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Pattern transfer processes for the NanoFrazor

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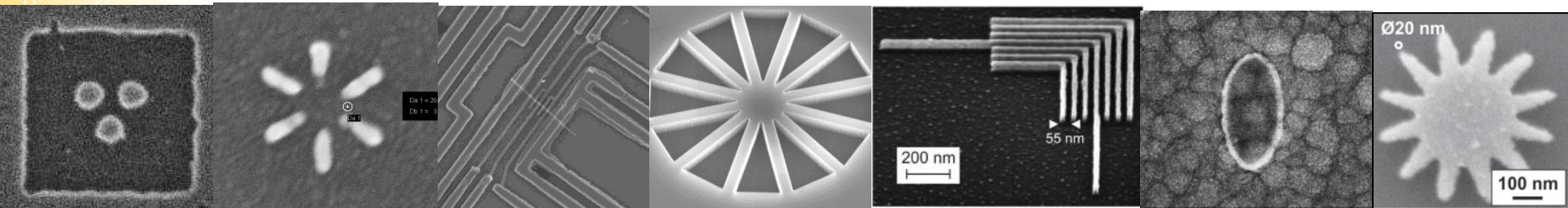
Outline

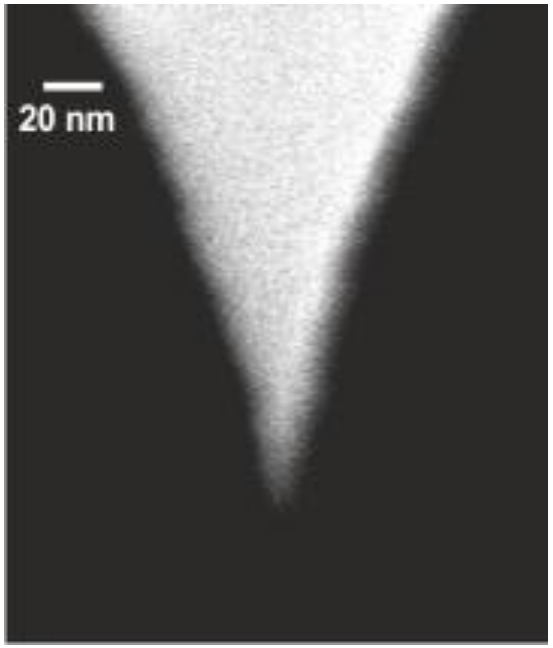
- Background
- High-resolution etch transfer
- Simple lift-off
- High-resolution lift-off
- 3D etch transfer
- Other processes

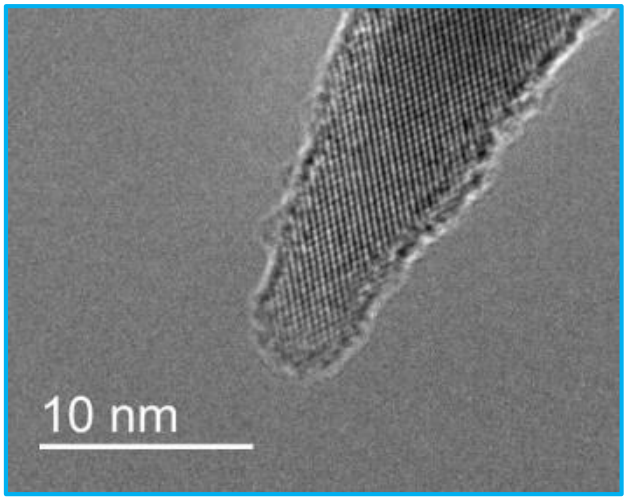


Background

- The tips of the NanoFrazor offer exquisite sharpness, with sub-10 nm tip diameters
- The tip itself is a cone shape – deeper writing results in broader features
- Highest resolutions are thus achieved with shallow patterning

- As a side note: Best heat transfer for deep / 3D patterning is achieved with broader tips
- Sharp tips are typically found towards the centre of the wafer, broad tips typically towards the edge





Examples: complex high-resolution shapes

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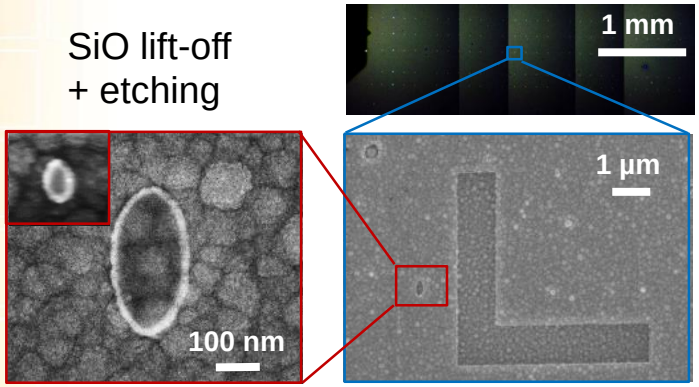
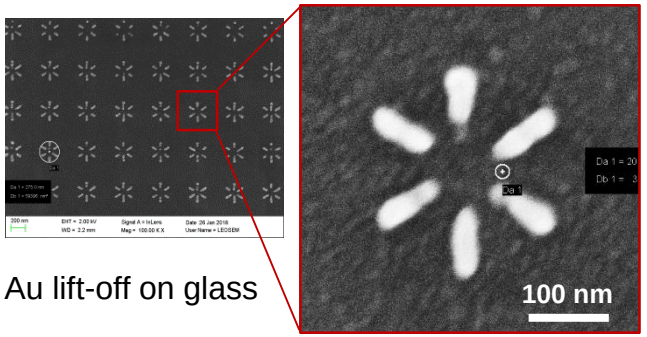
in contrast to using e-beam:
no proximity correction necessary => easy to make small complex geometries

Magnetic ellipses

SiO lift-off
+ etching

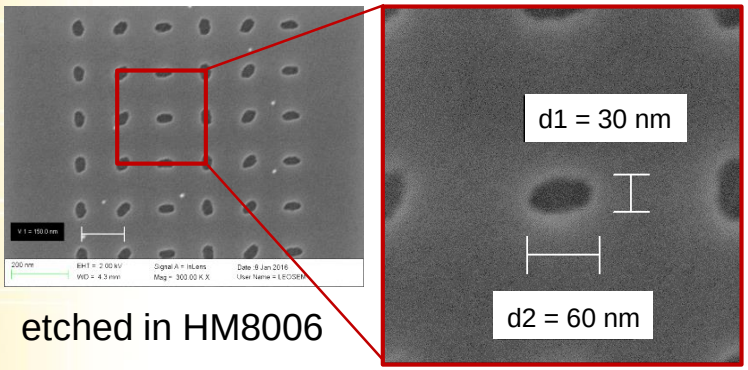


Plasmonic antennas



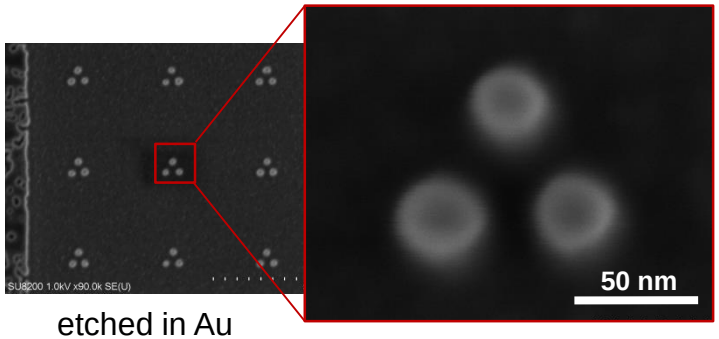
Au lift-off on glass

Rotating Elliptical Quantum Dots



etched in HM8006

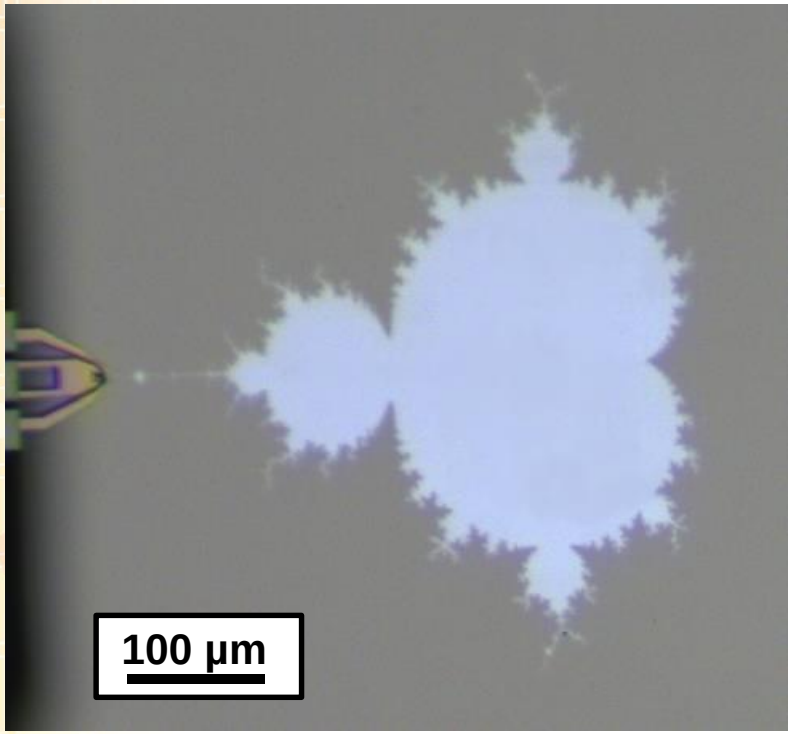
Trimer



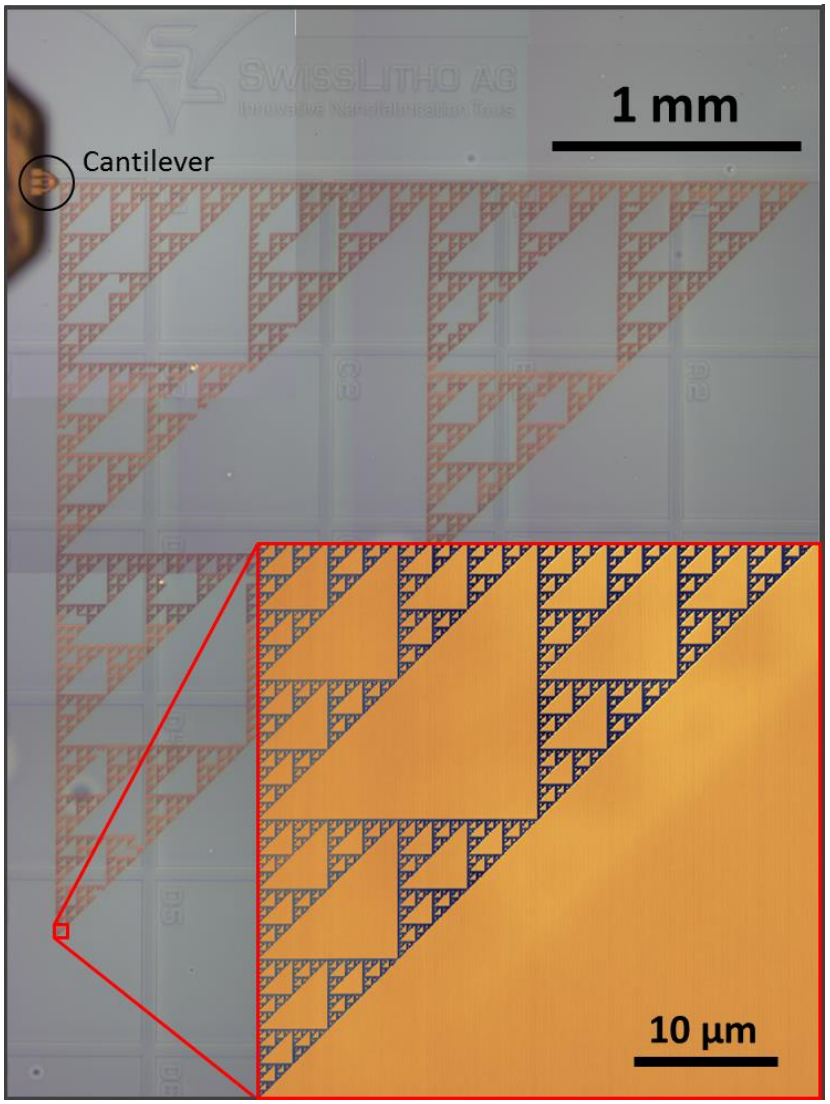
etched in Au

«Large area» patterning

Written with an automatic script



Mandelbrot Fractal



Sierpinski Triangle

High-resolution pattern transfer (RIE)

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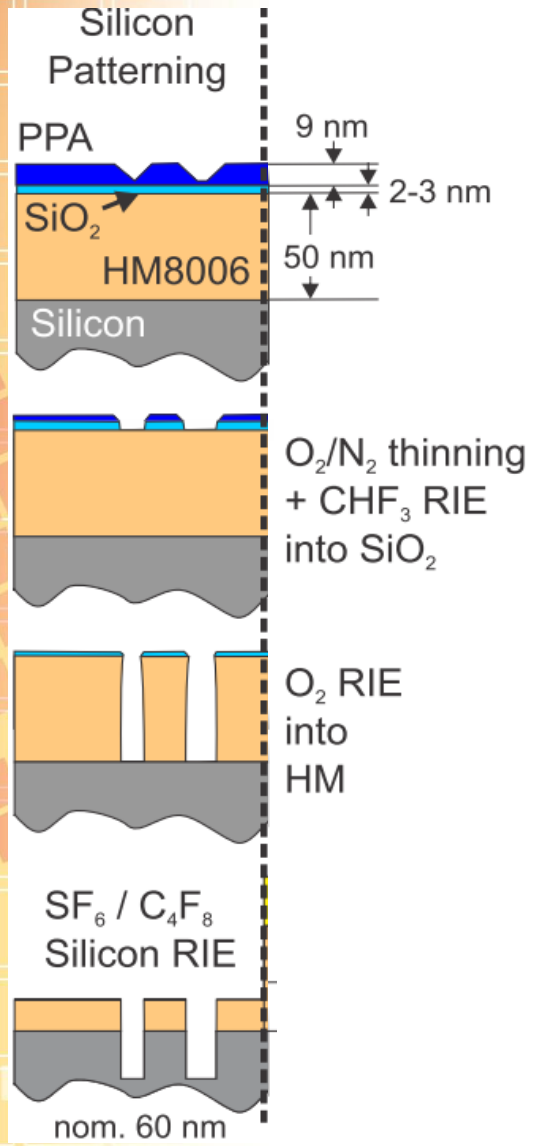
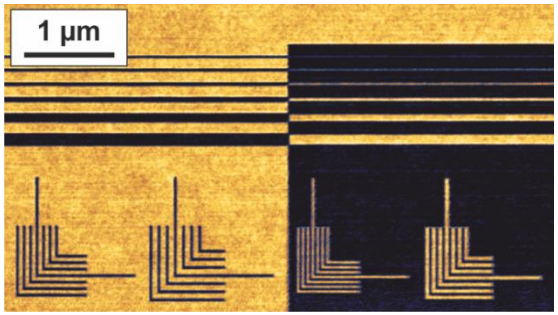
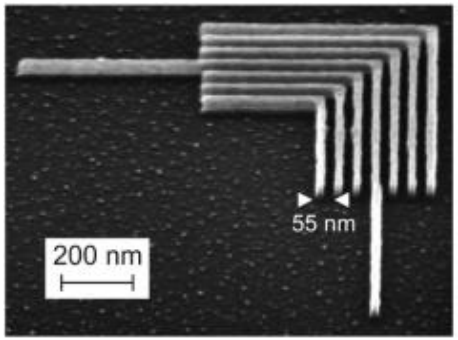


27.5 nm HP in PPA

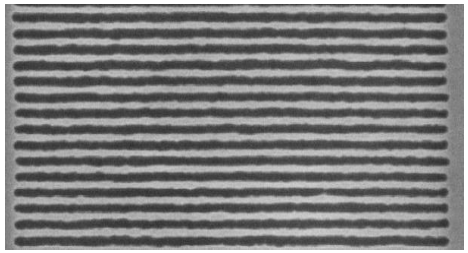


in Silicon

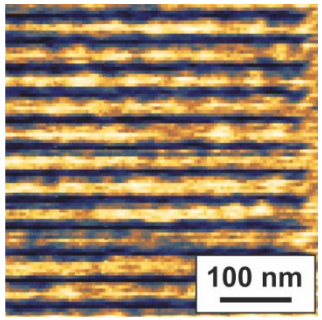


Cheong *et al.*, Nano Letters, (2013)

13.8 nm HP in Silicon

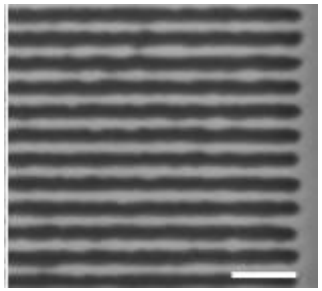


18.5 nm HP in PPA

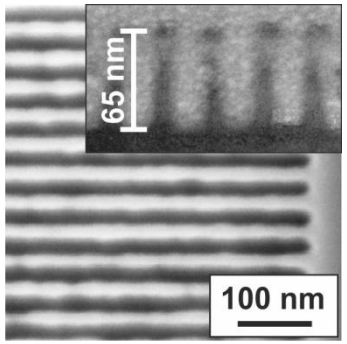


4 nm deep

in HM8006



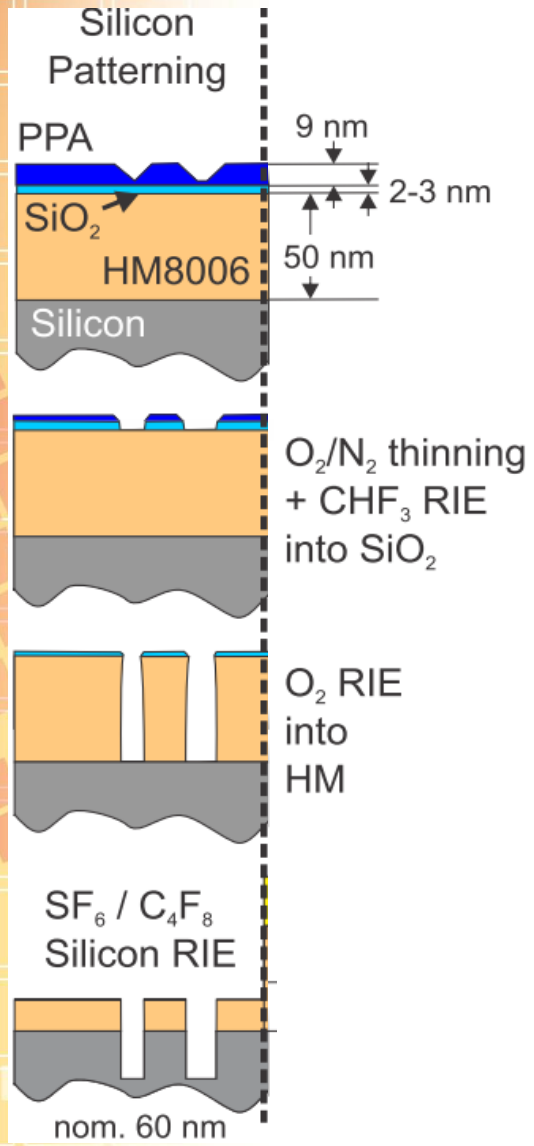
in Silicon



65 nm deep
3 nm (3σ) LER

Wolf *et al.*, JVSTB, (2015)

High-resolution pattern transfer (RIE)



Key points:

- This transfer process uses an oxide hard mask for contrast / depth enhancement.
- The shallow features are transferred from PPA into the hard mask with e.g. a CHF3 RIE (critical step)
- As the layer is very thin, the etch rates need to be calibrated for good control
- Evaporated SiO2 gives a more homogeneous layer than sputtered; better line edge roughness
- After transfer into SiO2, an O2 RIE is used for depth enhancement

High-resolution pattern transfer (RIE)

The full process is described in: *Wolf et al., J. Vac. Sci. Technol. B 33 (2015)*

1. Prepare PPA solution of 0.5%

1. Solvent is Anisole ($CH_3OC_6H_5$, 0.995 g/mL, bp: 154°C)
   or Cyclohexanone ($C_6H_{10}O$, 0.9478 g/mL, bp: 155.6°C)
2. For 1 mL use 5 mg of PPA and 0.995 g of solvent
3. Shake the solution well to get the PPA fully dissolved

2. Prepare solution for hard mask

1. The polymer hard mask layer is either HM8006 (Honeywell) or PMGI SFG-2S (Microchem)
2. For HM8006, prepare a diluted solution using ethyl lactate with the ratio 1:2 (HM:EL)
3. For PMGI, prepare a diluted solution using G-Thinner TM™ (Cyclopentanone with PMGE) with the ratio 1:1 (PMGI:GT)

3. Spin coating hard mask

1. Clean sample, dry and heat it to get the water off the surface (e.g. 1 min hot plate 150°C, further cleaning steps might involve a barrel asher or a HF dip)
2. Cover sample with solution and spin for 35 seconds at 3000 rpm
3. Bake at 225°C/90 sec (HM) or 200°C/60 sec (PMGI). The resulting layer is 20 nm thick.

4. Deposition of silicon oxide

1. The intermediate layer is a thin (3 nm) silicon oxide layer. This layer should be as homogeneous and smooth as possible. Usage of an evaporator (eg. Evatec BAK 501) is superior to sputtering.

High-resolution pattern transfer (RIE)

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5. Spin coating PPA

1. Optional: clean the sample using a gentle oxygen etch in a barrel asher (e.g. Tepla BA, oxygen plasma for 10 s at 100W)
2. Deposit 12 nm of PPA
   Spin coat with 0.5% solution for 35 seconds at 2000 rpm. Bake at 90 °C for 3 min.

6. Patterning high resolution pattern

1. For this process the standard settings are:
   Pixel size 5-10 nm
   Target depth 10 nm

7. Etch transfer of masks

1. All the processes to etch the PPA, SiOx, HM can be done in an anisotropic etch tool as the RIE NG80 (Oxford) or similar.
2. Etch of the residual PPA layer (4 sccm O2 and 16 sccm N2, power 10 W, pressure 15 mTorr, rate is ≈20 nm/min)
3. Etch of the silicon oxide (20 sccm CHF3, power 100 W, pressure 15 mTorr, rate is ≈14 nm/min)
4. Etch of the polymer hard mask (20 sccm O2, power 20 W, pressure 15 mTorr, rate is ≈20 nm/min)

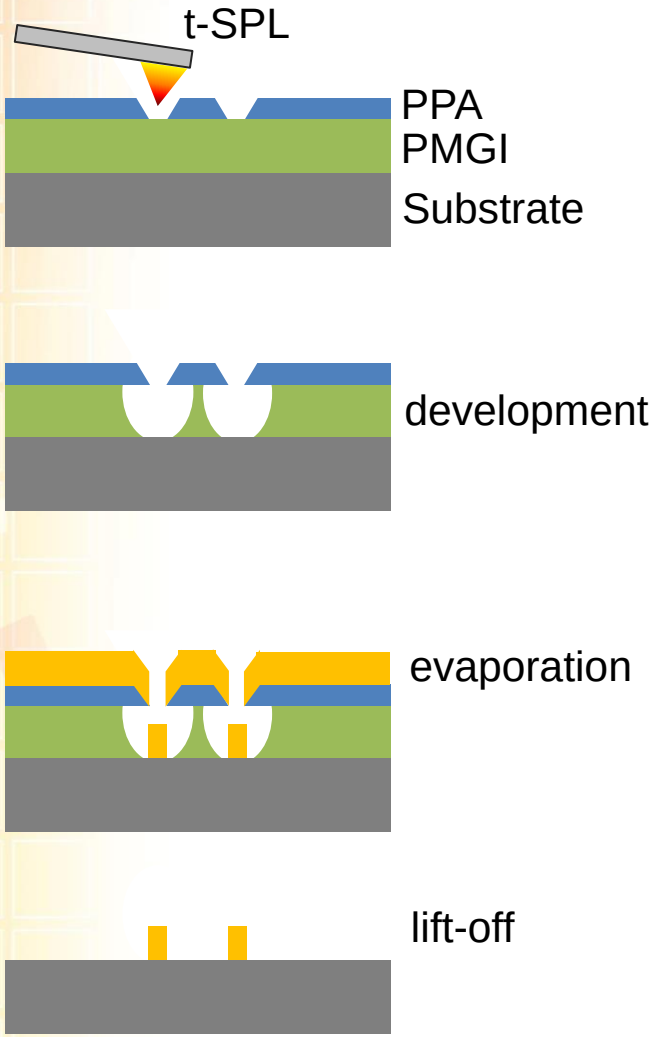
8. Etch transfer to silicon

1. The transfer to silicon is done in a DRIE, e.g. the Alcatel AMS 200.
2. Etch of the silicon (SF6 1.5:1 C4F8, power 1200 W, pressure 11 mTorr) The rate of silicon is ≈550 nm/min and the rate of the HM is ≈80 nm/min.
3. A thicker polymer hard mask than 20 nm allows for larger depths.

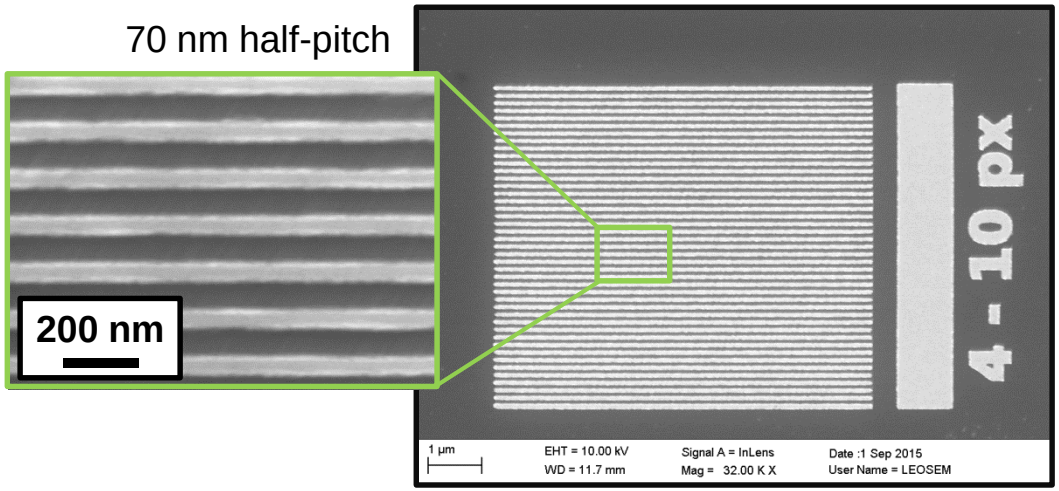
9. Cleaning of sample

1. To clean the sample from any polymer residual one can either apply a oxygen plasma or other oxidizing methods.

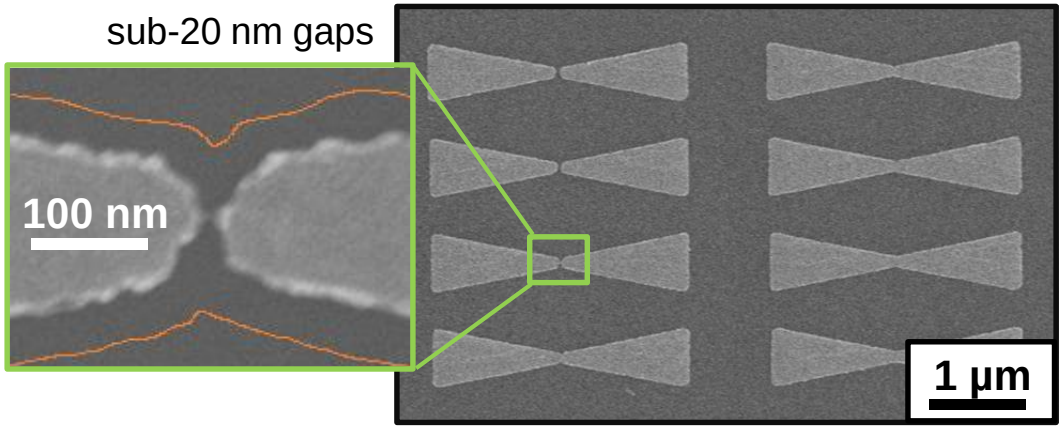
Lift-off process I



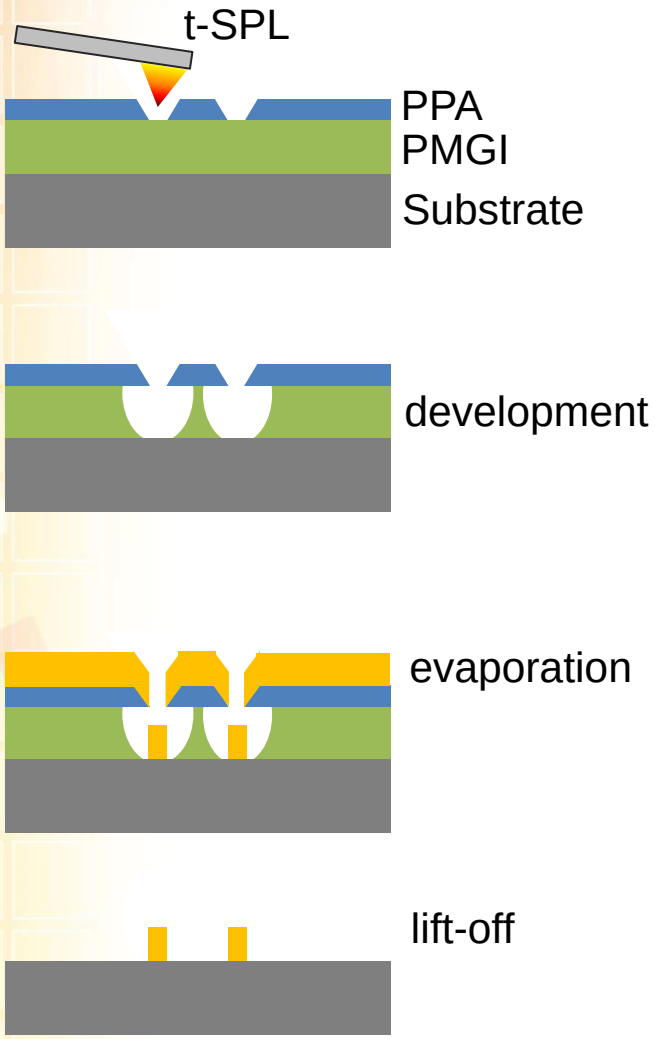
70 nm half-pitch



sub-20 nm gaps



Lift-off process I



Key points:

- Simple process, no RIE
- Relies on differential solubility, more robust
- The base layer is polymethylglutarimide PMGI (SFG 2S™, also known as LOR™) and the patterning layer is PPA.
- Thickness of the layers depend on the desired metal thickness. For example, for metal thicknesses up to 30 nm, 50 nm of PMGI and 20 nm PPA can be used.
- Stripping is done in a hot solvent.
- The disadvantages are the limitation of the design due the isotropic wet developing which might under-etch and lift small freestanding structures. Another issue are wings, which are formed if under-etched structures collapse due to capillary forces.

Lift-off process I

1. Prepare PPA solution of 0.5%

1. Solvent is Anisole ($CH_3OC_6H_5$, 0.995 g/mL, bp: 154°C)
   or Cyclohexanone ($C_6H_{10}O$, 0.9478 g/mL, bp: 155.6°C)
2. For 1 mL use 5 mg of PPA and 0.995 g of solvent
3. Shake the solution well to get the PPA fully dissolved

2. Sample preparation

1. Clean sample, dry and heat it to get the water off the surface (e.g. 1 min hotplate 150°C, further cleaning steps might involve a barrel asher or a HF dip).
2. Deposit PMGI (SFG 2S), cover sample with solution and spin for 35 seconds at 3000 rpm, after that, bake it at 200 °C for 1 minute. It results in a PMGI layer of 50 nm.
3. Deposit 20 nm of PPA, put few drops on sample, and spin for 35 seconds at 3000 rpm. Bake it at 90 °C for 3 min.

3. Patterning with standard resolution

1. For this process the standard settings are:
2. Pixel size 10 nm
3. Determine maximum write depth e.g. by writing a test structure in an unused area.
4. Set the target depth to this depth. Normally the maximum depth is about 10% less than the PPA thickness.
5. Write the desired pattern

Lift-off process I

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4. Development

1. Use 0.17 mol/L TMAH developer (eg. Diluted AR 300-47™) with a rate of 1 nm/sec. For 50 nm of PMGI it takes about 50 seconds to fully develop the sample. Do not stir.
2. Rinse the sample in water to stop the development, and move it quickly to isopropyl alcohol IPA, to remove the water (IPA has a lower surface tension, therefor might do less damage to the undercut layers). Finally dry with nitrogen.

5. Descumming (optional)

1. For a cleaner pattern remove 5 nm PPA with a barrel asher (e.g. Tepla BA; oxygen plasma for 5 seconds at 200W).

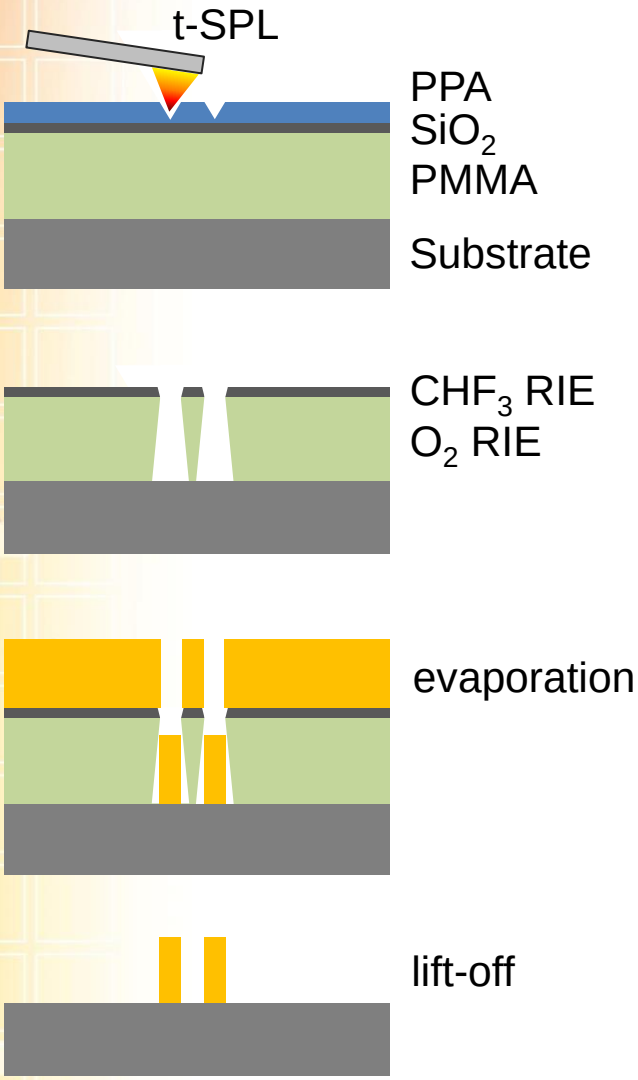
6. Metal deposition

1. Deposit up to 25 nm metal, e.g. 3 nm titanium and 22 nm platinum. Preferably using an evaporation tool. As a general rule, the layer should not be thicker than half the sacrificial layer thickness (PMGI).

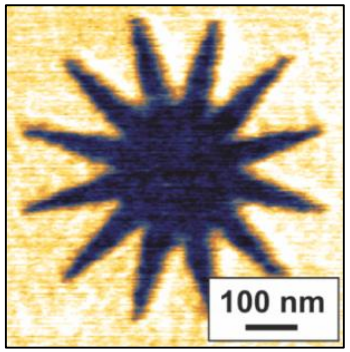
7. Lift-off the metal

1. Put the sample for 30 minutes into hot remover such as N-Methyl-2-pyrrolidone NMP. PMGI is very well soluble in NMP. (ask your facility responsible person for the maximum allowed temperature for the remover that you are using). Attention, NMP is a hazardous chemical! Alternatively NEP can be used.
2. (For a faster lift-off use a scotch tape before the hot remover. Just press it gently on to the sample and rip it off. Only the metal should stick on the tape, not the polymers.).
3. If the metal does not lift-off, sonication could improve the lift off.

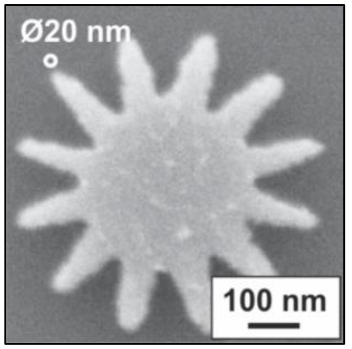
Lift-off process II



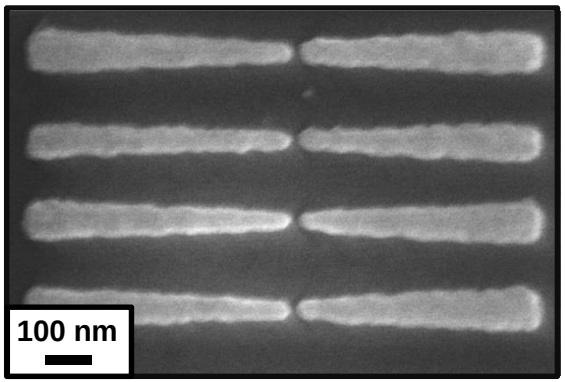
after t-SPL in PPA



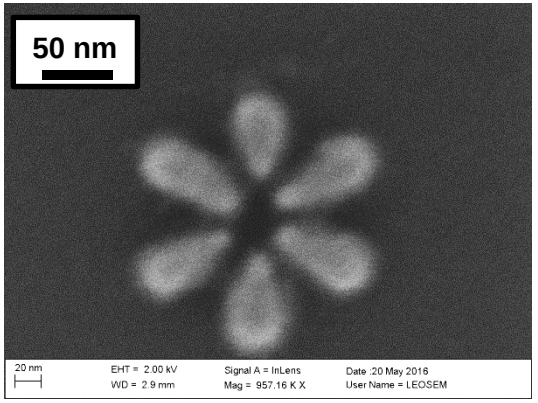
after lift-off with 30 nm Ni



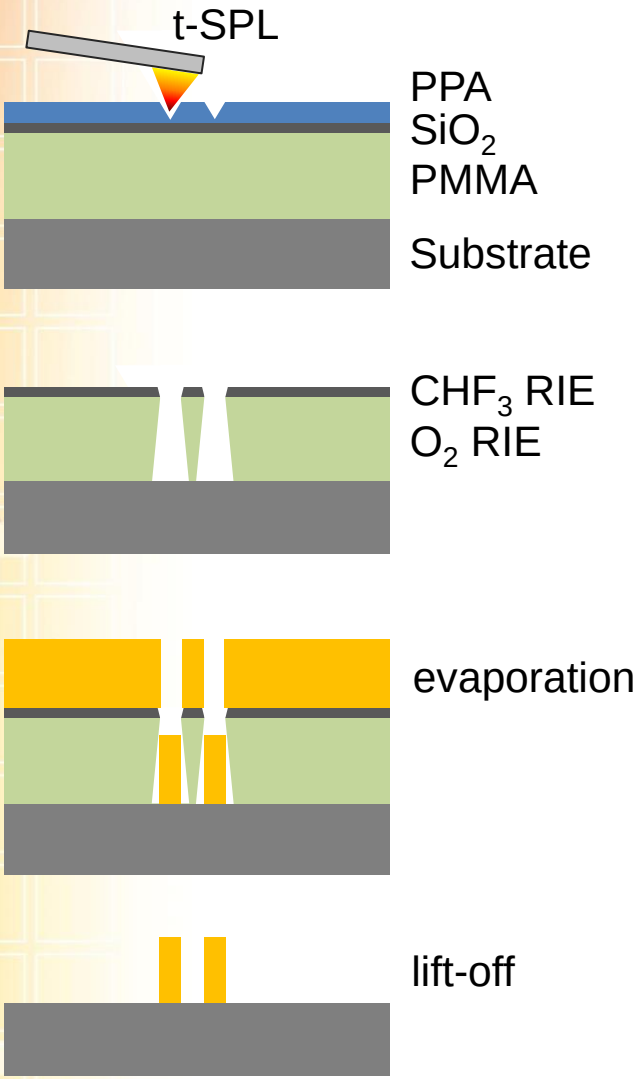
Wolf et al., JVSTB, (2015)



Bow tie antennas (30 nm Au)



Lift-off process II



Key points:

- RIE etch to achieve undercut
- Low isotropy of RIE allows high resolution
- Process steps similar to high-resolution transfer process, with different underlayer.

Lift-off process II

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(Differences to high-resolution transfer process)

1. Replace polymer hard mask (Steps 2 and 3)

1. Using the high resolution process for lift off requires to exchange the polymer hardmask (HM/PMGI) with PMMA. Good results are achieved with PMMA 950k, AR-P 672.02. Different dilution grades are available.
2. The thickness of the PMMA can be chosen arbitrarily, only limited by the etch resistance of the SiOx mask (e.g. 30 - 100 nm PMMA)

2. Layer deposition instead of silicon etch (Step 8)

1. For the lift-off process a broad range of materials can be deposited, e.g. metals, silicon oxide, or silicon nitride
2. Deposit the desired layer(s). As a general rule, the thickness of the evaporated layer should not exceed half the thickness of the PMMA layer.

3. Lift-off the layers

1. Put the sample for 30 minutes into acetone. PMMA is very well soluble in acetone.
2. (For a faster lift-off use a scotch tape before the hot remover. Just press it gently on to the sample and rip it off. Only the evaporated layer on top of the polymer should stick on the tape, not the structures itself.)
3. If the layers do not come off, sonication could improve the results.

3D pattern transfer

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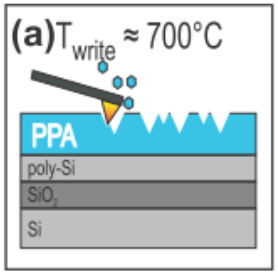
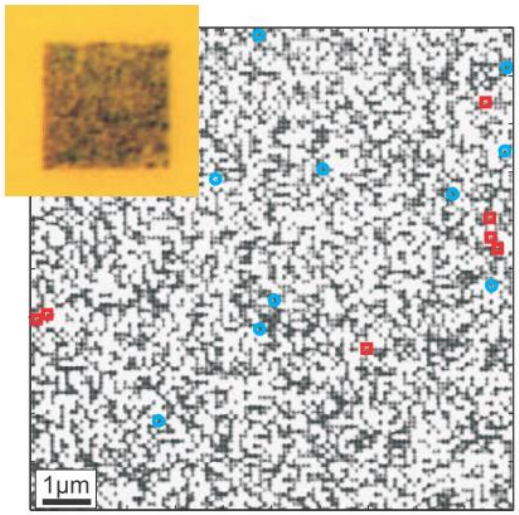
Direct RIE





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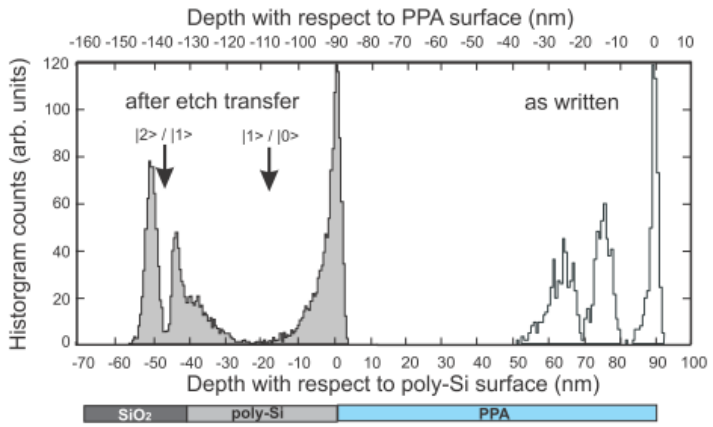
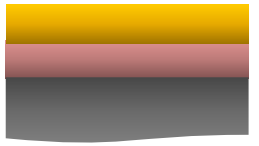
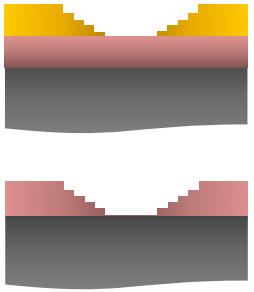


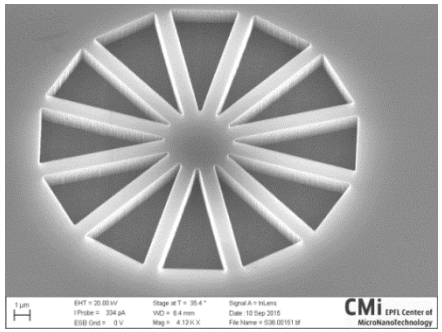
Holzner *et al.,* Appl. Phys. Lett., 99, 023110, (2011)

Hard mask for amplification

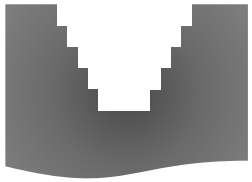


PPA
30 nm deep

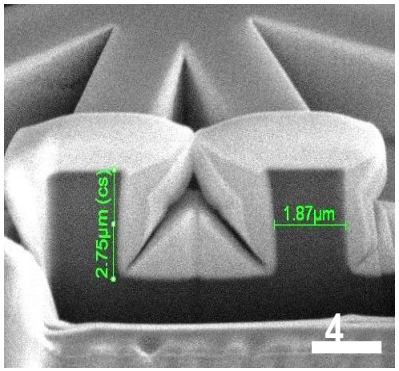




Si (2750 nm deep)



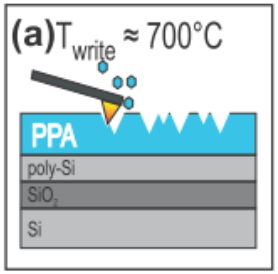
PPA
SiO_2
Si

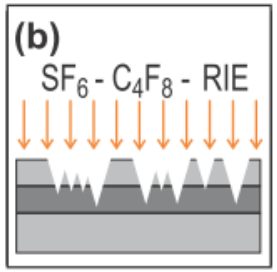


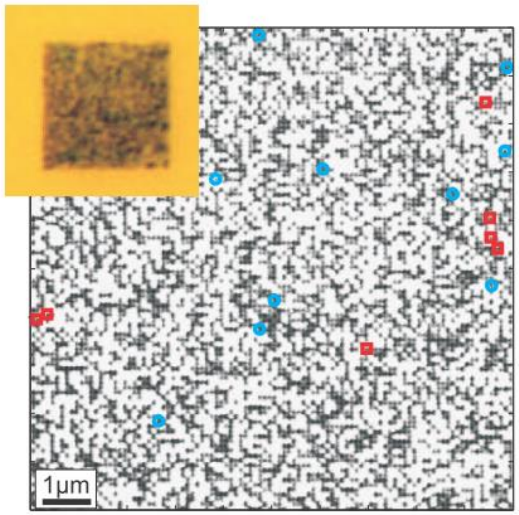
Yuliya Lisunova, EPFL

3D pattern transfer

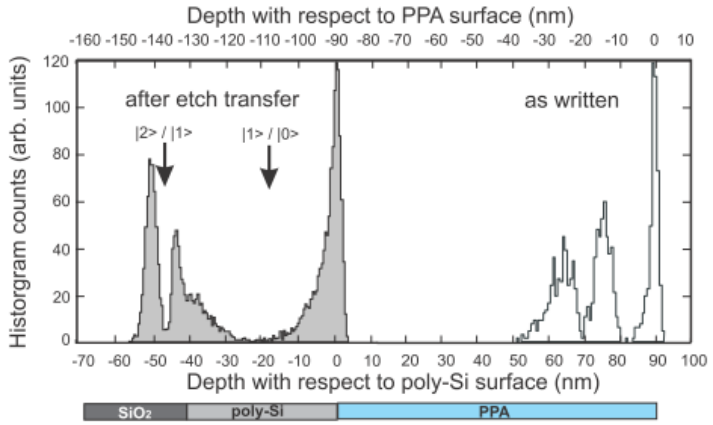
Direct RIE







Error rate: 10^{-3}



Holzner *et al.,* Appl. Phys. Lett., 99, 023110, (2011)

Key points:

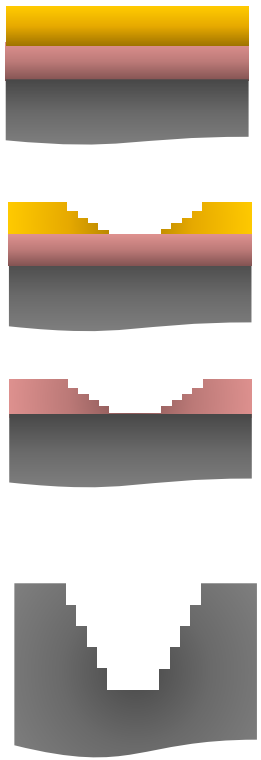
- Depth enhancement defined by etch contrast
- Etch contrast varies with materials, sample size, RIE configuration, chemistry.
- Needs to be determined for the application.

3D pattern transfer

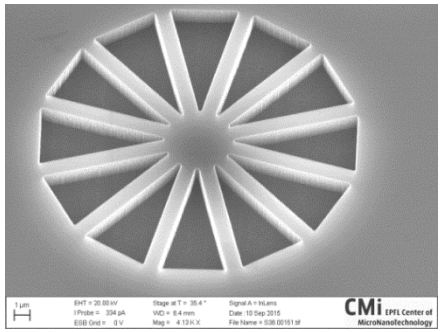
Key points:

- If larger depths are required, multiple layers can be used.
- Required patterning depth determined by layer choice and etch contrast(s).
- Etch rates, layer thicknesses and the etch timing are very important and have to be precisely controlled.

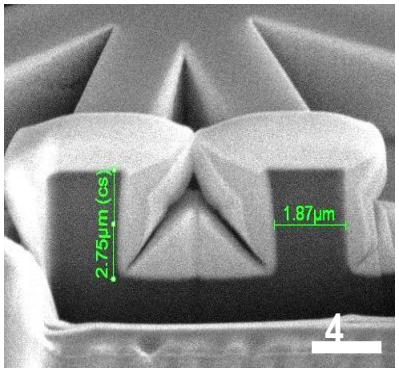
Hard mask for amplification



PPA
30 nm deep



Si (2750 nm deep)



Yuliya Lisunova, EPFL

3D pattern transfer

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1. Prepare PPA solution of 5%

1. Solvent is Anisole ($CH_3OC_6H_5$, 0.995 g/mL, bp: 154°C) or Cyclohexanone ($C_6H_{10}O$, 0.9478 g/mL, bp: 155.6°C)
2. For about 1 mL use 50 mg of PPA and 0.95 g of solvent
3. Shake the solution well to get the PPA fully dissolved

2. Sample Preparation

1. Clean sample, dry and heat it to get the water off the surface (e.g. 1 min hotplate 150°C, further cleaning steps might involve a barrel asher or a HF dip)
2. Deposit 100 nm of PPA, put few drops on sample, and spin for 60 seconds at 5000 rpm.
3. Bake the PPA for 3 min at 90°C to remove the residual solvent.

3. Patterning

1. For this process the standard settings are:
2. Pixel size 20 nm
3. Depth levels 2 – 60 (depth resolution is 1 nm)
4. Minimum patterning depth is 0 nm
5. Maximum patterning depth is 60 nm
6. Use the Feedback

3D pattern transfer

SwissLitho AG
Innovative Nanofabrication Tools

4. Thinning down the residual PPA

1. For a good transfer it is necessary to remove the residual PPA layer. In this case it is about 40 nm. A good way to do this is to use a RIE with an anisotropic oxygen etch. Still a small residual of 2-5 nm PPA should remain.
2. Etcher Oxford RIE NG80
3. 4 sccm O2 and 16 sccm N2, power 10 W, Pressure 15 mTorr
4. Measured etch rate is about 12 nm/min

5. Transfer pattern into silicon or hard mask material

1. Use an anisotropic dry etch to simultaneously etch the substrate and, with a lower rate, the PPA. The etch selectivity between PPA and substrate determines the achievable depth. This depends on many factors, and thus needs to be configured for each application.
2. With an etch selectivity of 3:1 (Si:PPA) and 60 nm pattern depth, a transferred depth of 180 nm is possible

6. Larger depths

1. Use an intermediate layer like silicon oxide. This way, the pattern is first transferred from PPA into silicon oxide, and in a second step from silicon oxide to silicon with different chemistry. Depths larger than 4 microns have been achieved.
2. The required silicon oxide layer thickness is calculated from the desired depth, and the etch contrast of silicon oxide to silicon for the selected etch chemistry.
3. The PPA thickness is then determined according to the etch contrast of PPA to silicon oxide. Note that an additional thermal buffer layer of ca. 40 nm should be added to the thickness of the PPA layer.

3D replication directly from PPA

SwissLitho AG
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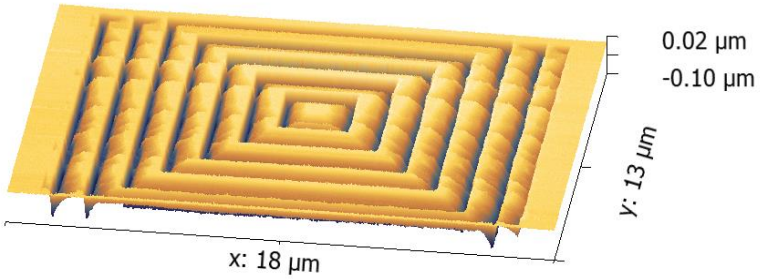
Nano-imprint

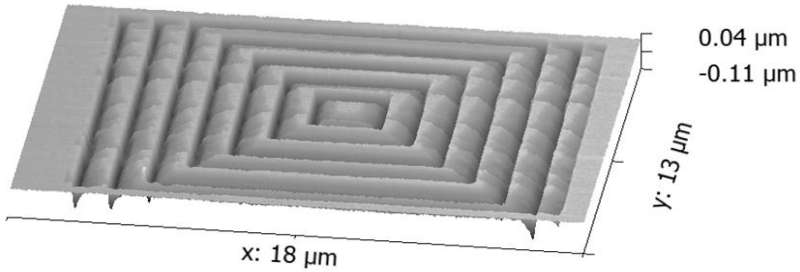
PPA

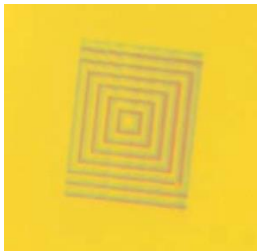


Soft Stamp

EVG SmartNIL
Direct replication
from PPA

UV NIL resist

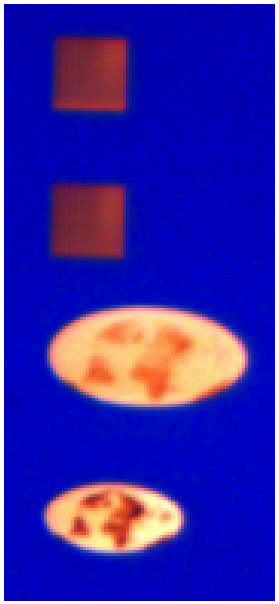




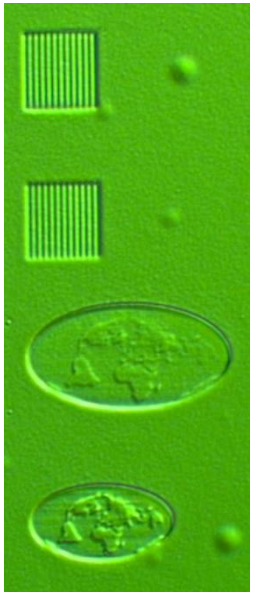
Simon Bonanni, SwissLitho AG
Thomas Glinsner, EVG

Plating

PPA



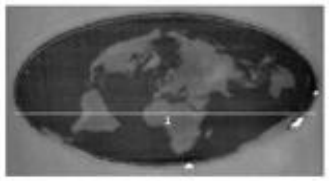
Nickel



Philip Paul, SwissLitho AG
Roger Bischofsberger, Applied MicroSwiss

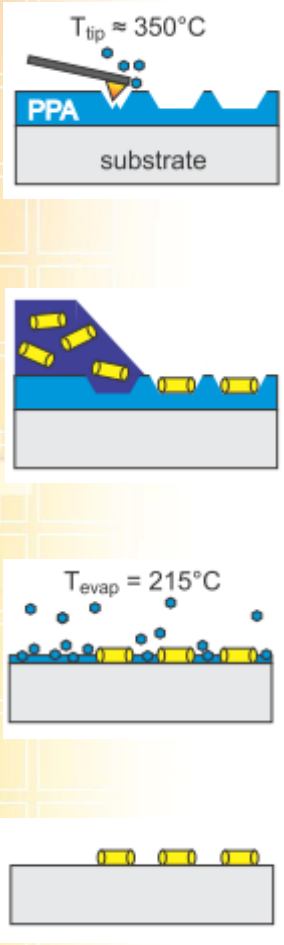
Injection Molding

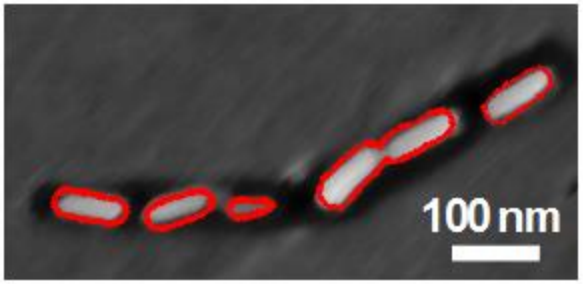
PMMA



Christian Rytka, FHNW

Directed placement of nanoparticles



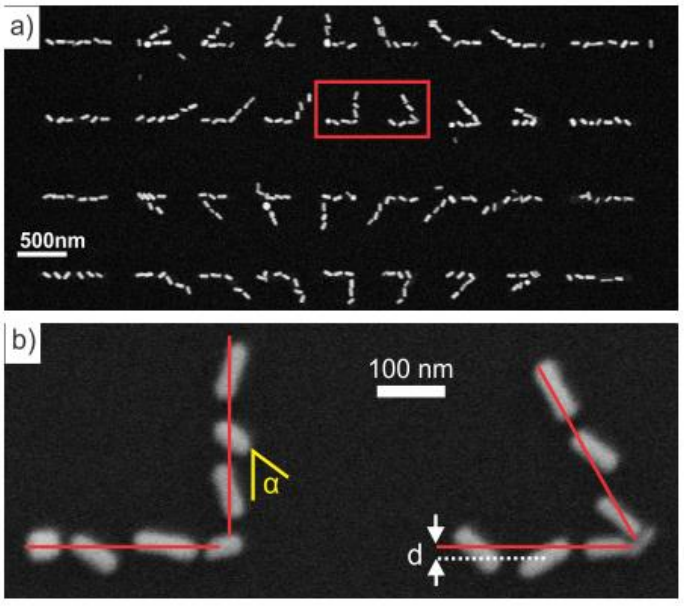


Overlay before (AFM) and after evaporation (SEM, red outline)

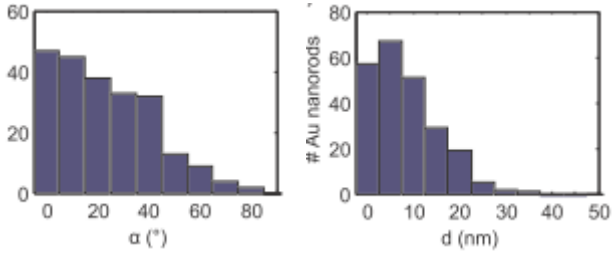
70 nm of PPA under the nanorods removed:

Lateral position and orientation of the Au nanorods is preserved!

Explanation:
PPA decomposes at T_g
$\Rightarrow$ no liquid phase
$\Rightarrow$ no dewetting



Off-axis displacement:
σ = 10.3 nm



Holzner et al., *Nanoletters*,11, 3957–3962, (2011)

Chemical Patterning

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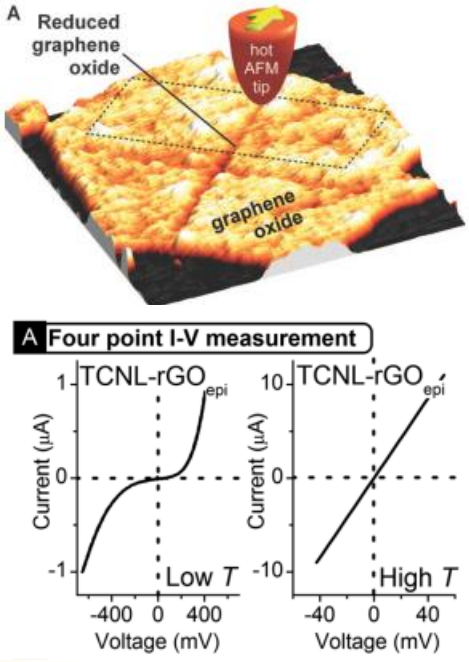
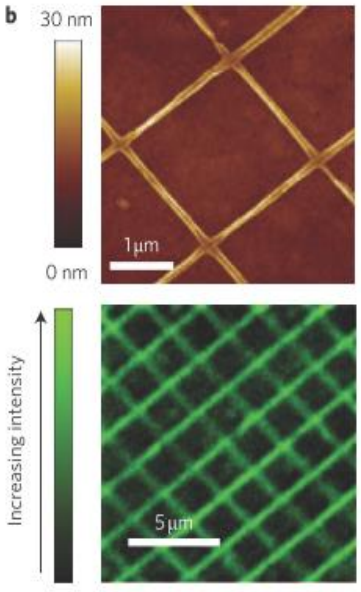
Graphene oxide



Local reduction of graphene oxide to create lines with a four orders of magnitude increase in conductivity

Wei *et al.,* Science, (2010)

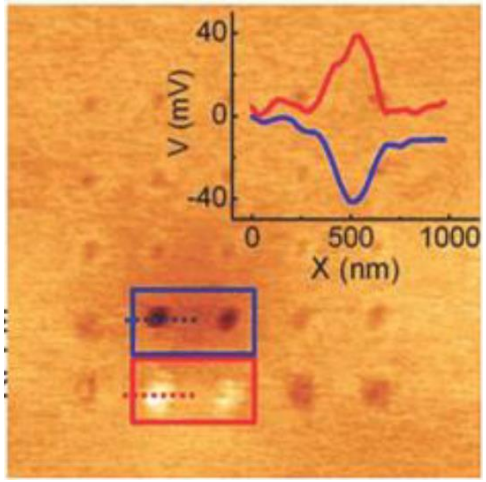
Organic semiconductors



Thermochemical conversion of a precursor to form poly(p-phenylene vinylene) (PPV)

Fenwick *et al*., Nat. Nano., (2009)

Ferroelectrics



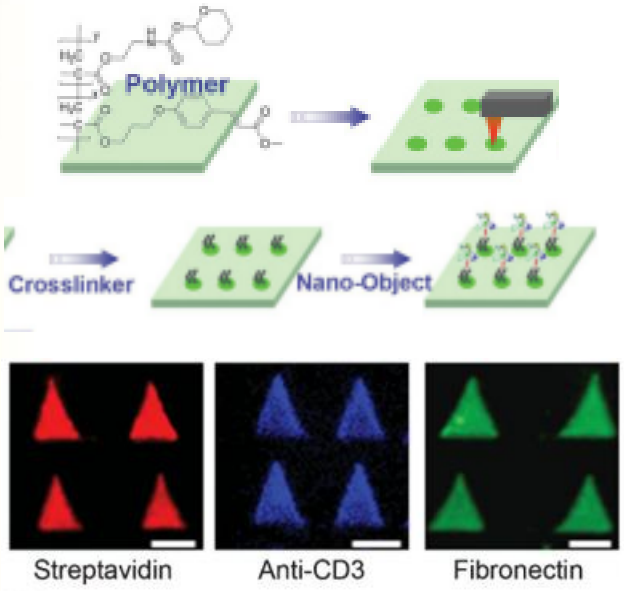
Local crystallization to write ferroelectric nanostructures on plastic, glass or silicon

Kimi *et al.,* Adv. Mat., (2010)

Chemical Patterning

SwissLitho AG
Innovative Nanofabrication Tools

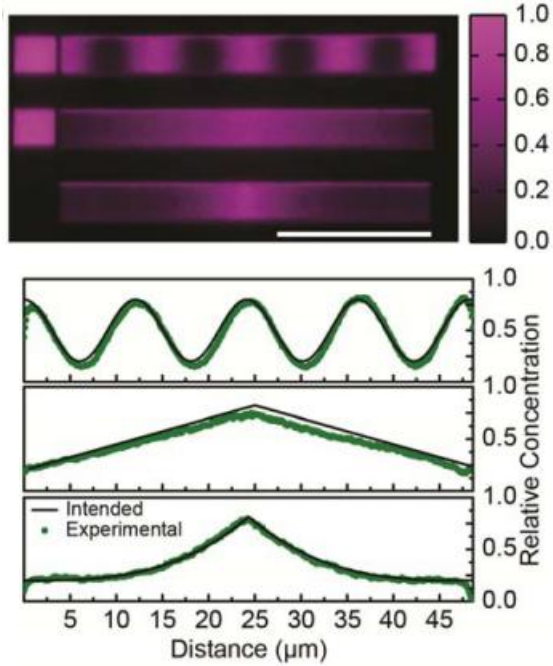
Thermally activated cross-linking



Nanoscale chemical patterning of amine, thiol, aldehyde or biotin to locally attach proteins or DNA.

Wang *et al*., Adv. Funct. Mat., (2010)

Chemical gradients



Local temperature variations result in local conentration variation of amine groups.

Carrol *et al*., Langmuir, (2013)