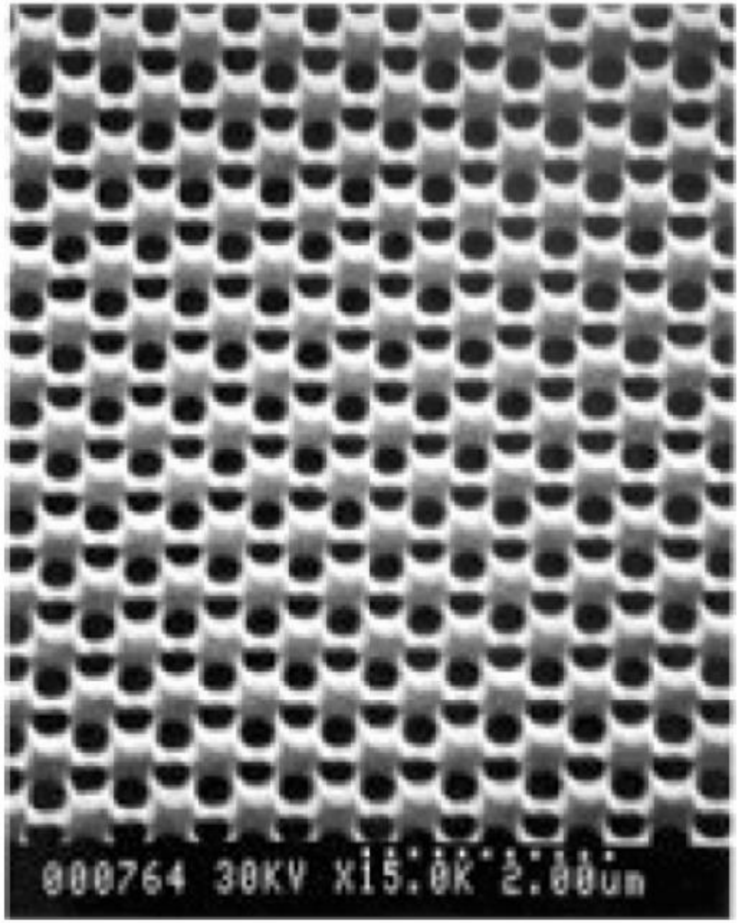
Application areas

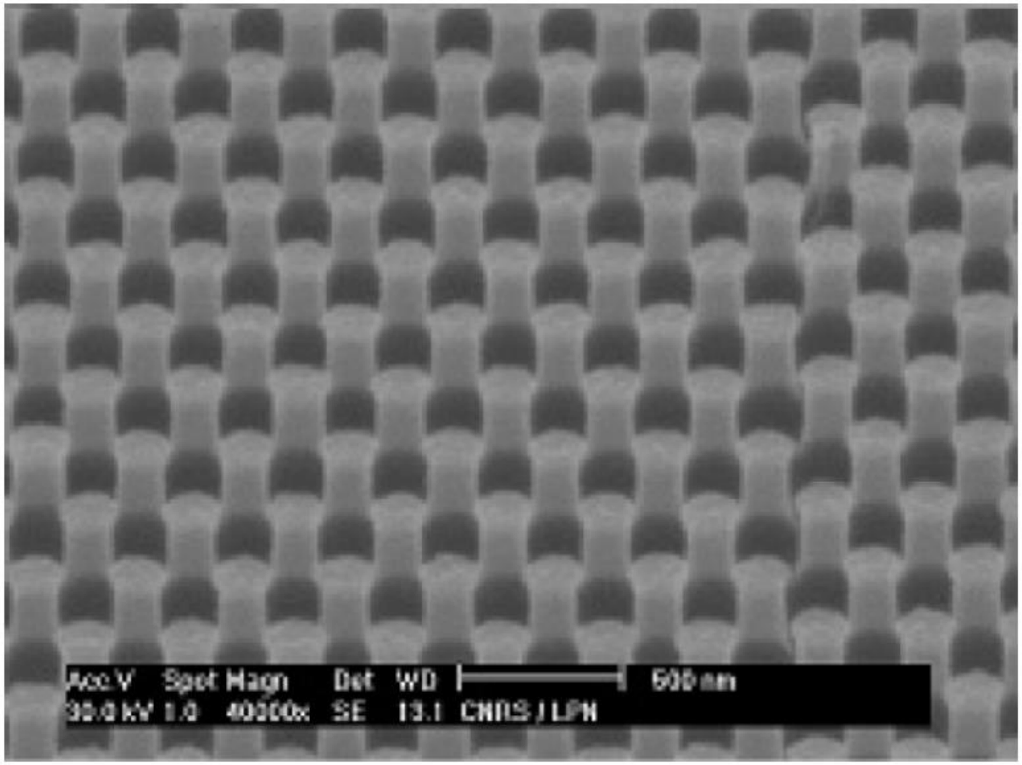
- Microelectronics
- Nanomagnetism
- Nano-optics
- Chemistry and biology

More examples…



Array of magnetic dots (Co) with period 60 nm (storage density 180 Gbit/in^2), made by nanoimprint lithography and lift-off. *Left* : Atomic force microscopy (AFM) image. *Right* : Magnetic force microscopy (MFM) image.

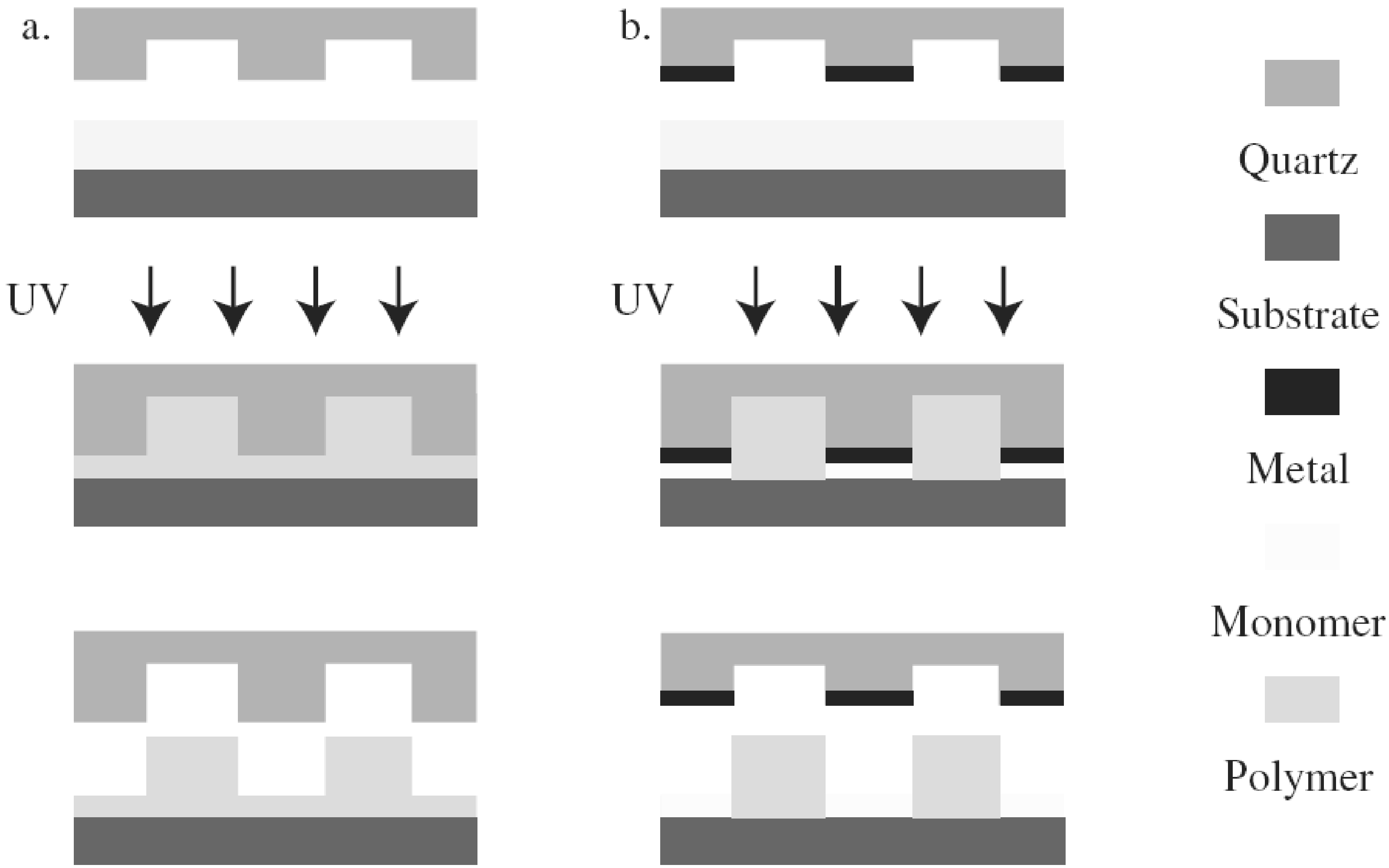




Graphite-type array on a polymer layer, for use as an etch mask for the underlying substrate in order to obtain functional photonic crystals.

Nanopillar array integrated into a microfluidic channel to improve the separation of DNA molecules by capillary electrophoresis on a chip.

UV nanoimprint lithography



UV nanoimprint lithography

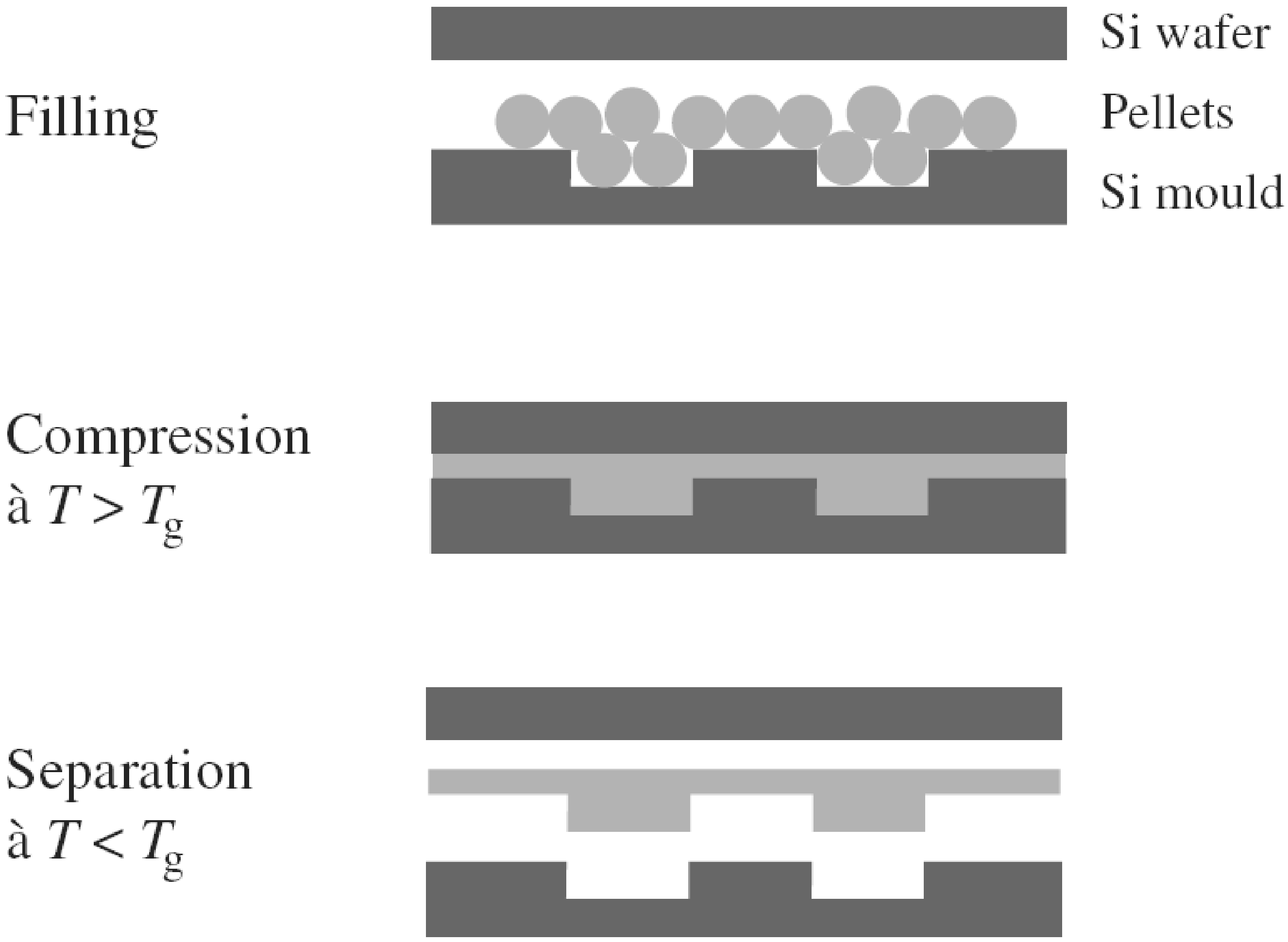
- Two main steps:
  1. Moulding a viscous pre-polymer and catalyzer mixture at room temperature
  2. Photopolymerizing

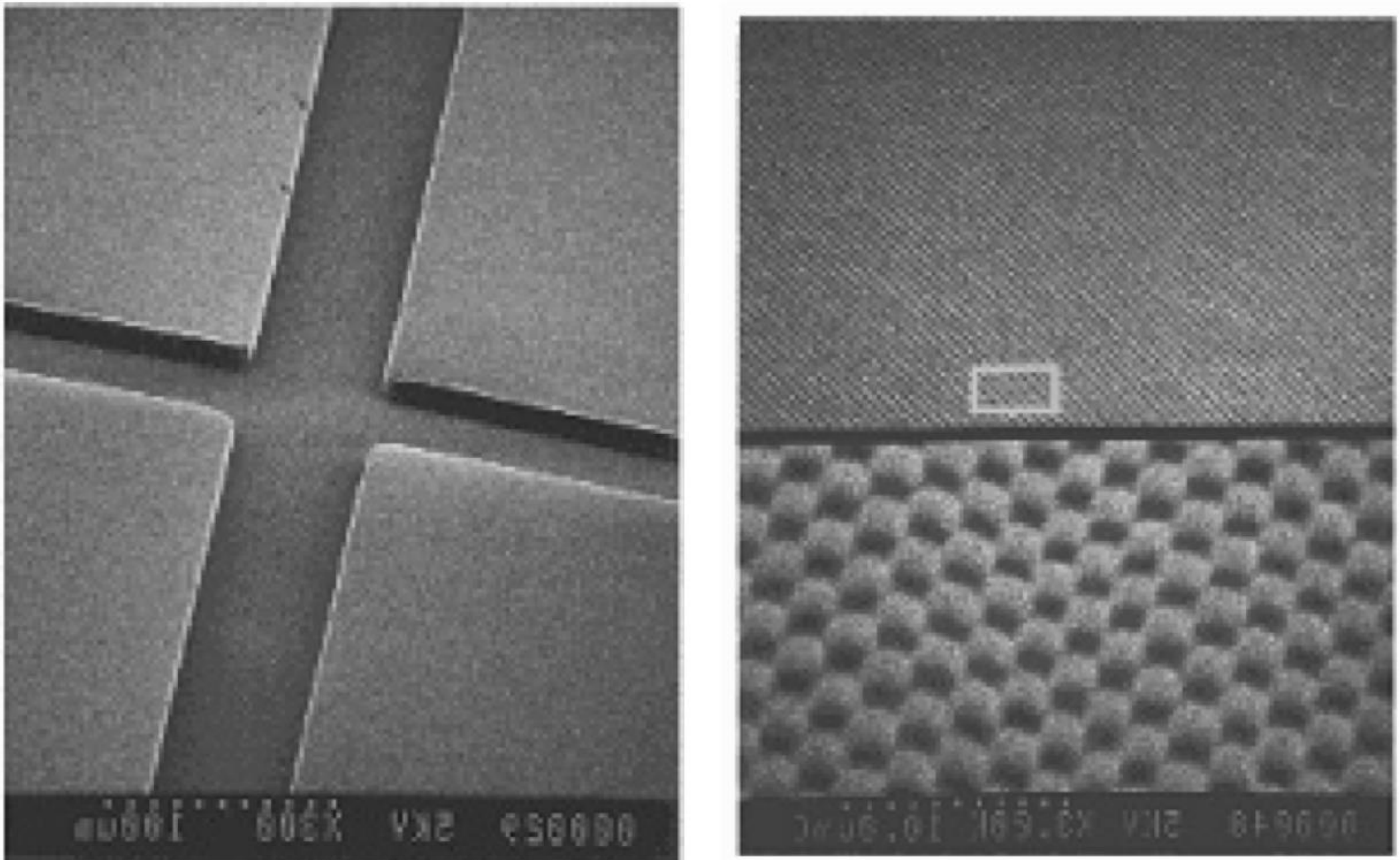
- Advantages
  – Works at room temperature and low pressure using a quartz template
  – High duplication rate (high throughput) and possibility of high precision alignment

Nanoembossing

- Forming nanostructures on the surface of a bulk material
  - Functional nanostructures
  - All-plastic devices
  - Can reproduce any pattern
- Three different approaches:
  1. Direct imprint on the surface of a plastic wafer
     - Temperature below T_g
     - Relatively high pressure
  2. Imprint of nanostructures on a polymer film
     - Deposited on a rigid substrate
     - No subsequent etching step
  3. Compression of thermoplastic polymer pellets
     - Temperature above T_g
     - Forms a nanopatterned wafer

Nanoembossing



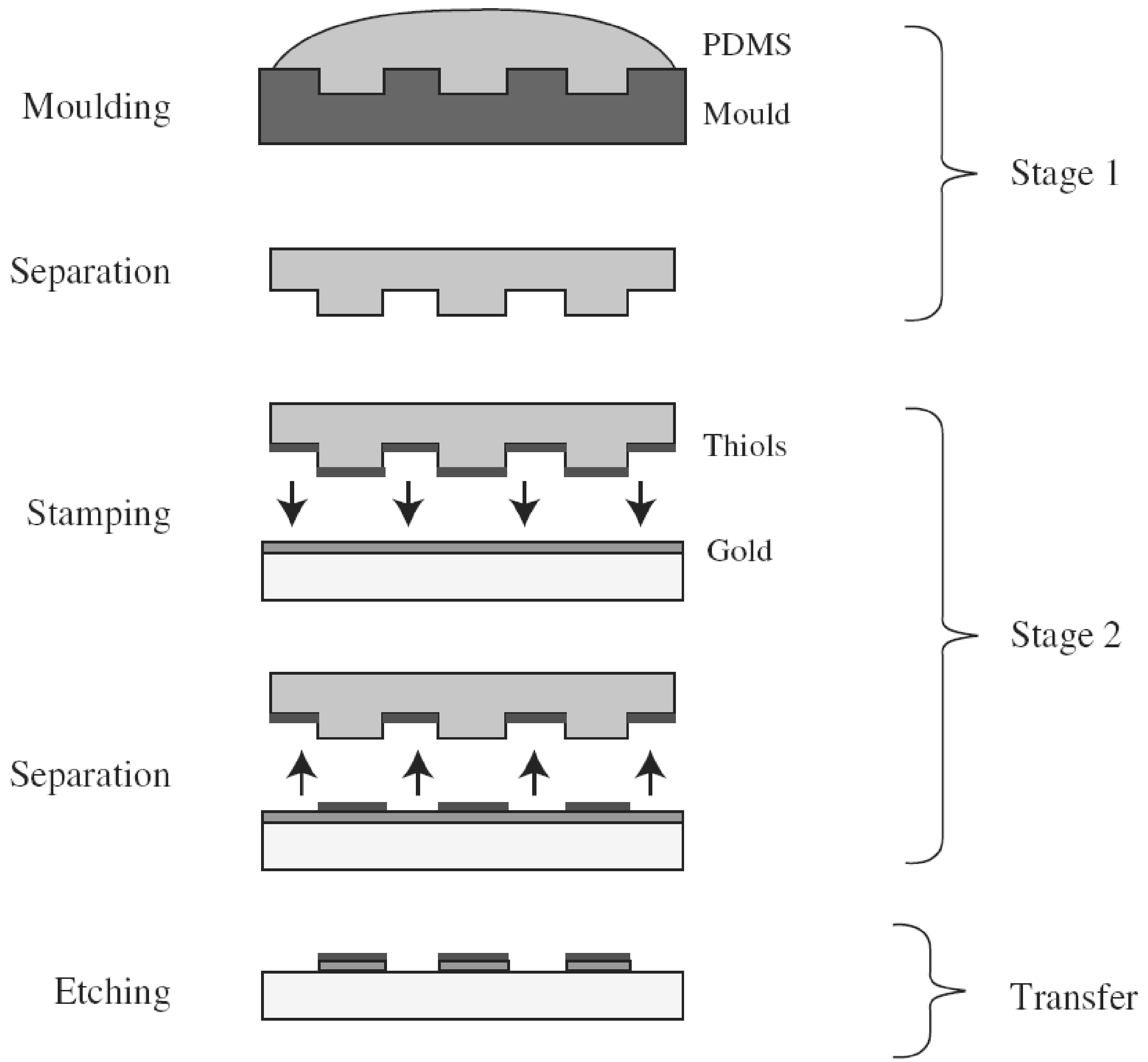


Microchannel (*left*) and nanostructures (*right*) made by nanoembossing with PMMA pellets and an etched silicon mould.

Soft lithography

- Use elastomer, polydimethylsiloxane (PDMS), as a mould or ink stamp
  - PDMS is a silicone oil polymer formed by the monomer $–OSi(CH_3)_2O–$
  - “Soft matter”
- Advantages
  - Can pattern large areas in a single step
  - Can pattern curved surfaces
  - Low cost, simple, rapid
- Disadvantages
  - Diffusion of the printed molecules limits resolution
  - Stamp suffers deformation and distortion

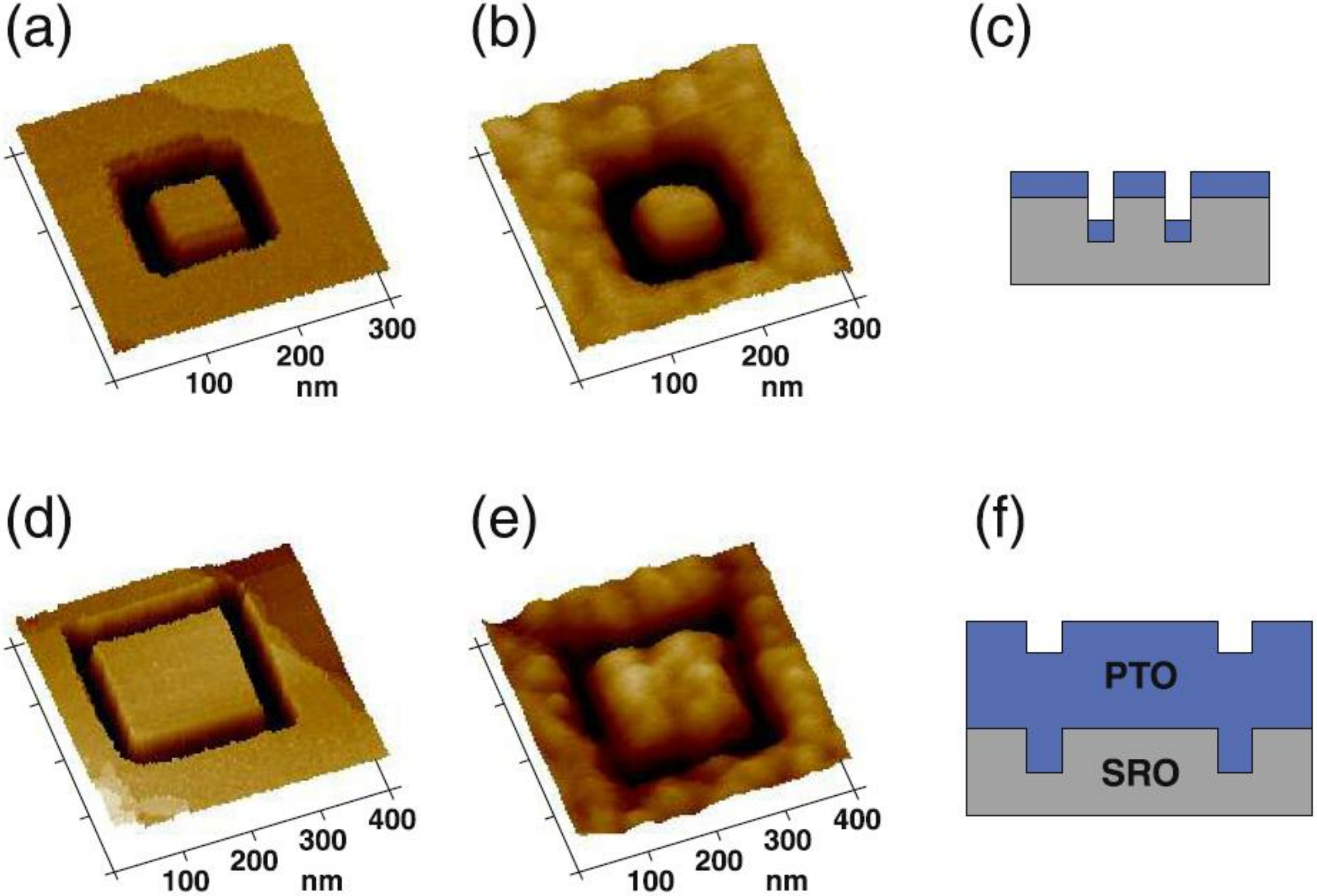
Soft lithography



Near-field lithography

- Non-standard replication method → near-field optical lithography
  - Expose a thin film of resist through a mask in perfect contact with the substrate
  - Resolution ~100nm
- Other near-field techniques include methods where a tip is used to scan a surface
  - Scanning tunneling microscopy (STM)
  - Atomic force microscopy (AFM)
  - Scanning near-field optical microscopy (SNOM)

NTNU research



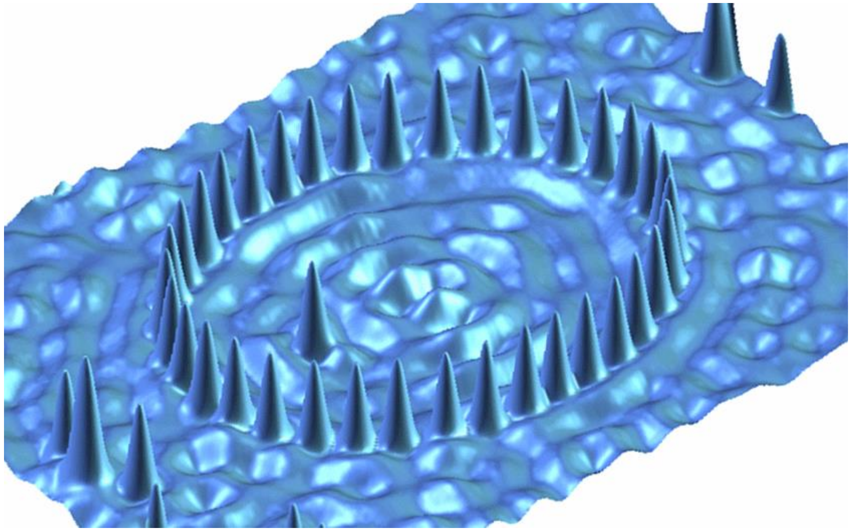
STM topography images:
Templates defined in a $SrRuO_3$ (SRO) thin film surface by STM lithography

AFM topography images:
$PbTiO_3$ (PTO) nanomesas obtained after (b) 4 nm and (e) 16 nm thick PTO film depositions on SRO templates

The ideal growth of PTO on a nanostructured SRO template for 4 nm thick (c) and 16 nm thick (f) depositions.

C. C. You *et al.*, *Nanotechnology*, 2009

- A scanning tunneling microscope can displace atoms one by one to fabricate patterns on a surface and design simple electronic devices involving a single molecule



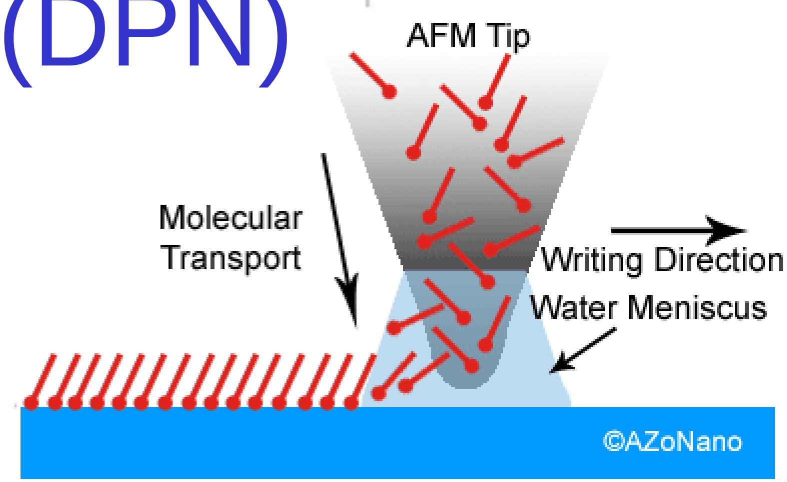
Elliptical quantum corral:

•Co atoms were deposited at sub-monolayer coverage on a Cu(111) at 7K in UHV

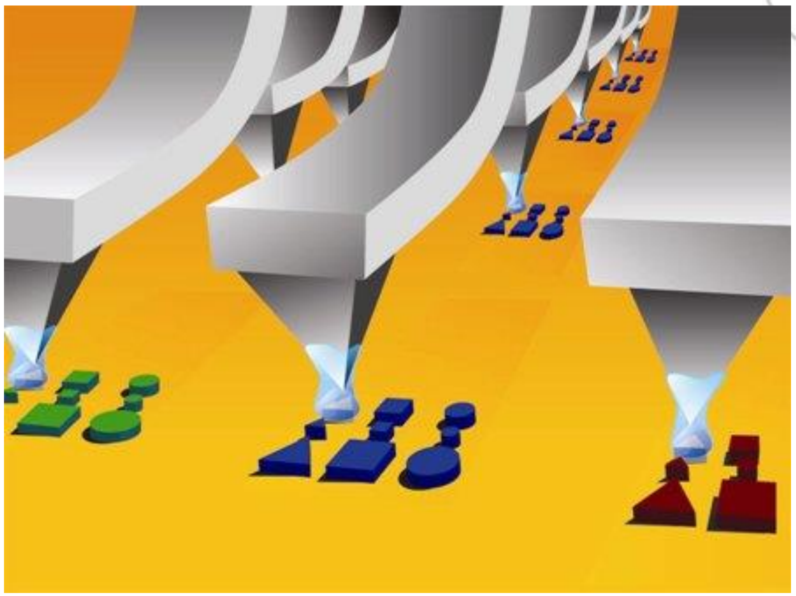
•STM measurements were performed at a 4.3 K sample temperature

http://commons.wikimedia.org/wiki/Category:Scanning_tunneling_microscope_images

Dip-pen lithography (DPN)



- Associates AFM and microcontact printing
- Resolution ~10 nm
- Example:
  - The AFM tip is coated with a solution of organic molecules, usually thiols, which are then deposited locally by self-assembly on a suitably prepared substrate (gold for thiols)



Key elements of DPN

- Can write complex patterns with different colors or molecules
- Molecules are transferred through the solvent meniscus
- Can write with many tips in parallel → as many as 55,000 tips can write simultaneously.

IBM’s millipede system

- Heated ”AFM tip” indent a polymer film.
- Indent = ”1”

  Absence = ”0”
- The same tip reads back the bit patterned by noting resistance changes in the tip resulting from improved heat transport from tip to polymer