NTNU

Norwegian University of Science and Technology

TMT4320 Nanomaterials
November 2nd, 2016

- TNN-Chapter 6-ZnO and TiO_2 nanoparticles, nanolithography

Wikipedia

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.

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

BULK SINGLE CRYSTAL GROWTH

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

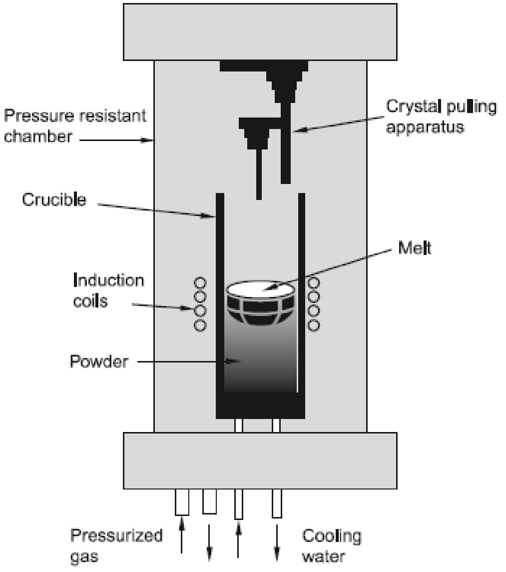

Fig. 6.15 Schematic diagram of the melt growth system.

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

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)

Metal organic precursors ($(CH_3)_2Zn$, $(C_2H_5)_2Zn$) 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

Chemical synthesis

Thermal evaporation

Pulsed laser deposition

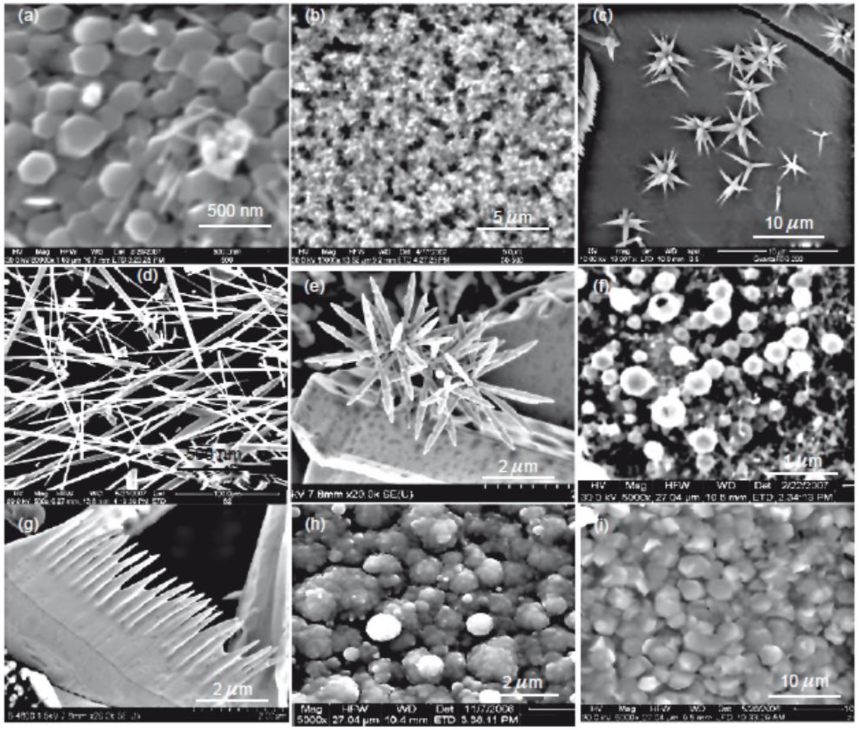

Fig. 6.16 SEM images of ZnO nanostructures synthesized using different techniques. ZnO (a) hexagons, (b) wires and (c) tetrapods by chemical synthesis route (d) ZnO wires, (e) tetrapods, (f) spheres, (g) brush grown by thermal evaporation technique and (h) ZnO spheres and (i) hexagons grown by pulsed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

ZnO nanoparticles

Applications of ZnO nanostructures

PIEZOELECTRIC SENSORS

BIOSENSORS

SOLAR CELLS

GAS SENSORS

ZnO nanoparticles

Applications of ZnO nanostructures

PIEZOELECTRIC SENSORS

ACS APPLIED MATERIALS & INTERFACES

Research Article

www.acsami.org

Sponge-Templated Macroporous Graphene Network for Piezoelectric ZnO Nanogenerator

Xinda Li,[†] Yi Chen,[†] Amit Kumar,[†] Ahmed Mahmoud,[‡] John A. Nychka,[†] and Hyun-Joong Chung*,[†]

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ZnO nanoparticles

Applications of ZnO nanostructures

PIEZOELECTRIC SENSORS

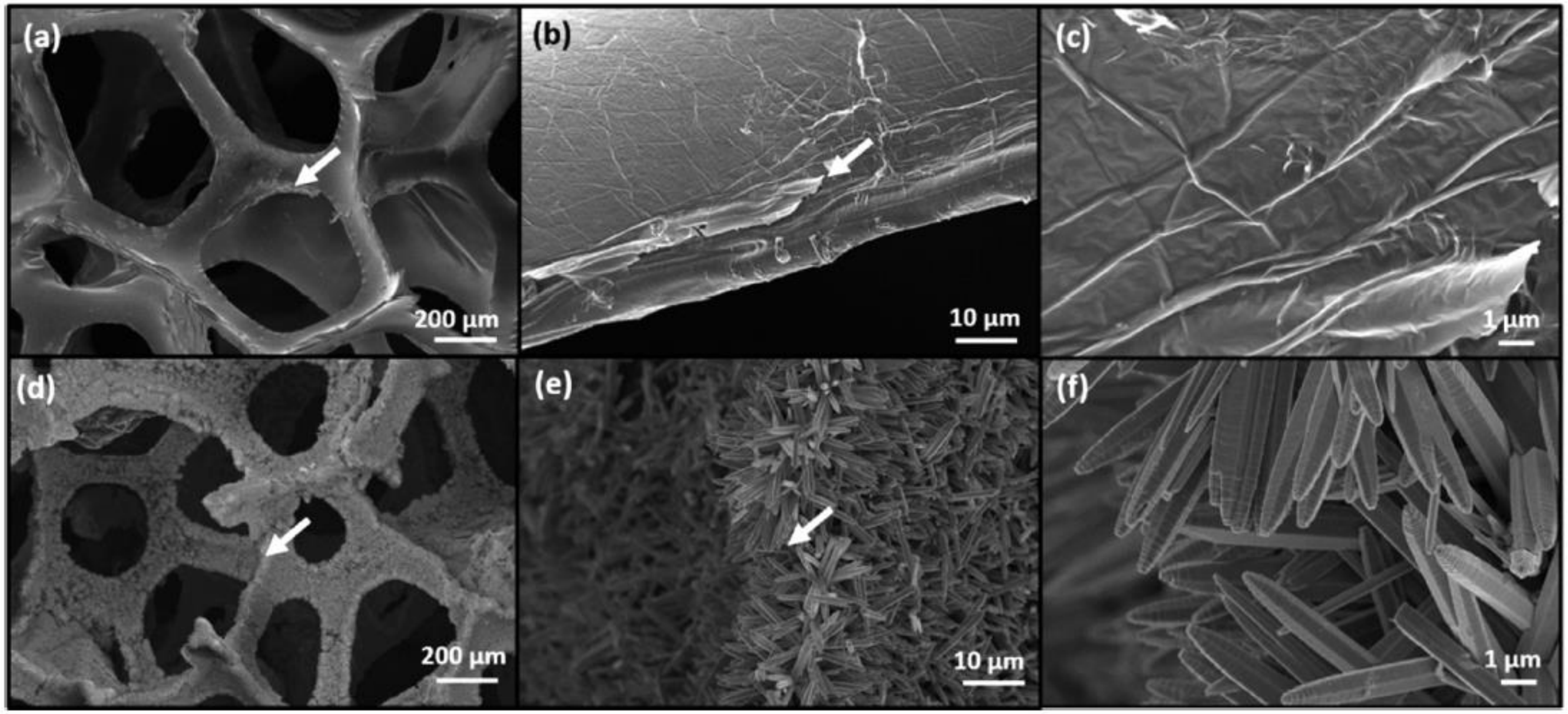

Figure 2. (a−c) SEM images of RGO@PU with different magnification. (d−f) SEM images of ZnO@RGO@PU with different magnification. White arrows indicate the locations for the zoom-in.

ZnO nanoparticles

Applications of ZnO nanostructures

GAS SENSORS

Sensors and Actuators B 239 (2017) 36–44

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Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Enhanced performance of novel calcium/aluminum co-doped zinc oxide for CO_2 sensors

CrossMark

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ZnO nanoparticles

Applications of ZnO nanostructures

GAS SENSORS

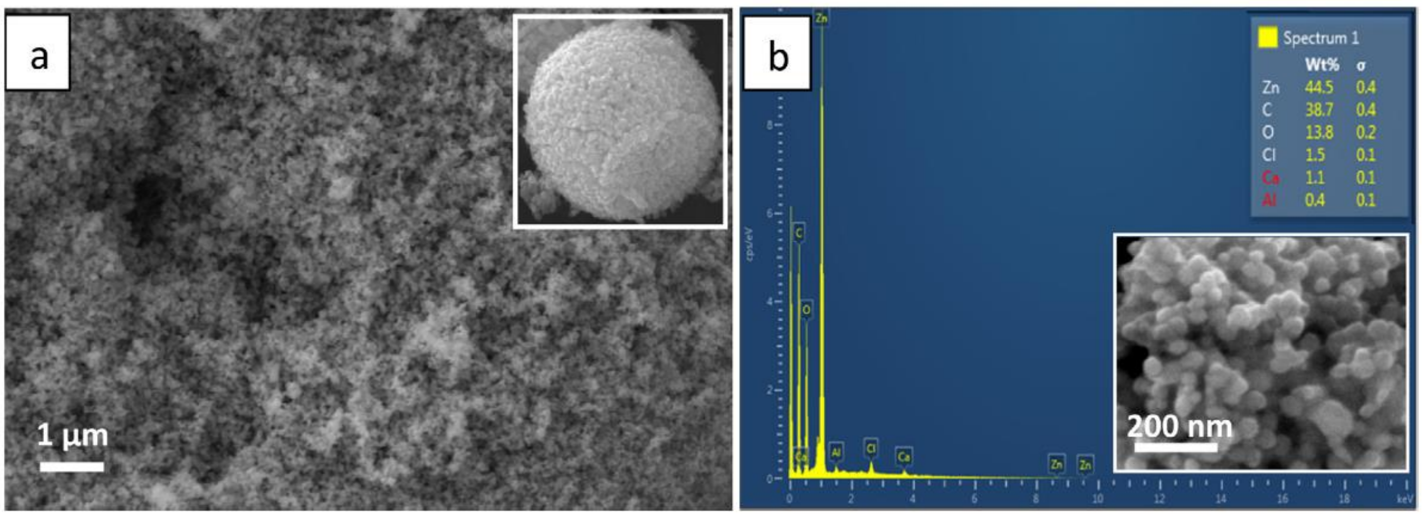


Fig. 1. a) SEM image showing the typical porous structure of the ZnO:Ca3Al1 printed sensing layer. Inset shows the image of one of the spherical aggregate composed of smaller single grains. b) EDX pattern taken from image in inset showing the size of the single grains.

TiO_2 nanoparticles

Crystal structure of TiO_2

❖ Three allotropic forms: brookite (orthorhombic), anatase (tetragonal) and rutile (tetragonal).

❖ Rutile is high temperature phase

❖ Anatase and brookite converts into rutile on heating

TiO_2 nanoparticles

Applications

- ❖ Nano-titania applications in pigments, adsorbents, catalytic supports, gas and humidity sensors and coatings for self-cleaning surfaces.

- ❖ Anatase higher photocatalytic activity → Hydrolysis (break water into hydrogen and oxygen) → energy

- ❖ Rutile high refractive index, weatherability (oxidation and wear resistance and high thermal and chemical stability → pigments and coatings as well as sterilizing, deodorizing and anti-fouling properties

TiO_2 nanoparticles

Nanopowders

- Rutile and anatase in a variety of geometrical configurations: spherical powders, thin films, nanorods, nanowires, etc…

- Synthesis method:

    Hydrothermal → Antoine Dalod

    Chemical vapour deposition

    Microemulsion

    Sol-gel → Very effective method

TiO_2 nanoparticles

Nanopowders

❖ Synthesis method:

Sol-gel → Very effective method

Precursor: Tetrabutyl titanate

Temperatures of 800 ºC lead to transformation from anatase to nano-rutile powder

Precursor: Titanium n-tetrabutoxide

Calcination temperatures between 200 and 600 ºC.

TiO_2 nanoparticles

Nanopowders

❖ Synthesis method:

Sol-gel → Very effective method

Precursor: Titanium n-tetrabutoxide

Calcination temperatures between 200 and 600 ºC.

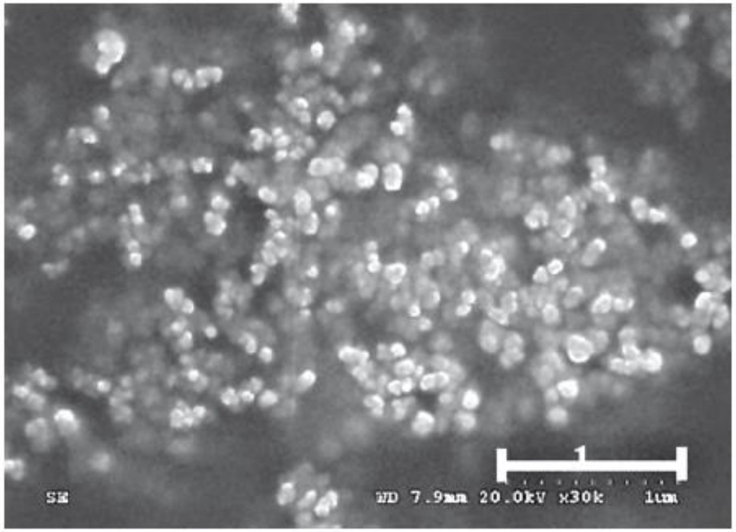
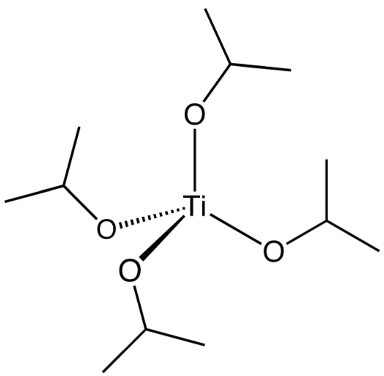


Fig. 6.17 Nanocrystalline titania. (*Source:* BS Murty, IIT Madras)

Hydrothermal synthesis

$$Ti\left(OCH\left(CH_3\right)_2\right)_4 + 2H_2O \xrightarrow{\text{hydrolysis}} TiO_2 + 4\left(CH_3\right)_2 CHOH$$

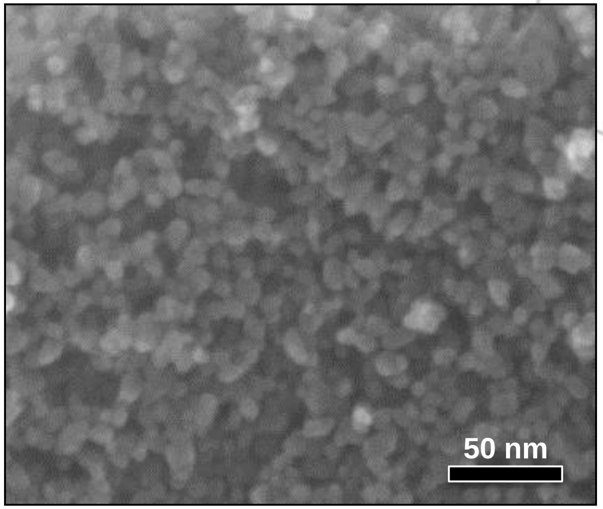
Parameters: temperature, time, filling factor, Ti/H_2O ratio



Titanium (IV) isopropoxide

200 °C – 2 hours
H_2O

125 mL



TiO_2 (anatase)
~10 nm

TiO_2 nanoparticles

Titania nanotubes (TNTs)

- They have large specific surface area, photocatalytic potential and ion-exchangeable ability
- Most common methods of synthesis
  - Template-assisted growth.
  - Hydrothermal methods

TiO_2 nanoparticles

Titania nanotubes (TNTs)

- Most common methods of synthesis
  - Template-assisted growth. Use of nanoporous membranes made anodic aluminum oxide. Difficulties in prefabrication and post-removal of the template and usually results in impurities.
  - Hydrothermal methods. More suitable for large-scale. Morphology and properties dependent of experimental parameters such as temperature, treatment time and type of precursors. Length of TNTs related with temperature.

TiO_2 nanoparticles

Titania nanotubes (TNTs)

- ❑ Template-assisted growth..

Advanced Materials Research *Online: 2011-07-04*
ISSN: 1662-8985, Vols. 295-297, pp 1279-1283
doi:10.4028/www.scientific.net/AMR.295-297.1279

In-situ Template Synthesis Titania Nanotube Array Films on Aluminum Plate

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TiO_2 nanoparticles

Titania nanotubes (TNTs)

- Template-assisted growth..

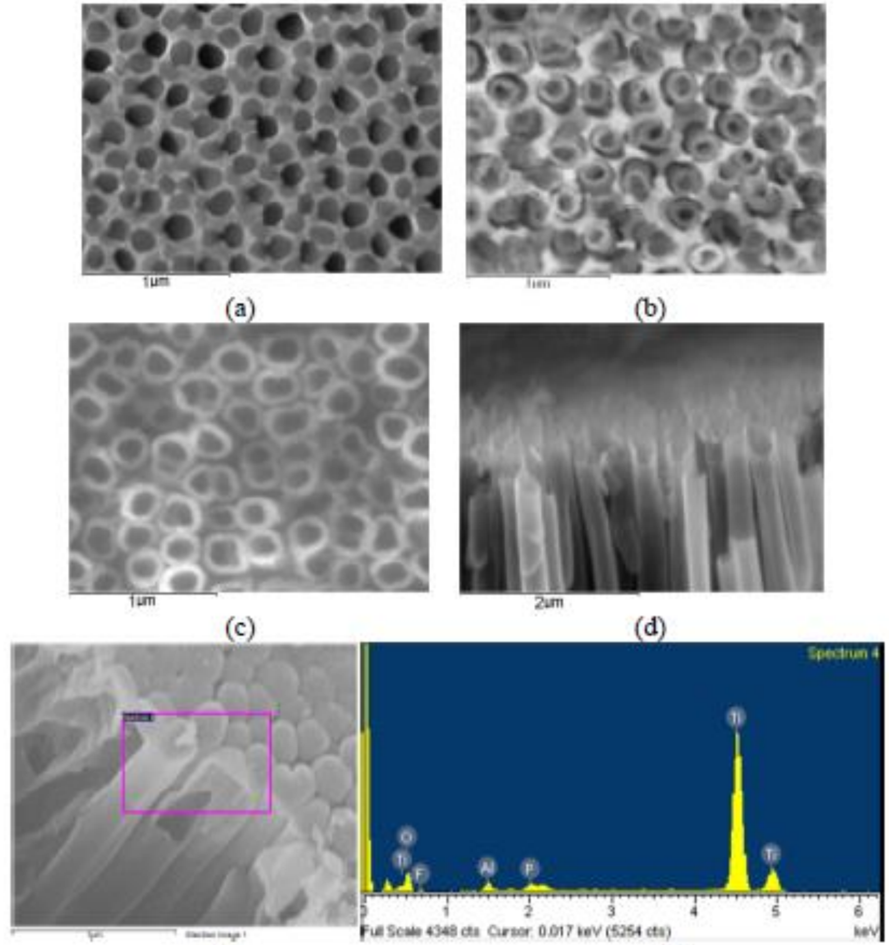

Fig. 1 FE-SEM images of AAO and TiO_2 nanotube array
(a) 0 min (AAO). (b) 30min. (c) 60min. (d) Cross-section of titania nanotubr array of (c).
(e) Bottom view of (c). (f) EDS diagram of selected area of (e).

TiO_2 nanoparticles

Titania nanotubes (TNTs)

- Hydrothermal methods.

Journal of Power Sources 283 (2015) 443–451

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Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

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Highly crystalline Titania nanotube arrays realized by hydrothermal vapor route and used as front-illuminated photoanode in dye sensitized solar cells

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Materials Science and Engineering School, Jingde Zhen Ceramic Institute, Jiangxi 333403, PR China

TiO_2 nanoparticles

Titania nanotubes (TNTs)

- ❑ Hydrothermal methods.

T. Zeng et al. / Journal of Power Sources 283 (2015) 443–451 447

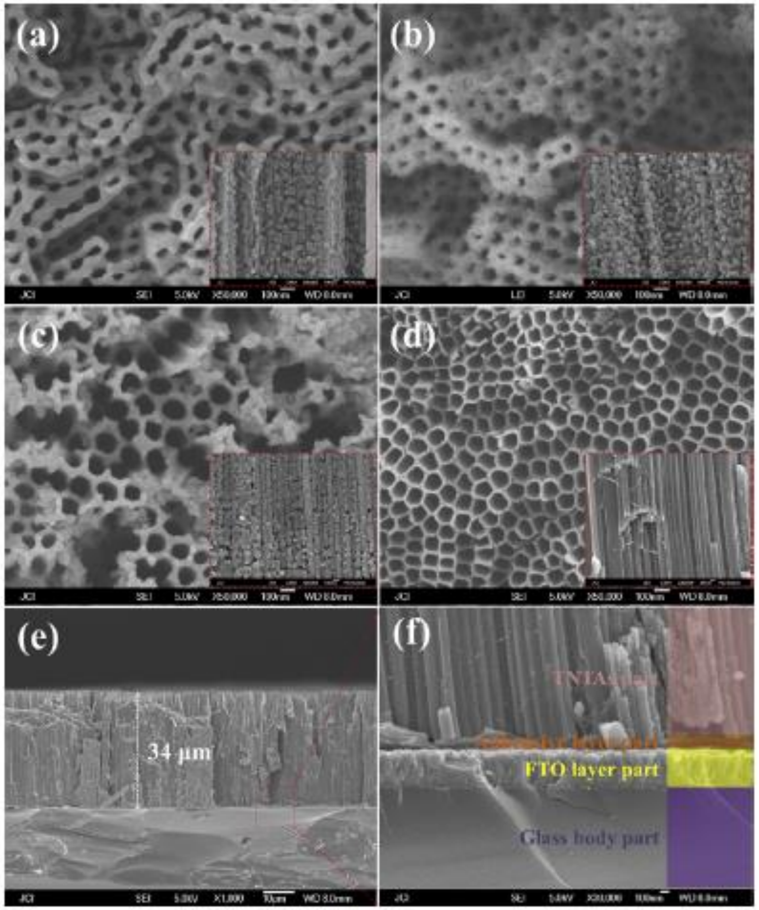


Fig. 3. FESEM images of the TNTAs photoanodes, (a) HV-160, (b) HV-180, (c) HV-200, (d) TA-450. (e) the cross-sectional view of the TA-450 TNTAs film transplanted on the FTO substrate. (f) present the corresponding zoom-in part from the red dash line rectangle in (e). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Nanolithography

Top-down approach

- 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

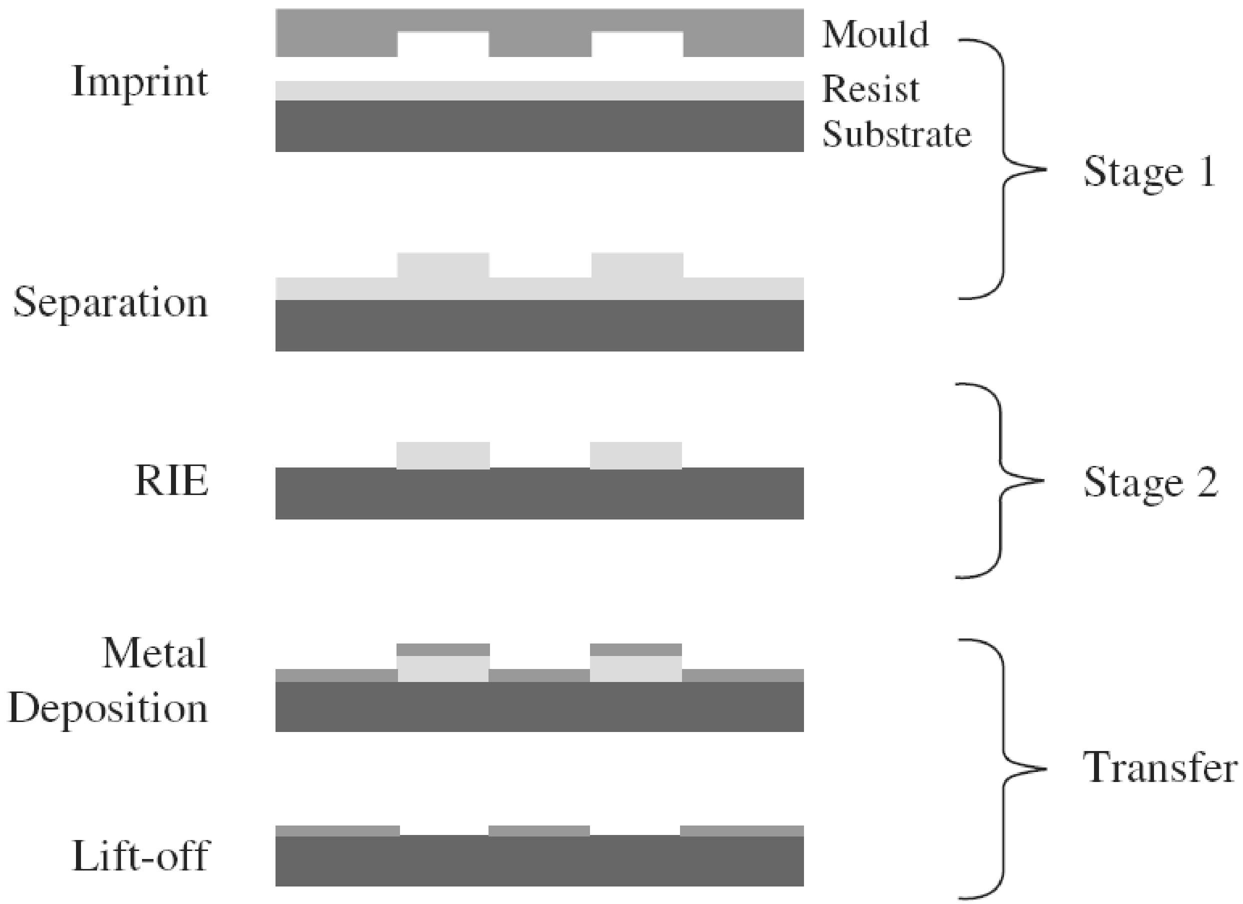
- Two-step process:
  - Patterns are stamped using a mould on a polymer (resist) layer deposited on the substrate;
  - The resist relief pattern stamped onto the polymer is treated by reactive ion etching (RIE) until its recessed areas are all removed

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

Nanoimprint lithography-types

- Thermoplastic nanoimprint lithography
- UV nanoimprint lithography
- Nanoembossing
- Soft lithography
- Near-field lithography
- Dip-pen lithography

Thermoplastic nanoimprint lithography



Thermoplastic nanoimprint lithography

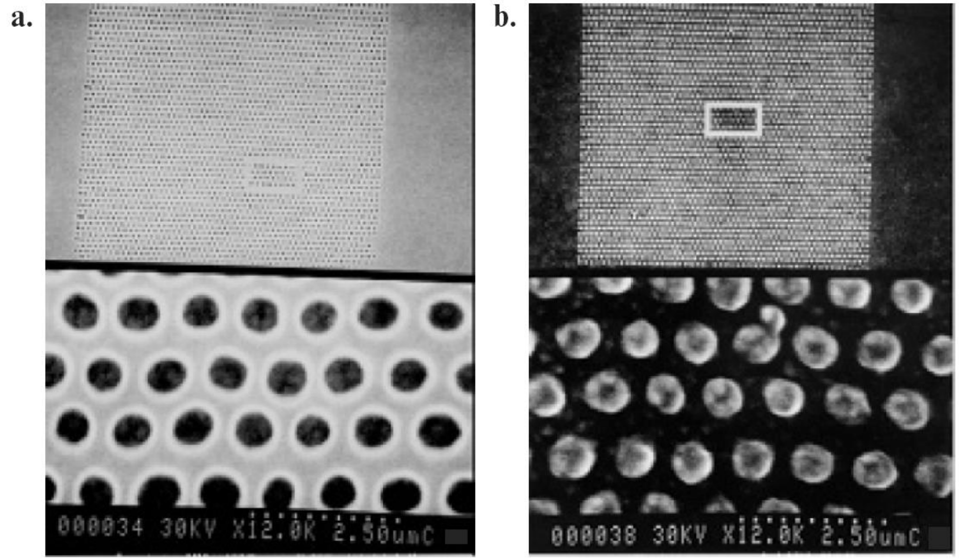
- Advantages
  - Very high resolution
  - High throughput production
  - Simple and cheap method
  - Easy to implement
  - Accessible and applicable in a wide range of situations
- Disadvantages
  - Potentially time consuming heating/cooling stages
  - Mould is necessary
- Mould
  - Typically produced 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

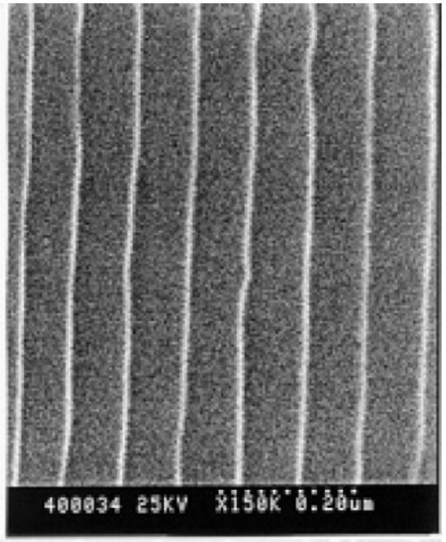
Examples of the trilayer process

- 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



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

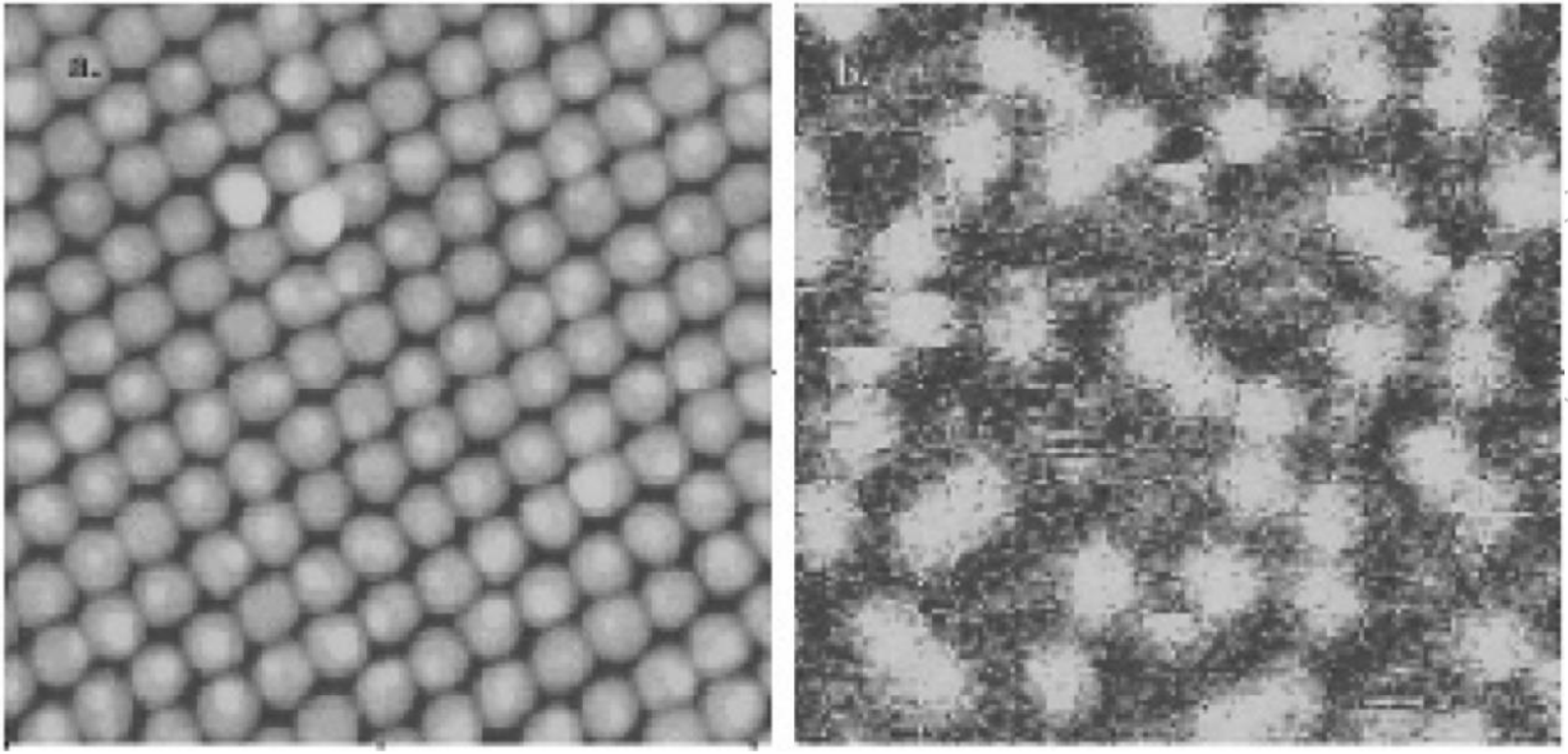
Array of silicon lines with width less than 10 nm, obtained by nanoimprint lithography and RIE of a silicon-on-insulator substrate.



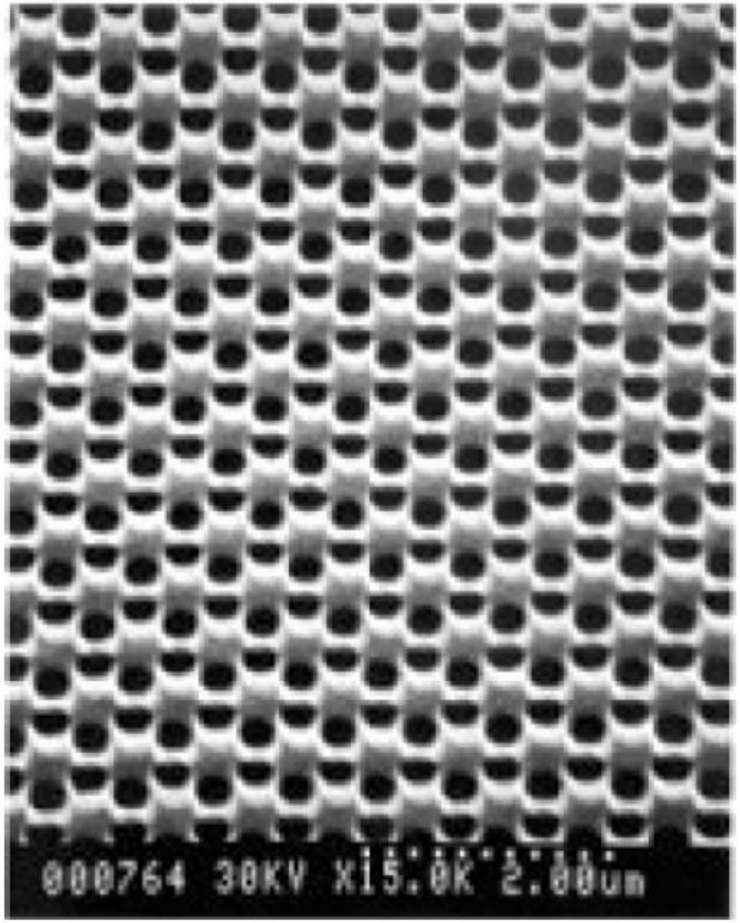
Application areas

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

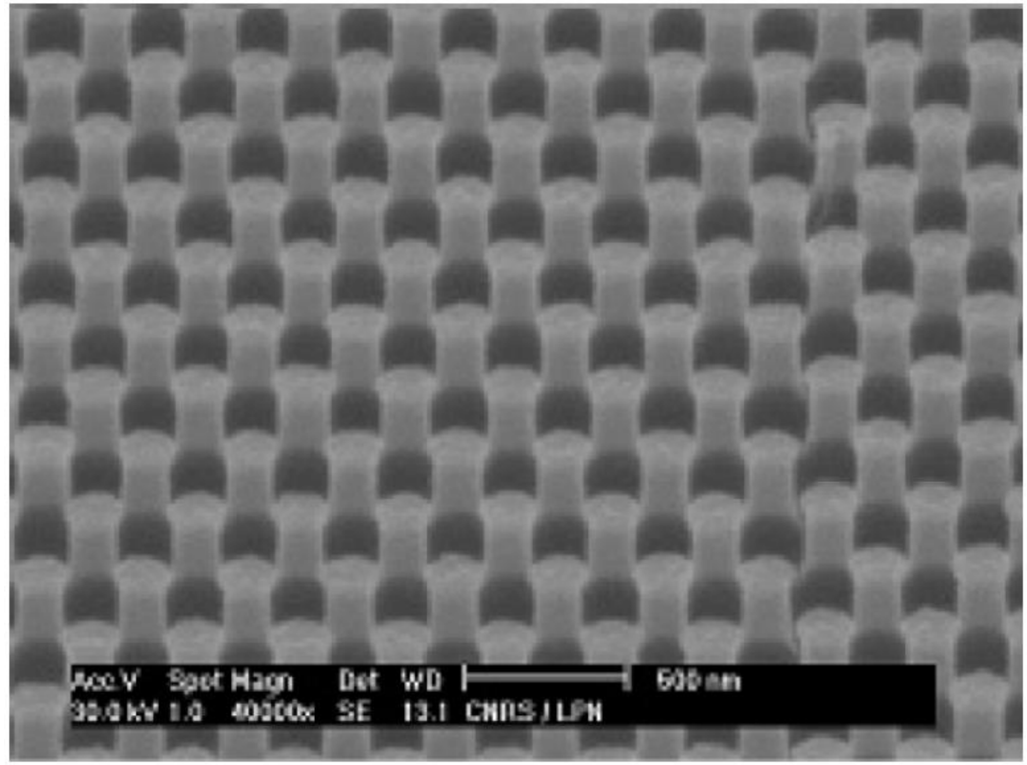
More examples…



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.

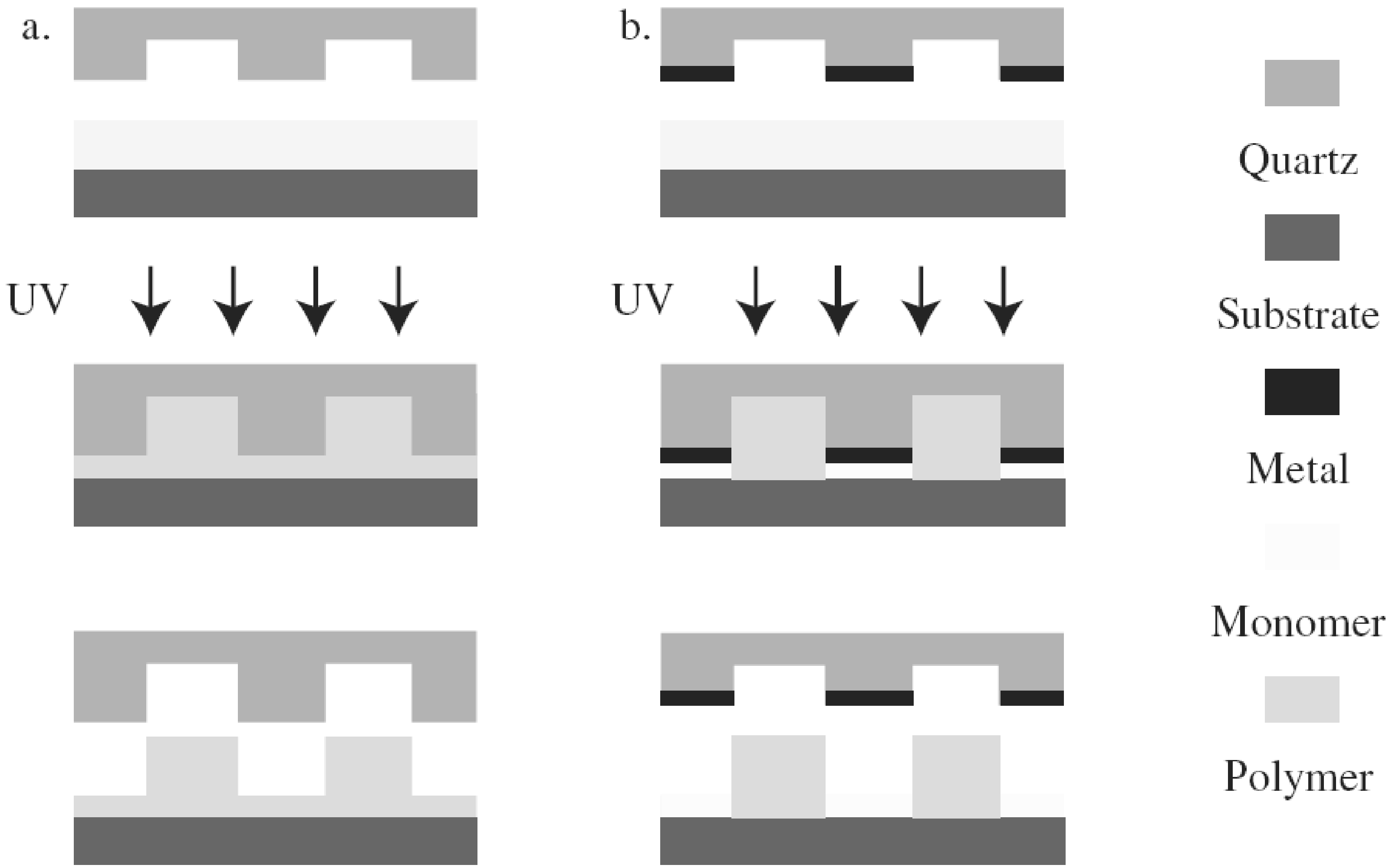


Graphite-type array on a polymer layer, for use as an etch mask for the underlying substrate in order to obtain functional photonic crystals.



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

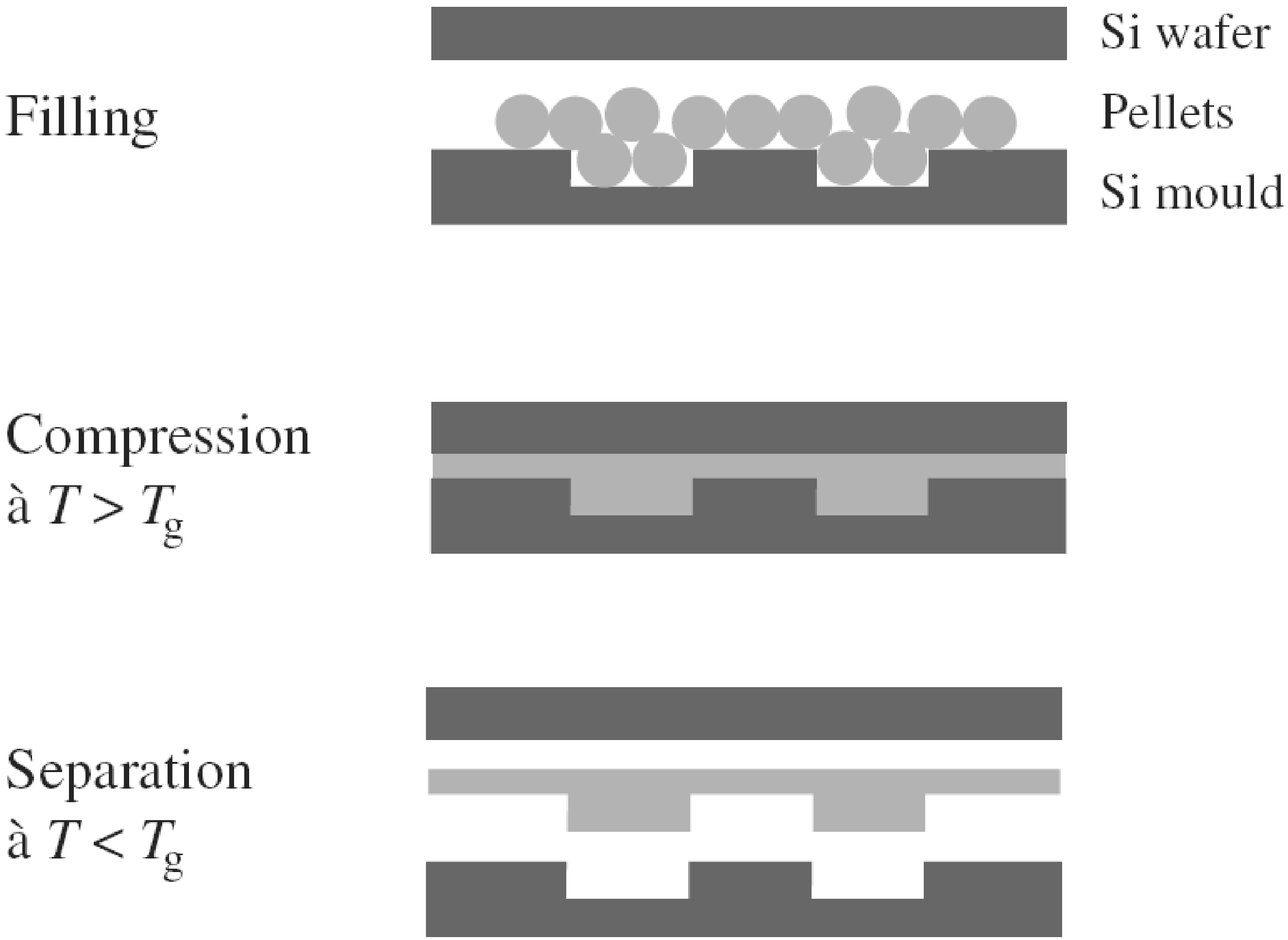
- Two main steps:
  1. Moulding a viscous pre-polymer and catalyzer mixture at room temperature
  2. Photopolymerizing

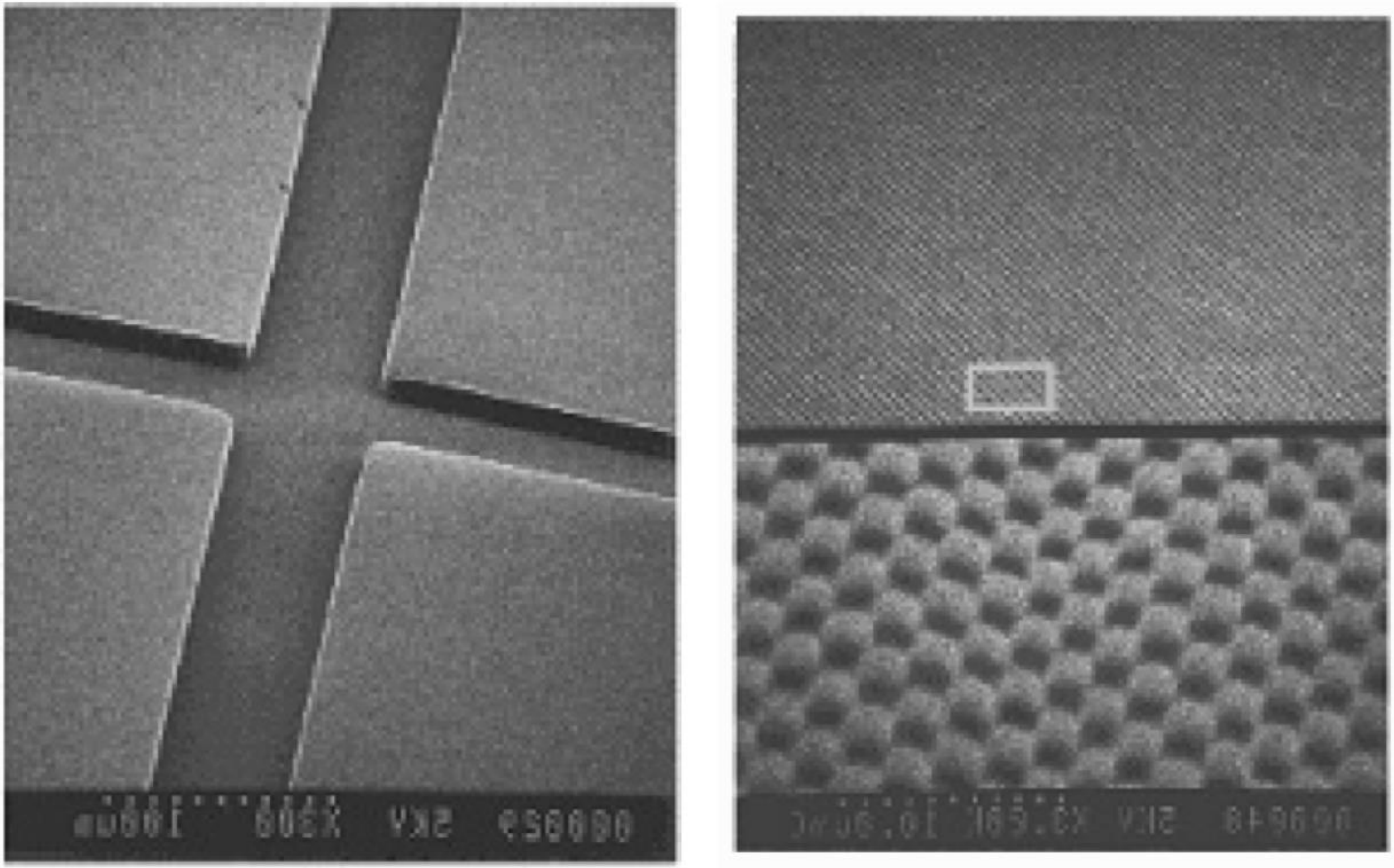
- Advantages
  - Works at room temperature and low pressure using a quartz template
  - High duplication rate (high throughput) and possibility of high precision alignment

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



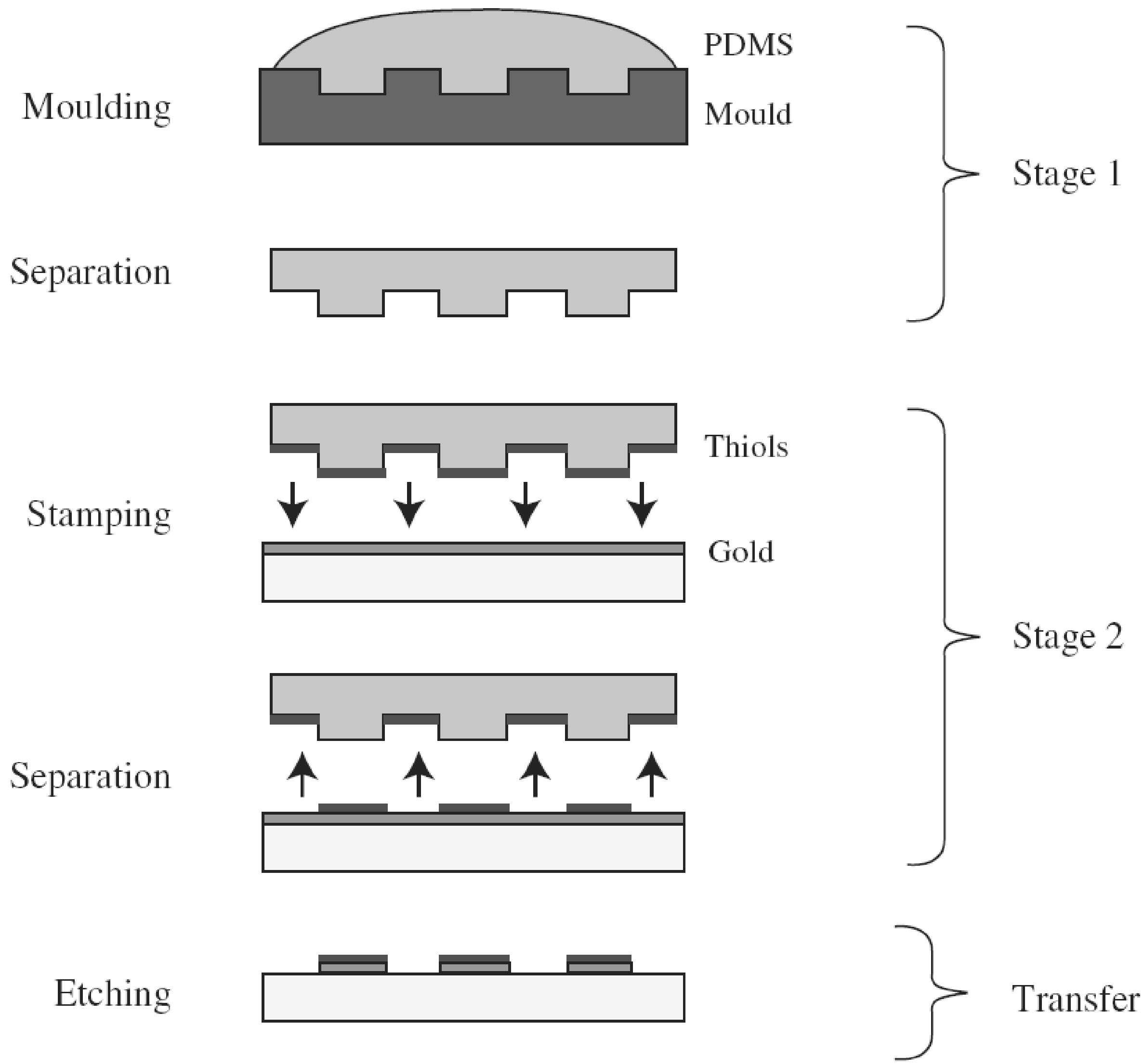


Microchannel (*left*) and nanostructures (*right*) made by nanoembossing with PMMA pellets and an etched silicon mould.

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

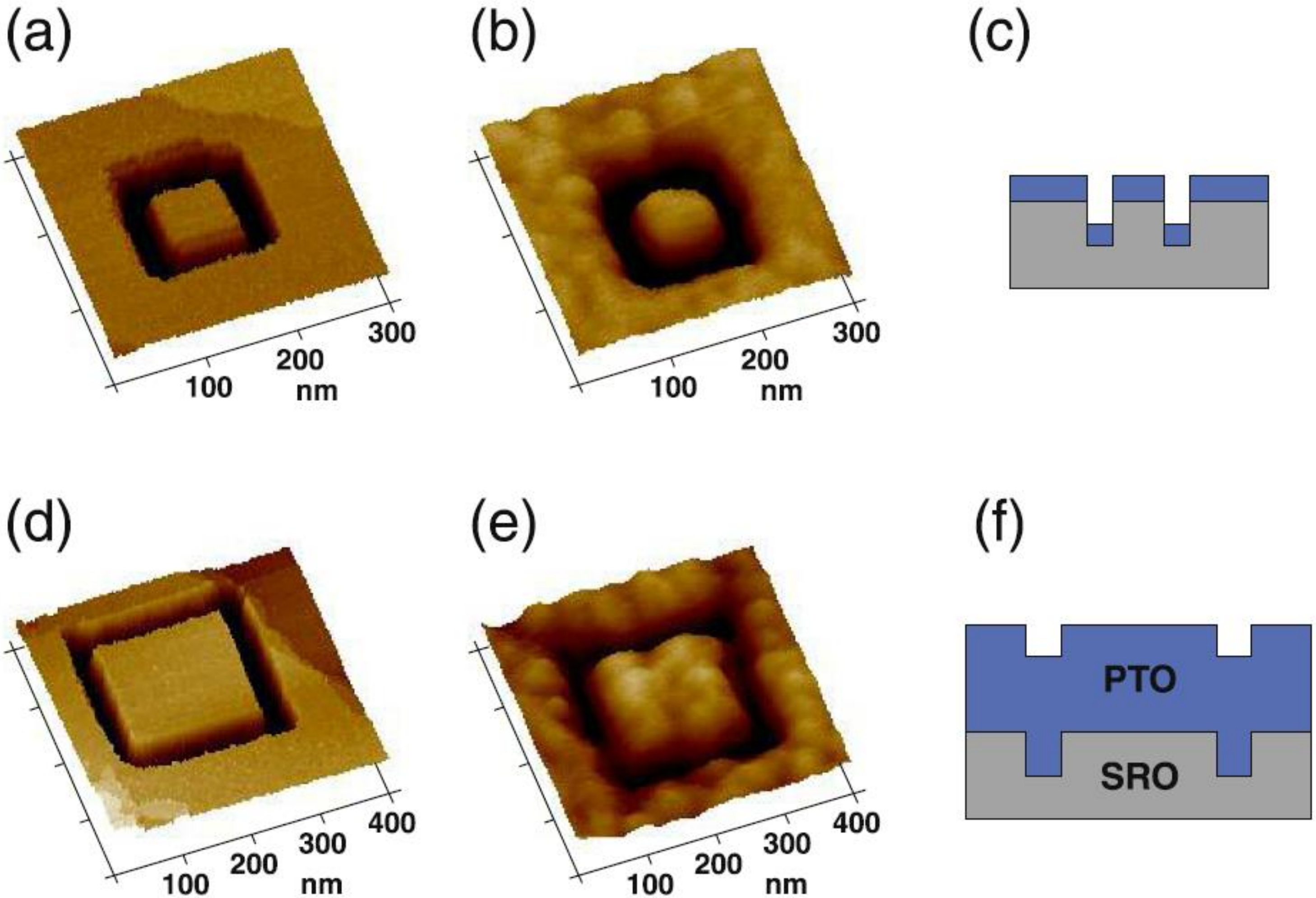
Soft lithography



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



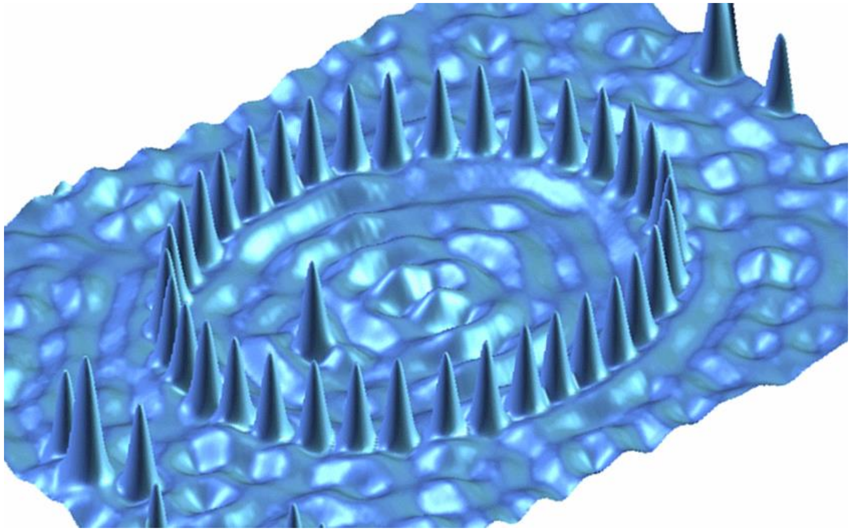
STM topography images: Templates defined in a $SrRuO_3$ (SRO) thin film surface by STM lithography

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



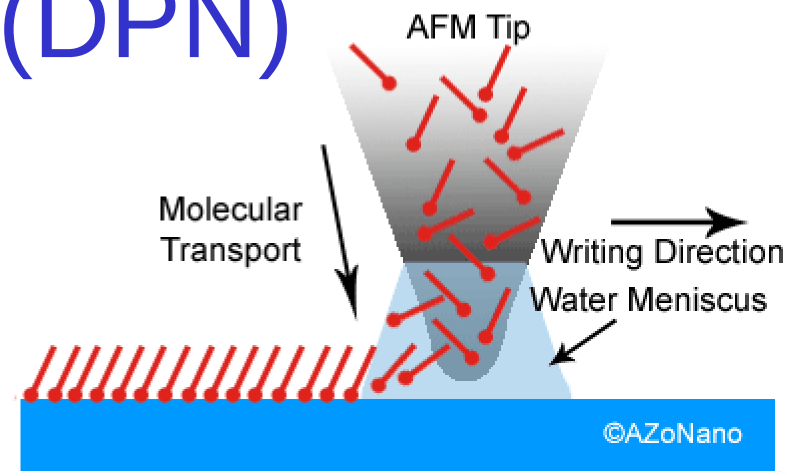
Elliptical quantum corral:

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

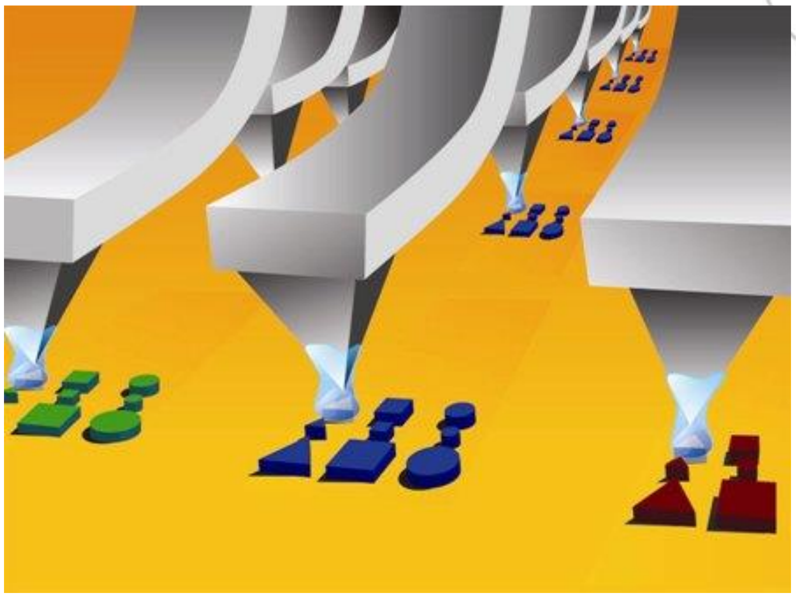
•STM measurements were performed at a 4.3 K sample temperature

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