Nanometer Scale Patterning and Processing

Spring 2016

Lecture 40

Nanoimprint Lithography (NIL) – Other NIL Approaches

- Section 9

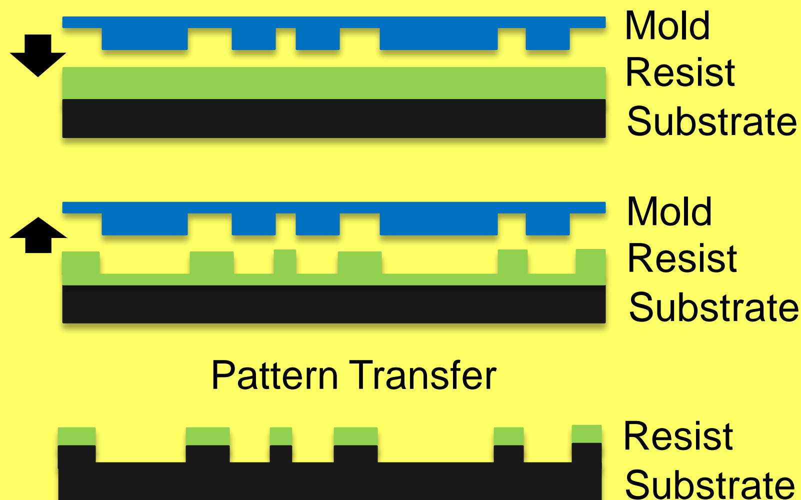
OTHER NIL APPROACHES

Emboss Metal at Nano-scale

- Nanoimprint Lithography
  - Transfers mold patterns onto the sample by mechanical deformation
  - Cost effective, repeatable and has high resolution

- Imprint metal films at nano-scale ???

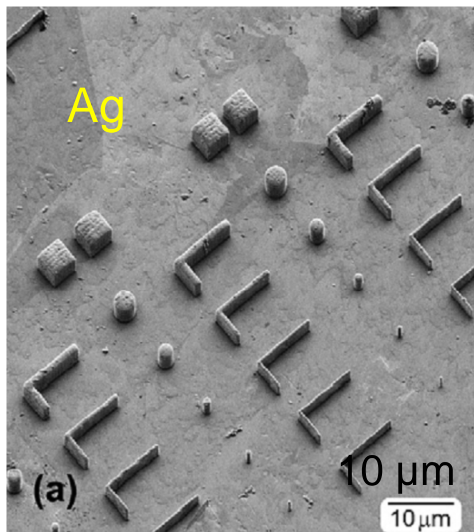
Macroscale



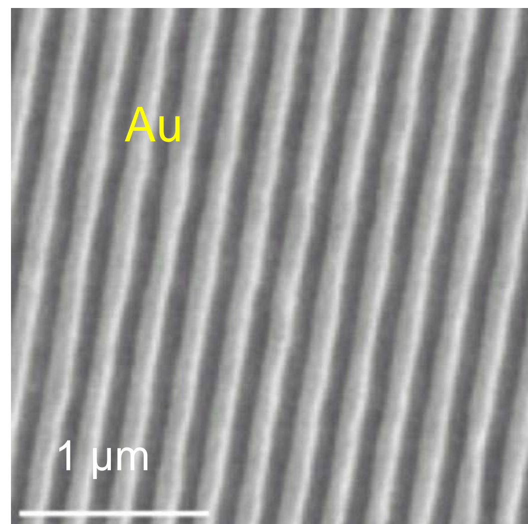
Alternative Direct Metal Patterning Methods

- Emboss metal at high temperature and high pressure
  - Temperature (≥ 400 °C). Pressure (≥ 300 MPa)
- Melt metal by laser irradiation and then form in quartz mold
- Direct imprint porous films or metallic nanoparticles
  - Not continuous film

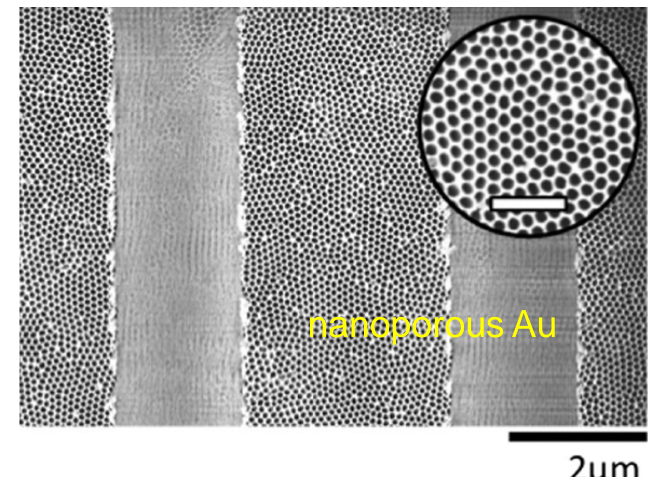
We want to develop a method that uses only conventional conditions (tools), yields high quality pattern and can be widely applicable in research



Buzzi, S. et al. *Appl. Phys. Lett.* 2009, *94*.

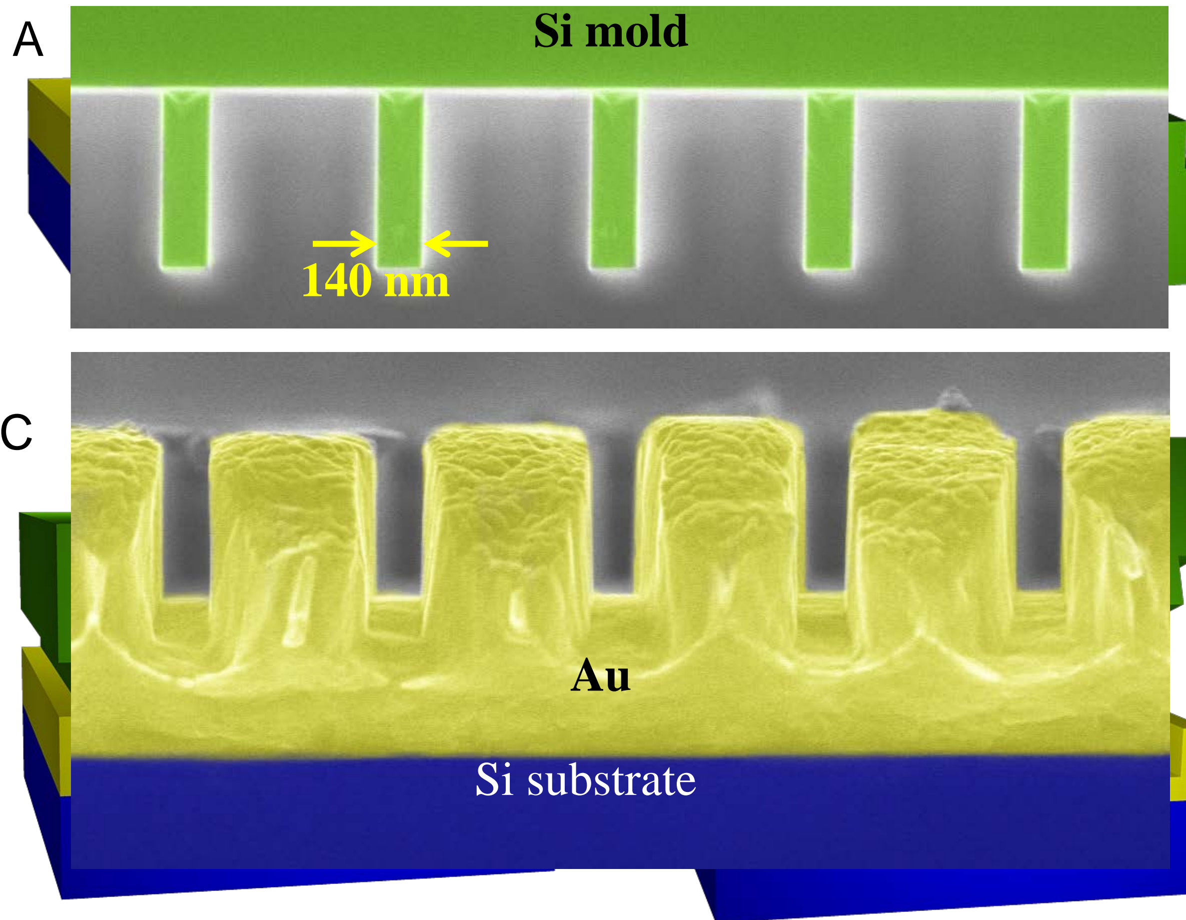


Cui, B. et al, *Nanotechnology* 2010, *21*.



Ryckman, J. D. et al, *Nano Lett.* 2011, *11*, 1857

Resistless Nanoimprint In Metal (RNIM)



Process flow:

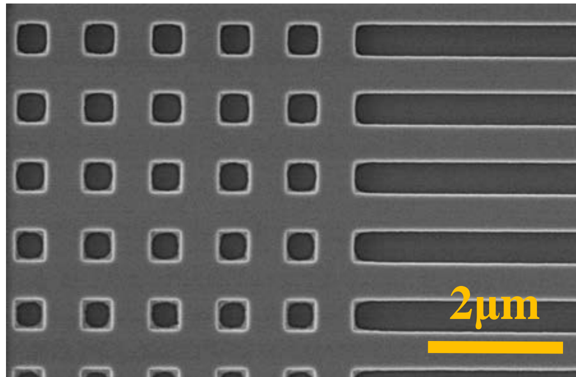
- A. Metal evaporation
- B. Pattern the mold
- C. Nanoimprint
  - Low Temperature 25-150 C
  - Low Pressure < 4 MPa
- D. Remove the mold

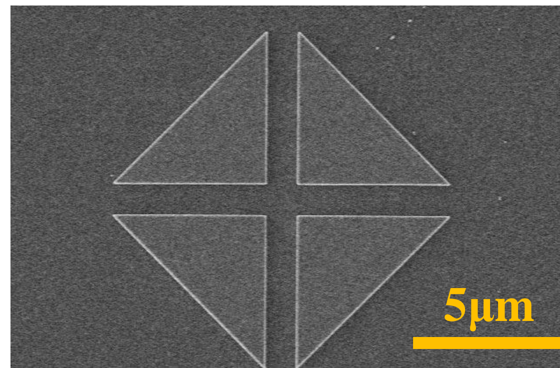
Varghese, L. T.[†], Fan, L.[†], et al (2013), *Resistless Nanoimprinting in Metal for Plasmonic Nanostructures.* Small. doi: 10.1002/smll.201300168

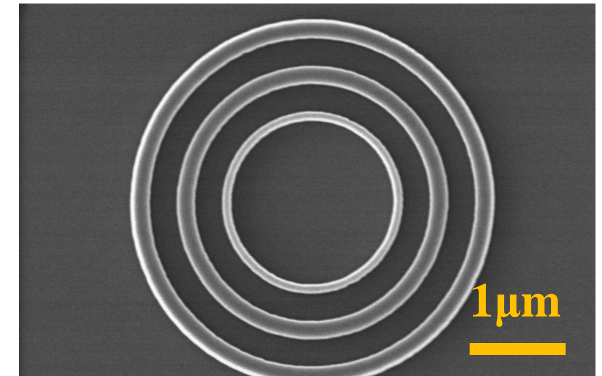
RNIM of Different Shapes

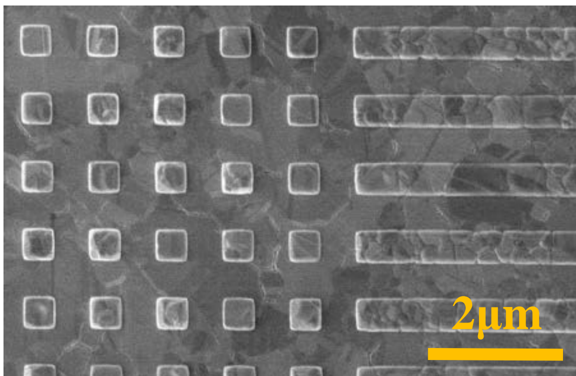
- Silver (Ag) and gold (Au) are ideal candidates
  - Ductile and malleable → Easy to deform
  - High conductivity and plasmonic resonance lies in visible wavelengths

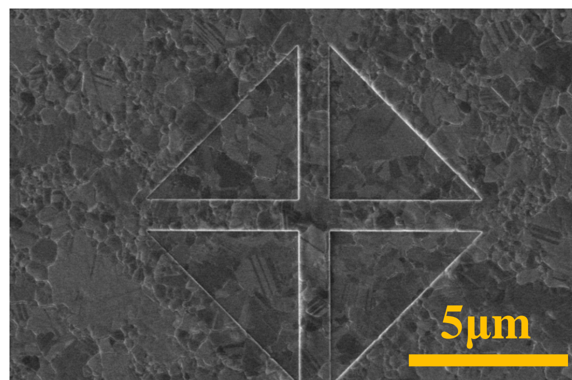
Si mold

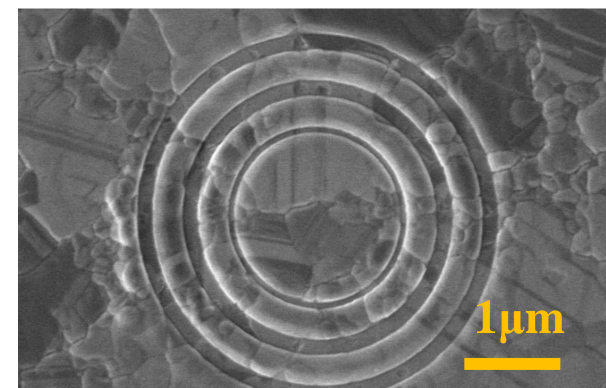












Ag film

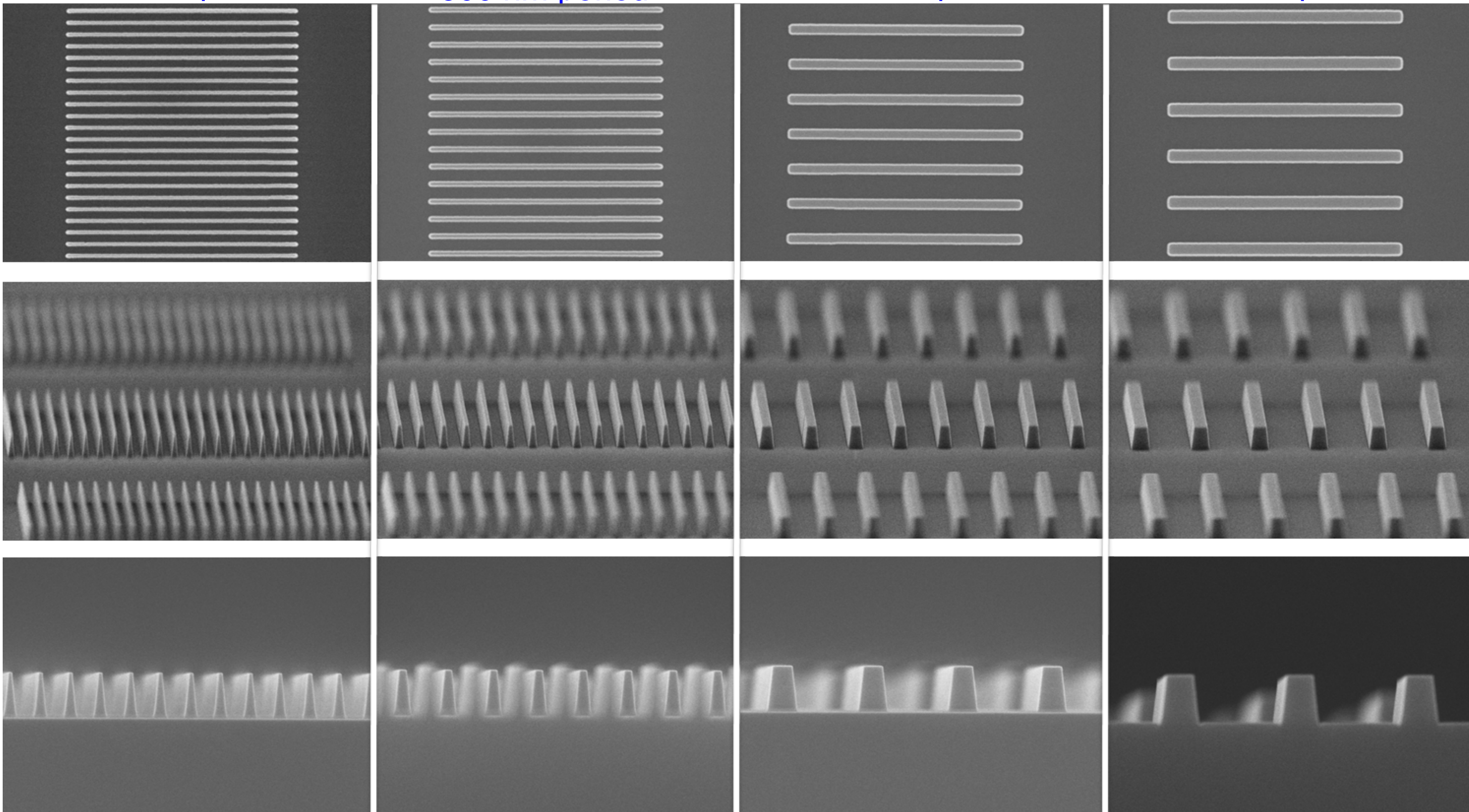
Gratings of Different Sizes: Mold

40 nm grating
200 nm period

75 nm grating
300 nm period

150 nm grating
600 nm period

200 nm grating
800 nm period



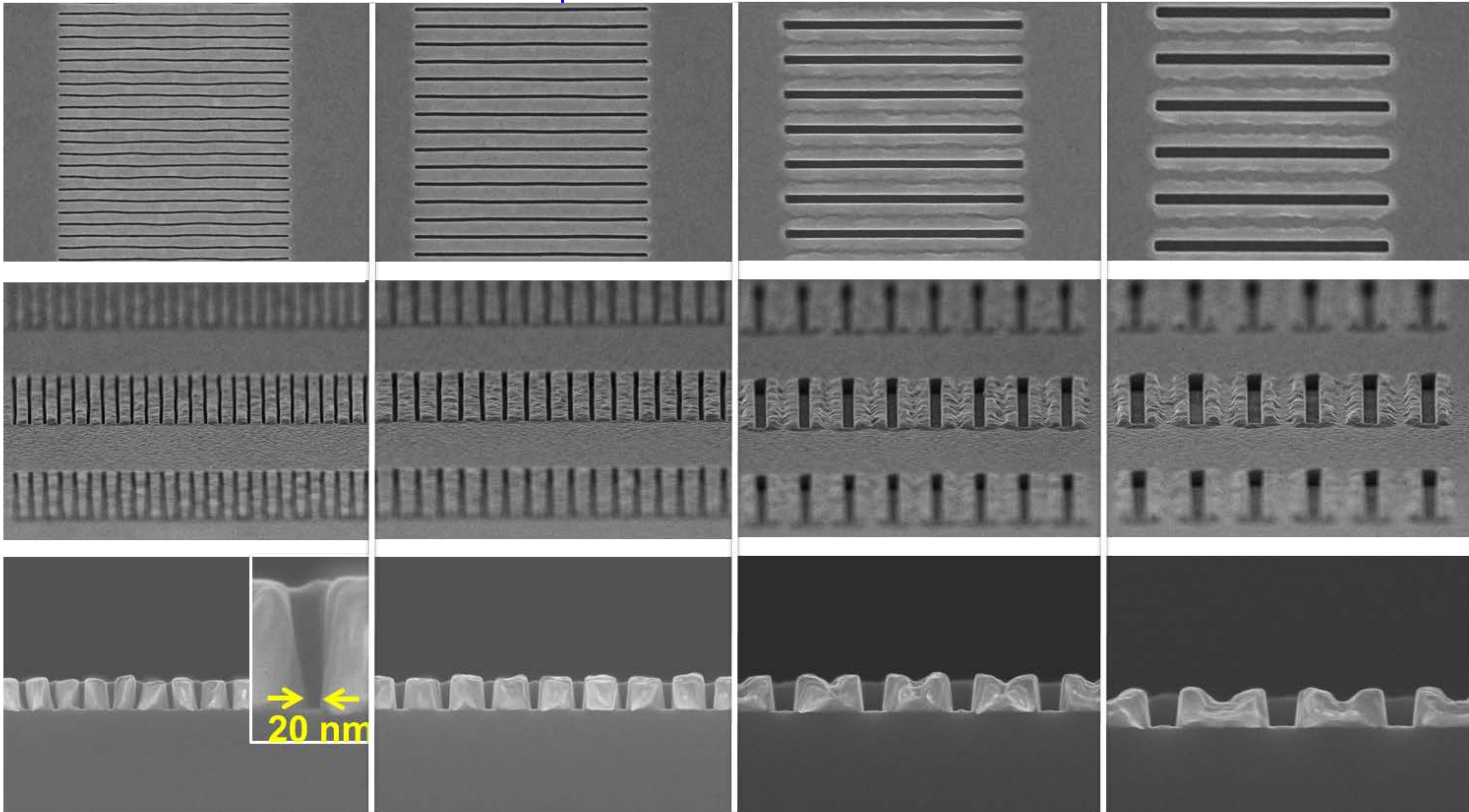
Gratings of Different Sizes: Ag

40 nm trench
200 nm period

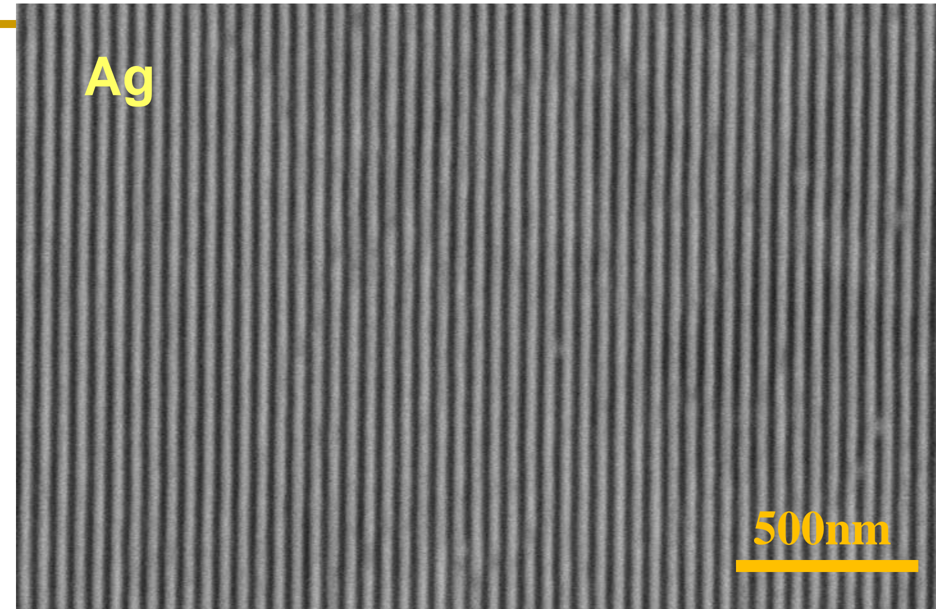
75 nm trench
300 nm period

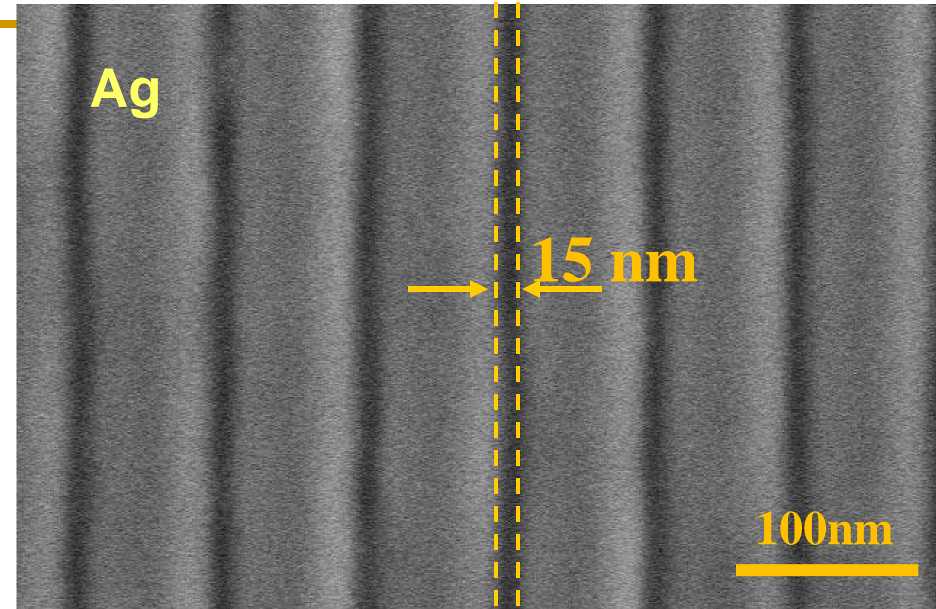
150 nm trench
600 nm period

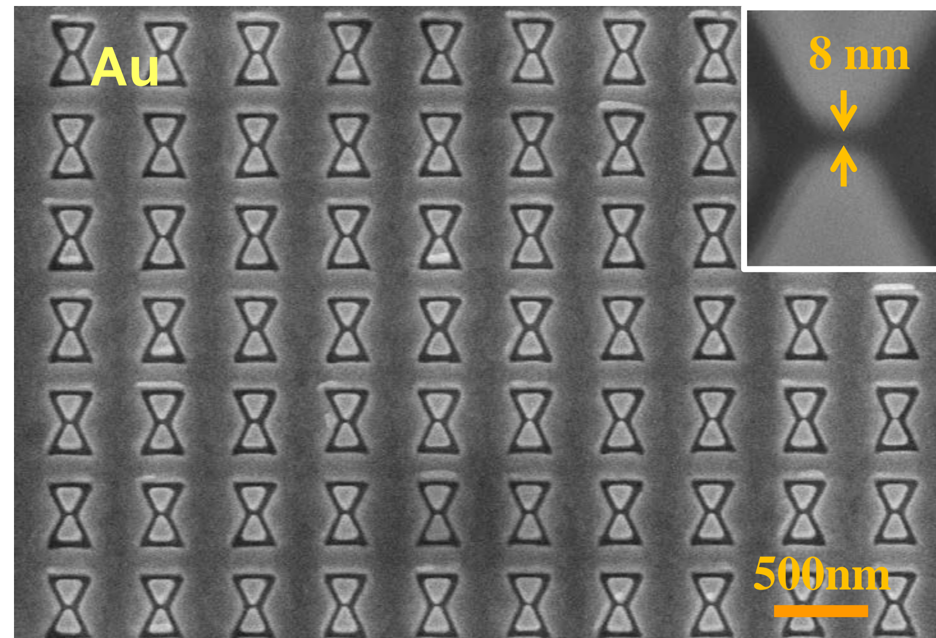
200 nm trench
800 nm period

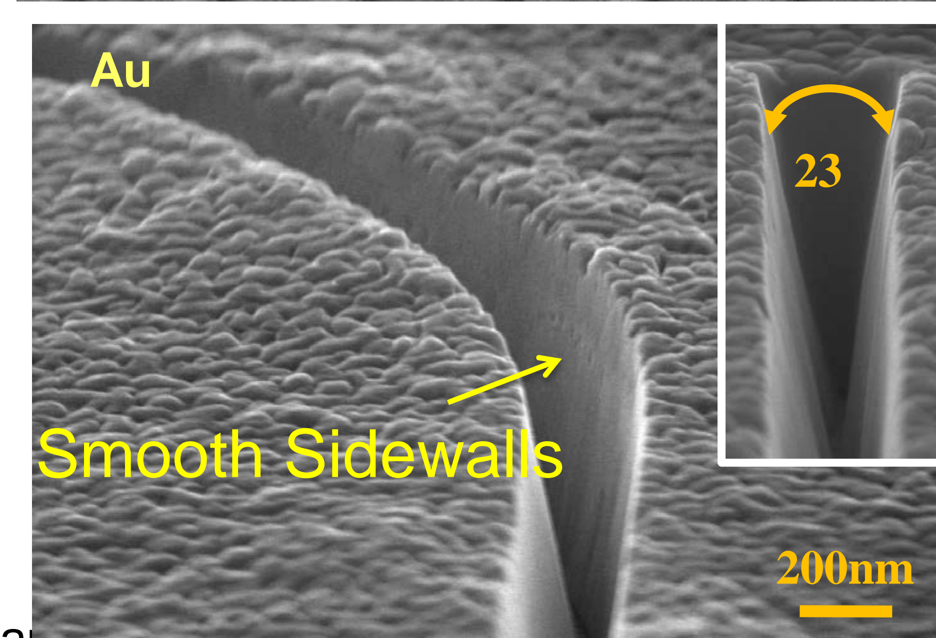


Sub-20 nm & 3D Pattern



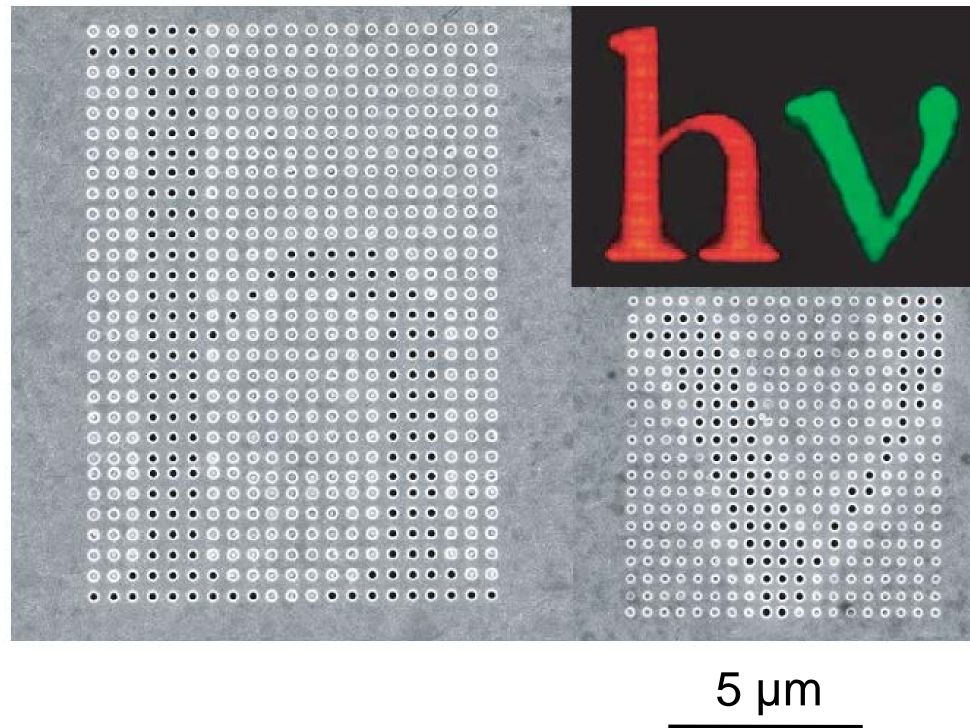






Extraordinary Optical Transmission (EOT)

- EOT produces enhanced transmission of light through sub-wavelength metal apertures via surface plasmon interaction

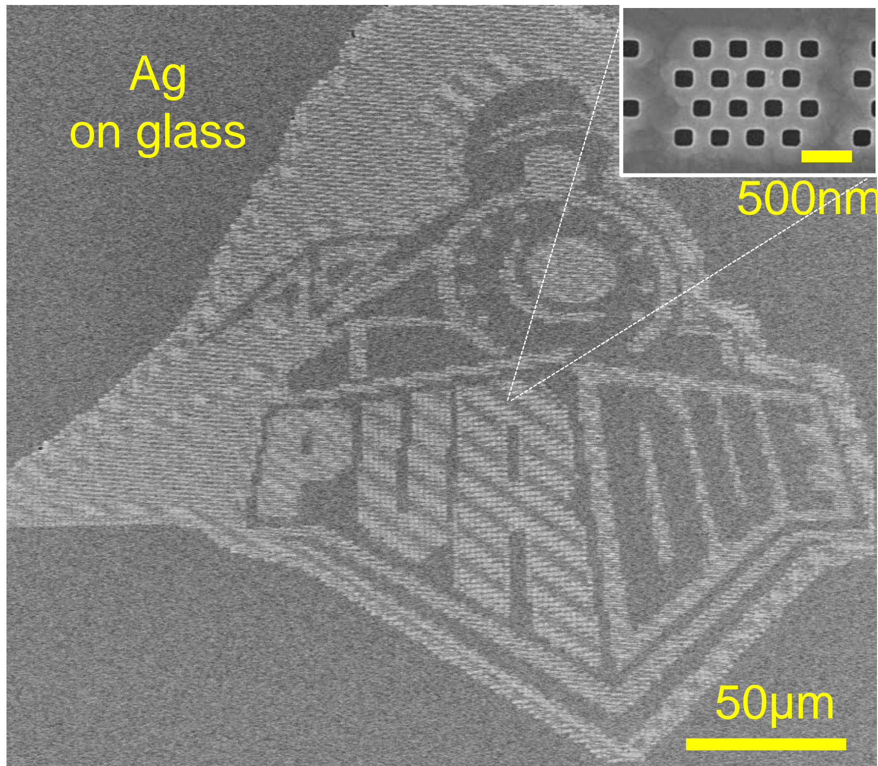


C. Genet and T. W. Ebbesen, "Light in tiny holes," *Nature* 445, 39(2007).

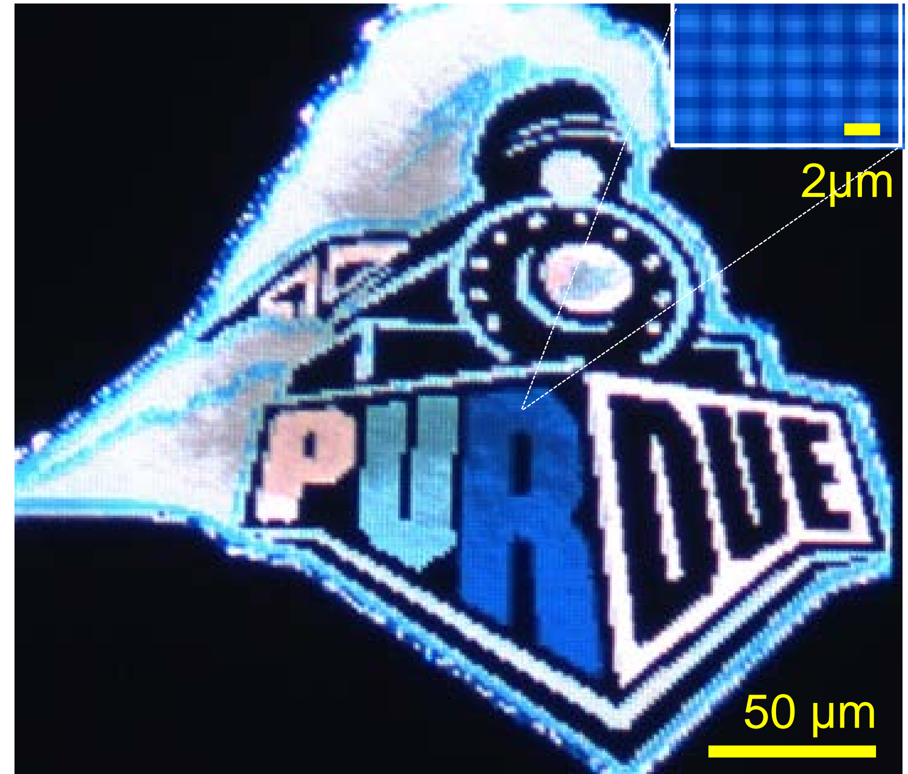
RNIM Application: EOT

- Our RNIM process can pattern metal directly on insulating substrates
  - No charging issues
- Large area patterns can be obtained in one step

SEM

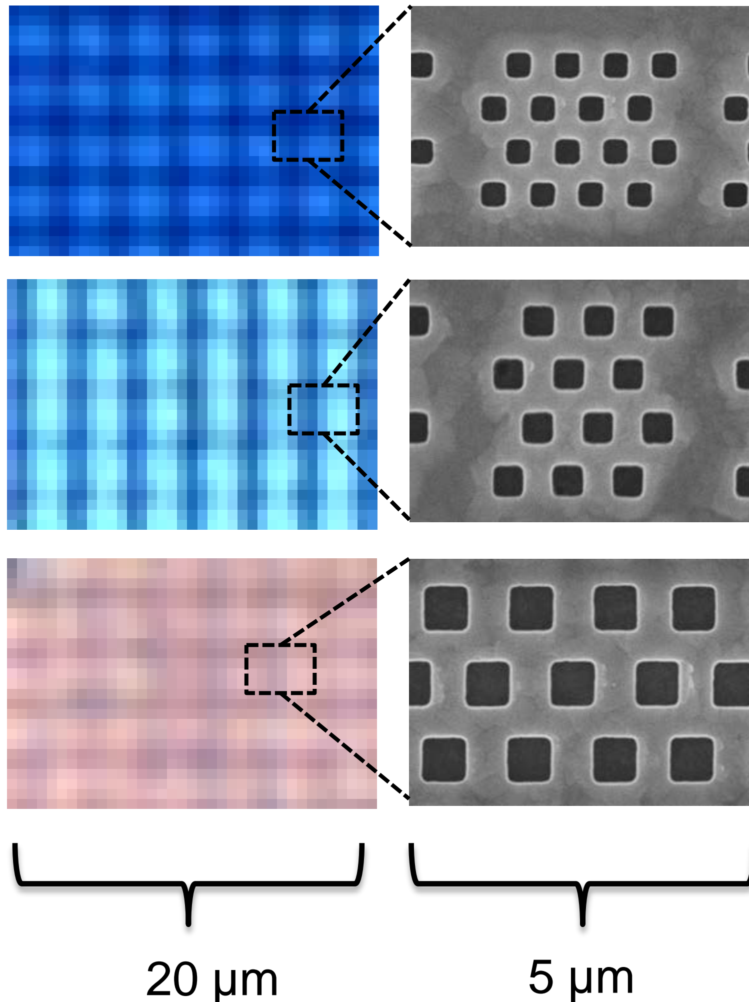


Optical Transmission Microscope

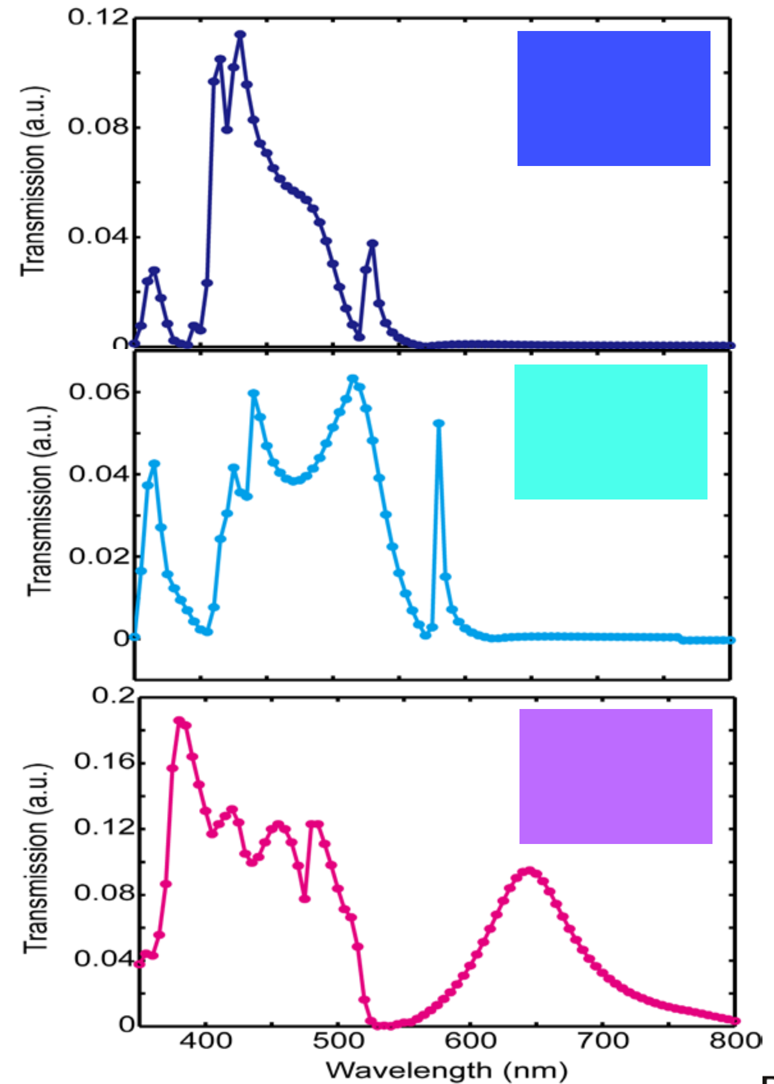


Each pixel

- Experiment

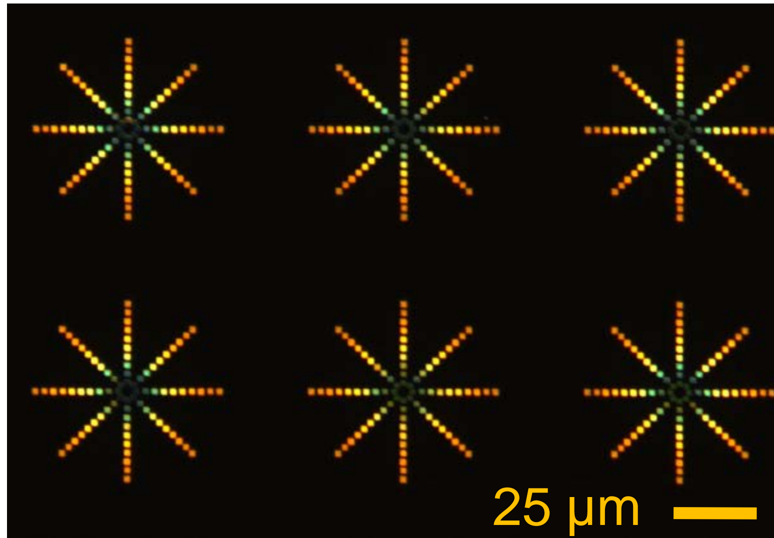


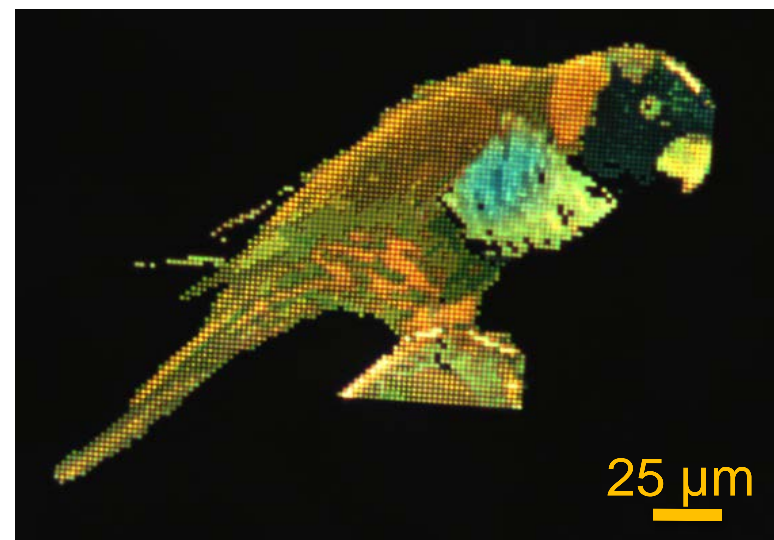
- 3D Simulation



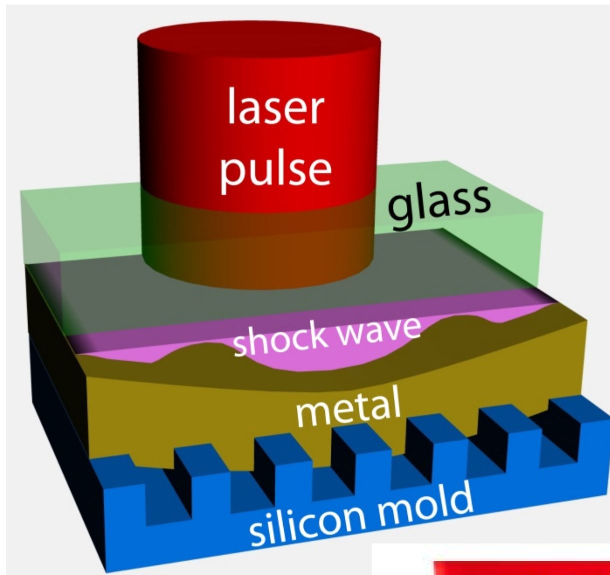
PURDUE
UNIVERSITY

Images Through Tiny Holes

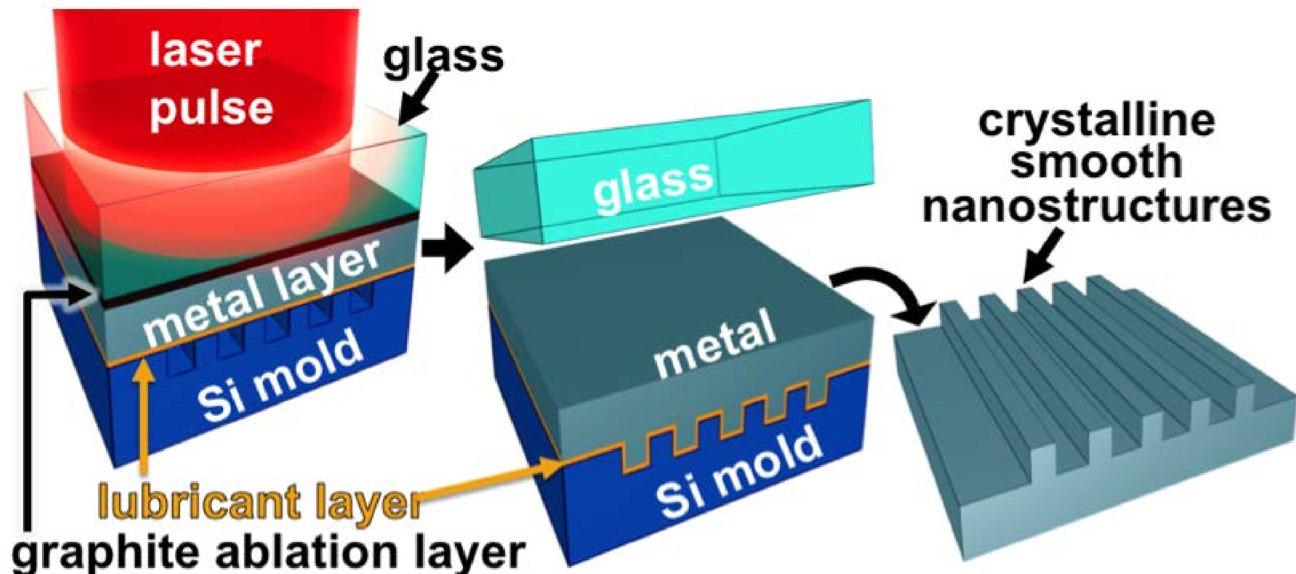




Laser Shock Imprinting (LSI)

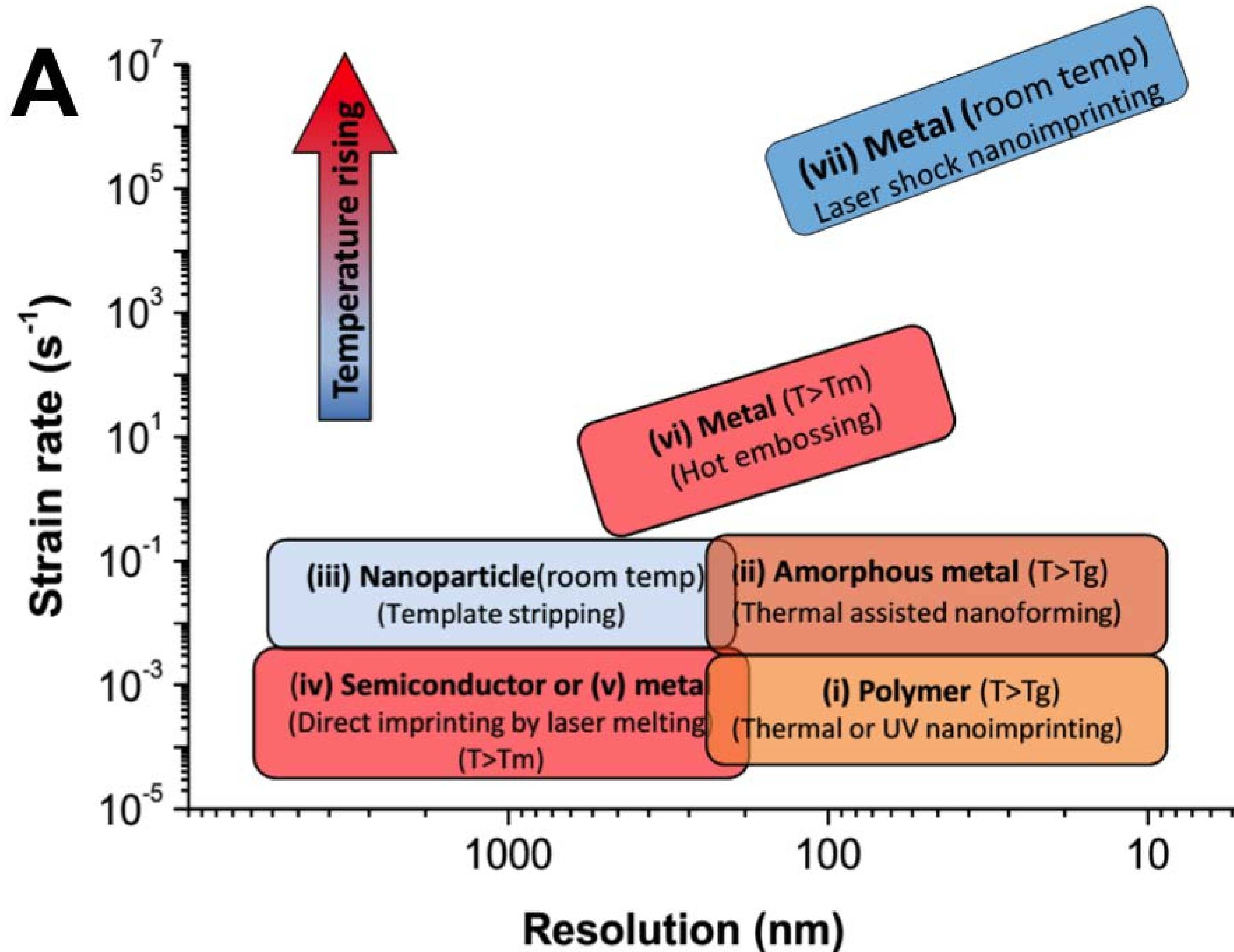


- Shock wave is generated between the glass cover the the metal film, creating a high-sped strain to press the metal into the silicon mold



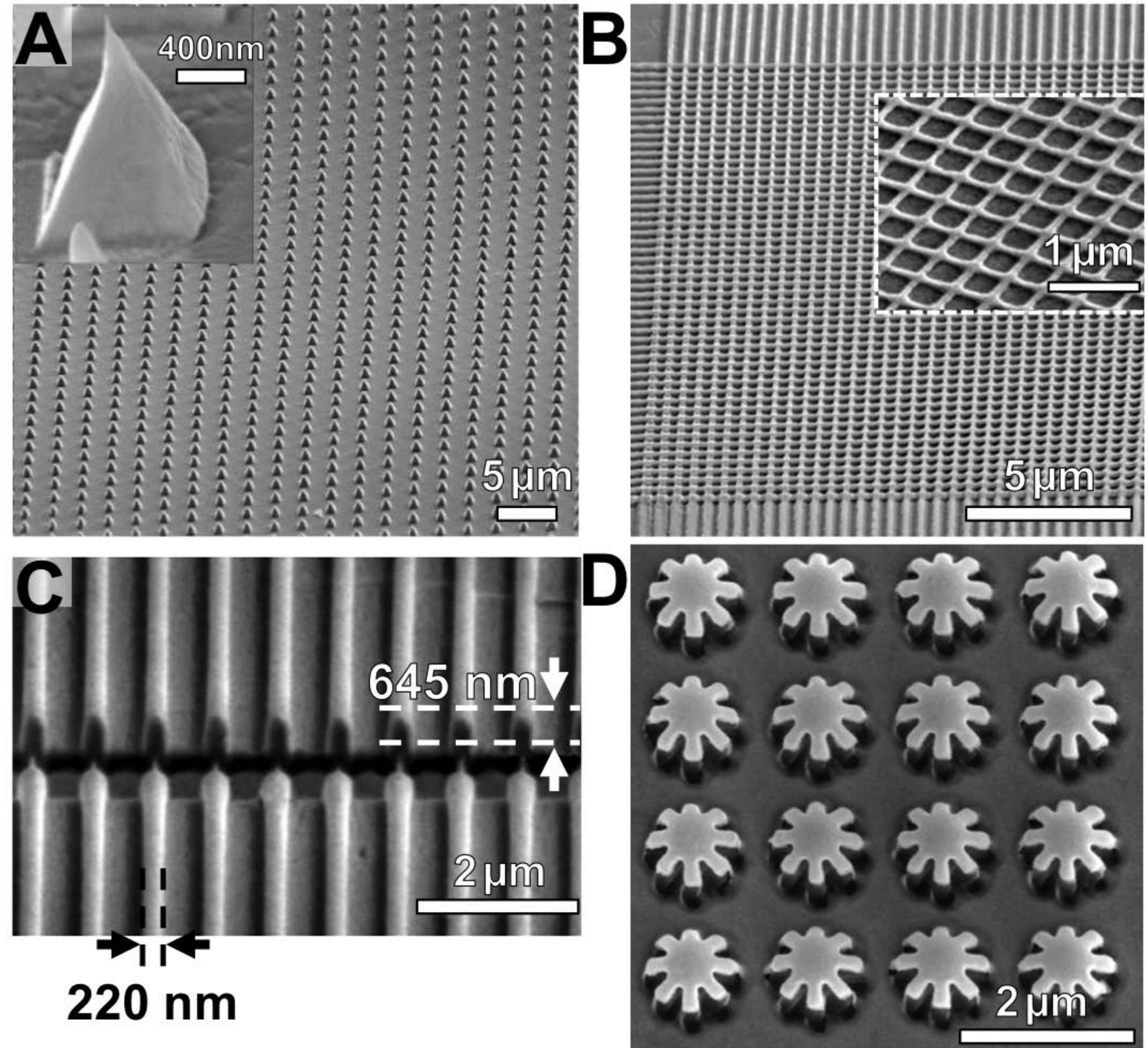
PURDUE UNIVERSITY

Importance of Strain Rate

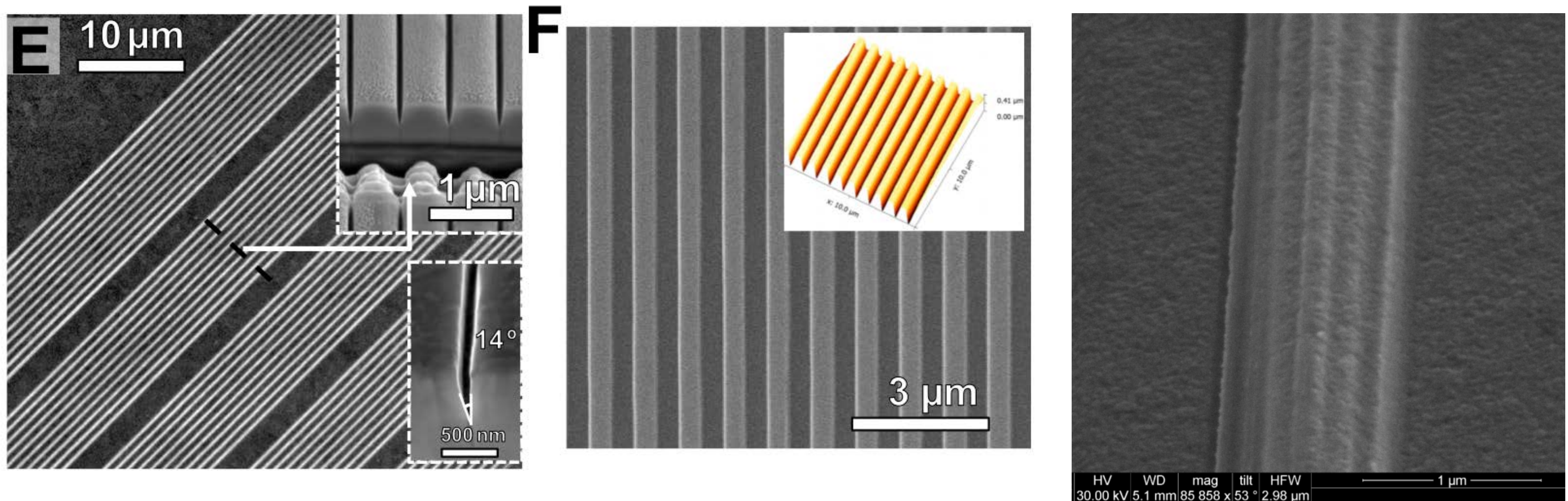


Unique Results

- A: Solid pyramids with sharp tips
- B: "Fish-net" structures for metamaterials
- C: High-aspect-ratio (heigh:width ~3) metal grating
- D: 3D "nano-gears"
- All are difficult (or impossible) to achieve with other methods

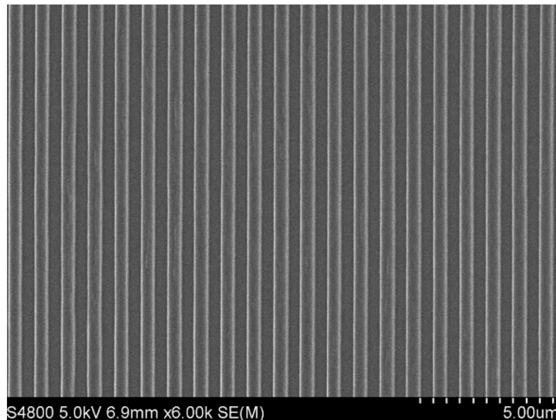


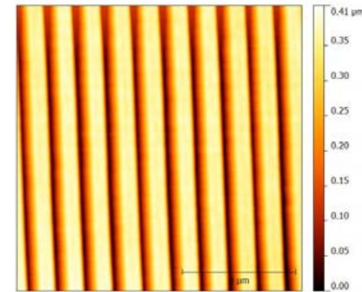
V-grooves and Smooth Edges

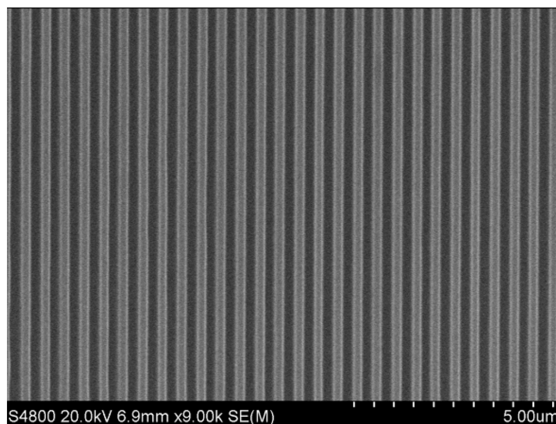


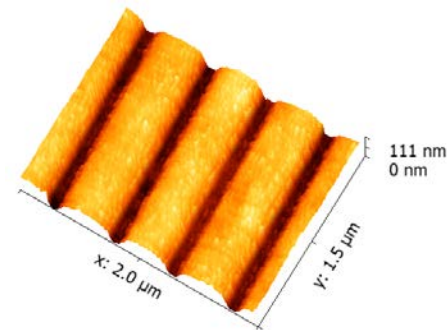
- V-grooves: much faster than using FIB
- No metal pile-up
- 3D patterning in one-step

Patterning of Hard Metal (Titanium)



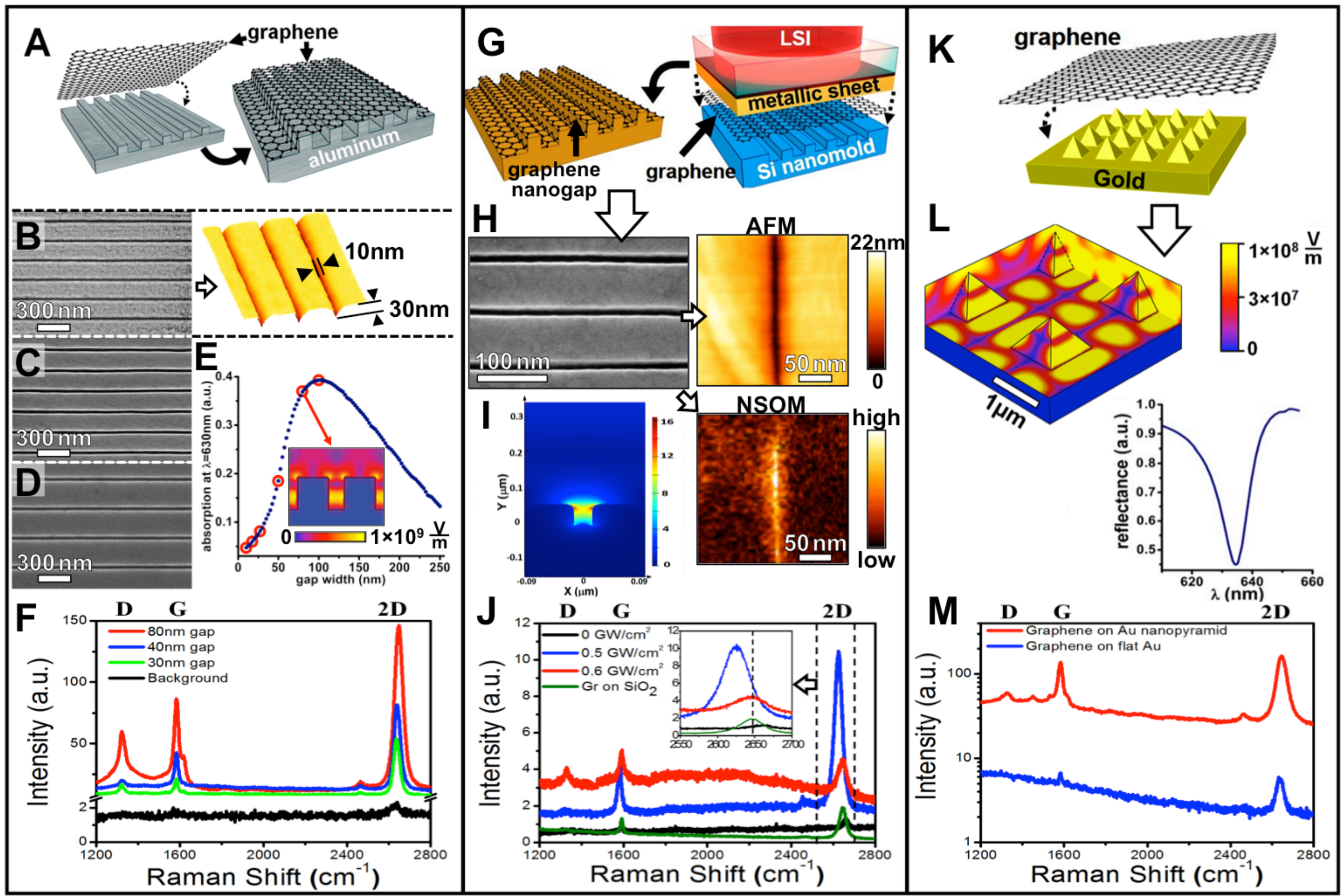






- Mohs Hardness: 6.0
  - Gold, Silver and Copper: 2-3
- Still smaller than Si hardness (7.0)

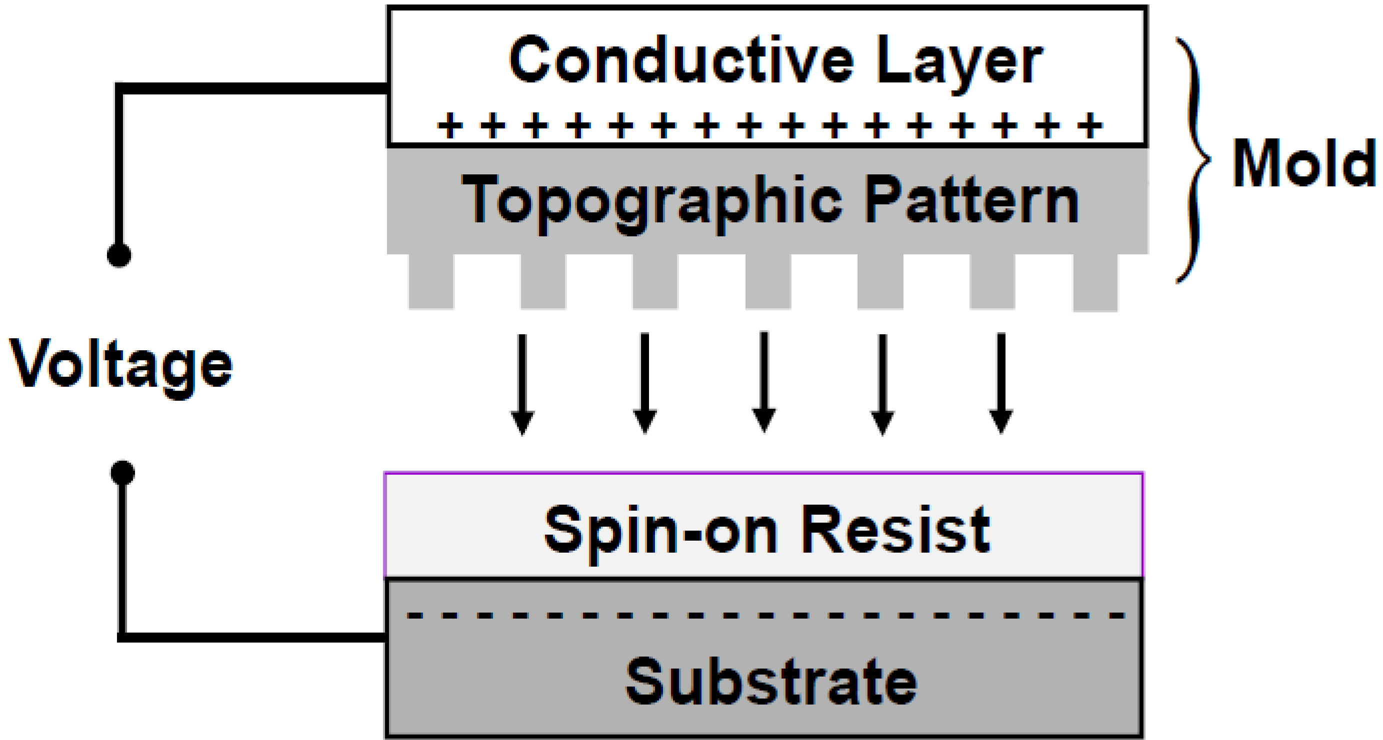
Application to Graphene/Plasmonic Structures



H. Gao *et. al, Science,* vol. 346, pp. 1352-1356, 2014

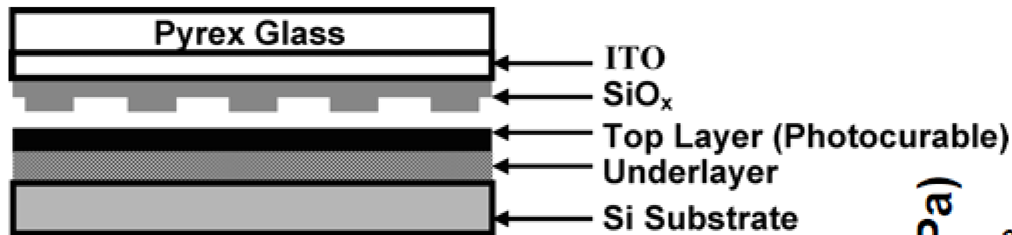
PURDUE UNIVERSITY

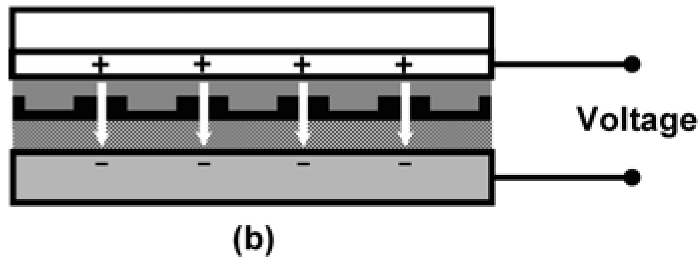
Electric field assisted NIL (EFAN)

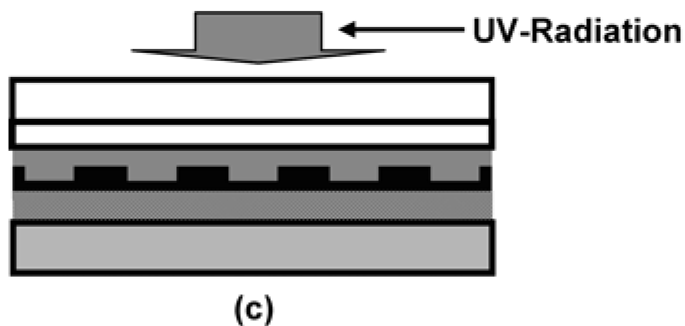


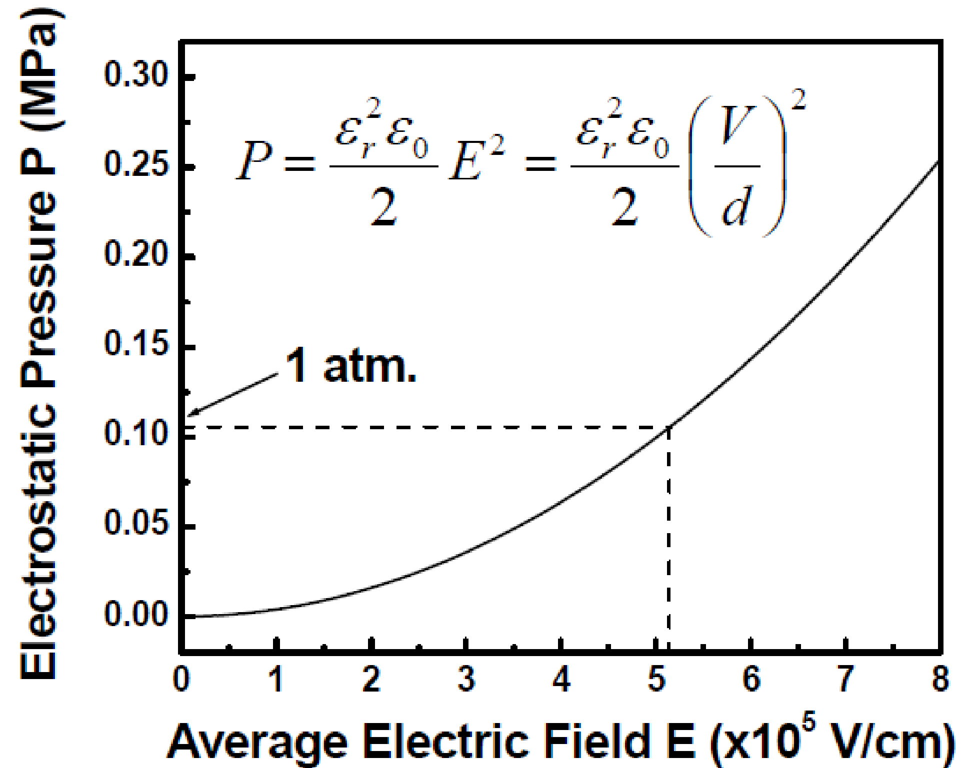
Principle of EFAN: a voltage is applied between the conductive layers on the mold and the substrate, generating an electrostatic force to press the mold into the resist layer.

EFAN process flow









Calculated effective electrostatic pressure (P) versus the required strength of the electric field.

A more accurate calculation

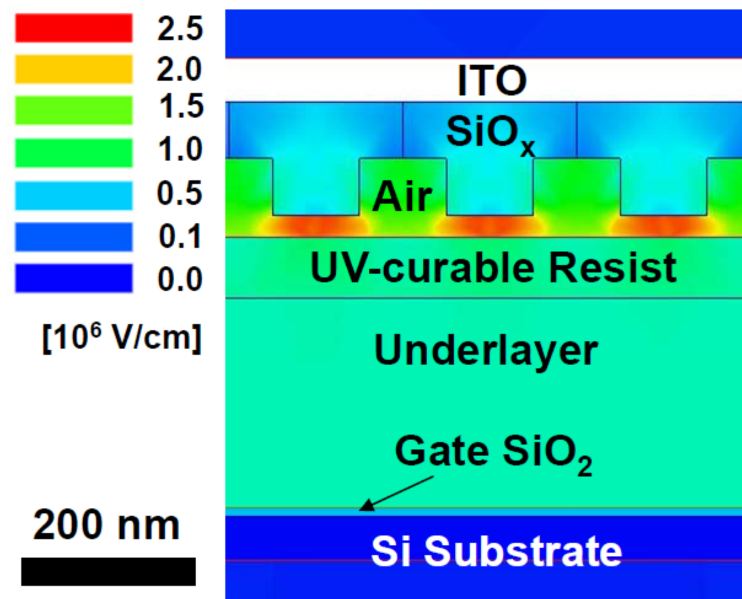
ITO (+)
d
Si (-)
(4) Finish
(3) Immersion
(2) Soft Contact
(1) No Contact

V = 40 volts
30 volts
20 volts

Electric Field E (V/cm): $2x10^5$, $3x10^5$, $4x10^5$, $5x10^5$, $6x10^5$, $7x10^5$

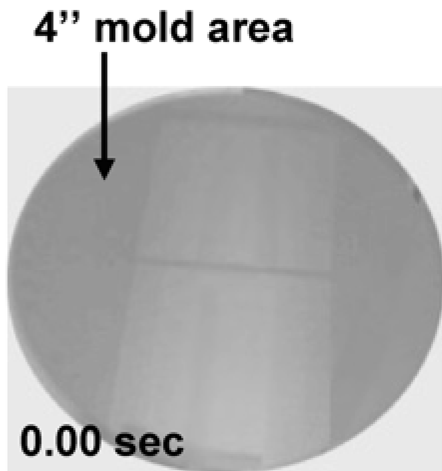
Electrostatic Pressure P (MPa): 0.00, 0.05, 0.10, 0.15, 0.20

Distance Between Electrodes d (nm): 400, 450, 500, 550, 600

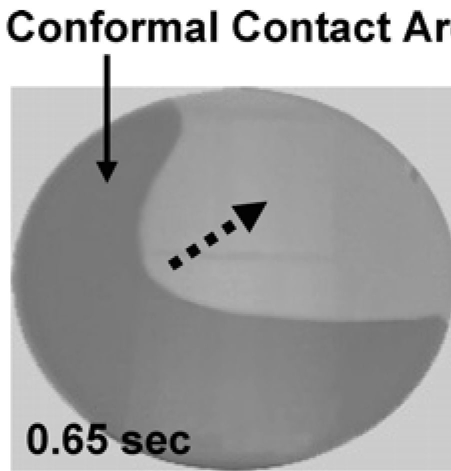


A 2D simulation of EFAN, which adds complete details of dielectric structures into the calculation of electric field.

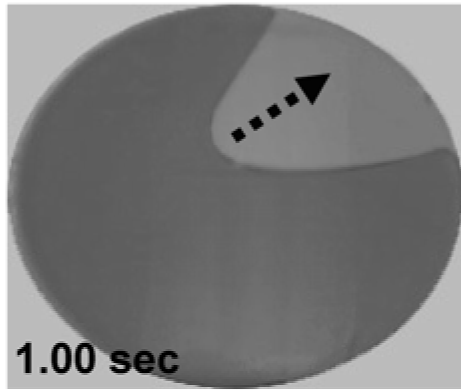
Propagation of contact area and imprint results



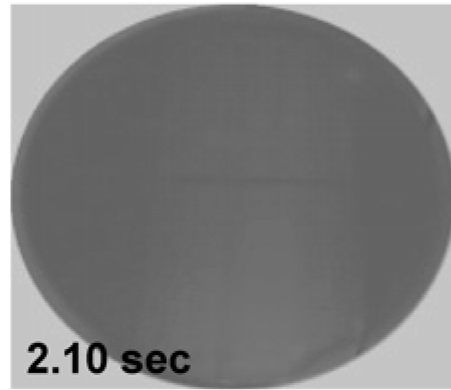
No conformal contact



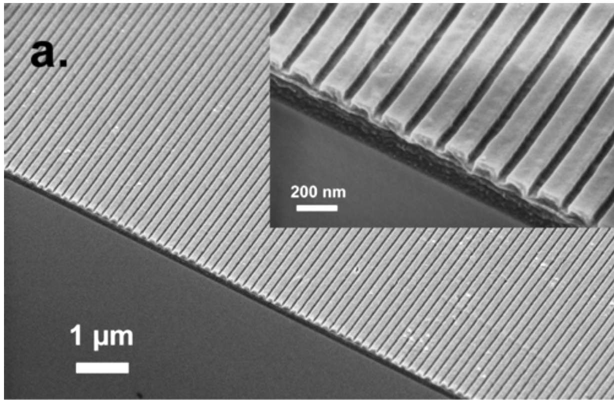
Propagation of the conformal contact area

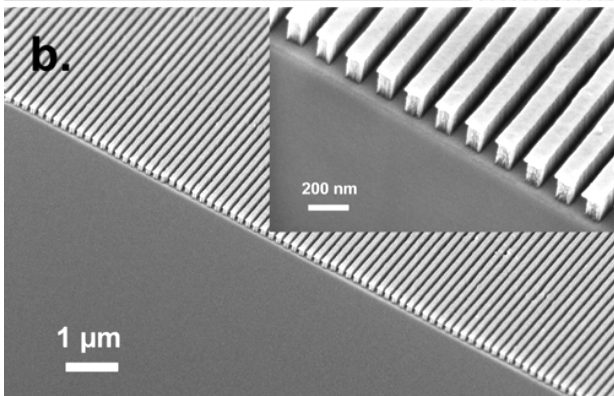


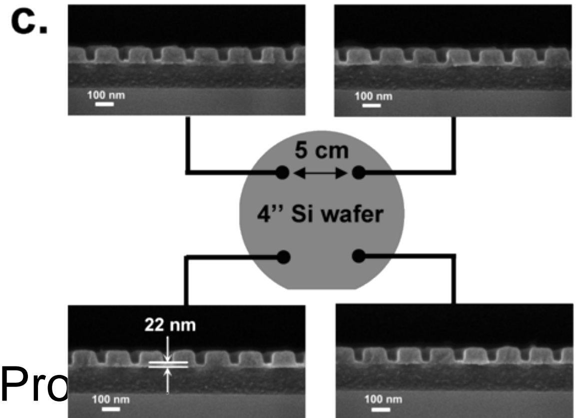
Propagation at t = 1 sec



Fully imprinted wafer at t = 2.1 sec



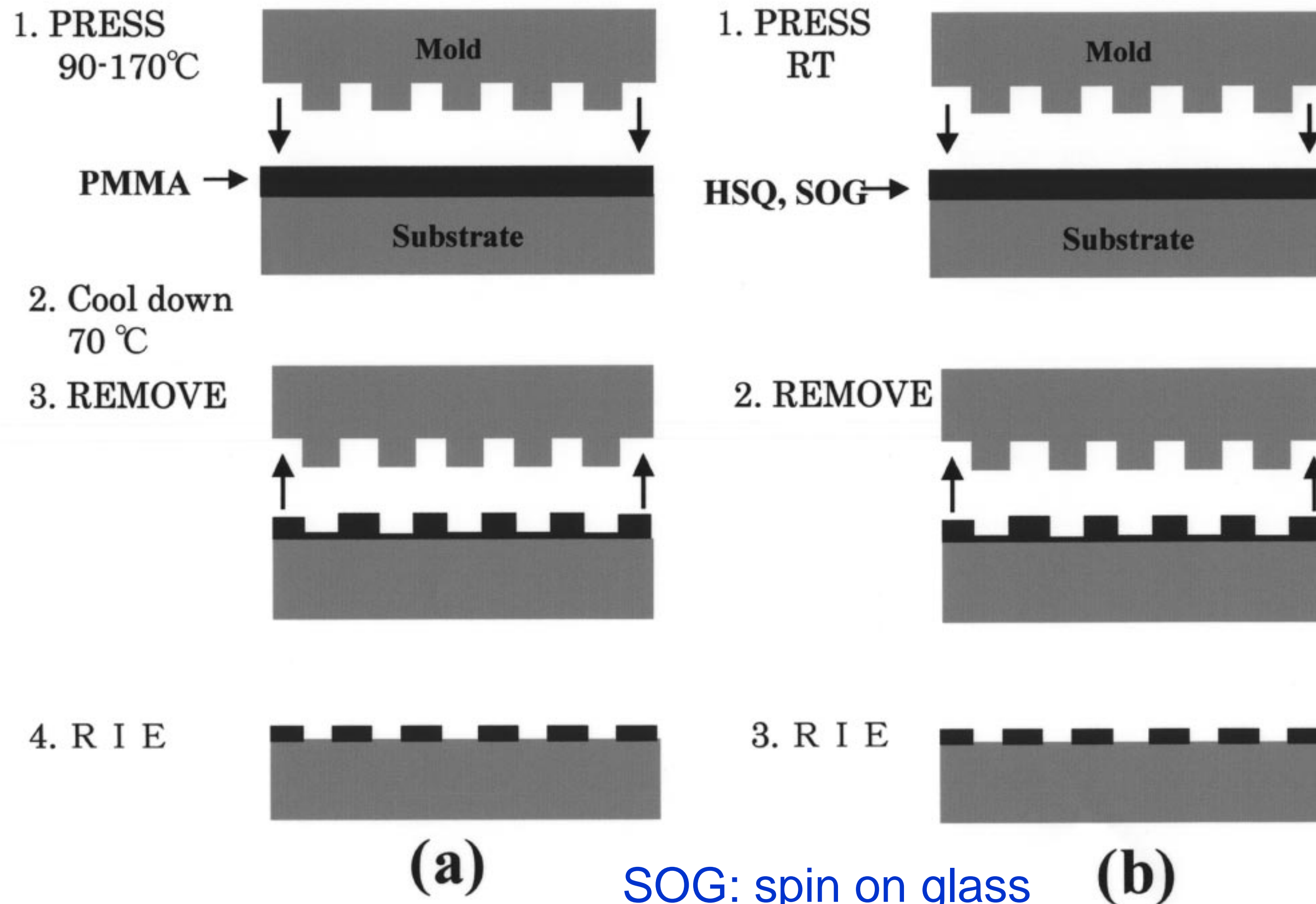




Room temperature ("thermal") NIL

RT-NIL process does not require a resist thermal cycle when pressing a mold onto the resist.

Use special material, such as hydrogen silsequioxane (HSQ), or ultrahigh pressure.



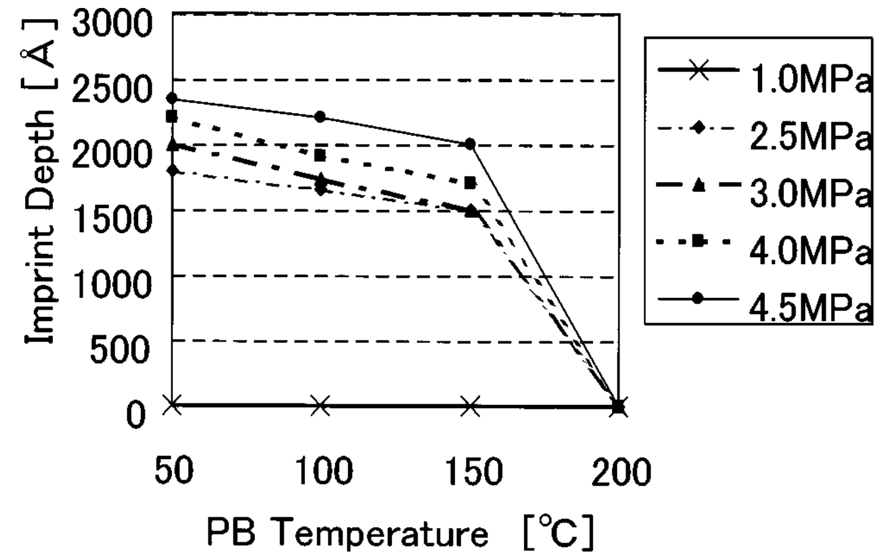
SOG: spin on glass

Matsui, "Room-temperature nanoimprint and nanotransfer printing using hydrogen silsequioxane", JVST B, 2003

Room temperature (“thermal”) NIL

Pre-baking is important:

- HSQ has a high viscosity without prebaking.
- The effect of prebaking HSQ is to remove the solvent init.
- The hardness of HSQ increases at around 150°C (so don’t bake at higher T).



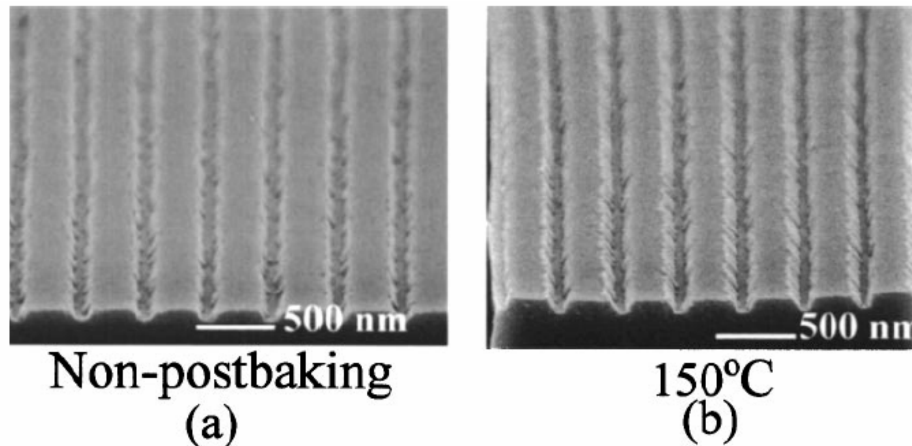


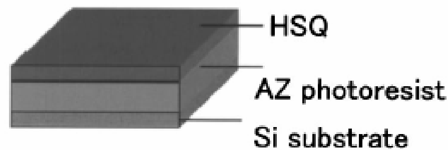
FIG. 5. HSQ replicated patterns with 100 nm linewidth after postbaking. (a) No postbaking and (b) baking temperature of 150 °C.

“Nanoimprint and nanocontact technologies using hydrogen silsequioxane”, JVST B, 2005

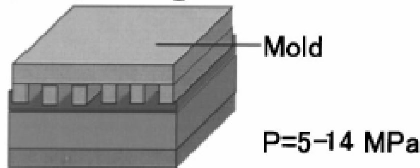
NIL results into HSQ at RT

1 min press time by RT-NIL at 40atm pressure.

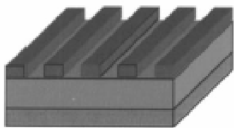
(1) Resist spin-coating



(2) Imprinting



(3) RIE(CHF_3) of the HSQ recessed area



(4) RIE(O_2) of the AZ bottom layer

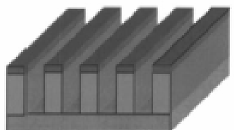
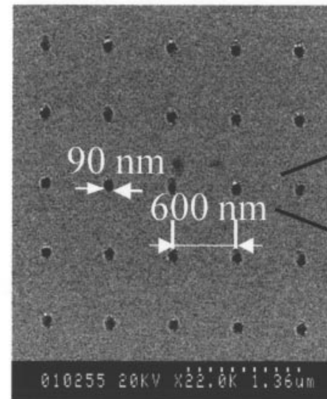
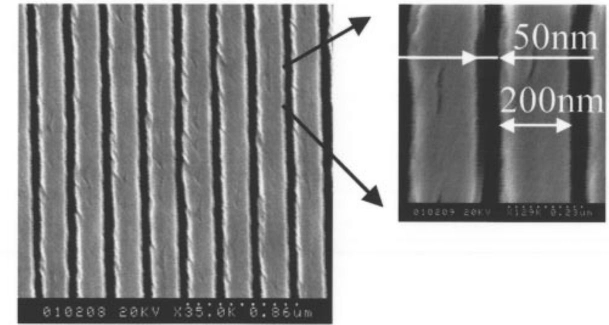


FIG. 6. Schematic of the RT-NIL process where a bilayer of HSQ (top layer) and *AZ* photoresist (bottom layer) is used.



(a)



(b)

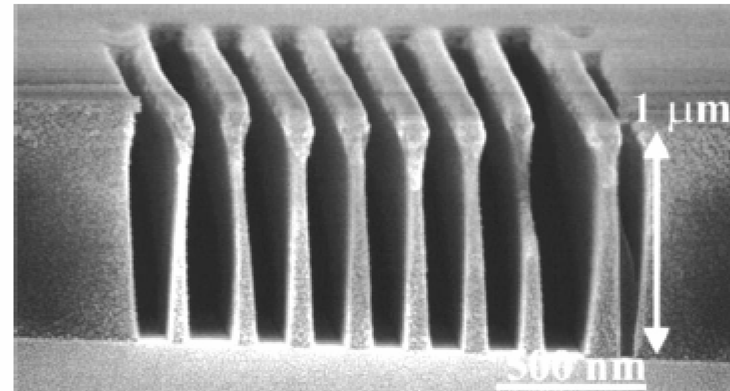


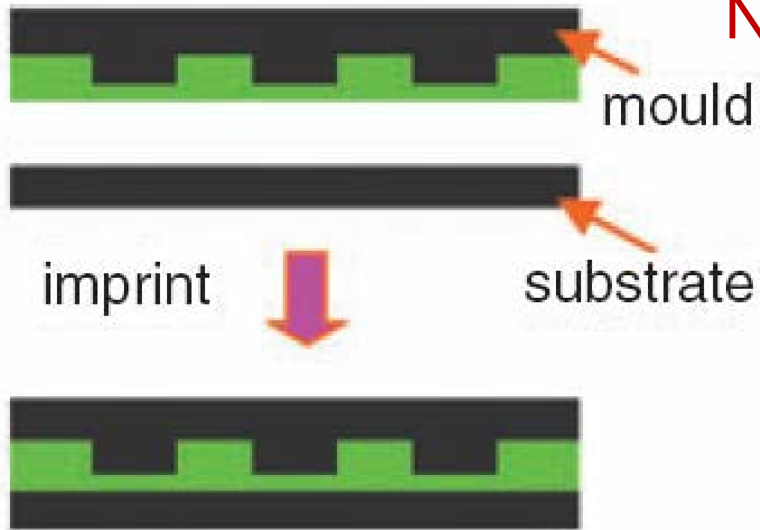
FIG. 8. SEM micrograph of a 100 nm linewidth, 1-μm-high bilayer structure after O_2 RIE.

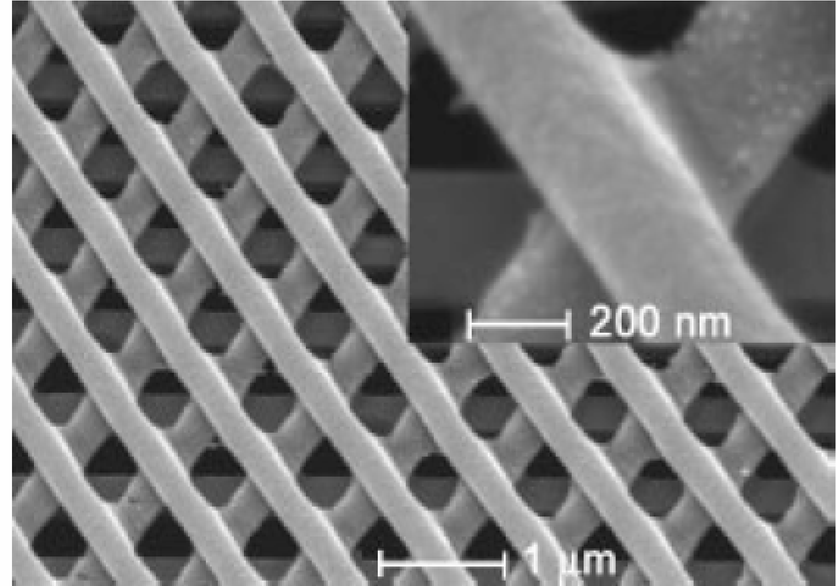
Etch rate ratio for AZ photoresist to HSQ (like SiO_2) is >100.

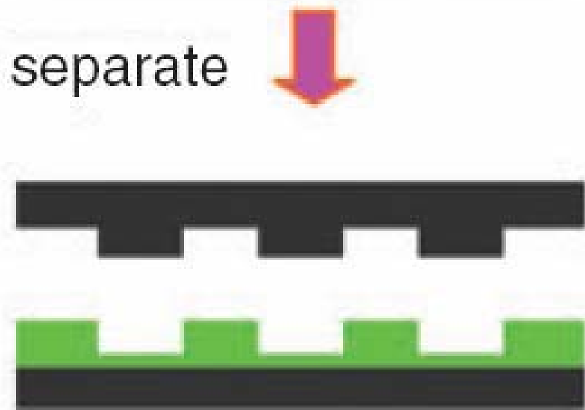
PURDUE UNIVERSITY

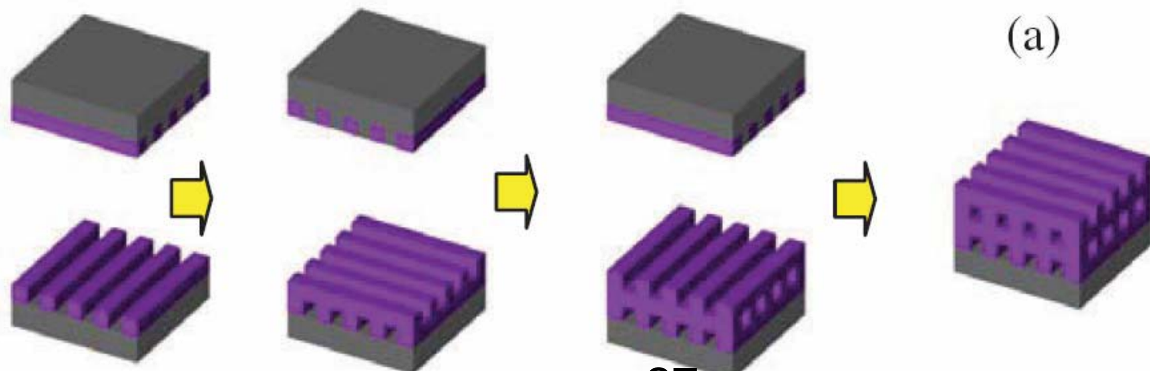
Reverse NIL and multi-dimensional patterning of polymer nanostructures

Layer-by-layer NIL (repeated reverse NIL)





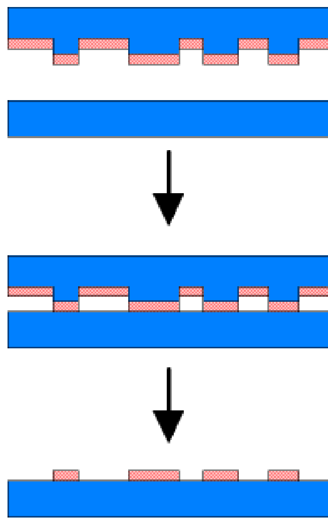




L J Guo, J. Phys. D 37, R123 (2004)

Imprint by inking

Inking process



$T \sim T_g$

Mold

PDMS pad impregnated with medium surface energy film

Selectively Surface Treatment

Protrusions with medium surface energy treatment

Sidewalls and trenches with lower surface energy treatment

Spin coat polymer and annealing

Ink to substrate

Bao…Guo, "Polymer inking as a micro- and nanopatterning technique", J. Vac. Sci. Tech. B, 2003, 21, 2749