Study of the transfer of a biosourced resin by thermal nanoimprint

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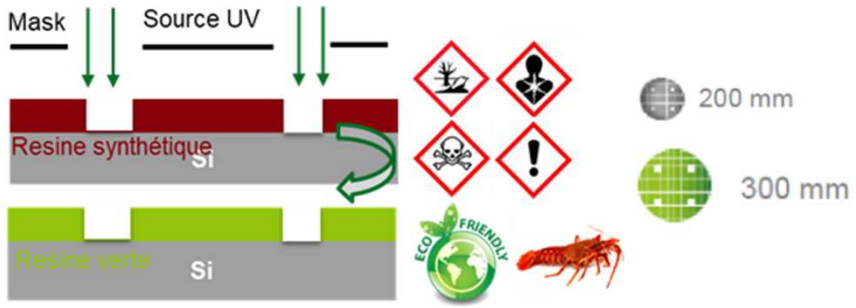
Context

- **Lithogreen** ANR project (ANR-19-CE43-0009) aims at the replacement of current (Deep) UV photolithography synthetic resists for micro/nanofabrication
- **Polysaccharides** from biomass as water developable eco-friendly (Deep) UV photolithography resist

From lab-scale to pilot line scale



Towards to eco-friendly resists

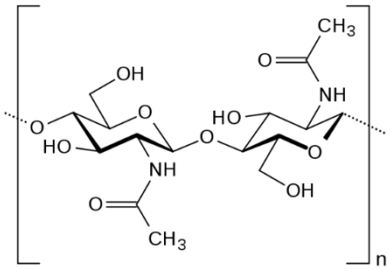
Lithography	Conventional resist	Bio-sourced resist
Photoresist. Photo-sensitive material Photo Acid Generator (PAG)	**Issued from petrochemical industry** *Polyacrylates, polystyrenic… resists* *Ionic or non-ionic salts (sulfonium…)*	**Polysaccharides extracted from natural sources** *Chitosan, Methylcellulose, Alginates, …*
Solvent. Solubility in solvent For cleaning (EBR + BS rinse)	**Organic solvents** *PGMEA, Ethyl Lactate, PGME…* *PGMEA*	**Deionized water**
Developer. To reveal 3D patterns	**Alkaline aqueous solution** *TMAH 2.38%*	**Deionized water**

From biomass source water soluble resist

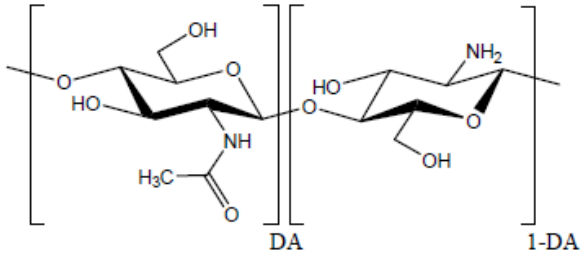
CHITOSAN PRODUCTION

Outer shells of crustaceans

Extraction



Deacetylation / Purification



Chitin

2nd most **abundant biopolymer** on earth

Prod. > 10,000 tons / year

Elieh-Ali-Komi D., Hamblin M. R. (2016)

Chitosan

with varying **M_w, DA**

CHITOSAN PROPERTIES

- ✓ **Film** forming and low surface roughness
- ✓ Good **adhesion** on Si substrate
- ✓ Production free of metallic ions
- ✓ **Sensitive to DUV** irradiation & E-beam
- ✓ Non-hazardous
- ✓ **Bio-sourced**, bio-degradable
- ✓ Soluble in low acidic-based water (pKa ≈ 6,5)

› **Chitosan used as water-soluble and developable photoresist**

anr

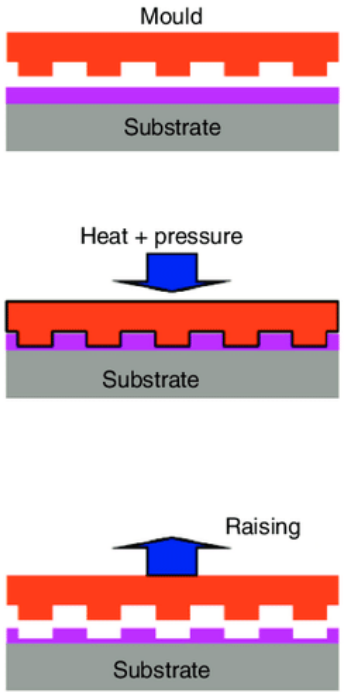
Nanoimprinting of Chitosan films ?

Objective : single-step nanoimprinting lithography of chitosan at **nanoscale without the introduction of additional chemistry**

→ Substrate : 2,5x2,5 cm², 300 nm de SiO_2/Si <100>

→ 250 nm thick films : C (chitosane) =1% (m/v), DA 35%, Mw=613 kDa, Mn=351 kDa, H_2O=13,5%

→ Silanized nanopatterned Si molds : microlines and nanodots features

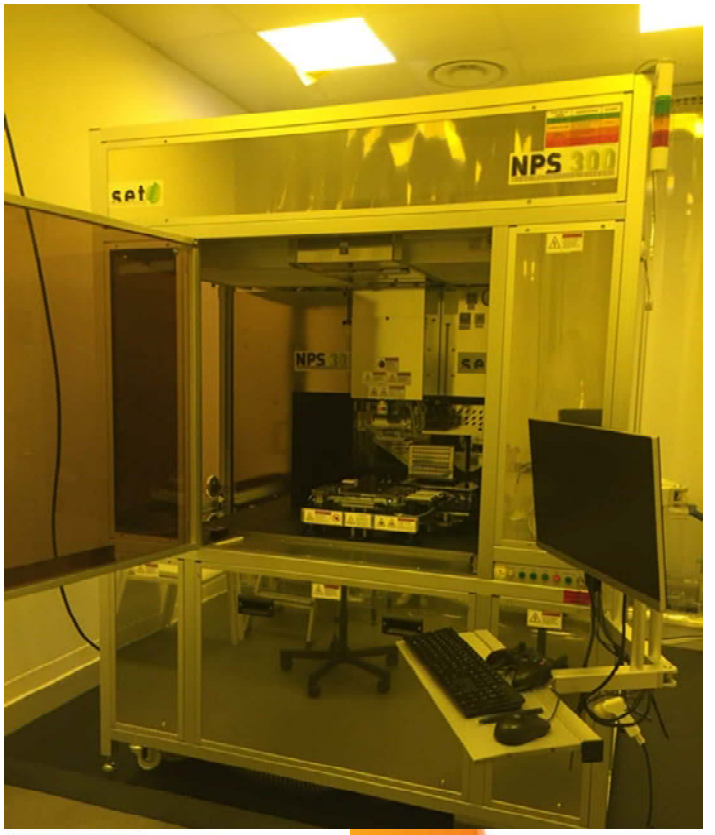


Y.G. Bi *et al,* Nanophotonics, 7 (2017)

Setting parameters Thermal Nanoimprinting :

- Chuck/Stamp temp : up to 450°C
- Pressure (force) : up to 4000 N
- *Step & repeat mode :*
  - *Stamp from : 2 to 40 mm²*
  - *Substrate : from 1 cm² up to 200 mm*
  - *Alignment < 300 mm*
- *UV NIL@365 nm*

SET NPS300 – Nano-Patterning Stepper



Thermodegradation of chitosane*

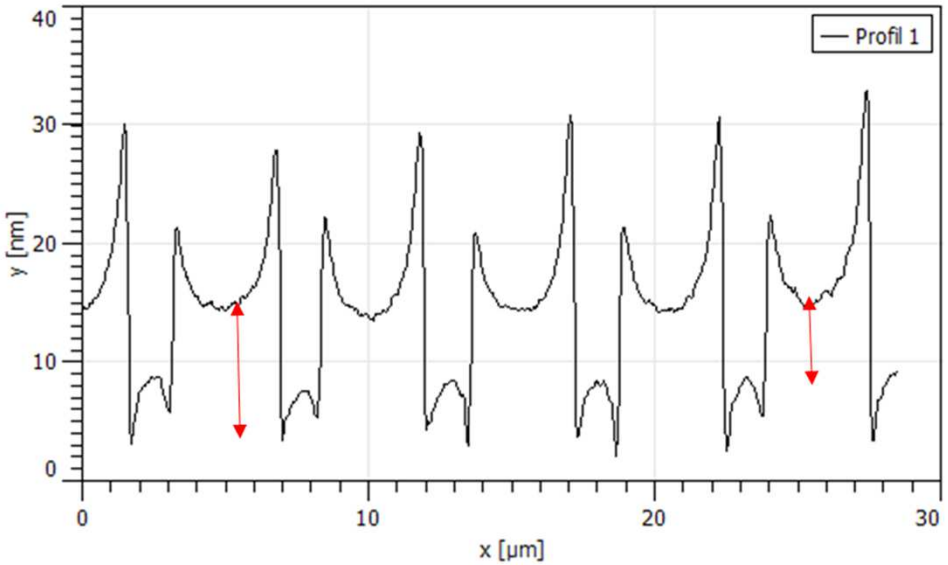
- Powder and film analysis: from room temperature to a “plateau” from 140°C to 200°C, the polymer only loses water. Then two phases of degradation
  - a first phase from 250°C to 350°C generates the formation of water, carbon monoxide, carbon dioxide and, depending on the AD, ammonia and acetic acid from the acetyl group
  - between 450°C and 750°C, this is the second degradation phase characterized by the formation of methane and a graphite-like carbon compound
- **No Tg observed** !

➔ **Softness vs. hardness of film during nanoimprint ?**

**Results from PhD thesis of M. Caillau “Green nanotechnology: polymers of biomass as eco-efficient resins for lithography” 05/10/2017 @INL*

First test

- Mold pattern : lines l= 3-4µm h=400nm, period 5µm
- T=150°C, during 1200s, F=4000N, during 1800s



<10nm

~ 6nm

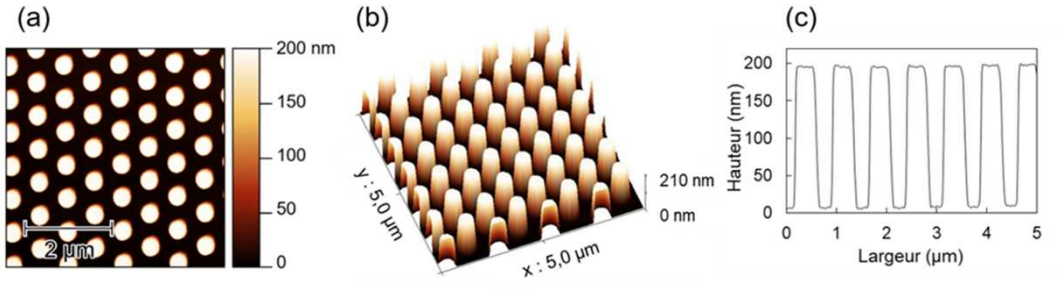
Observations :

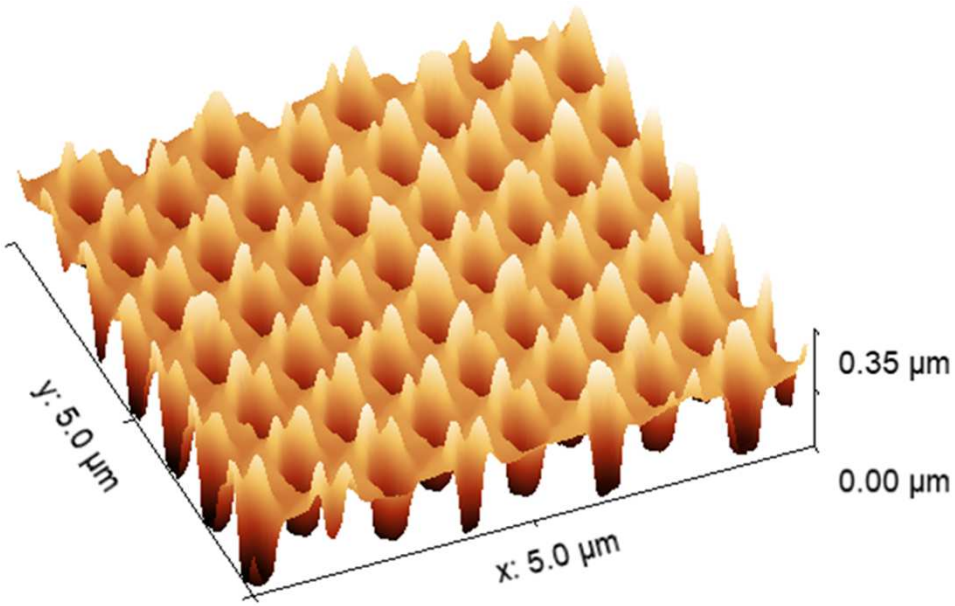
- Imprinted depth of 40-60nm at best !
- Strong ‘rabbit-ear’ effect
  - ✓ Wetting of chitosan along wall tranches of the mold
  - ✓ Incomplete filling of trenches
  - ✓ Pulling out during demolding step

➔ surface-to-volume ratio of trenches effect ?

Second test

- Mold pattern : Holes Ø500nm h=200nm, period 1µm
- T=180°C during 1200s, F=2600N during 2100s





Observations :

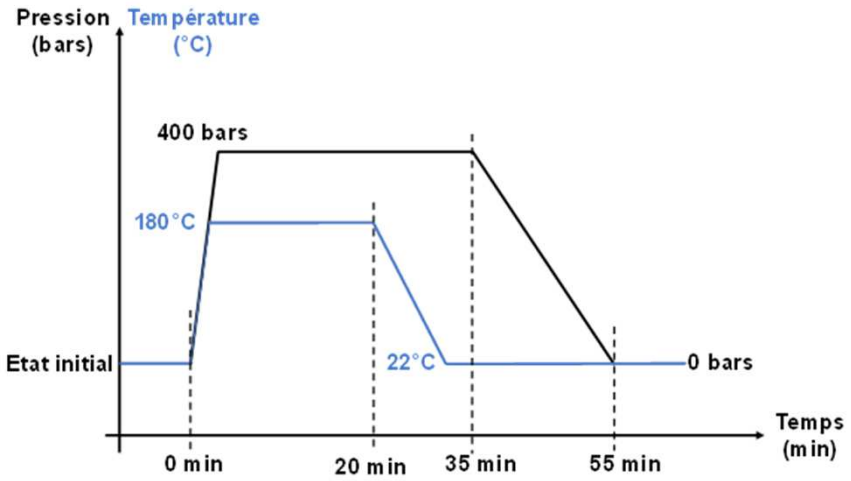
- Imprinted depth of 180 nm at best
- Less than 20 nm remaining resin at the bottom of the holes

- ‘rabbit-ear’ effect still present even by decreasing the dimensions

➔ Thermal/pressure to be adapted ?

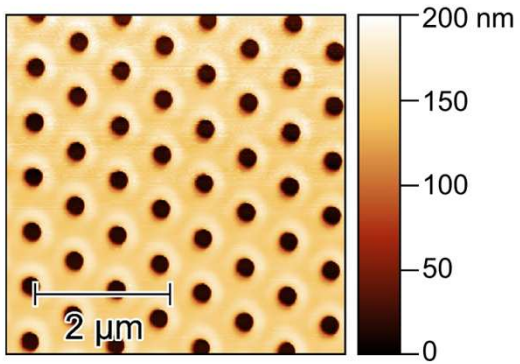
last test

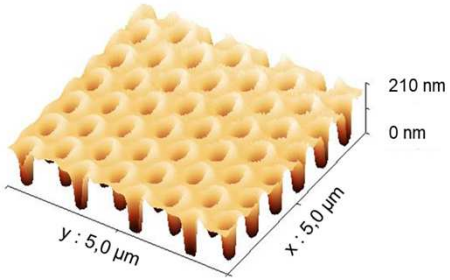
- Mold pattern : Holes Ø500nm h=200nm, period 500 nm
- Imprinting parameters :
  - ✓ Chuck and mold both heated @ 180°C (20 minutes)
  - ✓ F=2600 N during 2100 sec
  - ✓ Slow cooling and removal:
    - Pressure maintained when T↘ (15min)
    - Pressure drop by 2min steps

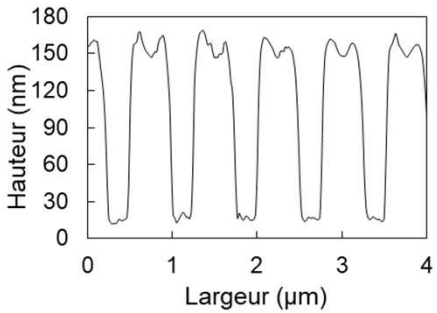


Last test nanoimprinted chitosan : AFM observations

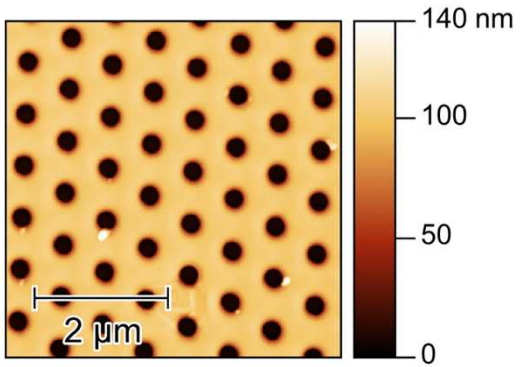
At border of sample

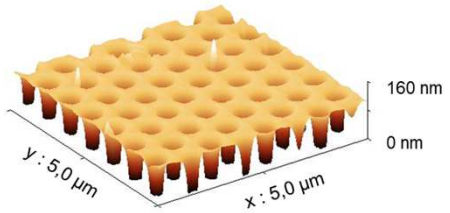


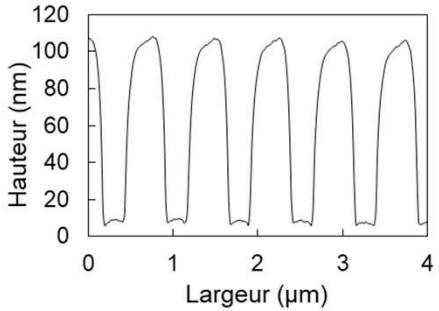




In the centre of sample







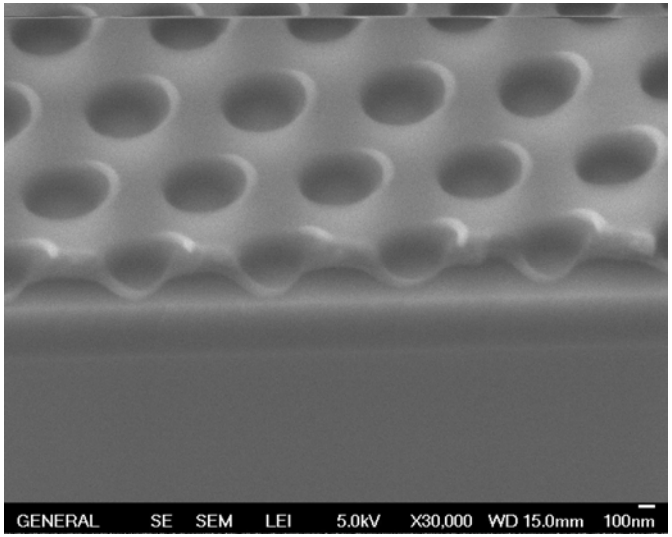
- Very nice and uniform imprinted surface
- Small ‘rabbit-ear’ at border ➔ thicker part ?
- Not perflecty flat surface in centre ➔ filling not achieved ?
- Still remaining resin at the bottom of the holes

cooling conditions well change the release

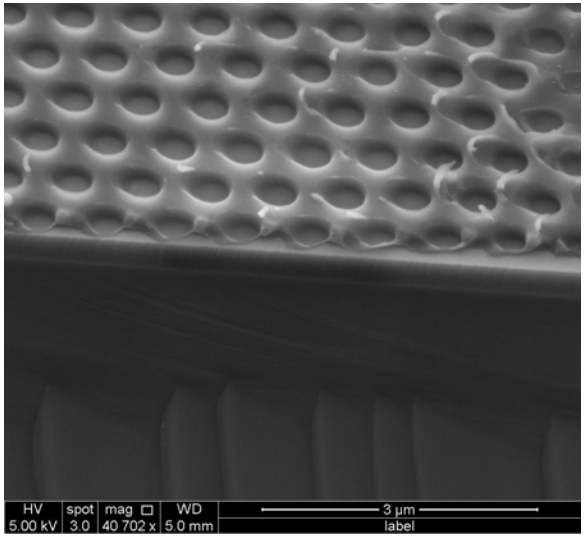
Chitosan-SiO2 hardmask transfer : descum step

RIE parameters : O_2=40sccm; P_T=50mT; RF=40W

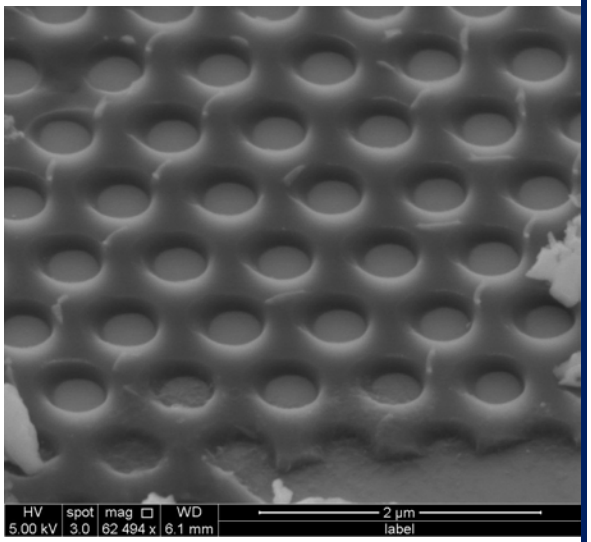
Before descum



After 3 seconds



After 3s +3s

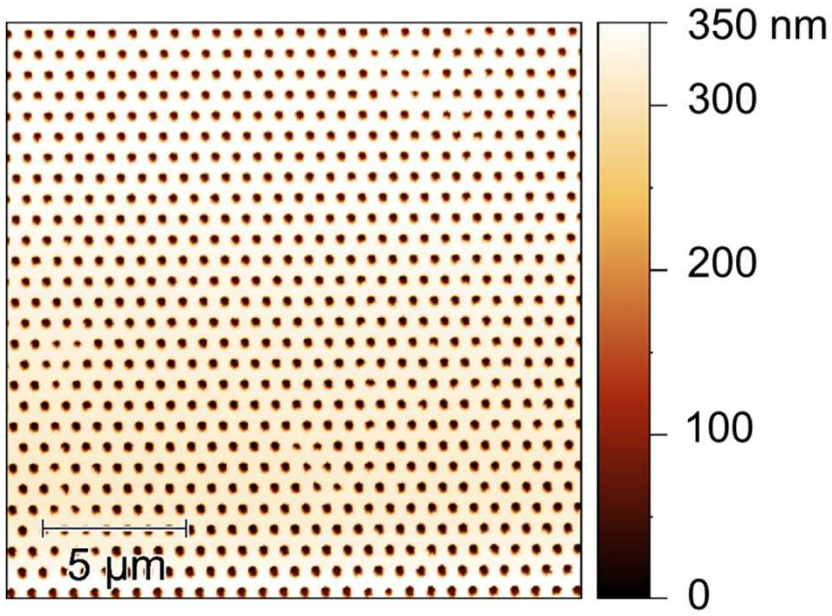


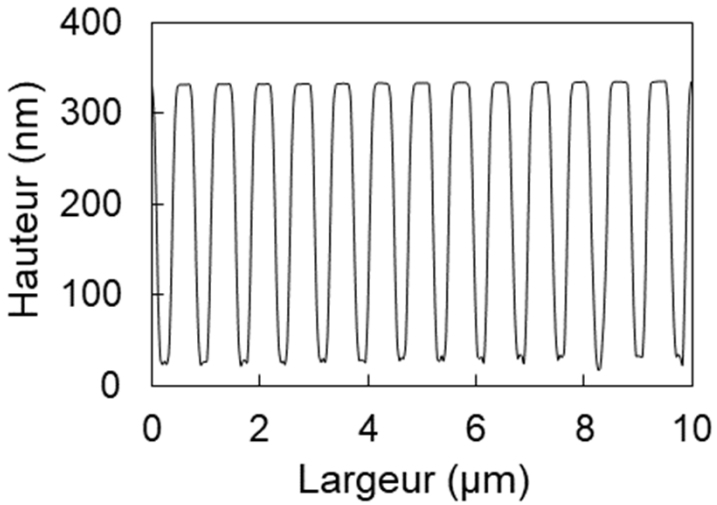
Only 6 sec are needed for a perfect descum !

Chitosan-SiO2 hardmask transfer after descum

RIE parameters : CHF_3=100sccm; P_T=50mT; RF=140W; t=8min

Stripping O_2=100sccm; P_T=100mT; RF=100W; t=2min

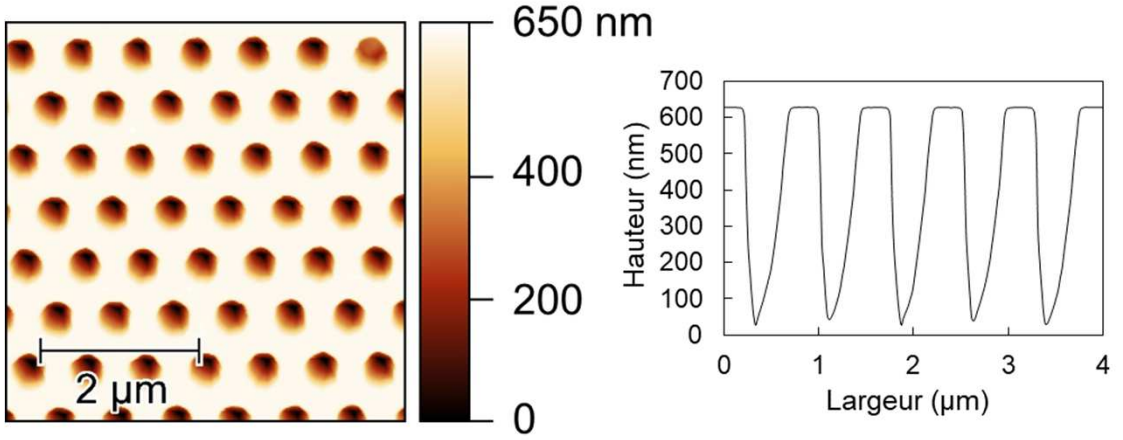




- Very nice and uniform surface
- Trenches : depth of 303 ± 1 nm – angle wall ≥ 70° (AFM tip limit)

SiO2 hardmask transfer in bulk Si

ICP-RIE parameters : O_2=4,5sccm; Cl_2=22sccm; P_T=0,3mT; P_{ICP}=100W; P_{RF}=143W; t=9min45s (RF bias = -340V)

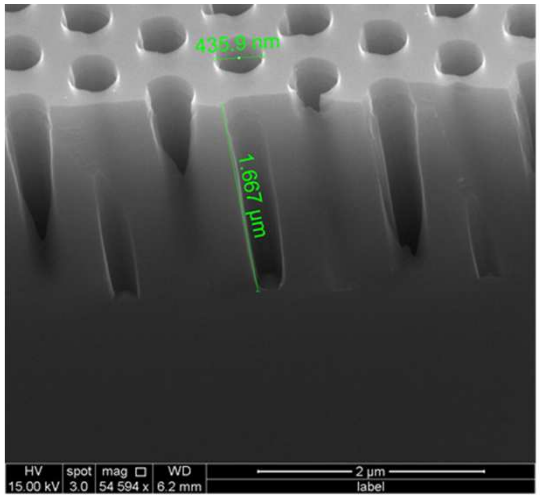


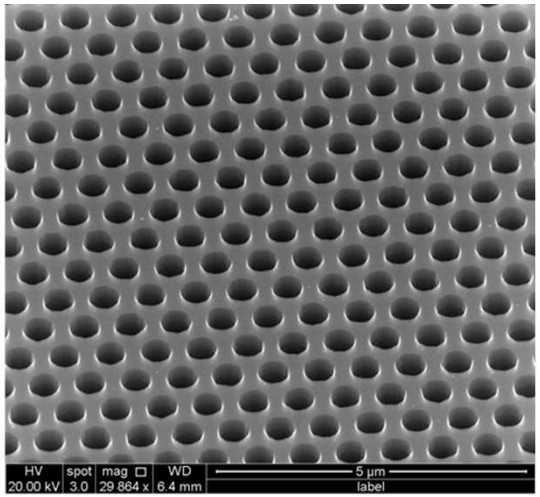
AFM : Very nice and uniform surface

- Trenches : depth of 600 minimum due to AFM tip limitations

SEM : Good vertical > 1,6µm deep holes

→ Respect of nanoimprinted features !





Concluding remarks

- Ability to use **biosourced resin** films without chemical additives in thermal nano-replication techniques under relatively mild conditions.
- Chitosan excellent properties under engraving plasmas (Descum + SiO2 transfer + Stripping) allow their exploitation in micro-nanofabrication

- Better imprinted chitosan when lowering cooling conditions and removal of mold

- To be tested ?
  - Lower Temperature
  - Pressure application at room temperature before heating
  - …

Acknowledgements

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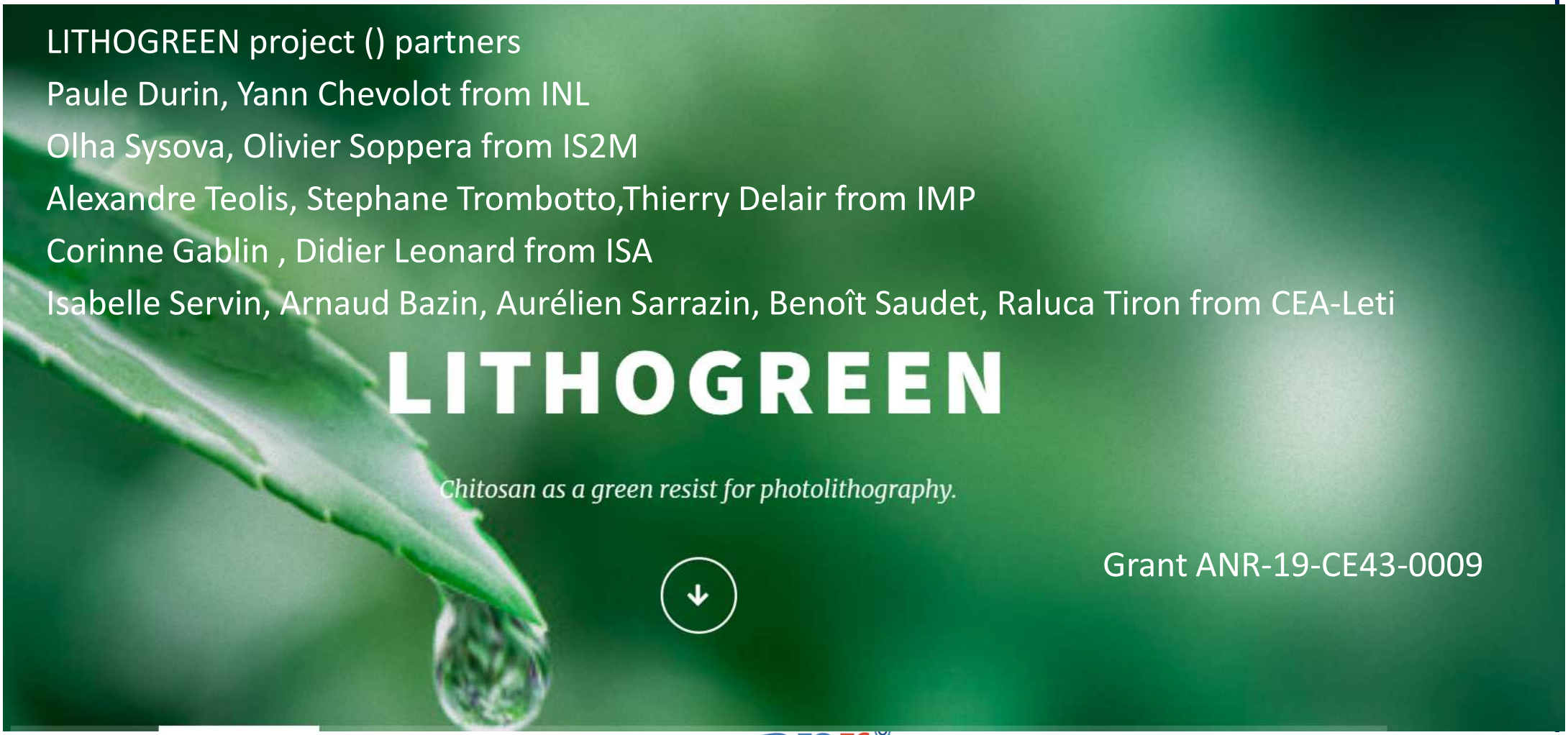

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