# Nanometer Scale Patterning and Processing

Spring 2016

## Lecture 38

## Nanoimprint Lithography (NIL) – NIL Mold Fabrication

- Section 7

# NIL MOLD FABRICATION

# Mold for thermal and UV-NIL

Mold: also called template, stamp, master.
Mold release agent: also called releasing layer, anti-sticking coating.
Separation: also called de-molding, de-embossing, release.

Overview:

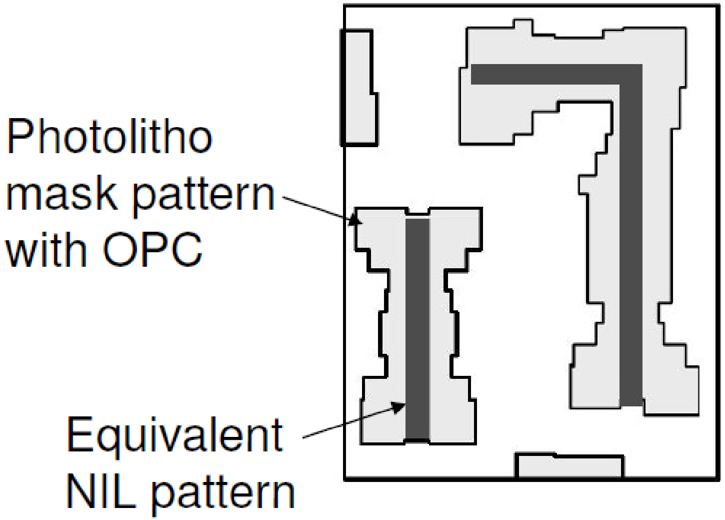
- Usually fabricated from Si, quartz or nickel, though polymer mold is becoming more popular and available.
- Feature fabrication at 1x vs. 4x for optical projection lithography, so critical dimension (CD) control at 1x more challenging.
- For instance, photomask needs ~250 nm resolution to print 65 nm features, NIL mold needs to be 65nm.

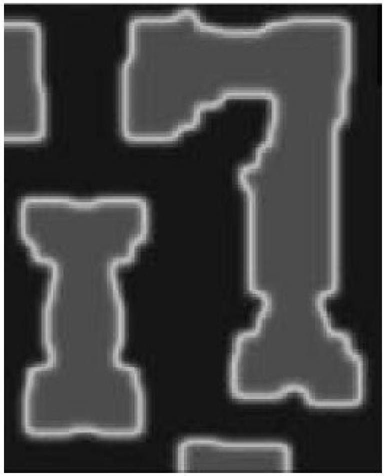
Desired properties:

- Defect free fabrication & inspection, repairable.
- Compatible to mold release agent coating.
- Mechanically durable (for reuse).
- Chemically durable (for cleaning).
- Low CTE mismatch with substrate (coefficient of thermal expansion).
- High imprint uniformity - uniform residual layer.

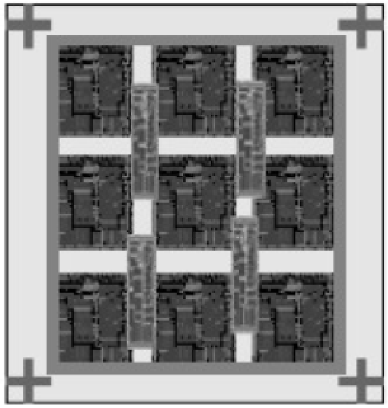
# Comparison with photomask

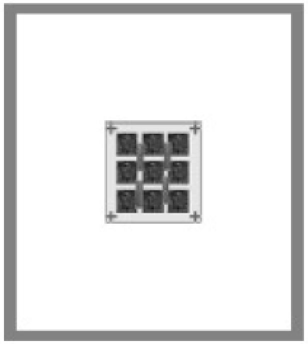
Optical projection lithography mask with OPC & equivalent NIL mold.





Photomask (4X)

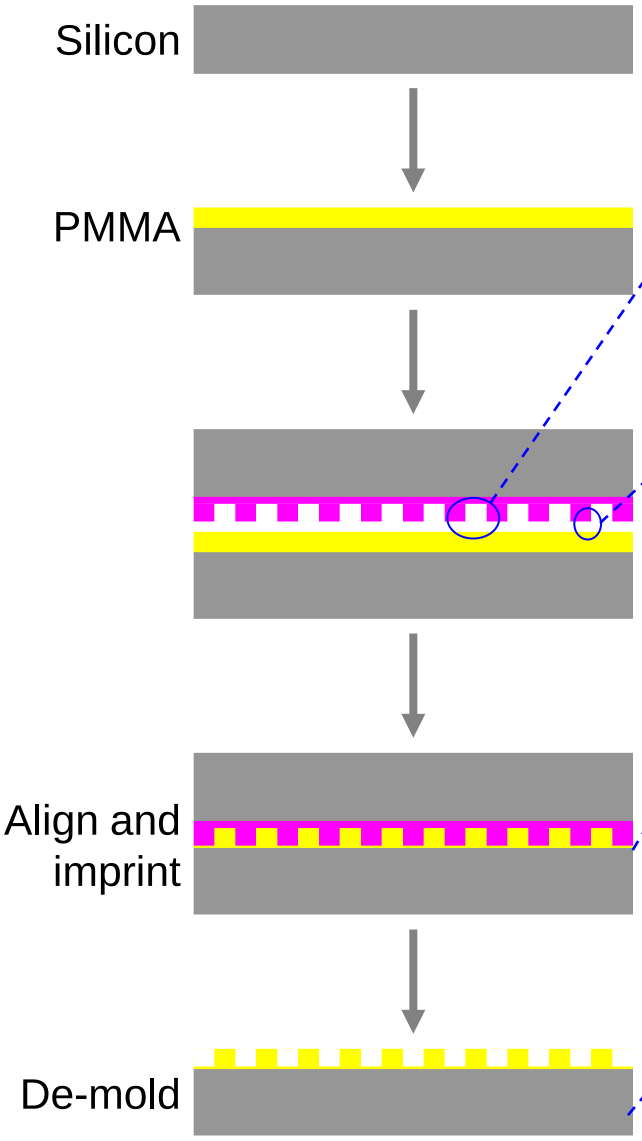




NIL Template (1X)

OPC: optical proximity correction

# Mold issues: profile, roughness, sticking

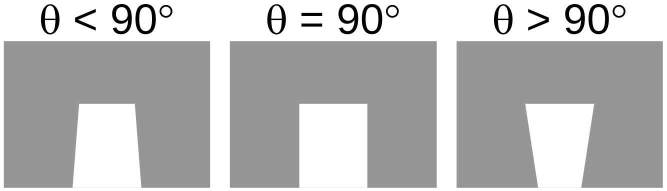

Silicon

PMMA

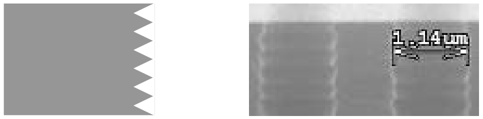
Align and imprint

De-mold

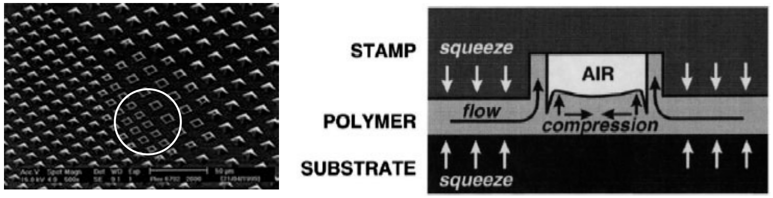
**Sidewall angle** (θ)



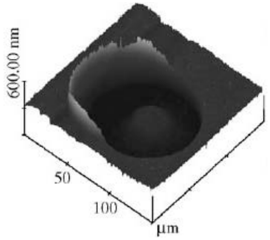
**Roughness** ($R_a$)



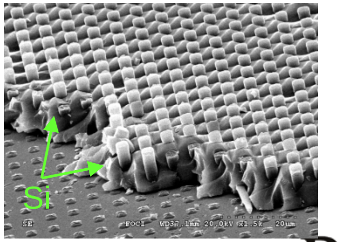
**Polymer flow and filling property**



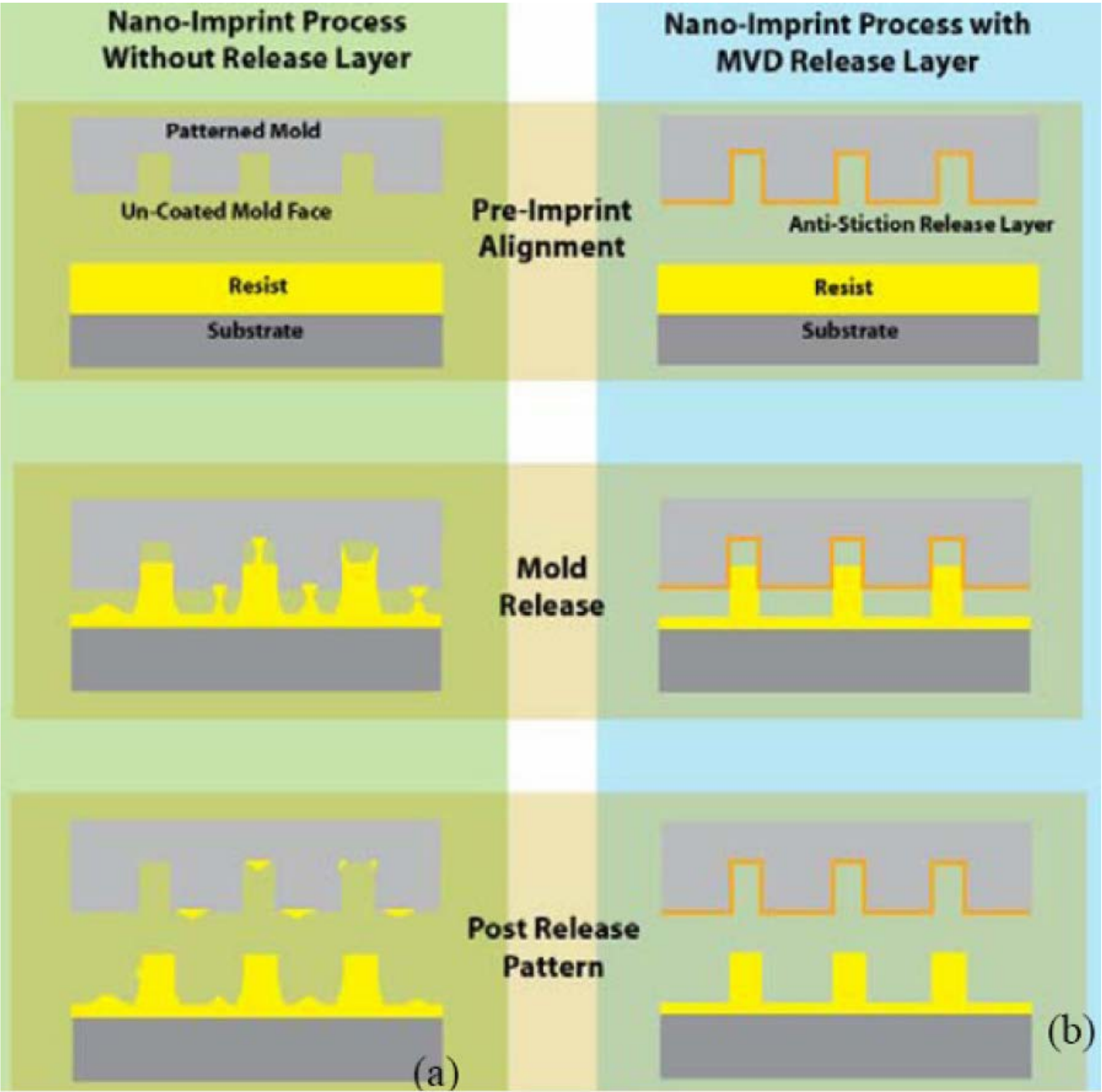
**Resist deform**



**Sticking**



# Importance of anti-stick coating



# Mold release agent: Teflon-like coating

Same idea as anti-stick cooking ware coating, but mono-layer.

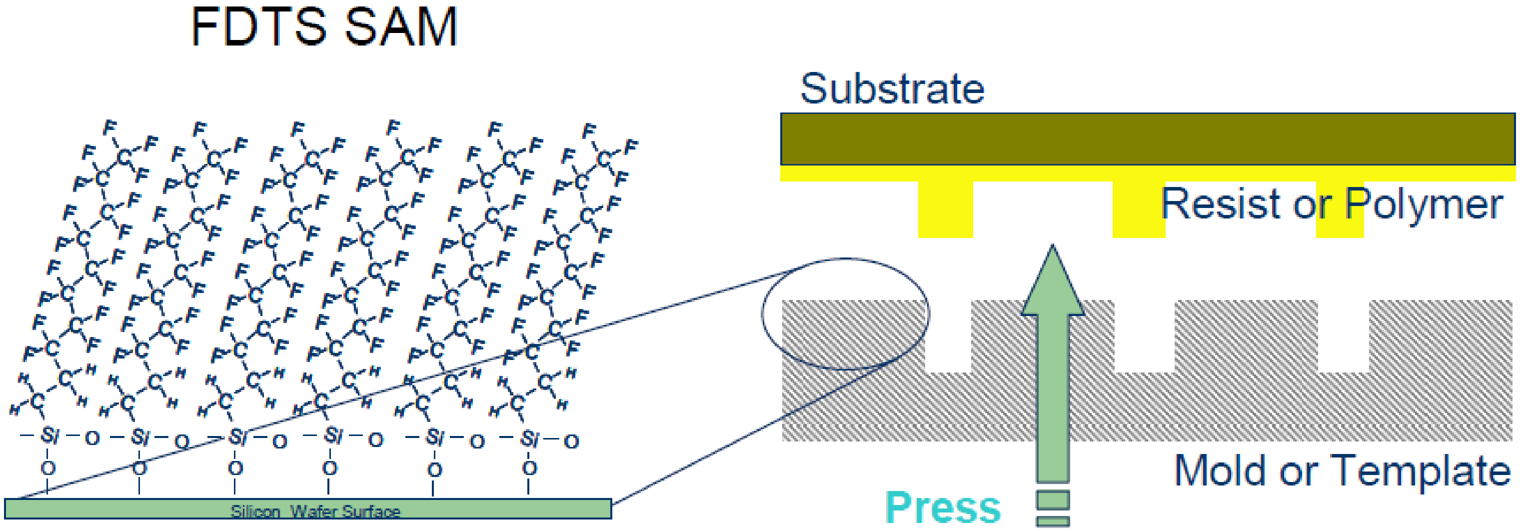
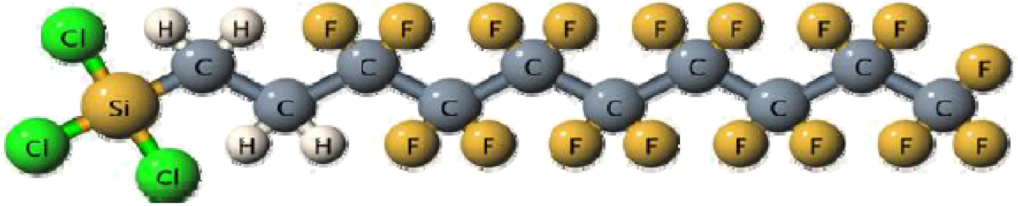


Fig. 2 SAMs used as a low energy release layer



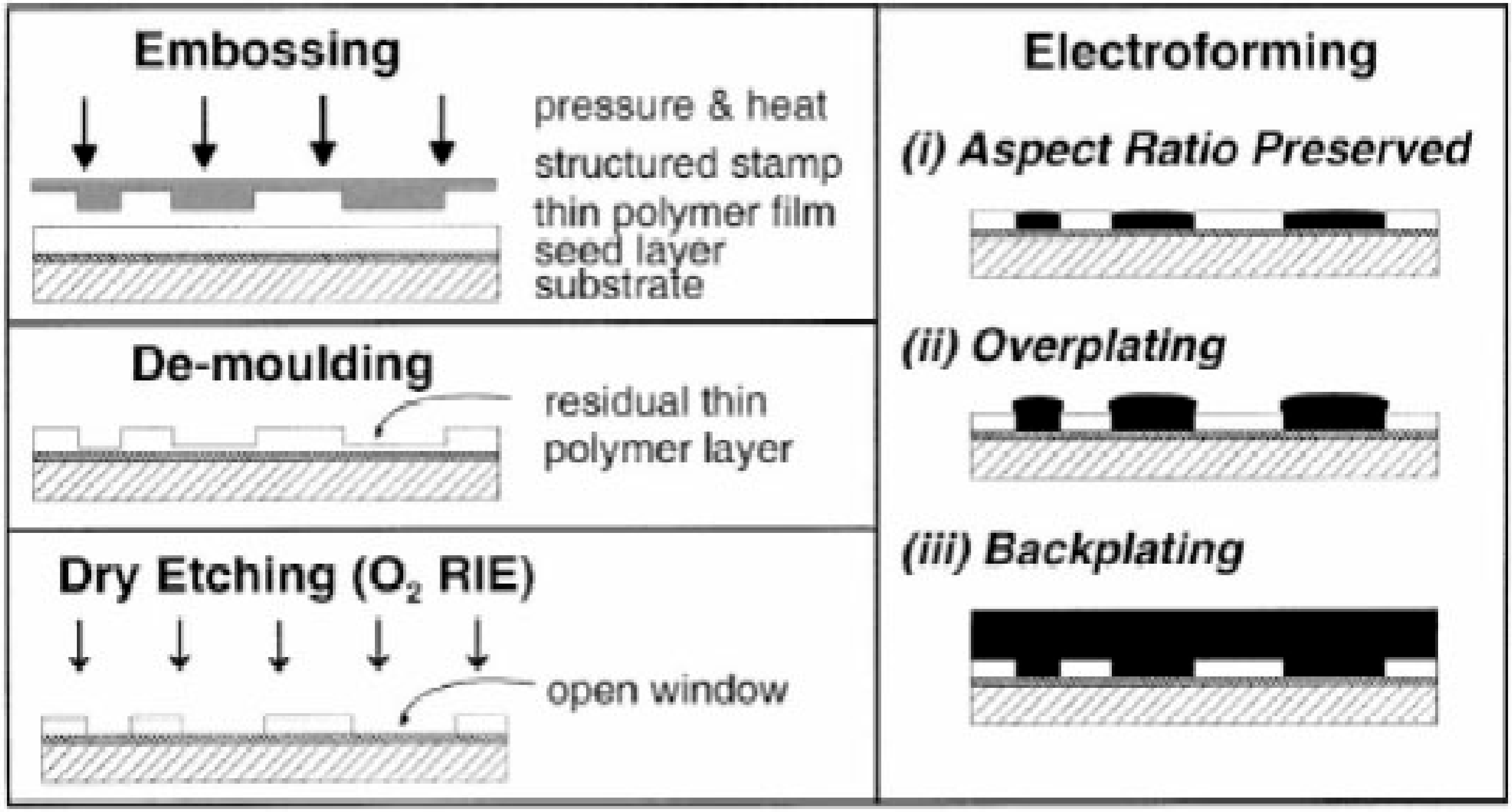
**Coatings are 100% conformal and extremely uniform.**

Finished template coated with an ultra-thin anti-sticking layer using molecular vapor deposition process (MVD$^{TM}$) from Applied Microstructures

Silane by simple vacuum coating: clean wafer by oxygen plasma, put wafer and a drop of silane inside a container, and vacuum the container. After >5 hours, take wafer out and bake 150$^{o}$C for 20min to cross-link the silane coating.

# Ni mold

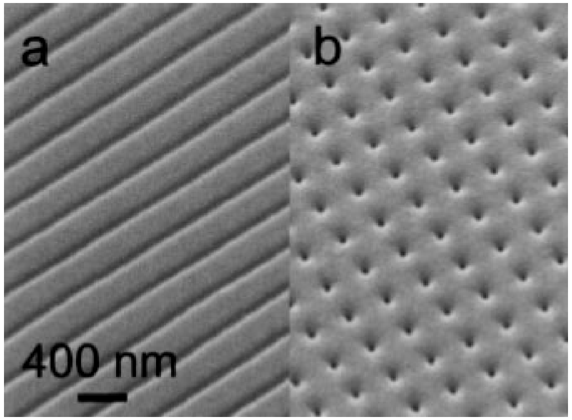
- Si or $SiO_2$ mold is most popular, but they are brittle.
- Metal mold is more robust and durable, used for making CD/DVDs.
- More difficult to fabricate,  takes days for electroplating to 100s um.
- Thickness is not uniform: much thicker (>2×) plating near wafer edges.
- Direct silane anti-stick coating to Ni not working, needs sputtering a thin (10nm) $SiO_2$.
- More used for hot-embossing onto thick plastics for micro/nano-fluidics applications.

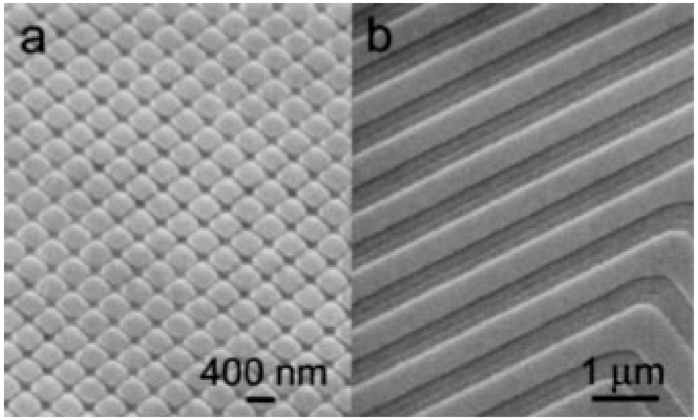


Source: Microelectron. Eng. 57-58 (2001) 375-380

# SEM images of Ni molds

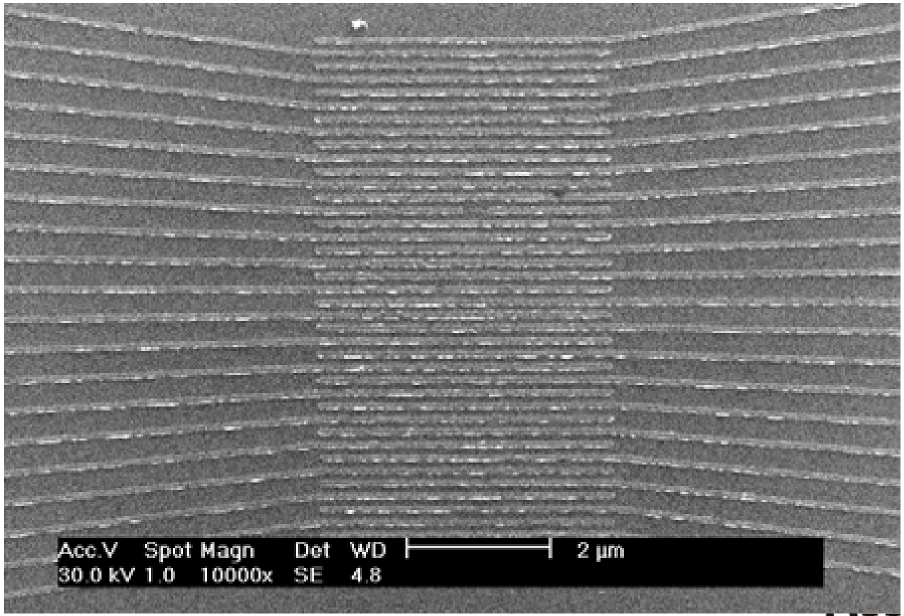
Mold by electroplating (follows profile in resist, good)





Mold by EBL and liftoff

Easier to pattern metal by liftoff. But metal structure by lift-off doesn't have vertical profile (Δ-shaped), and is of low height. The underneath Si is still brittle.



SEM image a of Ni/Si stamp showing 90nm channel-length inter-digited electrodes.

# Soft PDMS/PMMA mold for UV-NIL

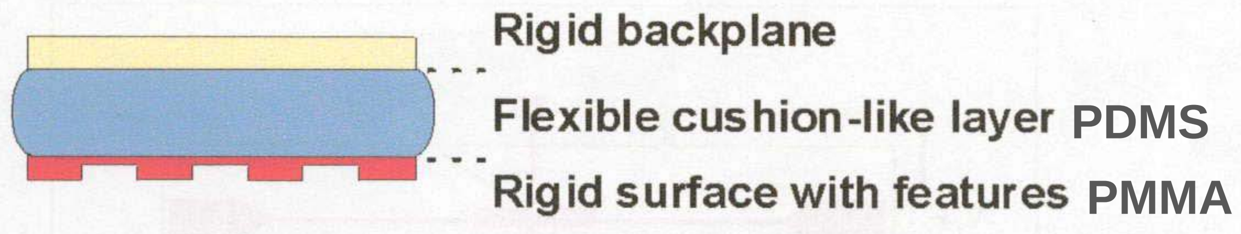
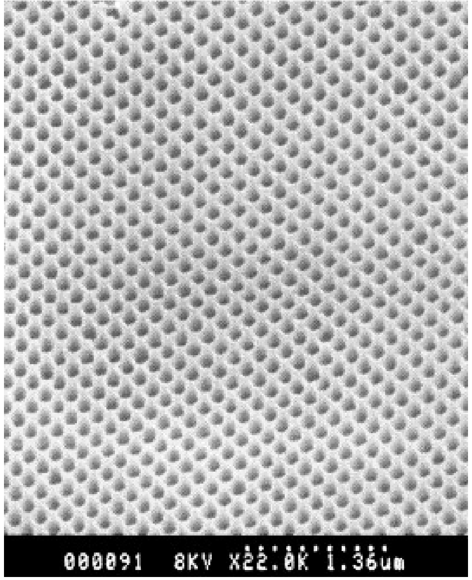
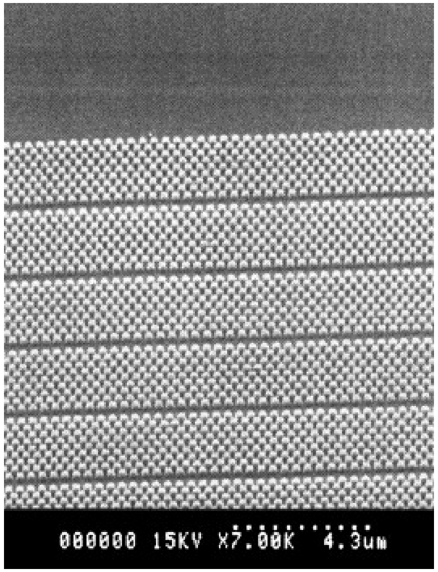


**Figure 7:** schematic overview of a possible multi-layer-stamp design, a flexible cushion like layer between a rigid backplane and a thin, rigid surface with the imprint structures

Mold: PMMA top layer cast and bonded on a PDMS buffer and a glass carrier.



Resist pattern: 0.1 atm imprint pressure, triangular lattices of 300nm period and 200nm pillar diameter.

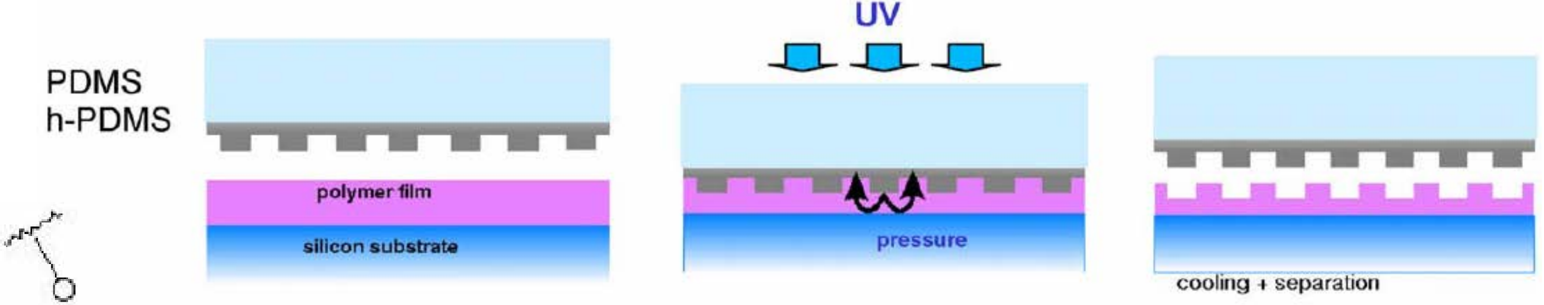


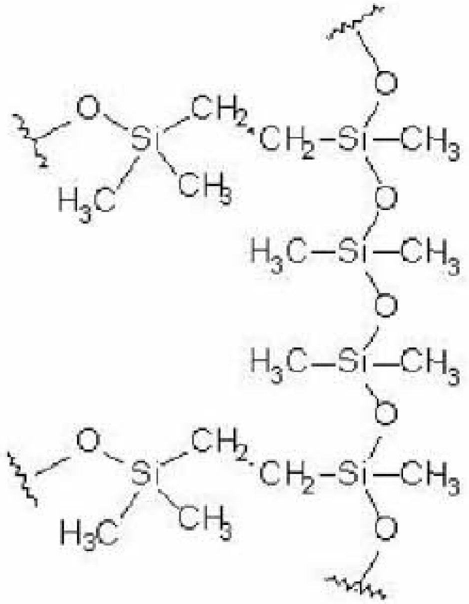
PDMS alone can be used as UV-NIL mold, but its nanostructure is not hard enough and will bend/collapse during NIL even at low pressure. It is good for $\mu$m-feature size UV-NIL.

Roy, “Enhanced UV imprint ability with a tri-layer stamp configuration”, MEE 2005

# Soft PDMS/hard PDMS mold for UV-NIL

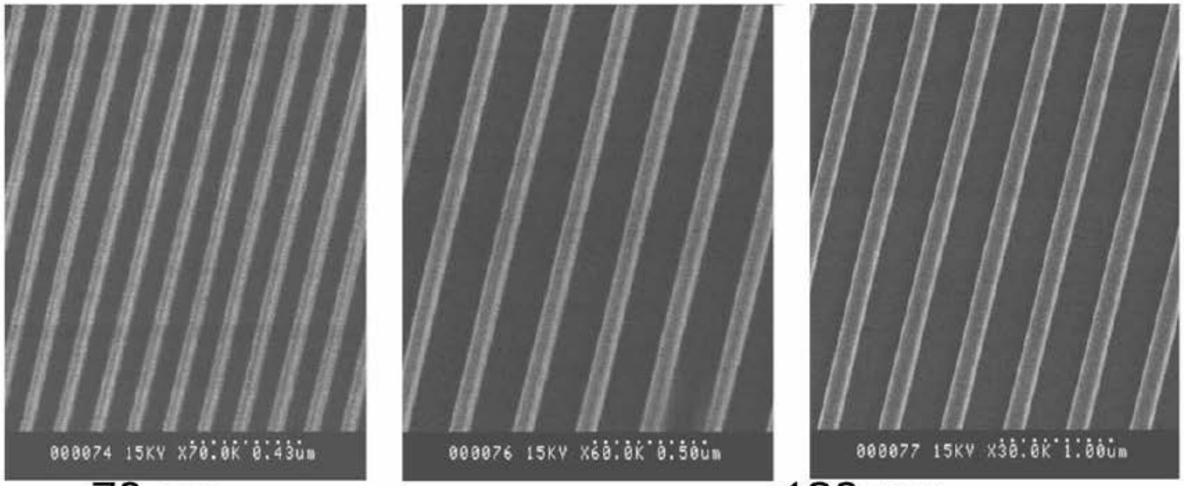
Hard PDMS: more cross-linked PDMS, but more brittle and less flexible





**PDMS**

Images of line gratings after NIL



70 nm

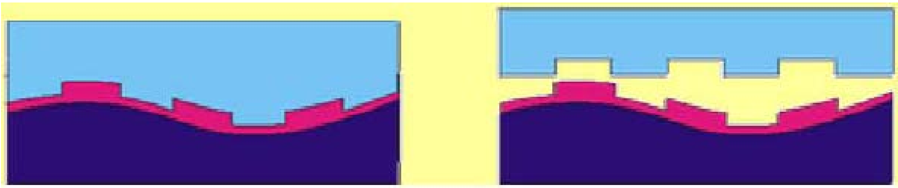
120 nm

**Use of a flexible mold :**

**for conformal contact,**

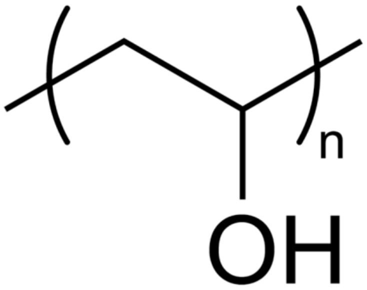
**even on patterned substrates**

**with surface irregularities**

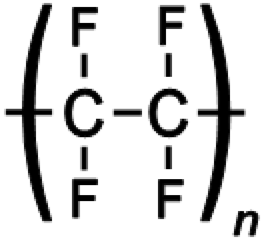


# Other polymer mold materials

PVA (polyvinyl alcohol): water soluble, can be one-time use mold (imprint and dissolve the mold with water)

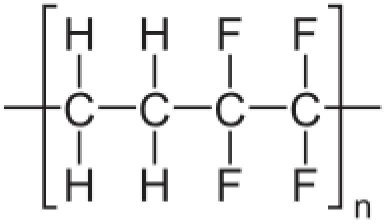


PTFE (Teflon, polytetrafluoroethylene), can be molded using a silicon mold at high temperature (>250°C). Low surface energy (no need for mold release agent), high strength, can do thermal NIL at high temperature.



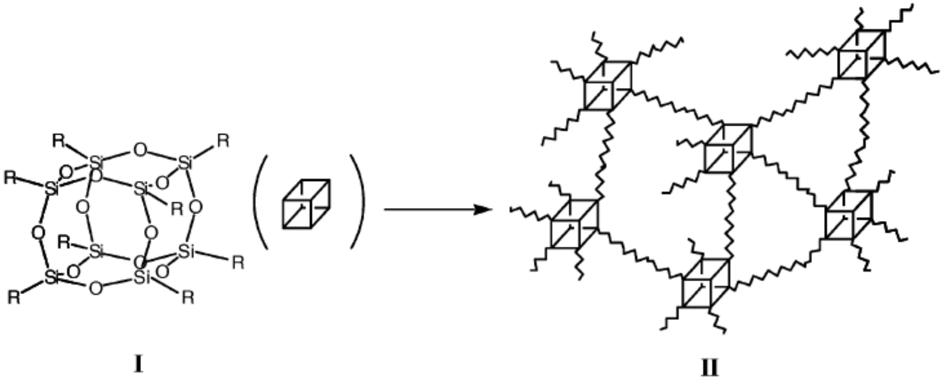
$-(CF_2-CF_2)_n-$

ETFE (ethylene tetrafluoroethylene), similar to PTFE, but mold is easier to fabricate from a master mold.



$-[CH_2-CH_2-CF_2-CF_2]_n-$

SSQ (silsesquioxane), similar to HSQ. After cross-linking the material is like $SiO_2$, which is easy to coat with mold release agent.



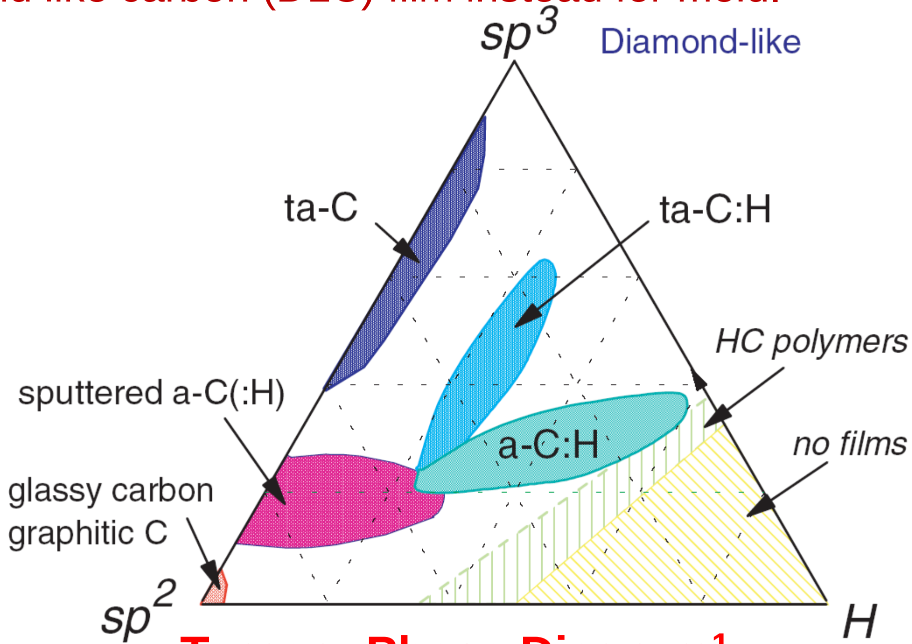
In principle, all cross-linked polymer can be used as NIL mold; however, most of them cannot be treated with mold release agent (hard to separate after imprint).

Barbero, “High resolution nanoimprinting with a robust and reusable polymer mold” (ETFE), Advanced Functional Materials, 2419 (2007)

# Diamond Molds

Diamond is hardest, but too expensive. Use diamond like carbon (DLC) film instead for mold.

- DLC is a synthetic meta-stable form of carbon.
- Amorphous network consisting of various fractions of hydrogen, $SP^2$ and $SP^3$ hybridized carbon.
- Common synthesis techniques
  - o Pulsed Laser Deposition
  - o Ion beam deposition
  - o Plasma Enhanced Chemical Vapor Deposition (PECVD)
  - o And many other techniques
- PECVD deposition uses hydrocarbon plasma in the presence of energetic ion bombardment.



**Ternary Phase Diagram[1]**

Why is DLC a suitable material for serving as the mold?

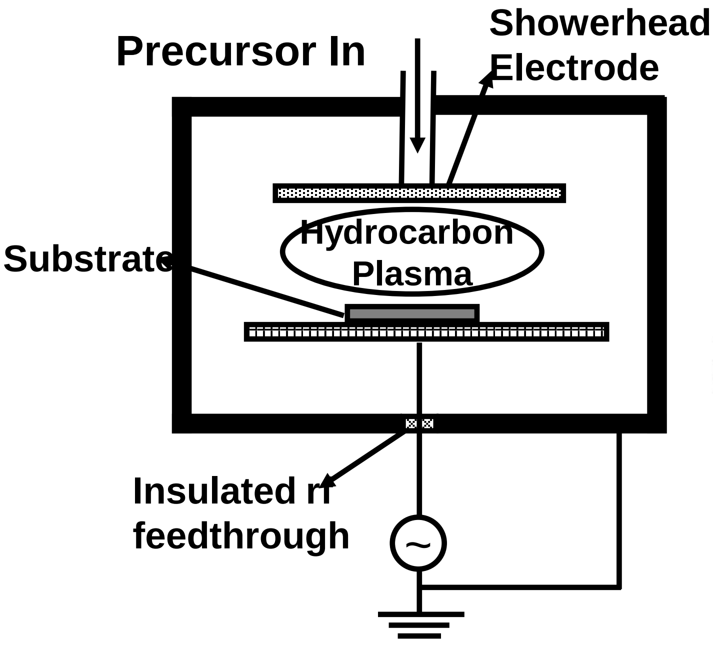
- Excellent hardness and wear resistance → 30-35 Gpa.
- Low energy surface → 35-50mN/m, may not need anti-stick coating.
- Controllable band gap → 1 to 3.5eV, for UV transparency.
- High chemical and corrosion resistance.
- Can be deposited on both Quartz and Si.

However, DLC deposition is very challenging, not readily available.

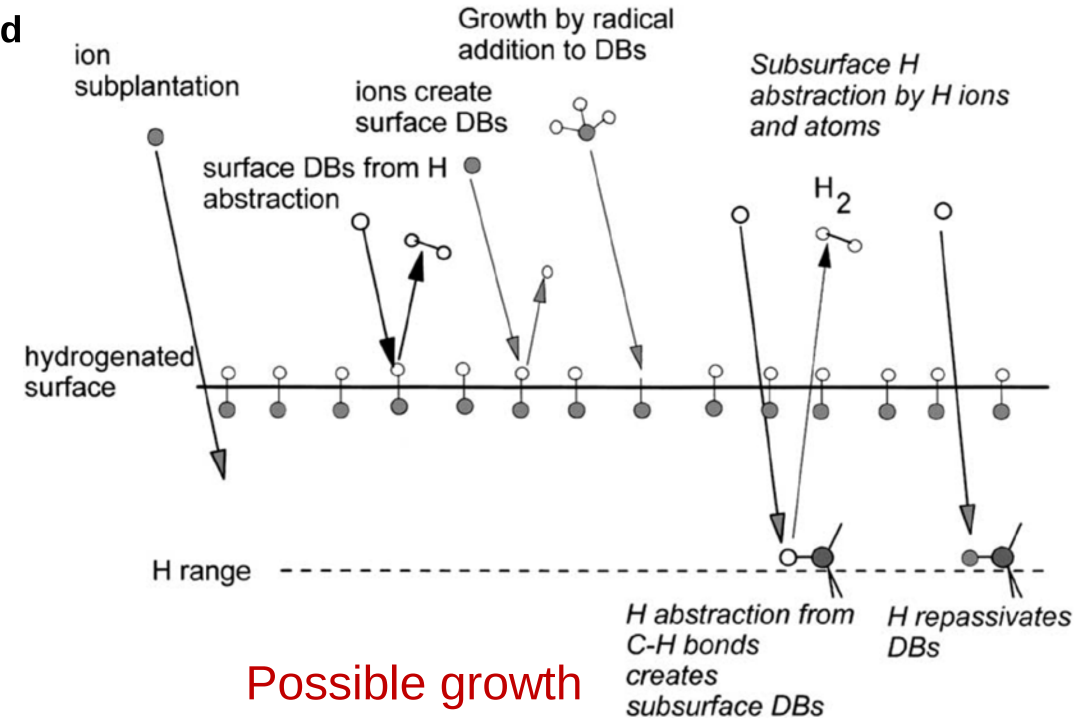
J. Robertson, Materials Science and Engineering R 37 (2002), 129-281

# DLC deposition by PECVD

Energetic Ions, radical and atomic species created in the plasma are all critical



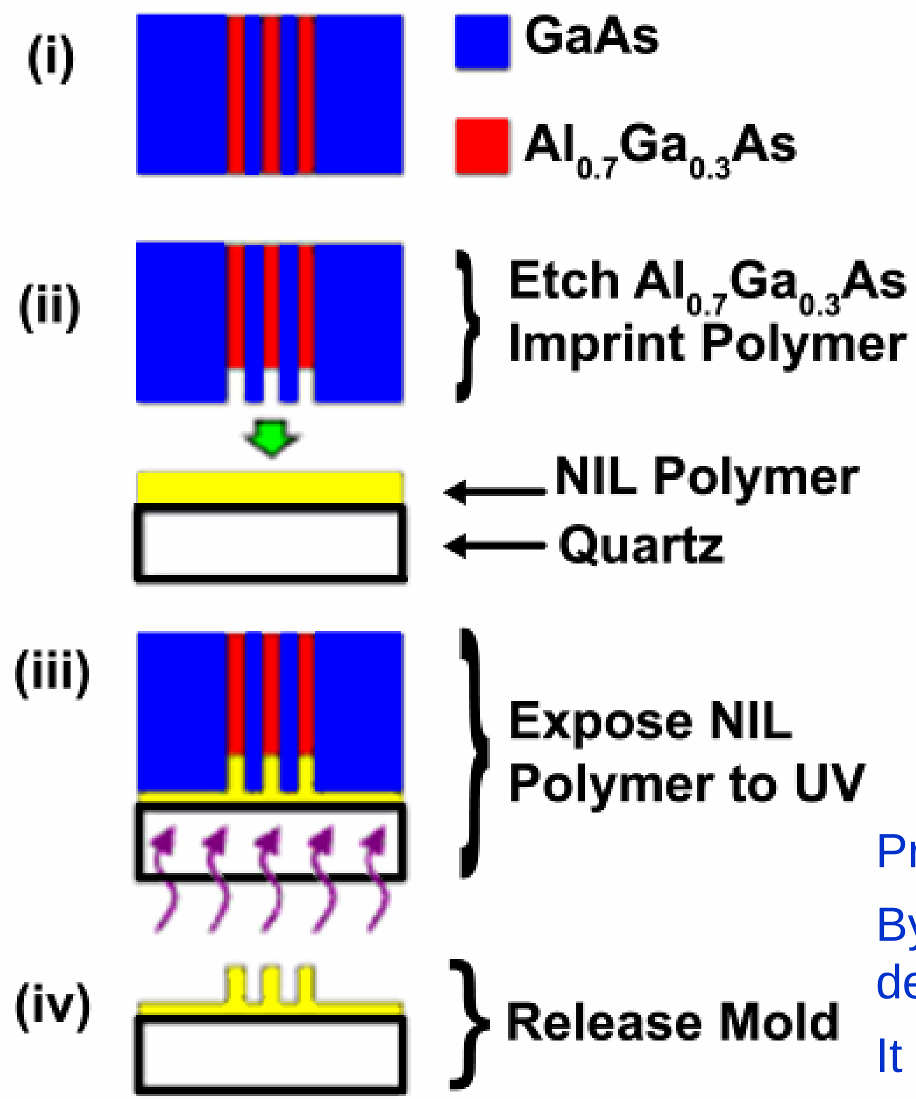
Typical PECVD reactor

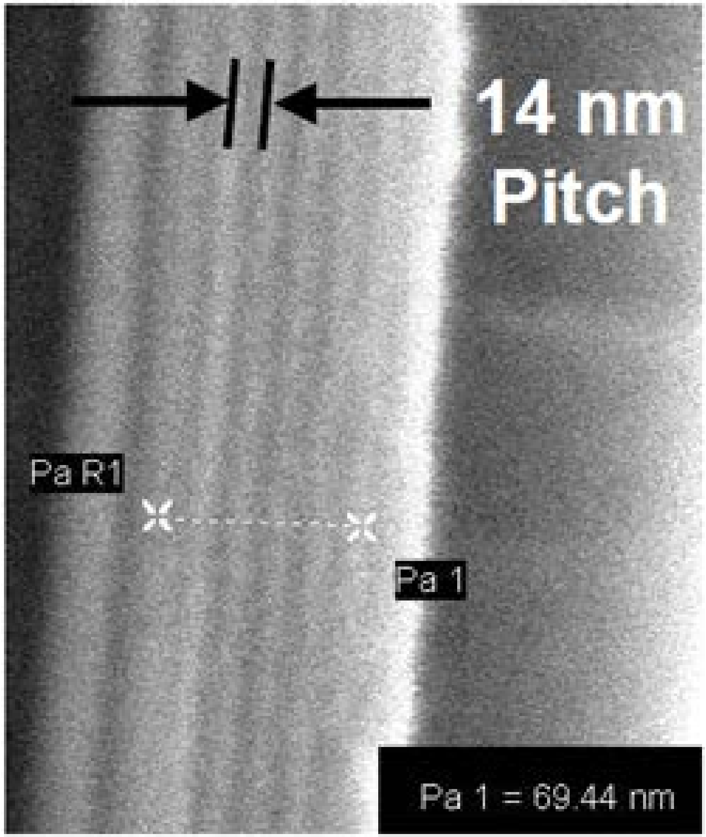


Possible growth mechanism

- DC and RF plasmas including microwave, capacitive and inductive-coupled plasmas.
- Typical PECVD reactor
  - o Reactor geometry, nature of RF coupling results in availability of energetic ions, radical and atomic species
  - o Auxiliary electrode to control the ion-energies
- Deposition mechanisms → sub-plantation model, cylindrical spike model, …

# Mold by MBE and selective wet-etching





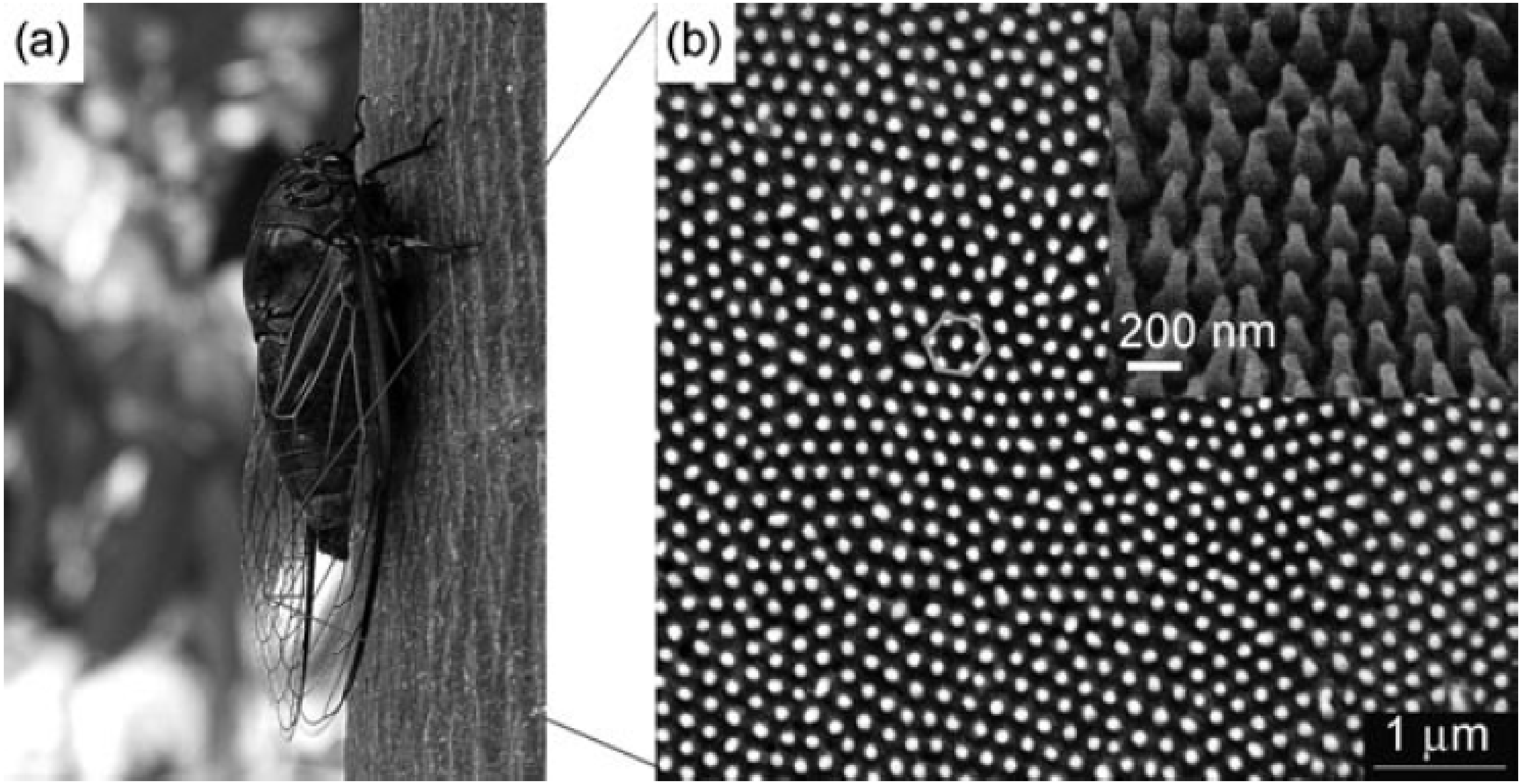
Precise control of pitch and line-width.

By far the highest resolution (~6nm) NIL is demonstrated using such a mold.

It is very difficult to write 14nm pitch grating using e-beam lithography.

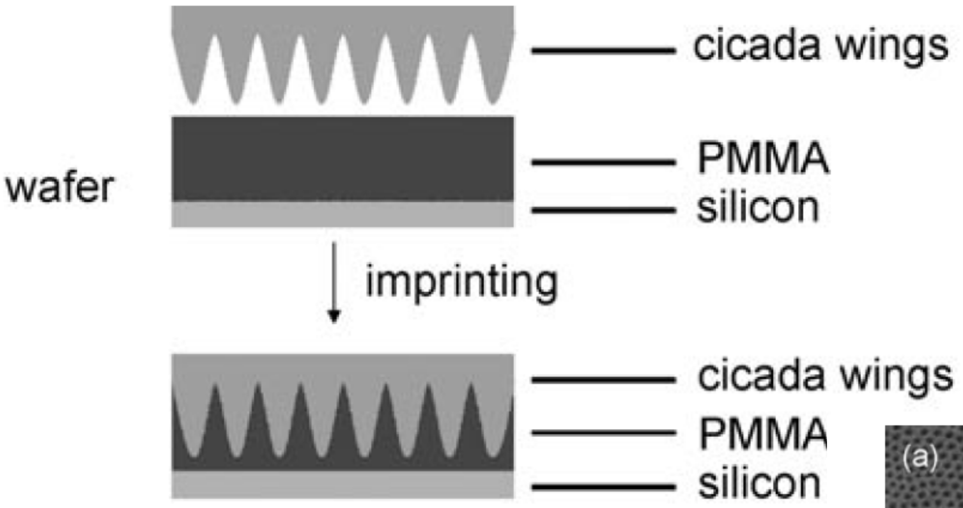
# Mold fabricated by nature

## Cicada Wings: a mold from Nature



The cicada wings consist of ordered hexagonal close-packed arrays of pillars with a spacing of about 190nm.
The height of the pillars is about 400nm and the diameters at the pillar top and bottom are about 80nm and 150nm, respectively.

# Results of NIL using cicada wing mold



Pressure ~40 bar; temperature ~190℃, 70℃ higher than the $T_g$ of PMMA; imprint time 3min.

The pitch between the wells is about 190nm, the well diameter is about 150nm, and the depth is found to be about 400nm; these are consistent with the mold.

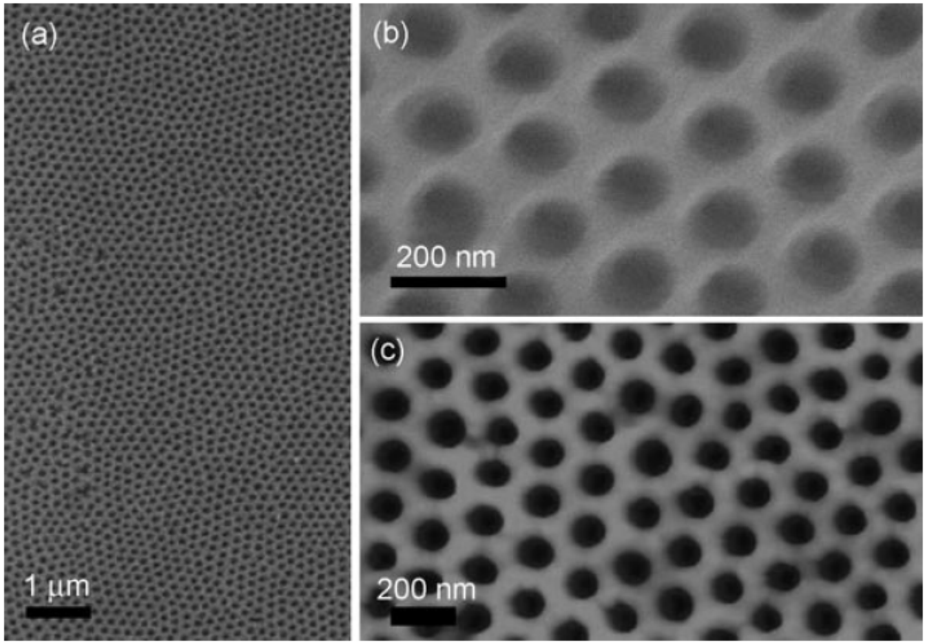
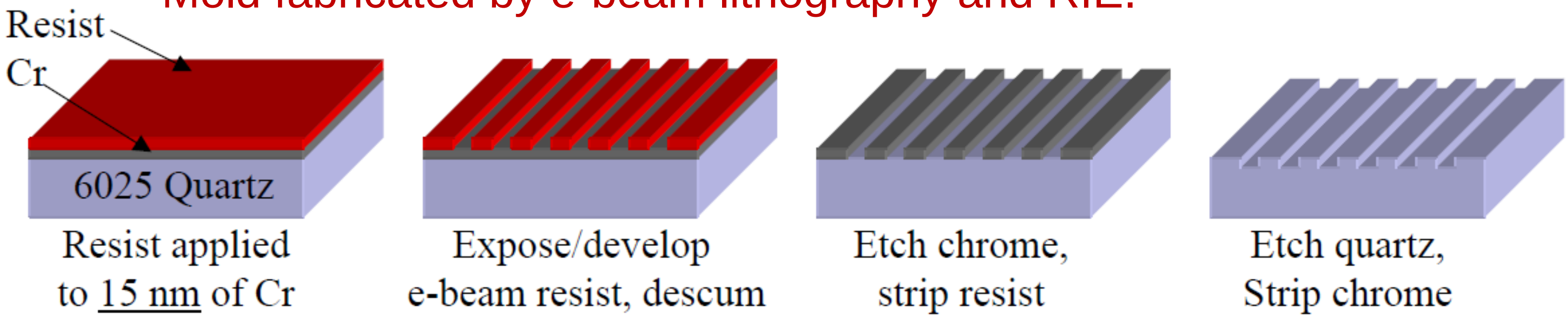


**Figure 3.** Results after imprinting using cicada wings as the stamp. (a) and (b) are SEM images of patterned PMMA with different scales. (c) is an AFM image of the patterned PMMA surface.

# Mold fabricated by engineers

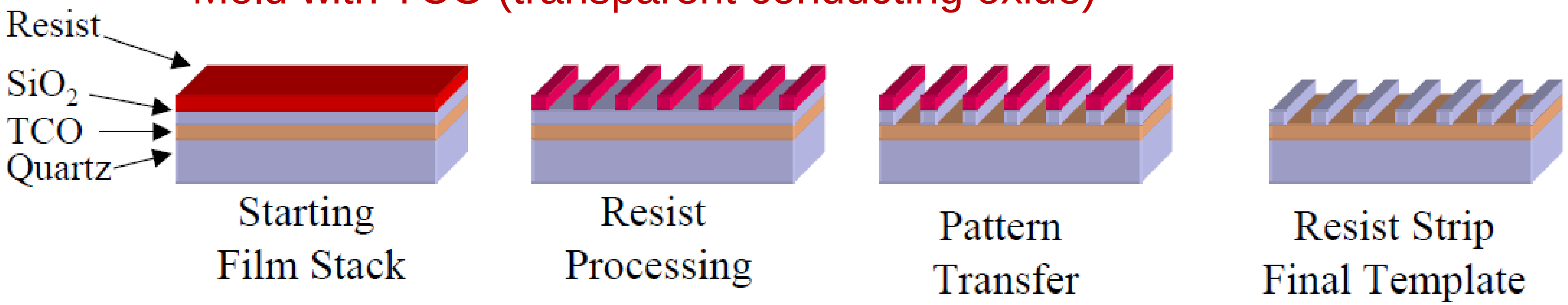
Mold fabricated by e-beam lithography and RIE.



Gas Chemistry: Cr – $Cl_2/O_2$; $SiO_2$ – $CF_4/O_2$

If no Cr RIE etch facility, Cr can be patterned readily by liftoff.

Mold with TCO (transparent conducting oxide)



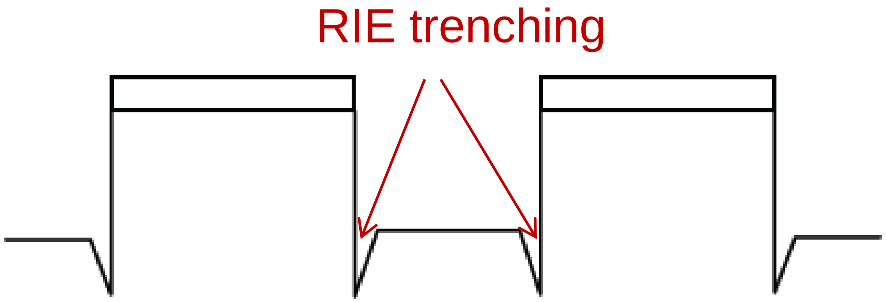
Incorporating TCO film in the mold has the following advantages:

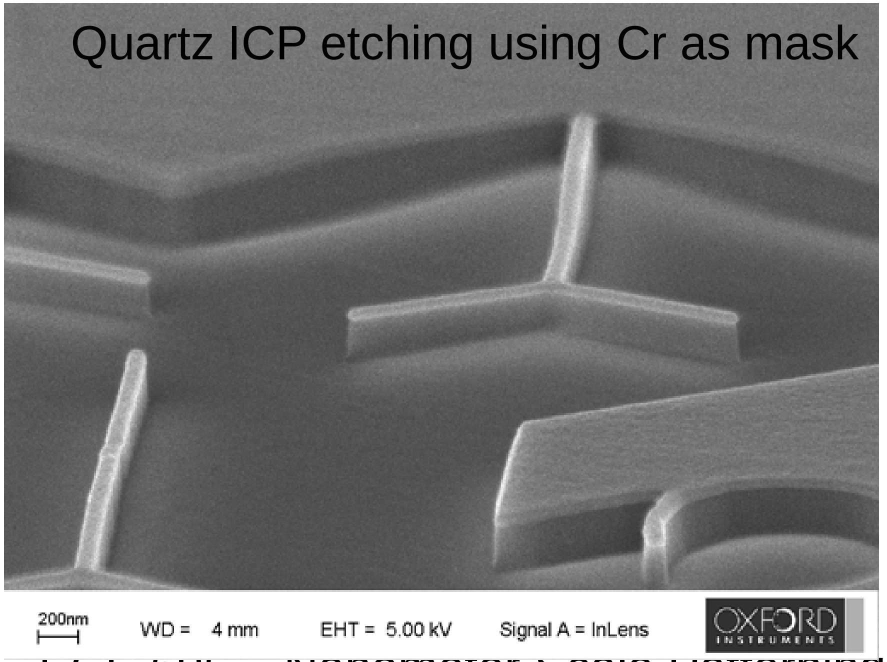
- Mold written by EBL without charge build-up.
- Final molds are easily inspected (both CD and defects) with SEM.
- It is still transparent for UV-NIL.

# Etching issues for mold fabrication

- Etch should be vertical or very near vertical.
- But NO negative slope allowed
- Trenching undesirable
- Smooth sidewalls desirable
- Uniform depth
- Uniform critical dimension (CD)

ICP etching offers better process control (ICP-inductively coupled plasma)


RIE trenching


Quartz ICP etching using Cr as mask

- Cr mask etch followed by quartz etch.
- 200nm depth for 30nm features (aspect ratio 7:1)
- Etch rate 85nm/min.
- Selectivity over Cr >170:1 (very high).
- 89-90°profile (very vertical)
- Smooth and trenching free.

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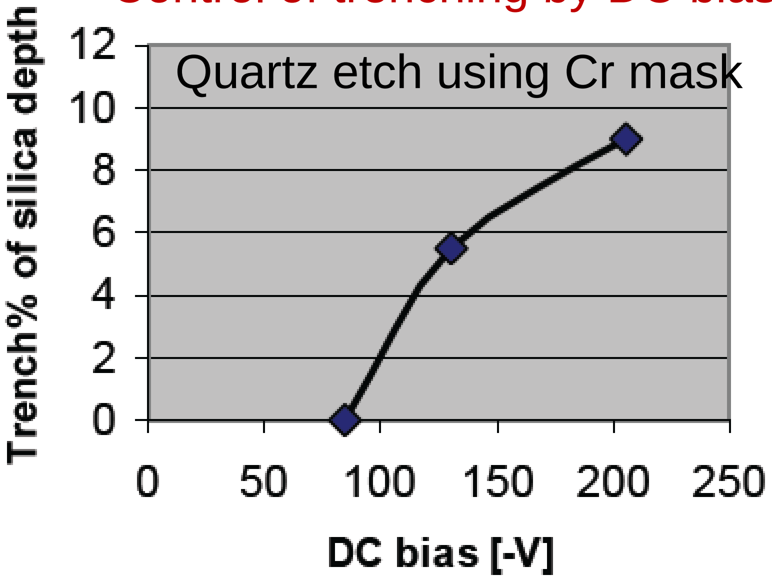
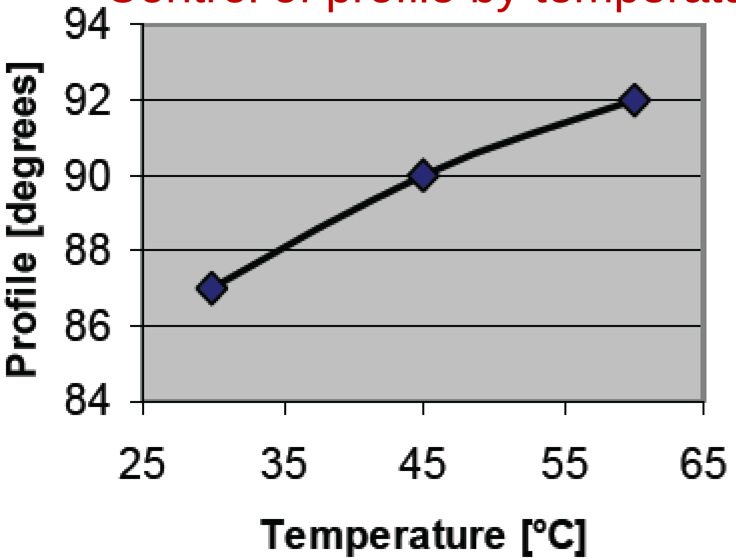
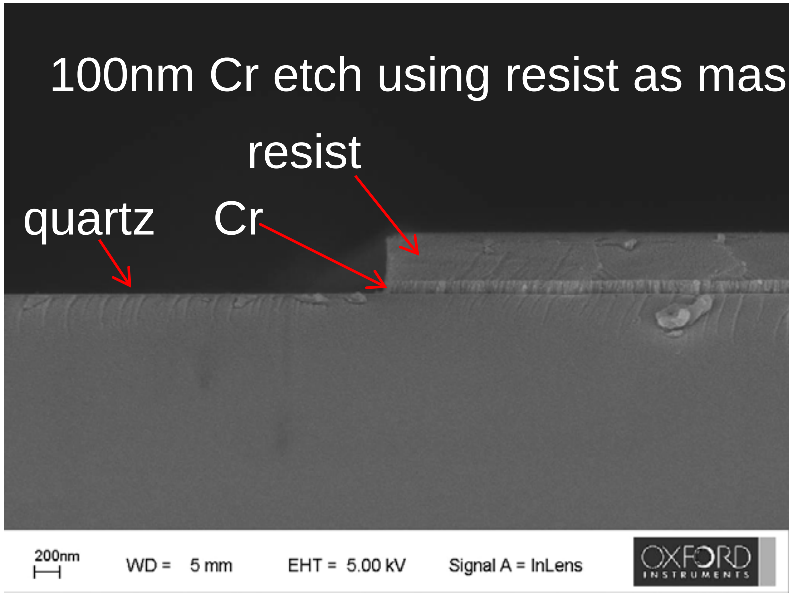
# ICP quartz mold etch: process control

Control of trenching by DC bias


Quartz etch using Cr mask

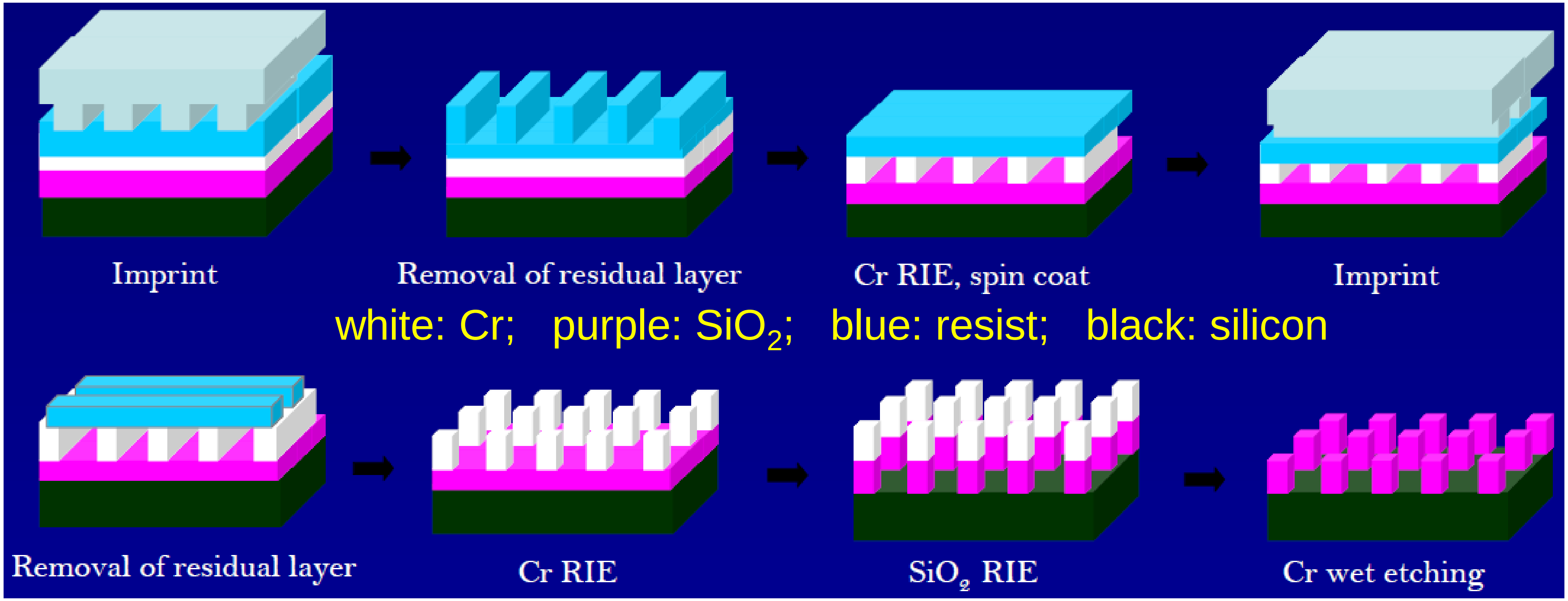
Control of profile by temperature



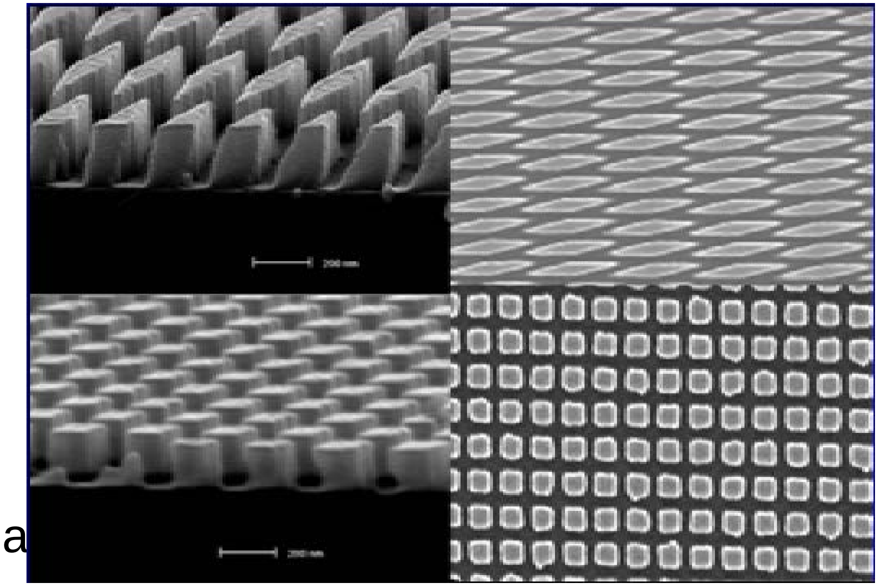

100nm Cr etch using resist as mas

Process gases: $Cl_2$, $O_2$ (+He).
Cr etch rate >15nm/min.
Uniformity <±4% (200mm wafer)
Profile >85°.
Delta CD<50nm.
CD control < ±1%.
Selectivity Cr : resist > 0.5 : 1 (resist dependent)

# Pillar array mold fabrication



white: Cr; purple: $SiO_2$; blue: resist; black: silicon



Pillar array (2D) mold fabricated from grating (1D) mold by two NILs