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CIN2
CENTRE D'INVESTIGACIÓ EN
NANOCIÈNCIA I NANOTECNOLOGIA

CSIC

Combinational Nanofabrication:
nanopatterning and self-assembly

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ICREA &
Catalan Institute of Nanotechnology
(ICN-CIN2)

40th Anniversary of LAAS-CNRS, Toulouse 7-9 October 2008

Collaborators

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S Arpiannen, J Ahopelto, *Micro-and Nanotelectronics, VTT, Finland*

A Genua,J A Alduncin, J A Pomposo, D Mecerreyes Centre for Electrochemical Technologies CIDETEC, Spain

R Farrel Centre for Research on Adaptive Nanostructures & Nanodevices (CRANN) and University College Cork, Ireland

Support

NaPa
Emerging Nanopatterning Methods

www.NaPaIP.org

The PHAT project

NaPANIL

SEVENTH FRAMEWORK
PROGRAMME

www.NAPANIL.org

sfi
science foundation ireland
fondúireacht eolaíochta éireann

PhOREMOST

Motivation

- Cost-efficient enabling nanofabrication technologies

  to unfold promise of nanotechnology

- Novel functionality suitable for heterogeneous integration

  to advance nanoelectronics

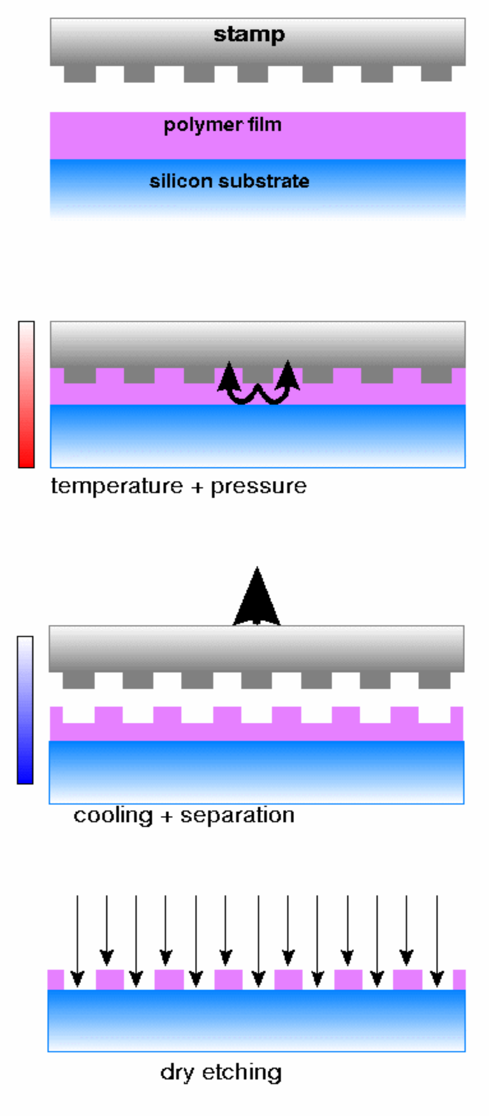
- Nanometrology

  to enable uptake by industry

Outline

- Nanoimprint lithography
    - Metrology
- Self assembly
    - Colloidal particles
    - Metrology
- Nanoimprint lithography and self-assembly
    - Selective growth of polymer brushes
    - Graphoepitaxy
- Self-assembly on SOI substrates
- Conclusions

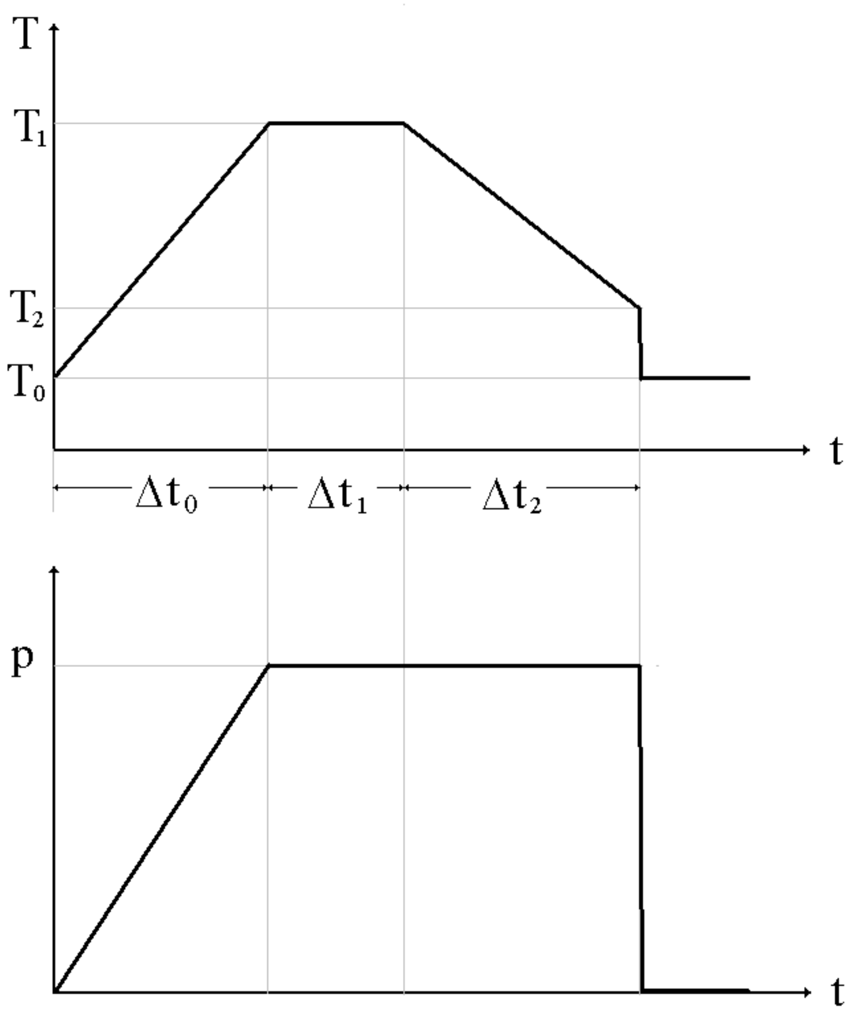
(Thermal) Nanoimprint lithography



PROCESS:

1. Heat to $T>T_g$
2. Bring stamp & sample into contact
3. Apply pressure
4. Cool down
5. Separation at $T<T_g$
6. RIE to remove residual layer
7. Lift off or pattern transfer by RIE or use printed functional polymer film.

Imprint Process Cycle

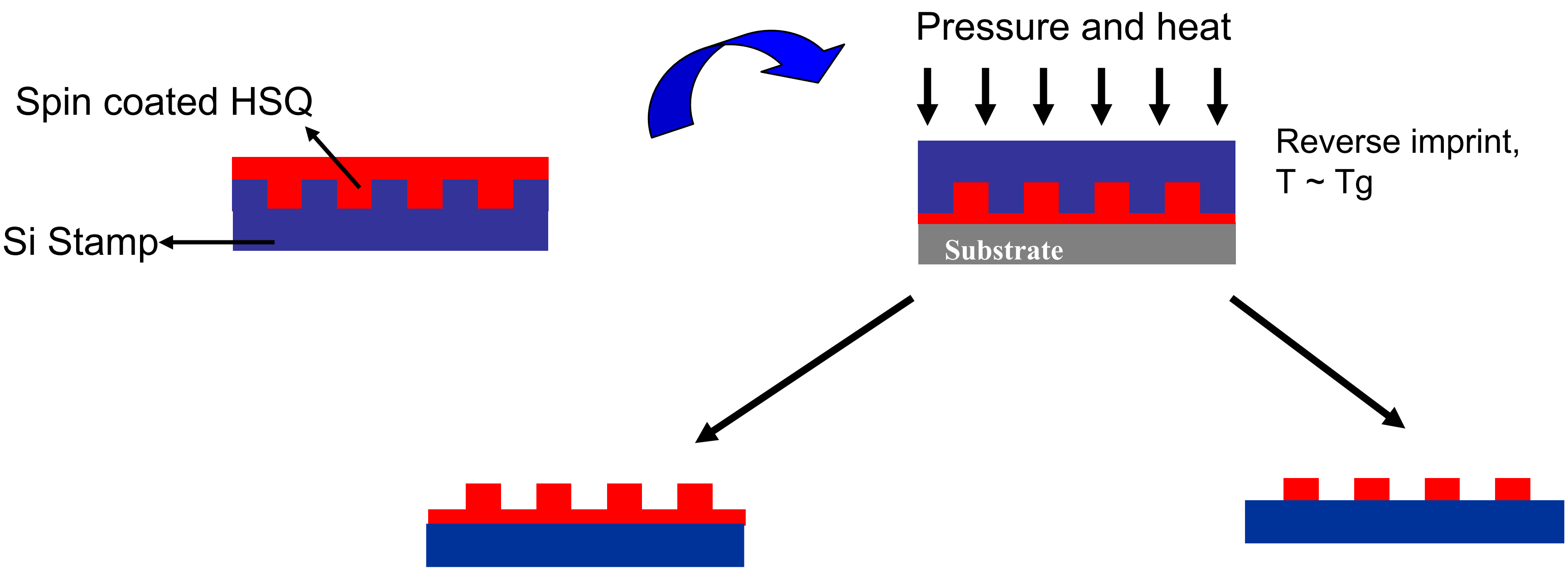


Typical parameters used in NIL

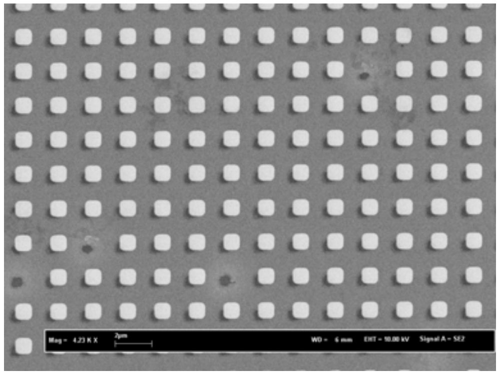
T_1 (°C) = 185
T_2 (°C) = 95
P (bar) = 30
Δt_1 (s) = 60
Δt_2(s) = 160

Temperature & pressure cycles

Reverse Nanoimprint Lithography



Whole layer transfer mode

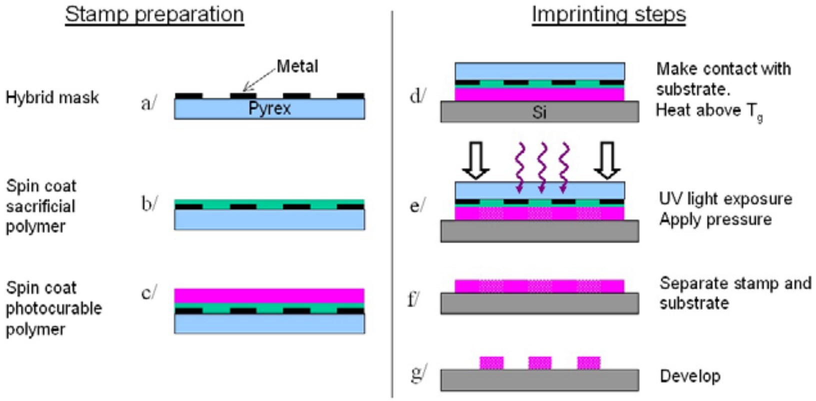


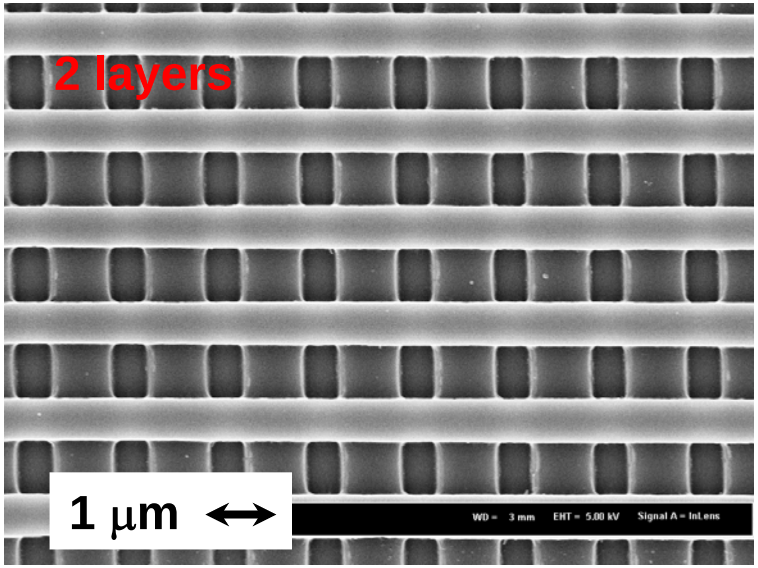
Inking mode

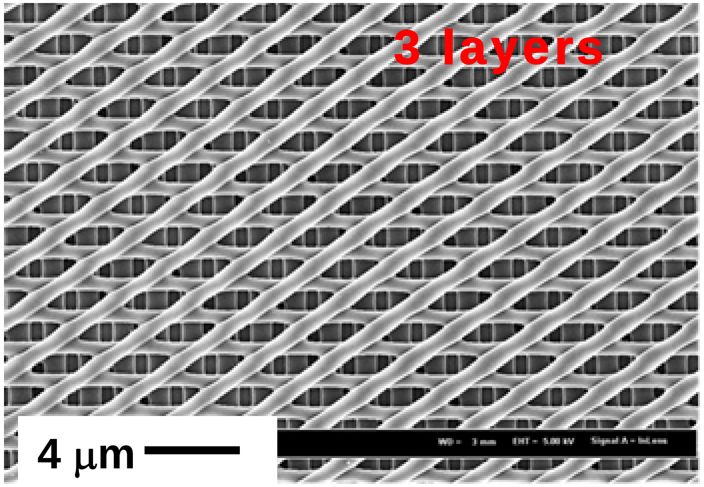
N Kehagias et al J Vac Sci Technol B **24**, 3002 (2006)

Reverse UV NIL technique

- No residual layer
- No need for anti-adhesive treatment of the stamp
- The same photocurable polymer is used
- High resolution (stamp dependent)
- High throughput (<2 min)





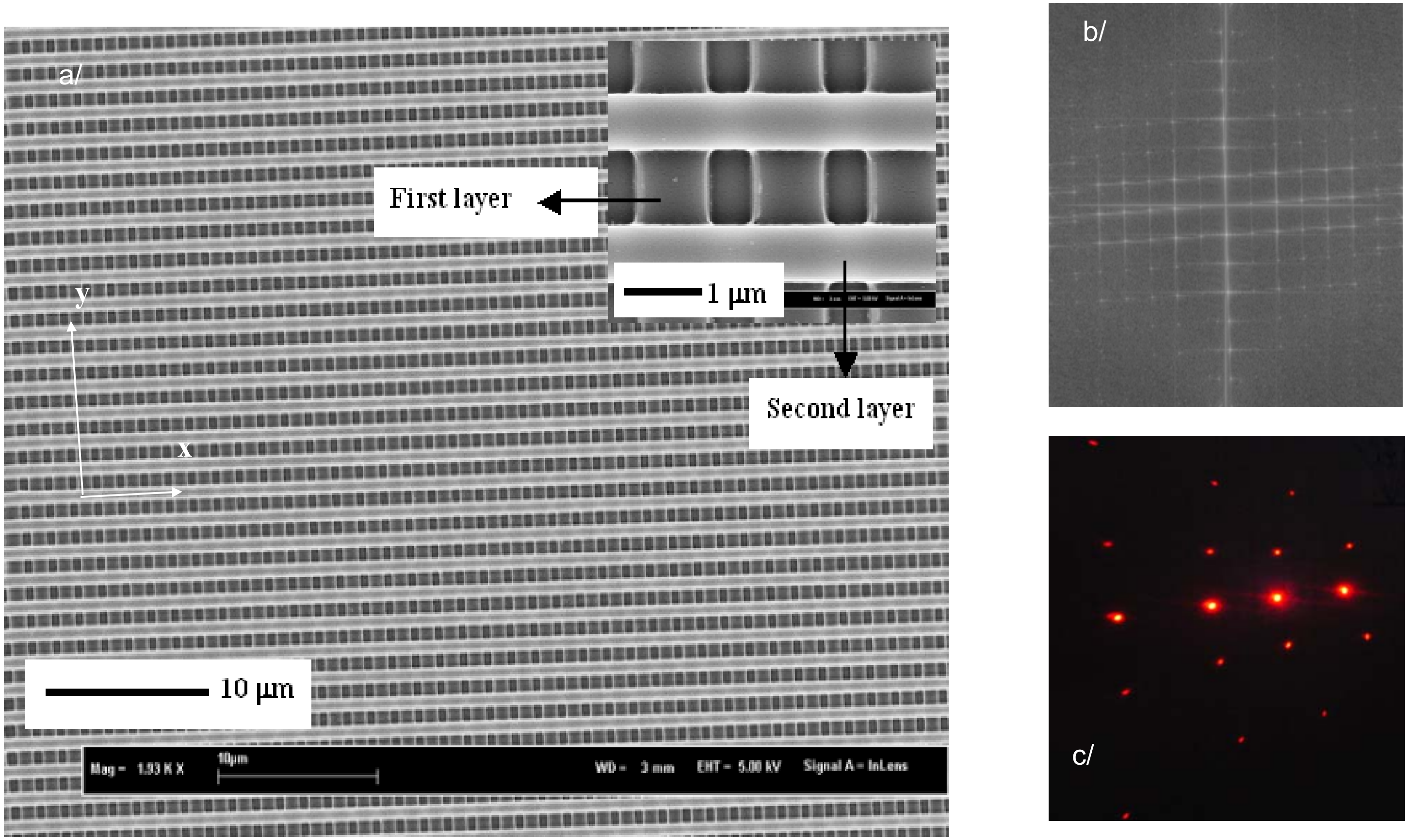


N. Kehagias *et. al*, *J. Vac. Sci. Technol. B* ***24****, 3002, (2006)*

N. Kehagias *et. al*, Nanotechnology, 18, 175303, (2007)

Patterned area 5 x 5 mm2

Polymer double layer grating by RUV NIL

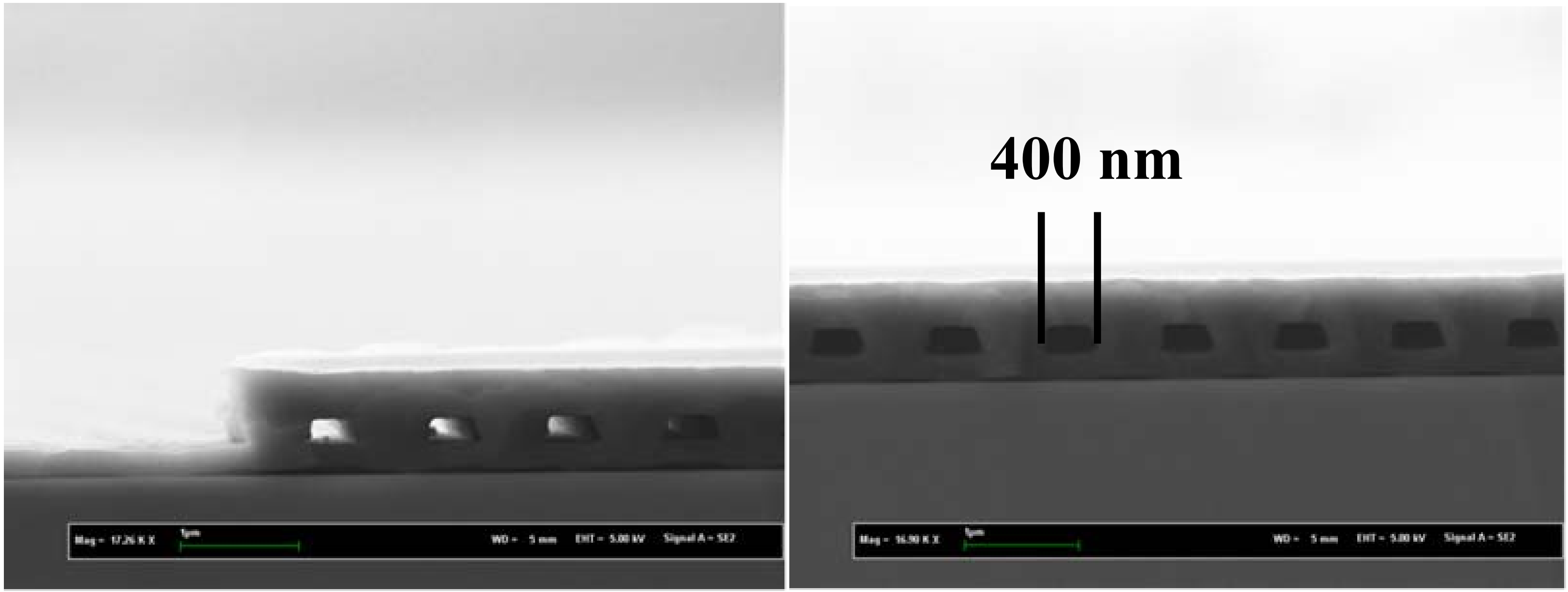


a/ SEM image of a large (>50µm) double layer grating. b/ Fourier transform of a/ showing good homogeneity of lines over the whole surface with limited dispersion in size and position c/ Far -field optical image of diffracted light by the 3D grating.

N Kehagias_*et al., J. Vac. Sci. Technol. B* ***24****, 3002, 2006*

NIL Development: 3D nanofabrication

Embedded nanochannels



Suitable for microfluidic applications

N Kehagias et al, 2007

Metrology techniques for nanoscale

- **SEM** → Resolution < 1 nm

  → For height, slope, profile, requires destructive cross-section. Requires conducting surface

- **AFM** → Resolution < 1 nm

  → Difficult to access between structures, sidewalls, corners – use of flared probe. Relatively slow.

- **Scatterometry** → Resolution < 50 nm +/- 2 nm

  → Lateral dimension, height and slope

  → Requirement of wavelength, polarization or angle variability.

- **Optical sub-wavelength diffraction** → Resolution 50 nm +/- 5 nm.

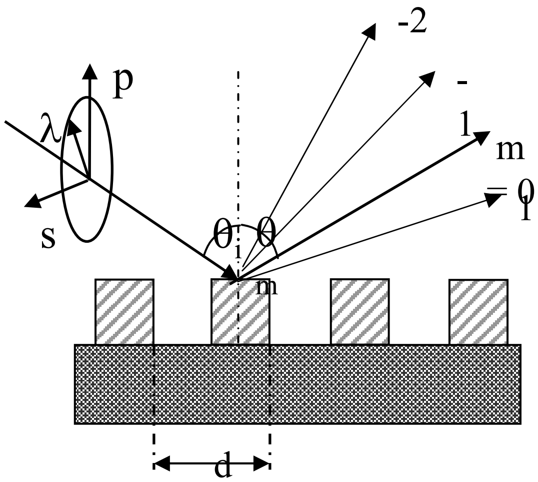
  → Lateral dimension and height

  → Monochromatic diffraction intensity

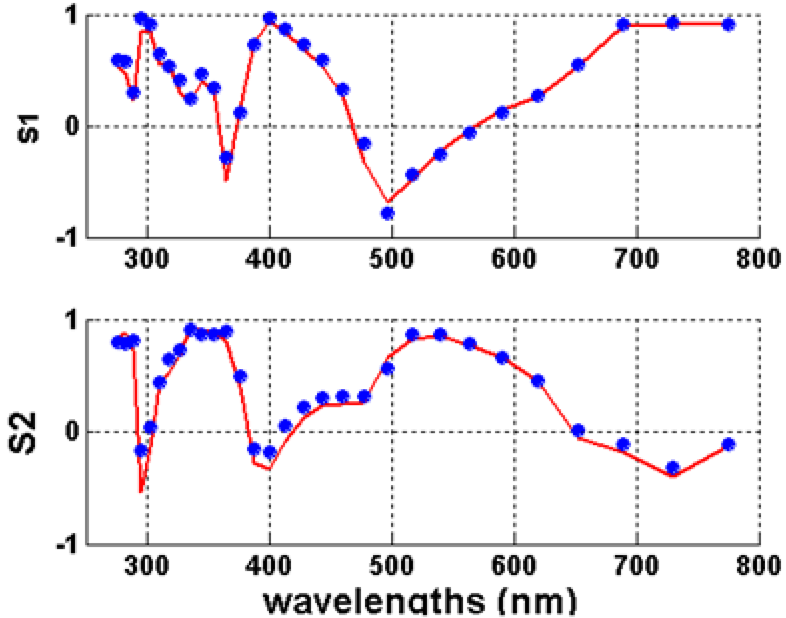
- **Photoacoustic metrology** → Resolution of acoustic λ ~10nm, in depth.

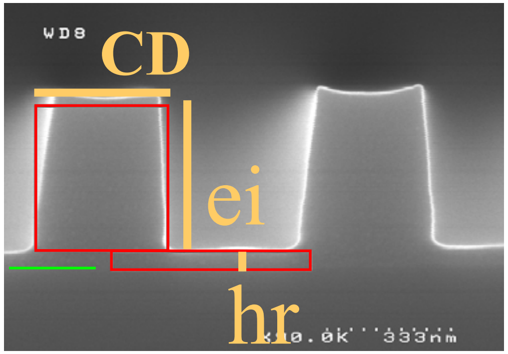
  → Lateral resolution currently 1μm.

Scatterometry: Direct measurement of CD, ei and hr



Spectroscopic ellipsometry + electromagnetic simulation using a description of the features with variable parameters CD, ei, and hr



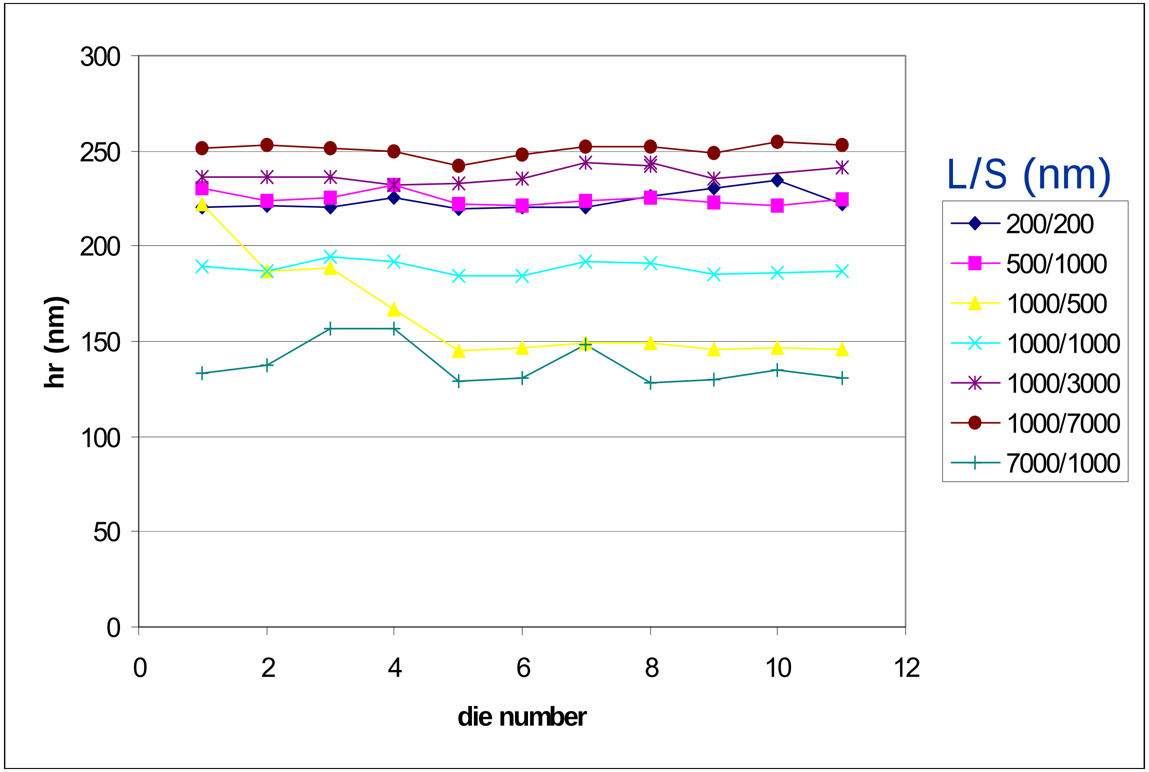


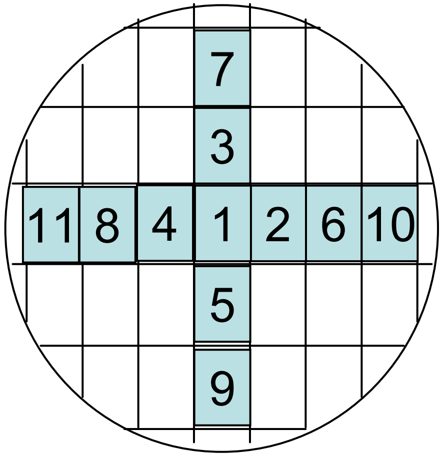
- ✓ Fast and non destructive
- ✓ Automatic characterization at the wafer scale
- ✓ Periodic features with CD< few microns
- ✓ Grating surface larger than the ellipsometer spot size
- ✓ Complex 3D structures: limited by calculation time
- ✓ Optical indices needed as a function of λ with high accuracy

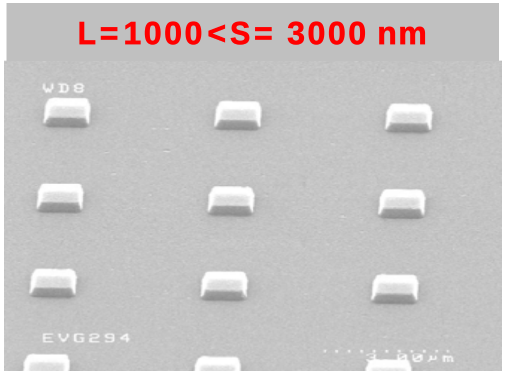
Patterns = gratings of lines (2D) or dots (3D)

Courtesy of Dr C Gourgon (CNRS-LTM) and Dr S Landis (LETI)

Scatterometry results in 3D square dots at wafer scale



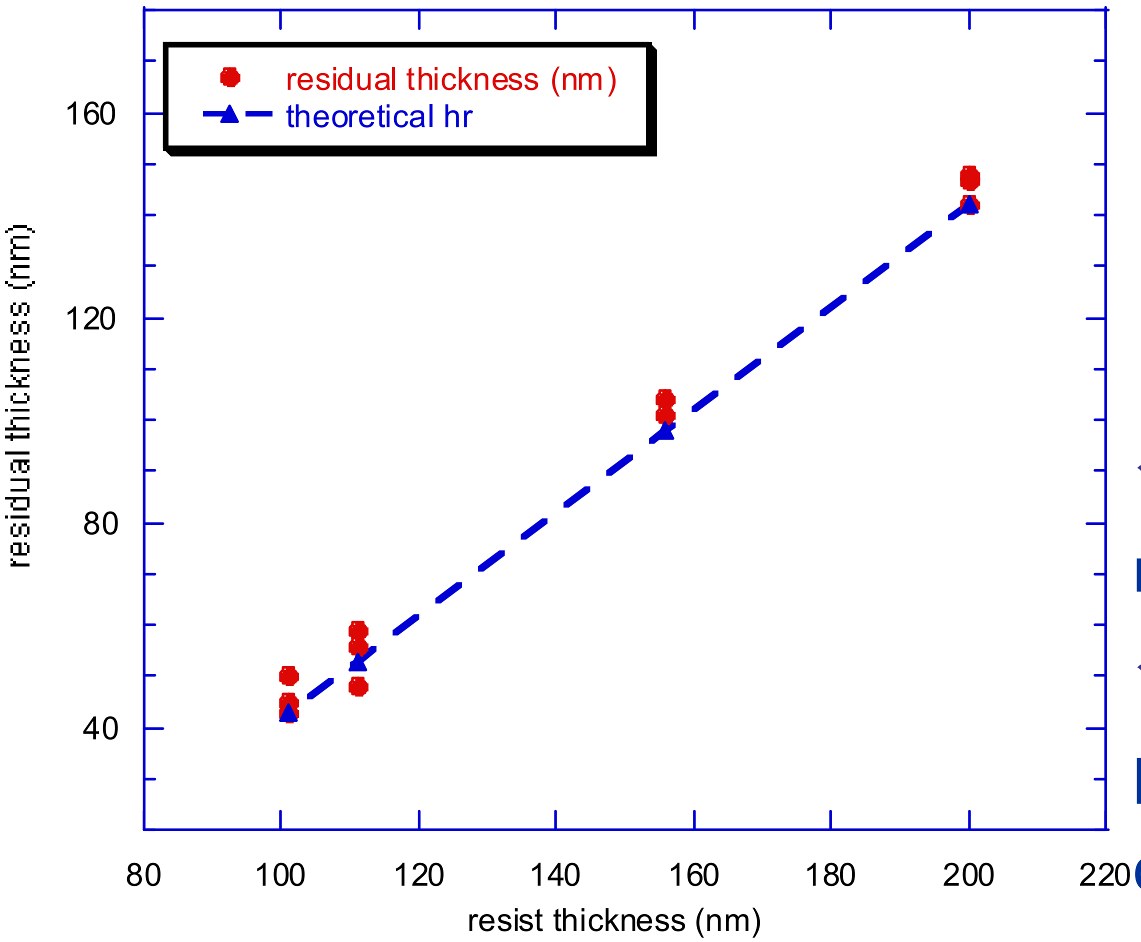



L=1000<S= 3000 nm

- Demonstration of the imprint uniformity at the wafer scale From die 1 to 11
- As expected the residual thickness depends on the filling ratio
- Higher uniformity for L<S due to complete filling
- Poor uniformity for L>S because initial thickness is not high enough to induce a complete filling

Courtesy of Dr C Gourgon (CNRS-LTM) and Dr S Landis (LETI)

Results of scatterometry on 50 nm lines



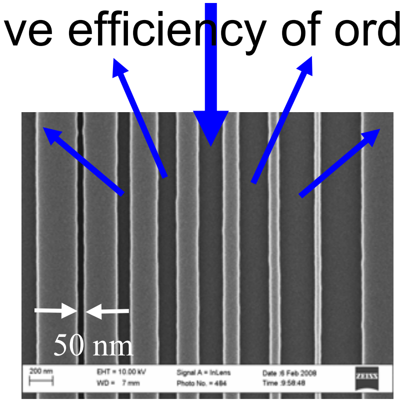
Hr depends just on the initial polymer thickness

- ✓ Demonstration of high reproducibility
- ✓ Demonstration of the potential high throughput: cycle times 2 min

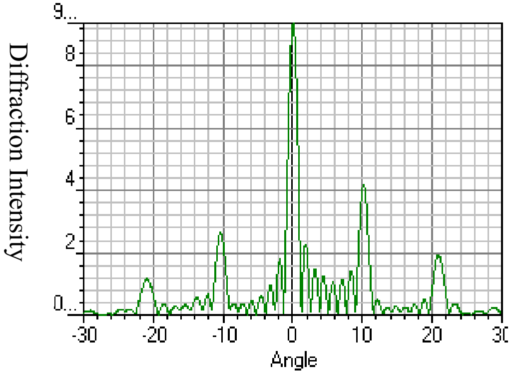
Courtesy of Dr C Gourgon (CNRS-LTM) and Dr S Landis (LETI)

Subwavelength diffraction

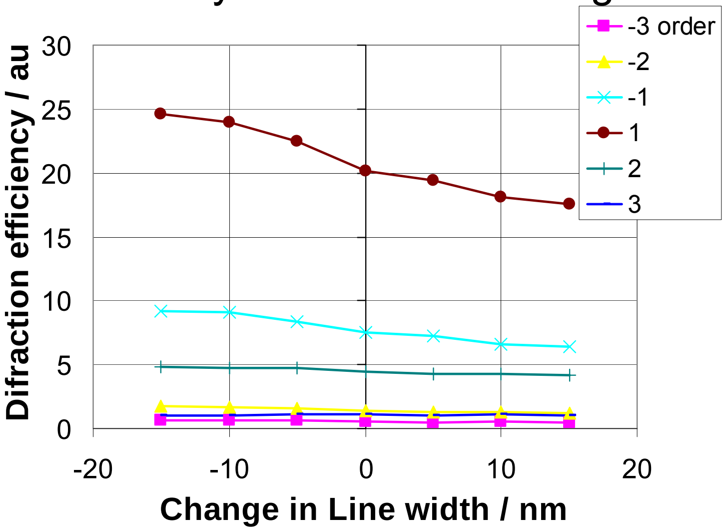
- Sub-wavelength features within periodic test structure : Line-width, height, defects affect the relative efficiency of orders in far-field diffraction.



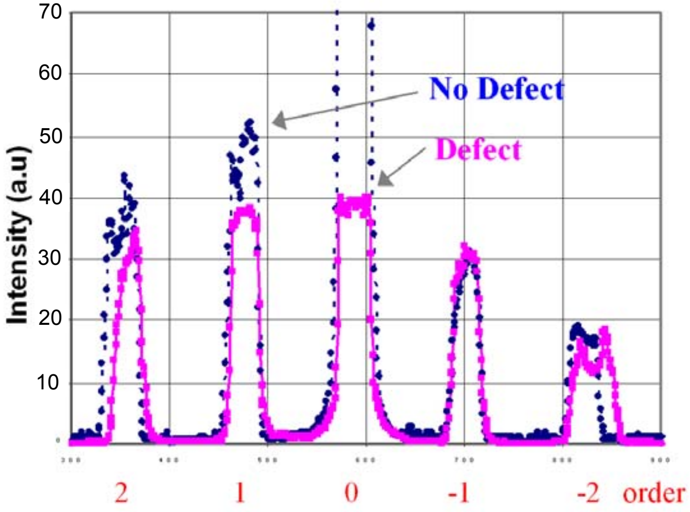
One period 2.8 µm



- Models (FDTD and Rigorous Coupled Wave Analysis) show sensitivity to dimension changes of <10nm



- Used to show presence of defect – missing 50nm lines



T. Kehoe et al, Sub-wavelength optical diffraction and photoacoustic metrologies for the characterisation of nanoimprinted structures, Proc. SPIE 6922 (2008) 69210F

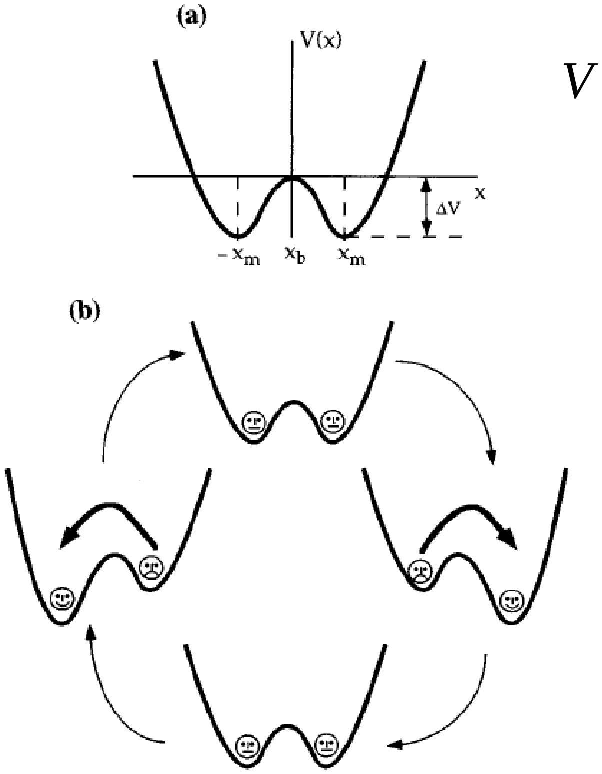
Figures of merit in self-assembly

Particle size	1-400 nm	methods
Size dispersion	2 %	methods
Ordering in 2D	?	SEM. FT
Ordering in 3D	?	Transmission?
Functionality	Early days	A multitude

Stochastic-resonance

Noise and nonlinearity concur to determine an increase of order in the system response

Symmetric double well potential



$$V(x) = (1/4)bx^4 - (1/2)ax^2$$

$$\Delta V = a^2/(4b)$$

$$V(x,t) = V(x) - A_0 x\cos(\omega t)$$

Transition rate between neighbouring potential wells

$$r_K = \frac{\omega_0\omega_b}{2\pi\gamma}\exp(-\frac{\Delta V}{D})$$

Kramer’s rate

$$2T_K(D) = T_\Omega$$

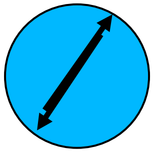
Noise strength D related to temperature T, Tomega= half period of driving force

L. Gammaitoni, Rev. Mod. Phys. 70, 223 (1998)

Sample preparation

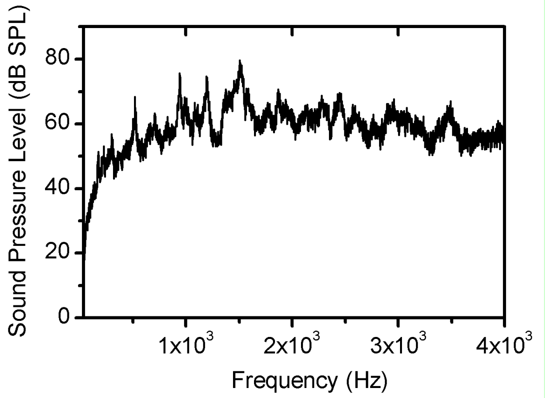
- Polymethyl-metacrylate (PMMA) spheres

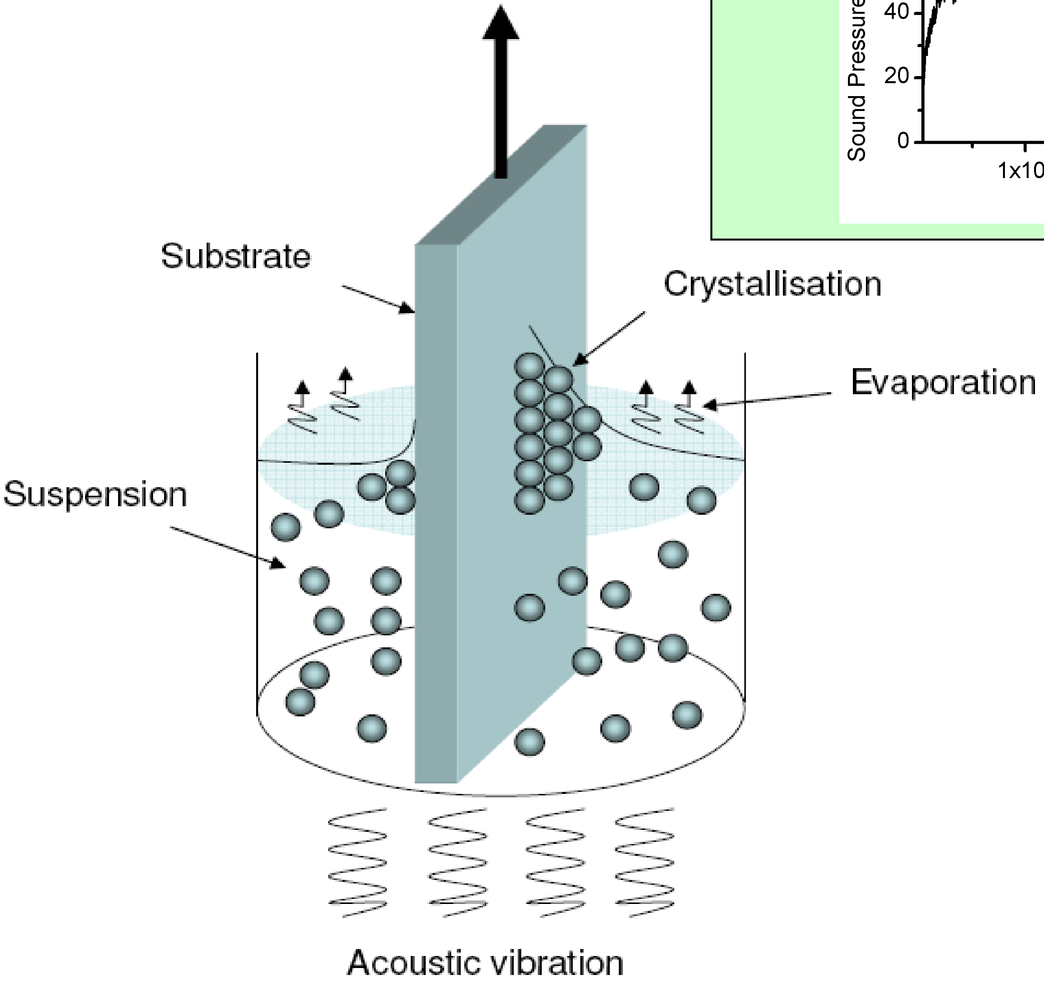
∅ = 368 and 530 nm



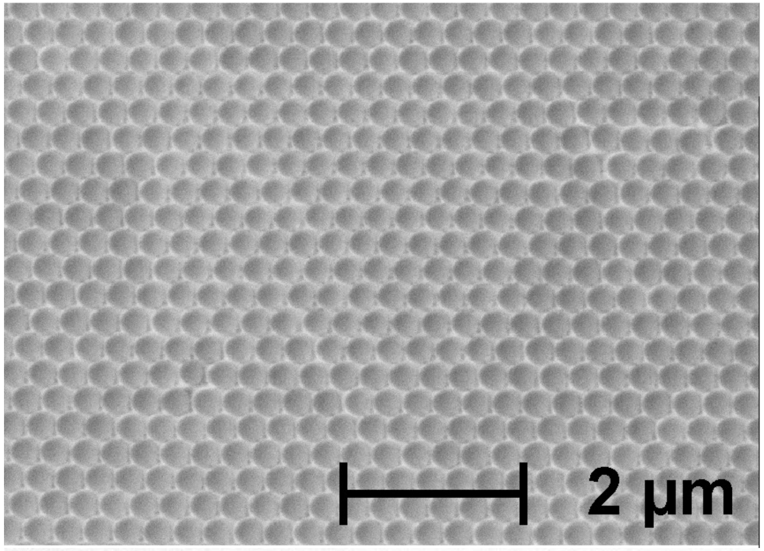
- 4 wt% dispersed in deionized water with 18 MΩ-cm resistivity.

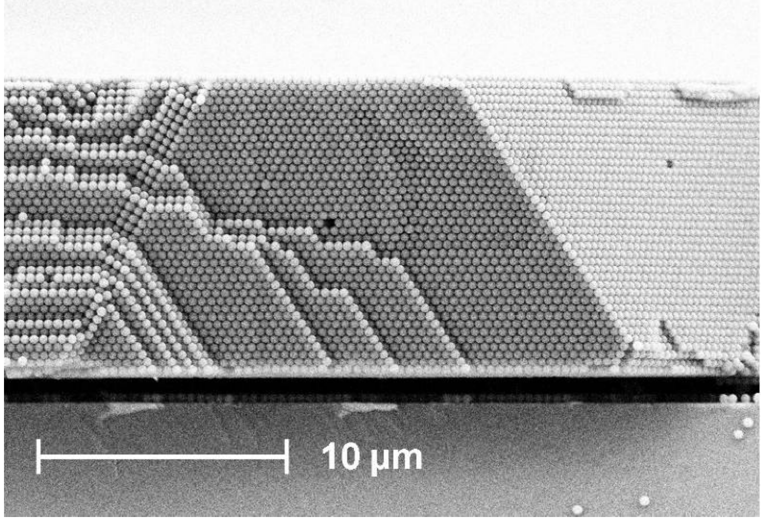
- Broadband random noise: 20 – 4,000 Hz

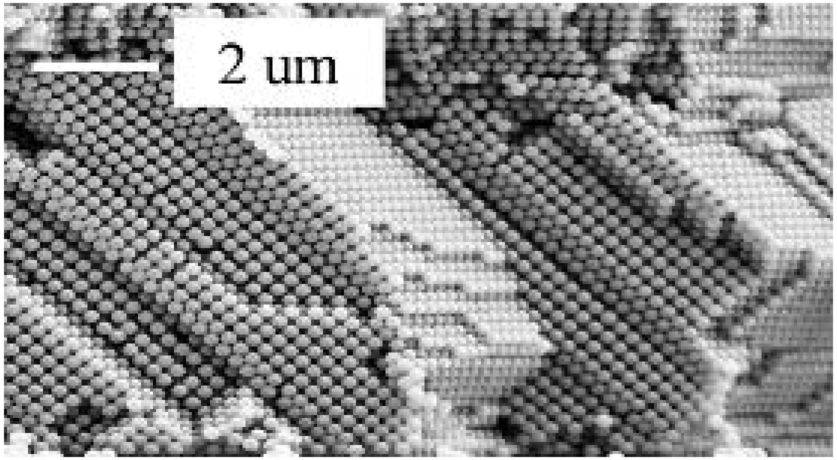




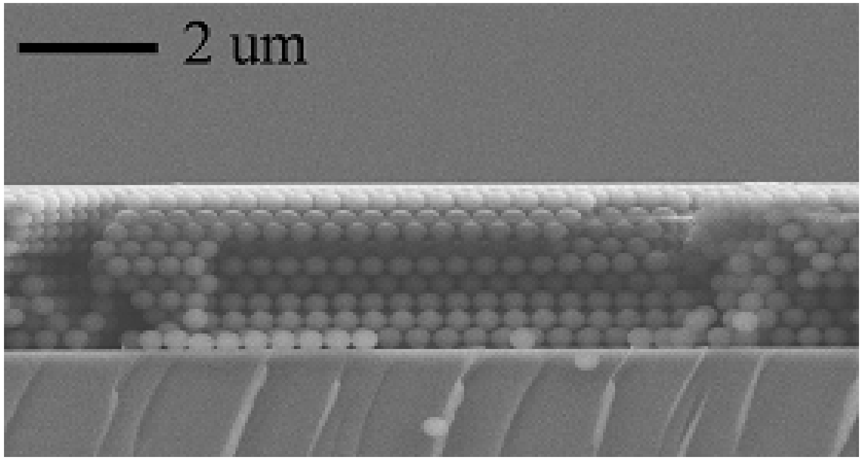
3D colloidal crystals: Quality improvement using acoustic noise



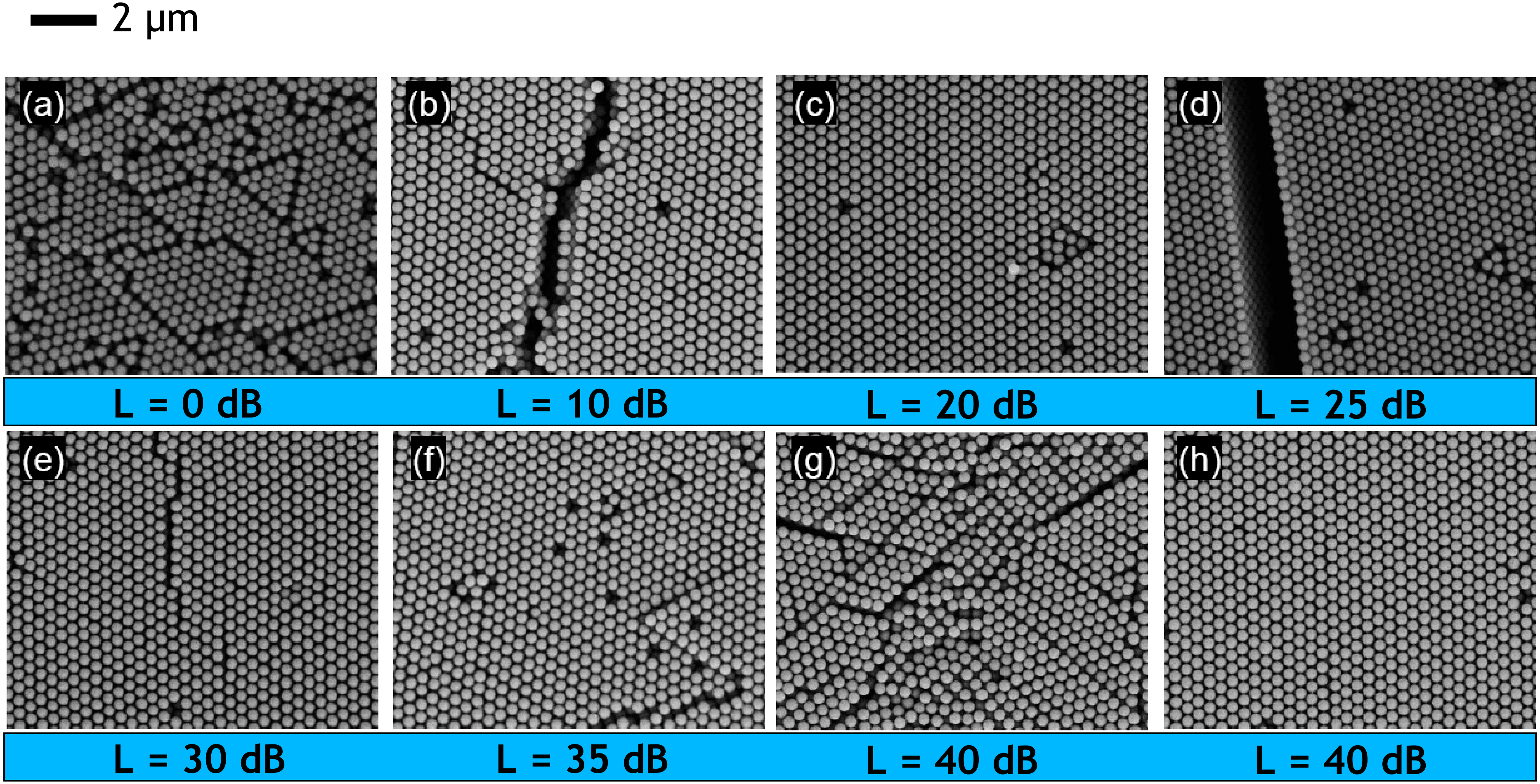




W Khunsin, G Kocher et al, to be published



Stochastic resonance in photonic crystals growth



L = 0 dB

L = 10 dB

L = 20 dB

L = 25 dB

L = 30 dB

L = 35 dB

L = 40 dB

L = 40 dB

-> L = 20 dB is calibrated to water displacement of 2.5 µm

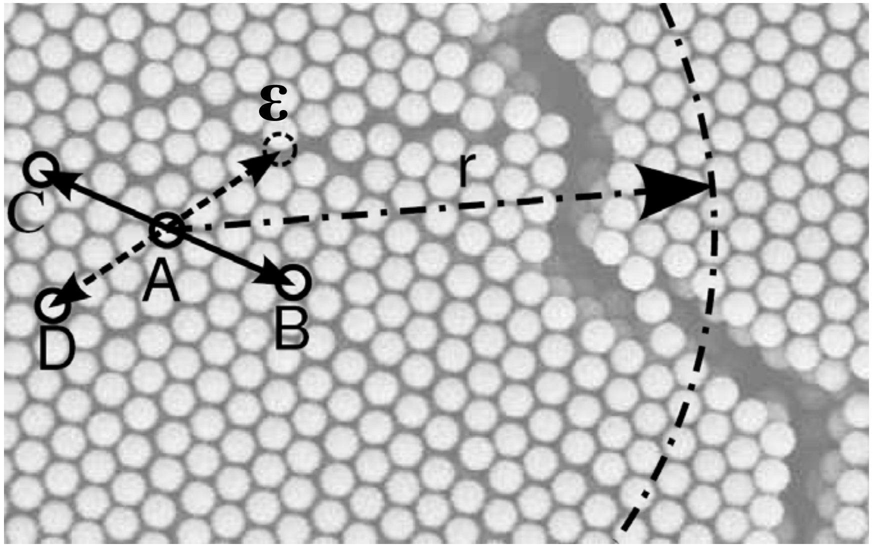
Quantifying order in self-assembly

- Define scale
- Make compatible with existing methods or at least acceptable
- In-line or a posteriori?
- Reliable?
- Suitable for a standard?

Concept of “*opposite beads*”

p(r) – probability of finding an opposite beads within a radius **r**, for a given tolerance parameter **ε** for the exact location of the spheres

At sphere ‘A’



$$p(r)=\frac{\sum_{A\neq B,C}\chi_r(\overrightarrow{AB})\,\chi_\varepsilon(\overrightarrow{AB}+\overrightarrow{AC})}{\sum_{A\neq B}\chi_r(\overrightarrow{AB})}$$

$$\chi_y(\vec{R})=\begin{cases}1 & if\ \ |\vec{R}|<y\\ 0 & else\end{cases}$$

Global sum: weighted average

$$\boxed{p(r)=\frac{\sum_A N_A(r)\,p_A(r)}{\sum_A N_A(r)}}$$

Conditions met by p(r)

- Scalar quantity (dependence on certain predefined orientation undesirable)
- Integral measure of a locally observable quantity
- Based on actual position of sphere (not on pixel representation of SEM image: contrast & focus dependent)
- Robust against missing spheres.

Comparison: ordered & disordered fcc crystal

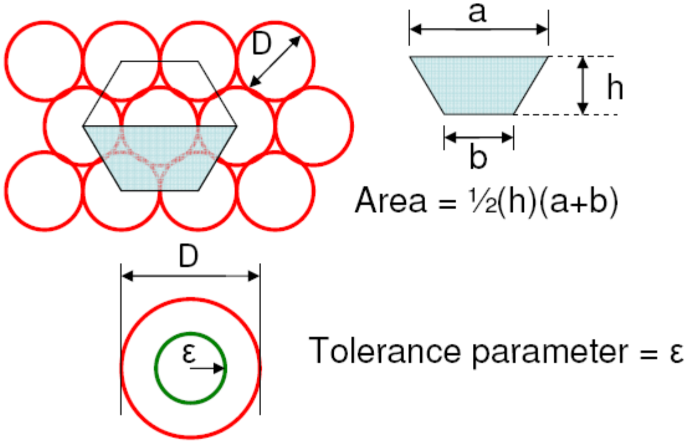
Perfectly ordered system

$$p(r)=\frac{\sum_A N_A(r)p_A(r)}{\sum_A N_A(r)}=1$$

Theory $0.04 \le p(r) \le 1.00$

Experiment $0.06 \le p(r) \le 0.46$

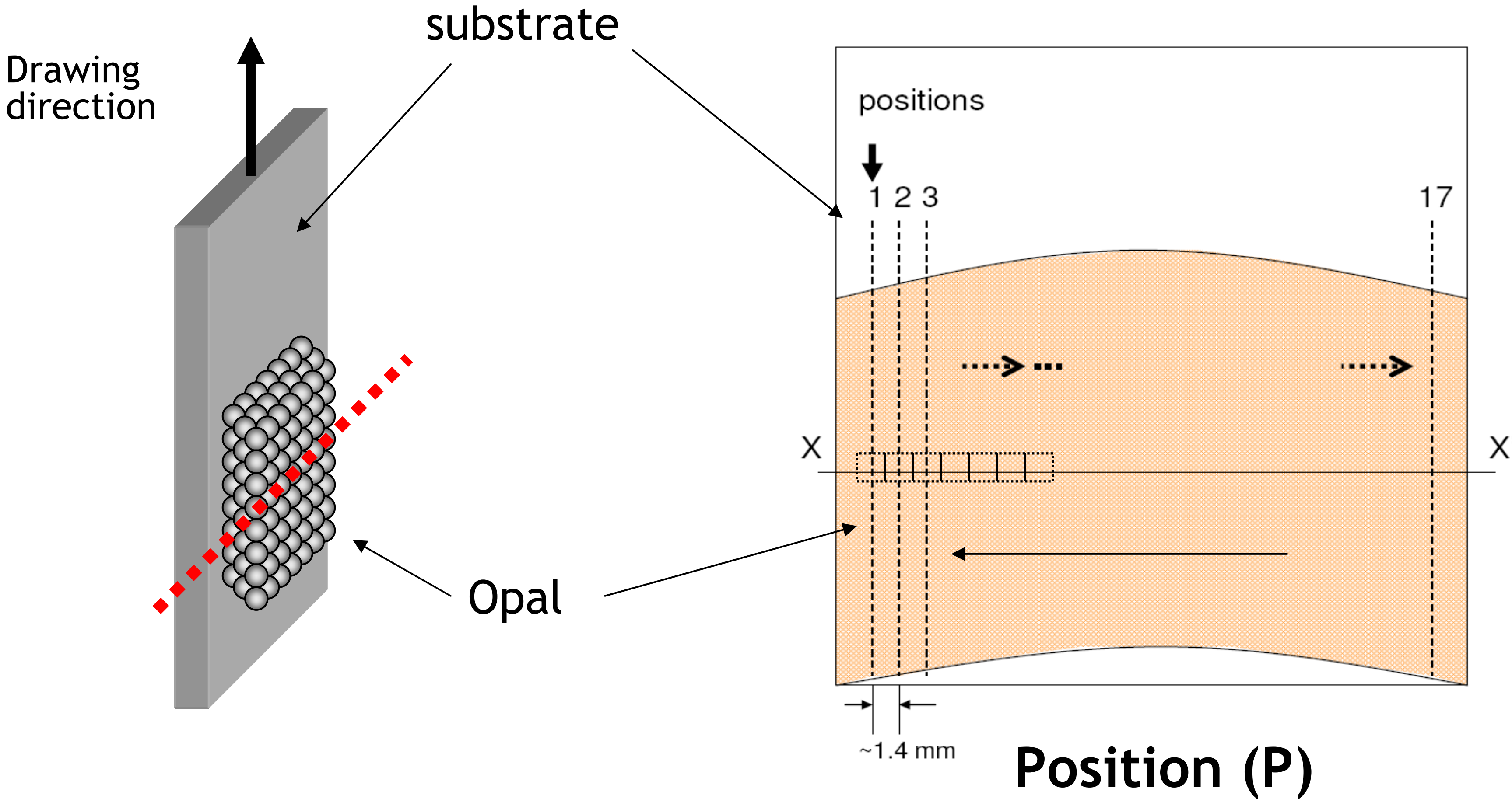
Completely disordered system



$$p(r)=\frac{1}{\frac{\sqrt{3}D^2}{2}}(\pi\varepsilon^2)=\frac{2\pi}{\sqrt{3}}x(\frac{\varepsilon}{D})^2$$

SEM imaging

SEM images of size 65 µm x 40 µm (resolution: 3072 x 2304 pixels)



Drawing direction

substrate

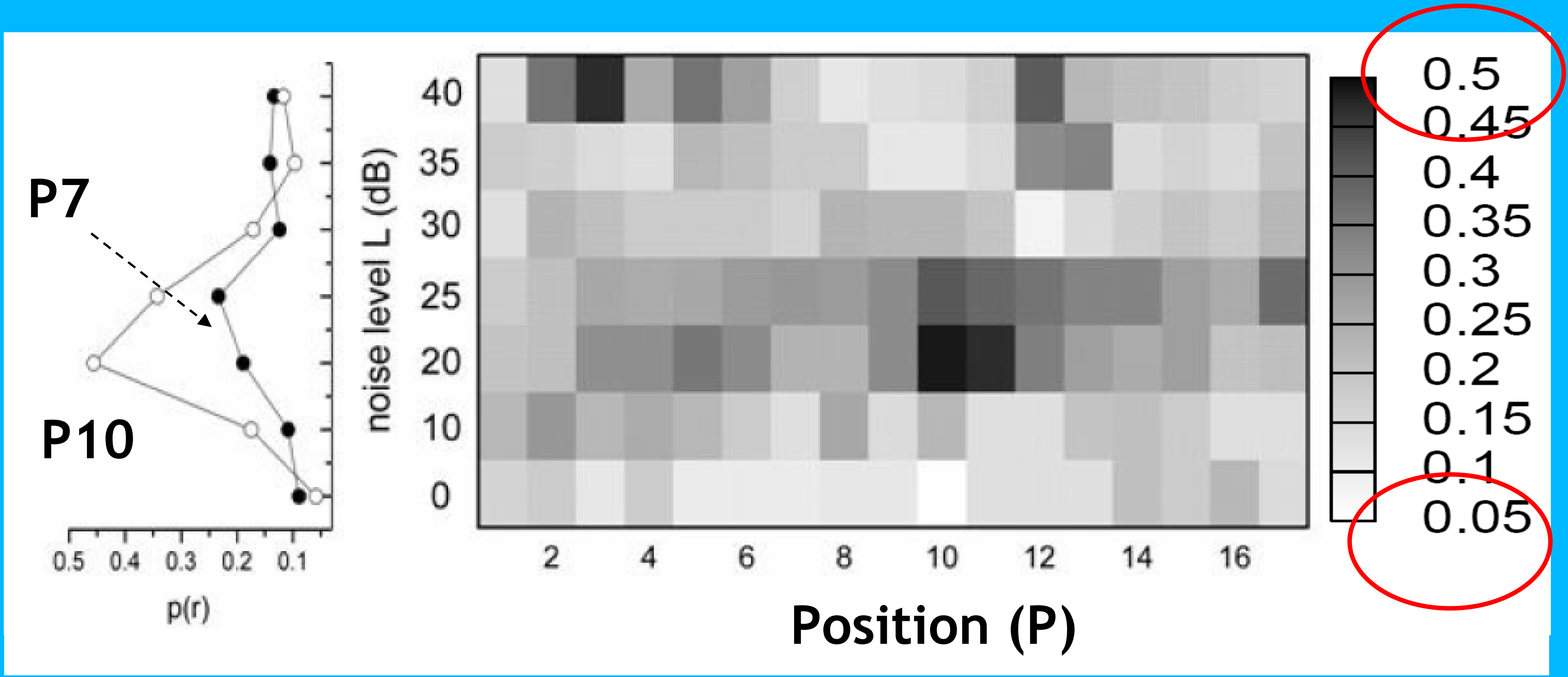
Opal

Position (P)

Stochastic-resonance in photonic crystal growth

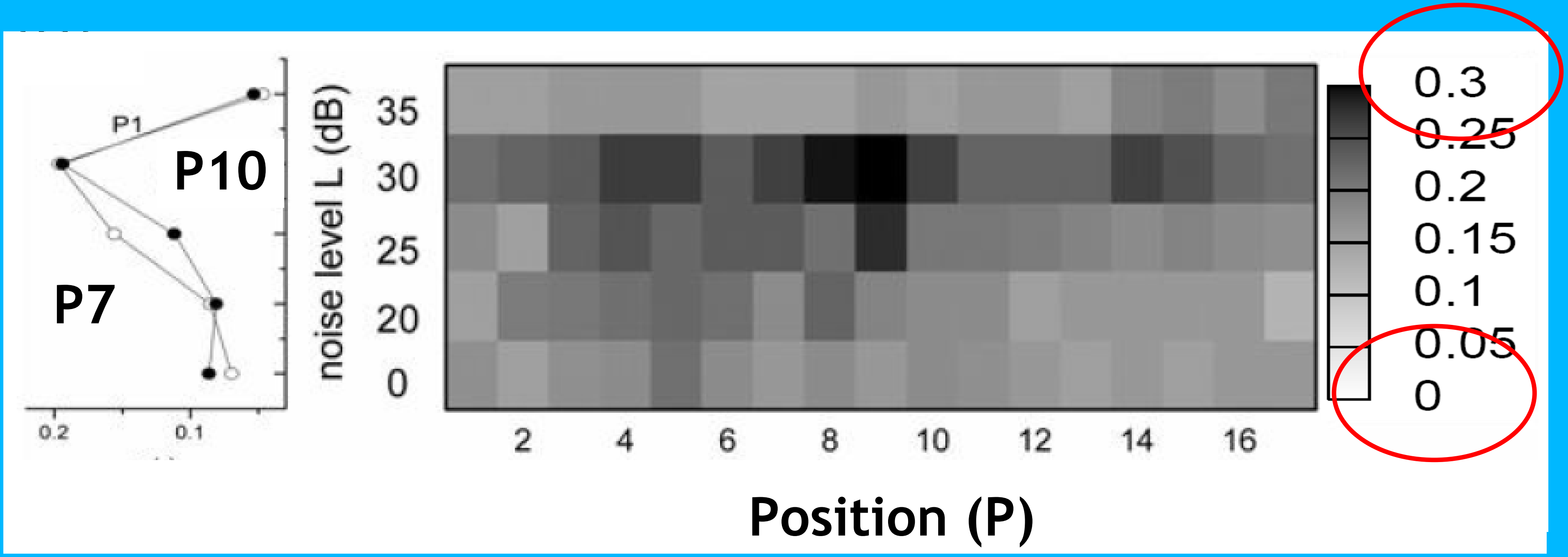
D = 368 nm

r = 5.5 µm ≈ 15D, and ε = 43 nm ≈ 0.12D



Stochastic-resonance in photonic crystal growth

D = 530 nm



So far …

1. We demonstrated a constructive role of noise in the crystallisation of self-assembled colloidal crystal

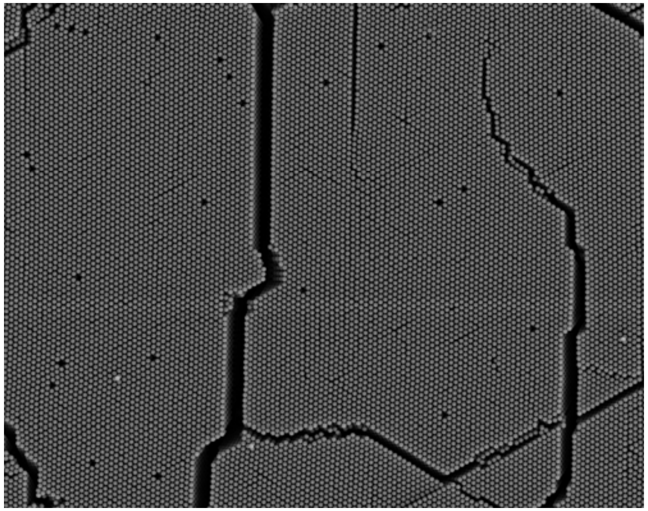
2. The optimum noise intensity corresponds to meniscus displacement of several lattice periods.

3. We propose a robust and generic approach to quantitatively analyse two-dimensional lattice ordering

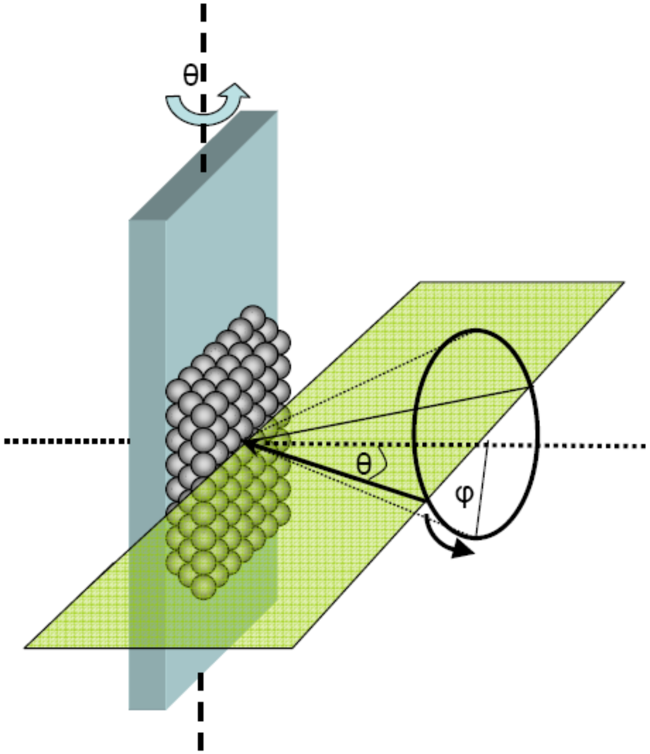
3 D ordering - Experimental approach

2D analysis

3D analysis

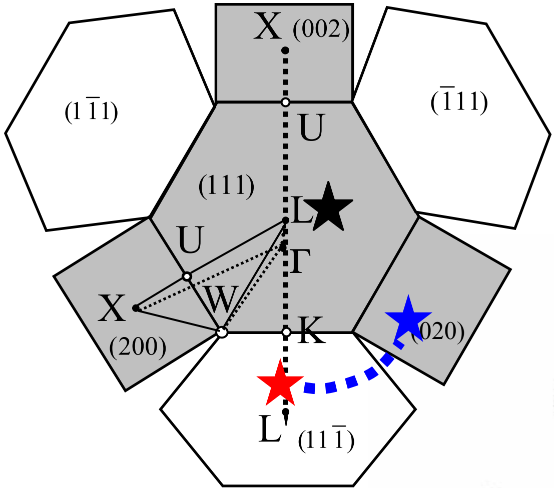


SEM images



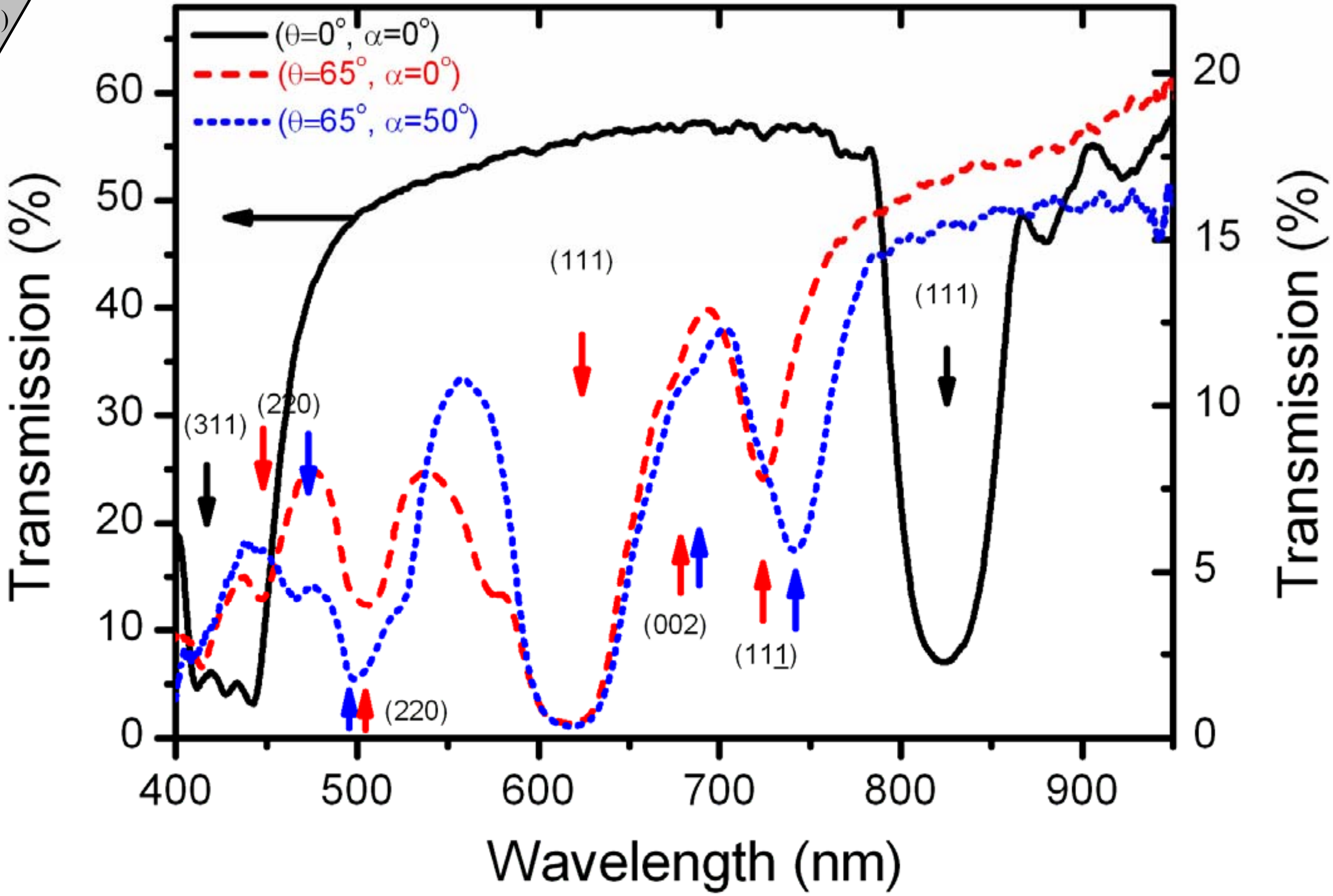
θ – incident angle
φ – azimuth angle

Transmission spectra

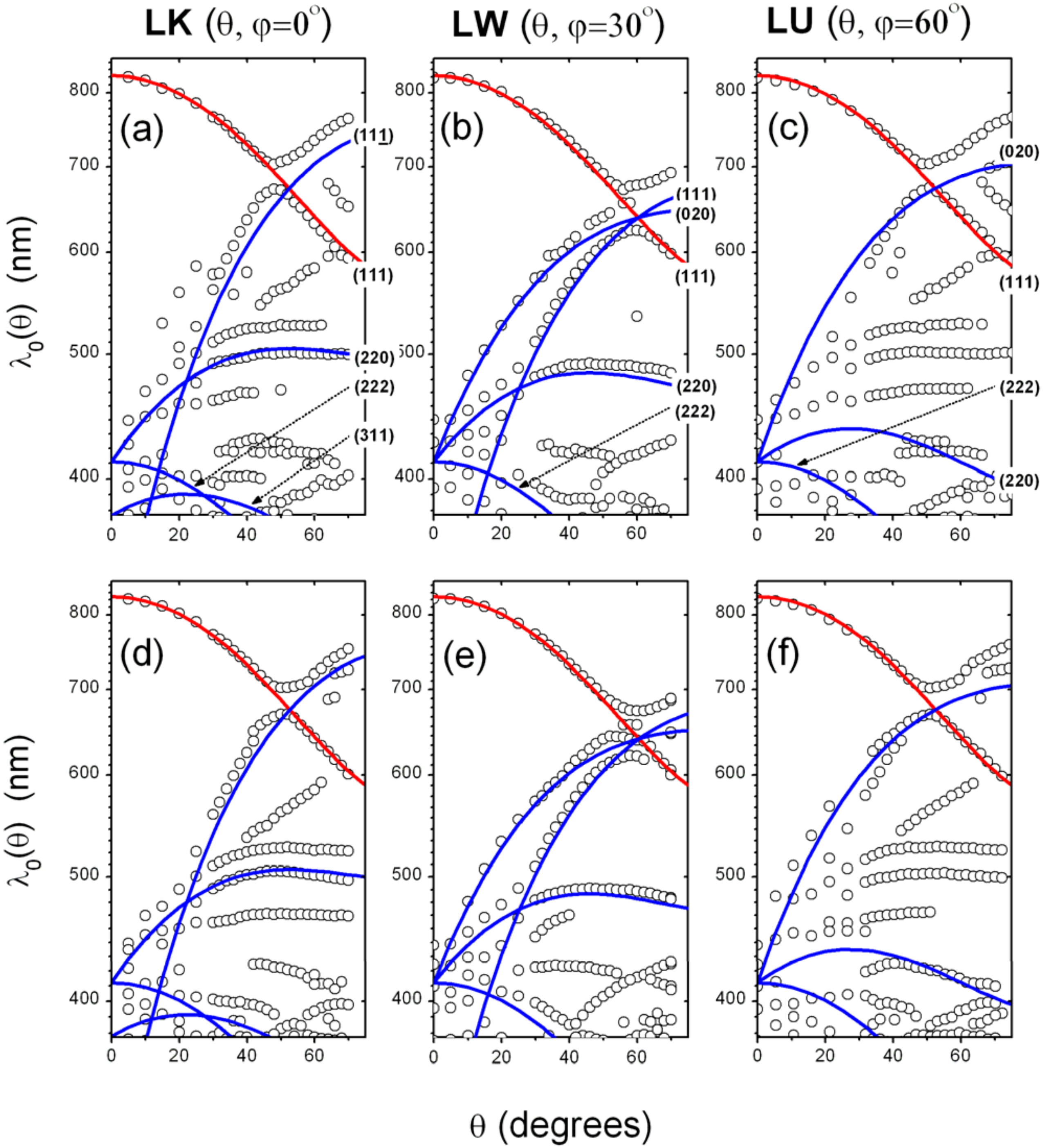


Bragg's Law

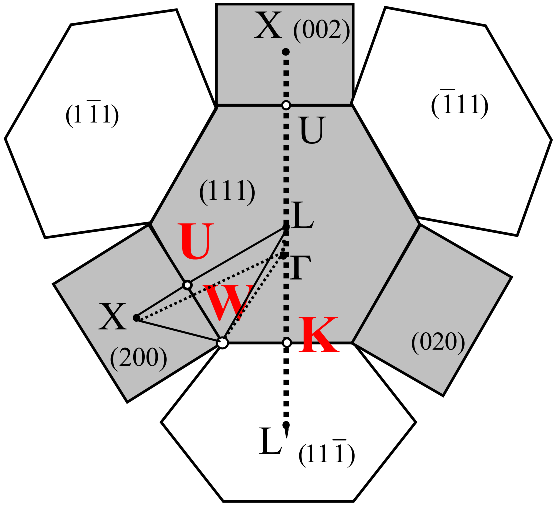
$$\lambda = 2 * n_{eff} d_{hkl} \sqrt{(1-\sin^{2}(\alpha_{hkl}))}$$



$\lambda_0(\theta)$ dispersion



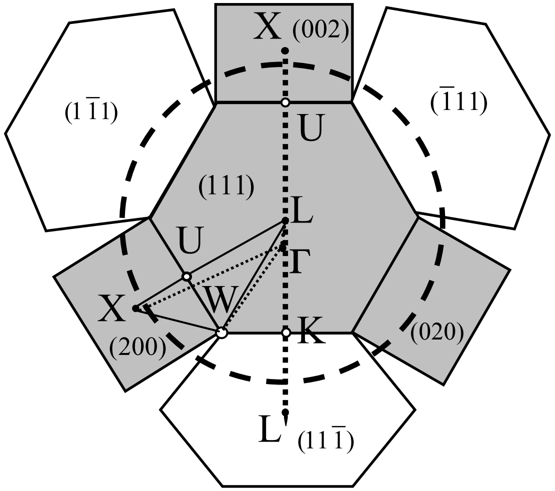
Without noise



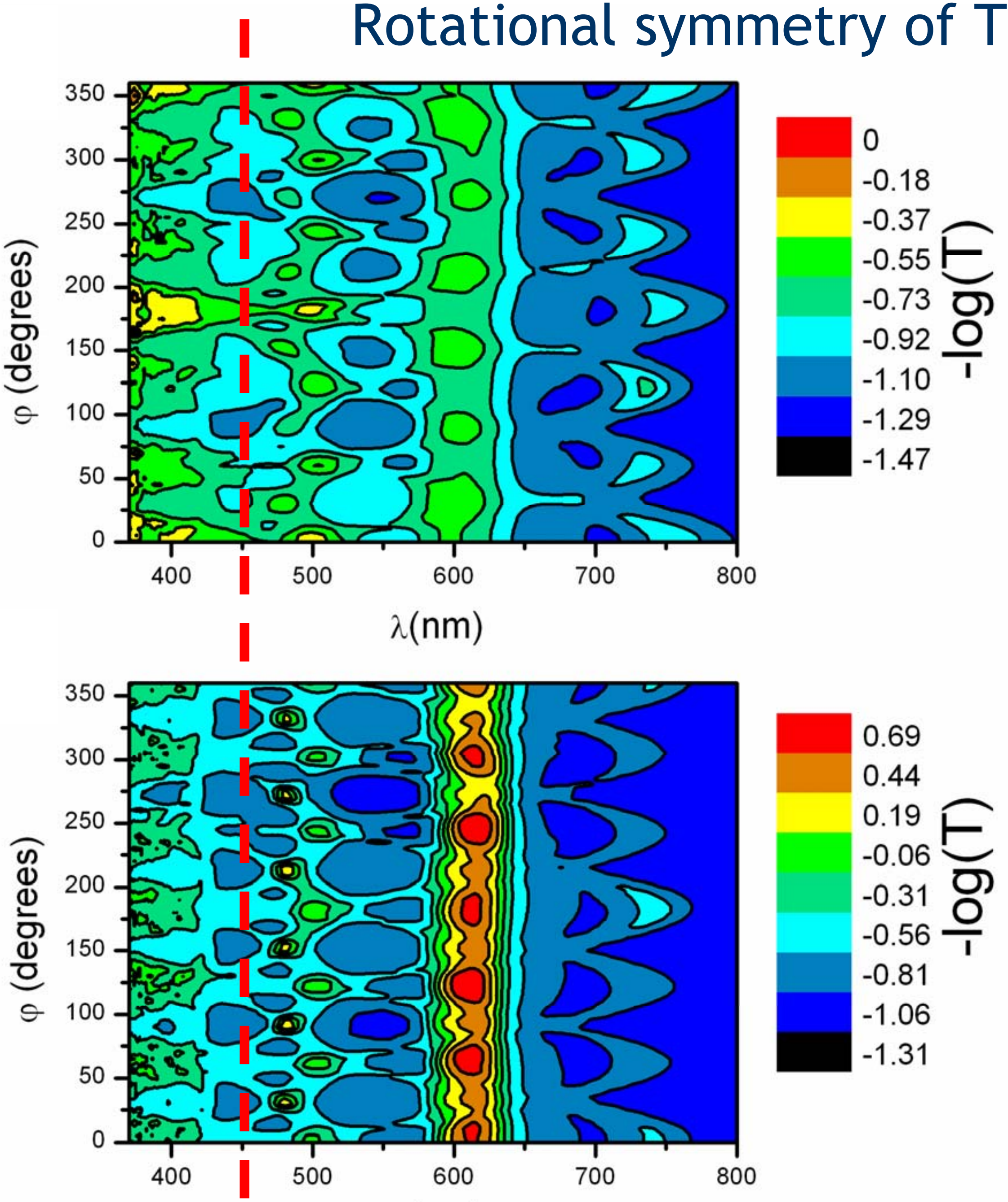
Noise

Rotational symmetry of T(φ)

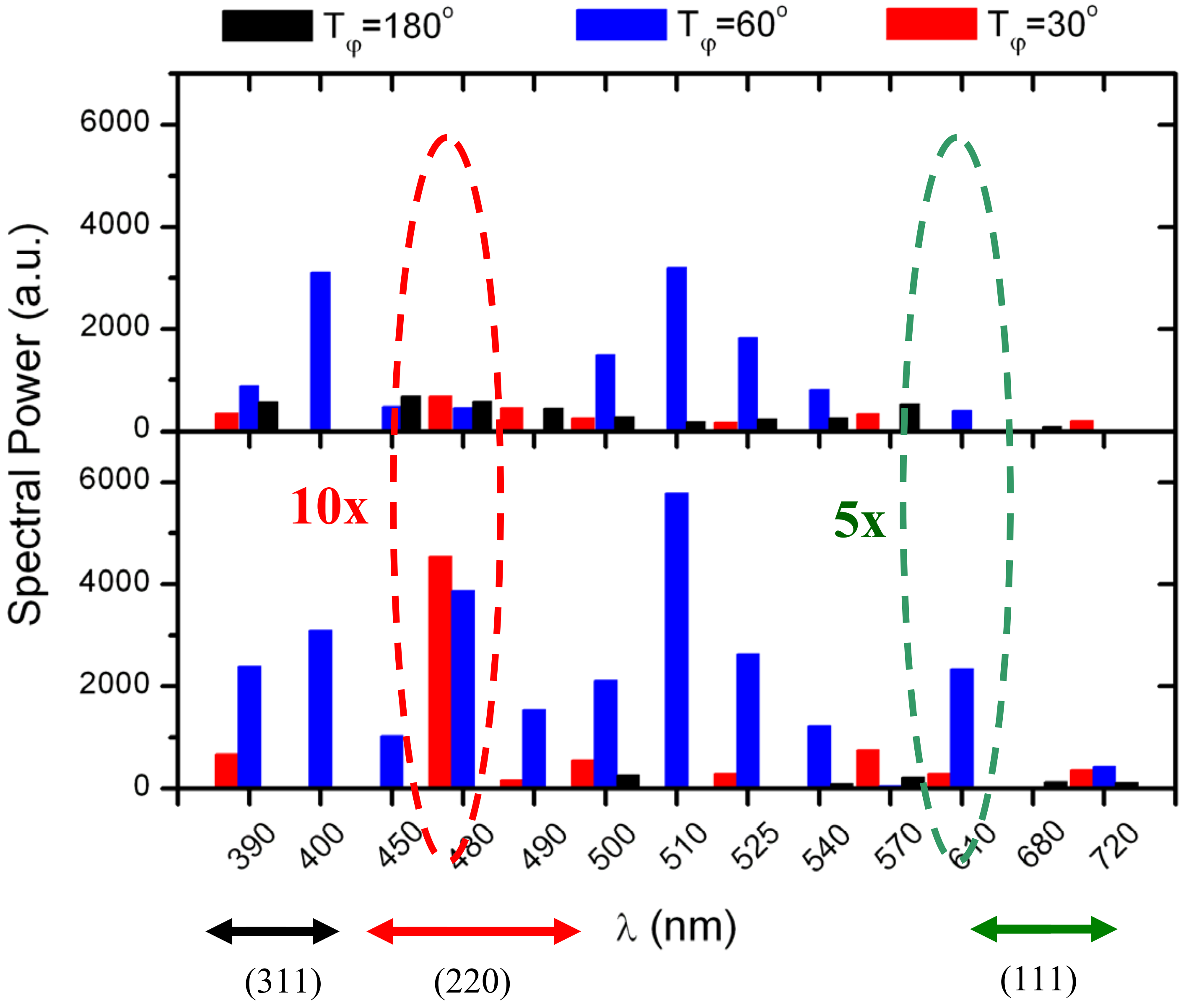
Without Noise



Noise



Noise Susceptibility: lattice planes-dependent



Without Noise

With Noise

So far ...

1. We demonstrate how to extract quantitative information from optical measurement irrespective of lattice symmetry.

2. Colloidal crystals grown by vertical deposition represent distorted fcc lattice

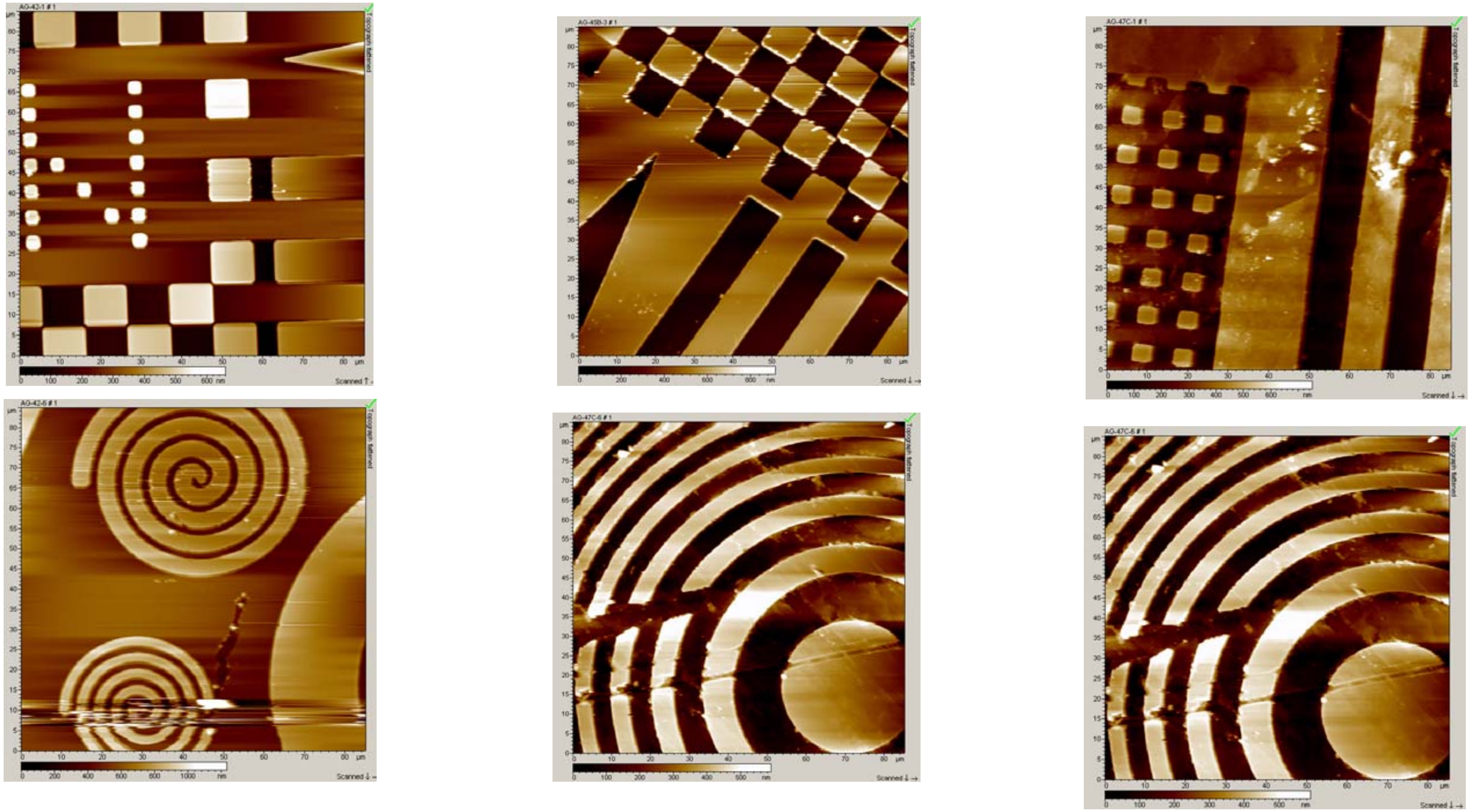
3. Noise-induced order is confirmed.

4. In a fcc lattice {220} planes are most sensitive to disorder in crystal.

Types of surface modifications

- Topographic: introduce additional patterns on nanoimprinted surfaces.
- Chemical: selectively modify sidewall or bottom/top surfaces.
- Electrical: conductive material selectively deposited or metallic nanoparticles in next printed layer.
- Magnetic: ditto.
- Mechanical: response tuned to force differentials

NIL test on functional PMMA, after growth of hydrphilic layer and hydrophobic layer



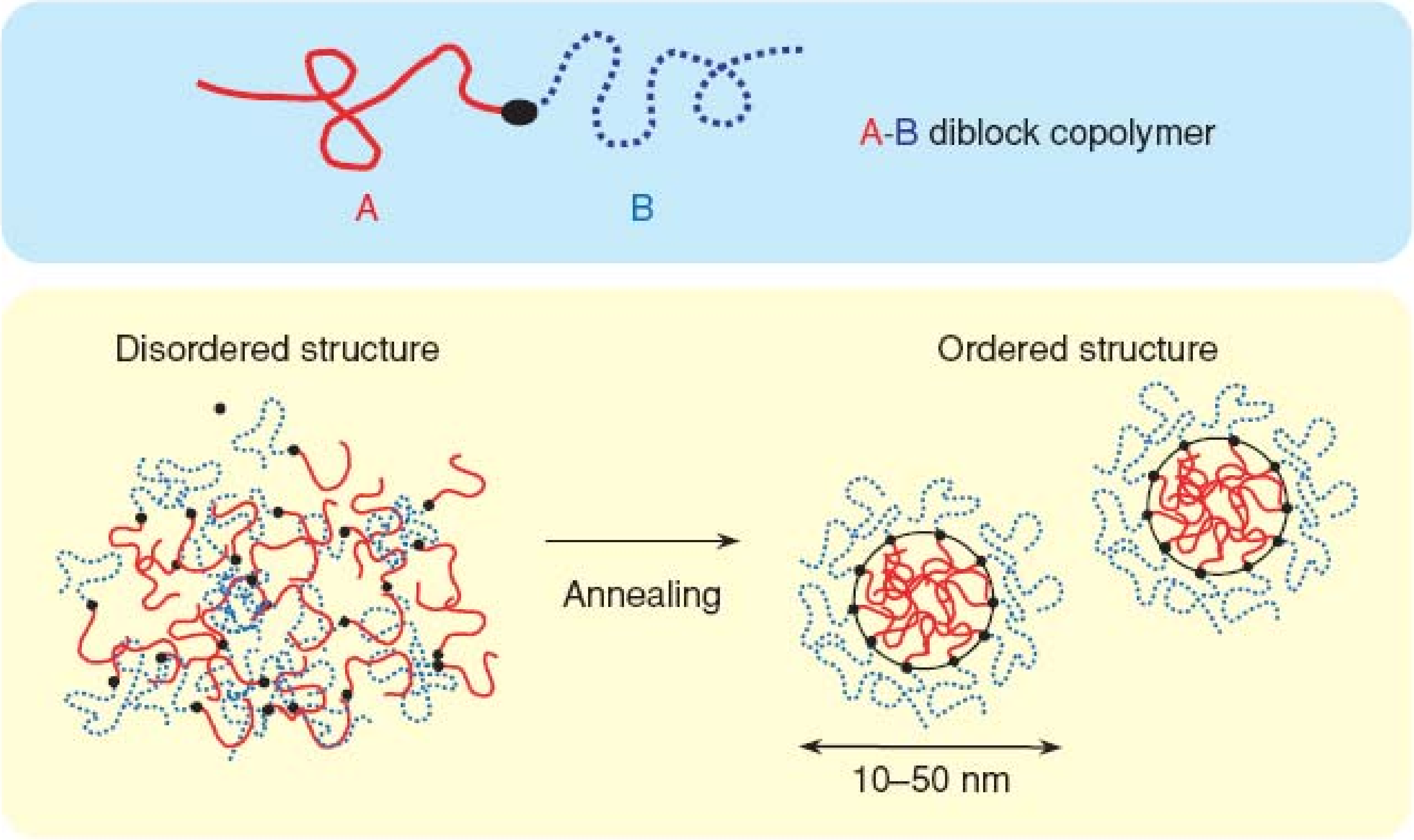
Water contact angle =
88 º

34.4 º

115 º

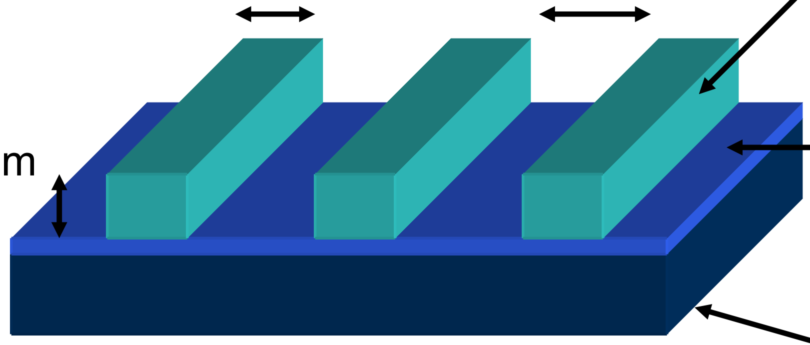
A Genua et al Nanotechnology **18,** 215301 (2007)

Towards molecular scale lithography



T Hamaguchi and H Hamaguchi, NEC Technical Review, **4**17 (2006)

Requirements for graphoepitaxy



Mesa width ~ 50 nm

Groove width
40 – 200 nm

Patterned sidewall material
- Test of both PS and PMMA wetting walls
- Fab-friendly materials

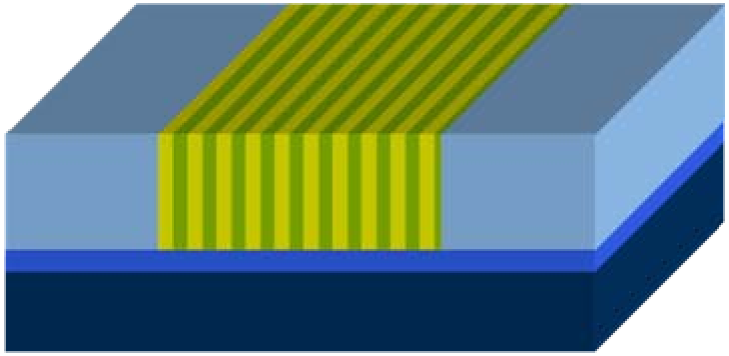
Wall height ~ 30 nm

Base must have surface OH groups to attach neutral polymer brush

Substrate

Patterned Silicon dioxide

Patterned HSQ after microphase separation



N Kehagias et al, in preparation

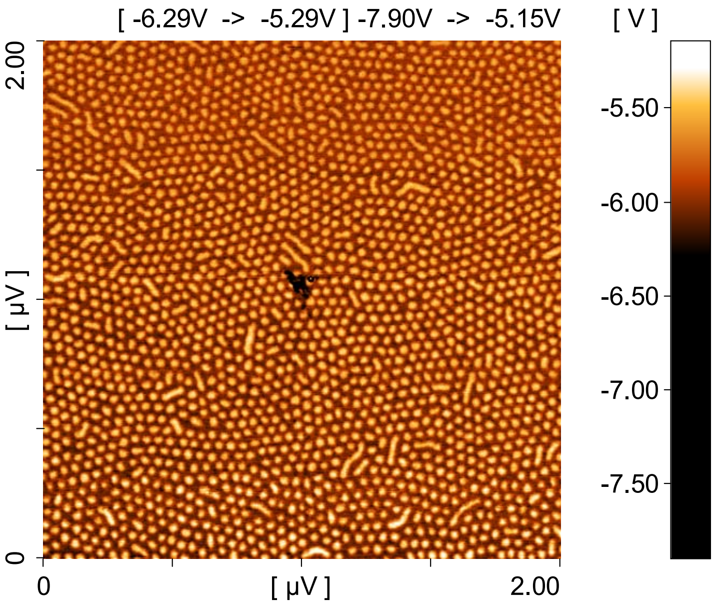
Our contribution so far

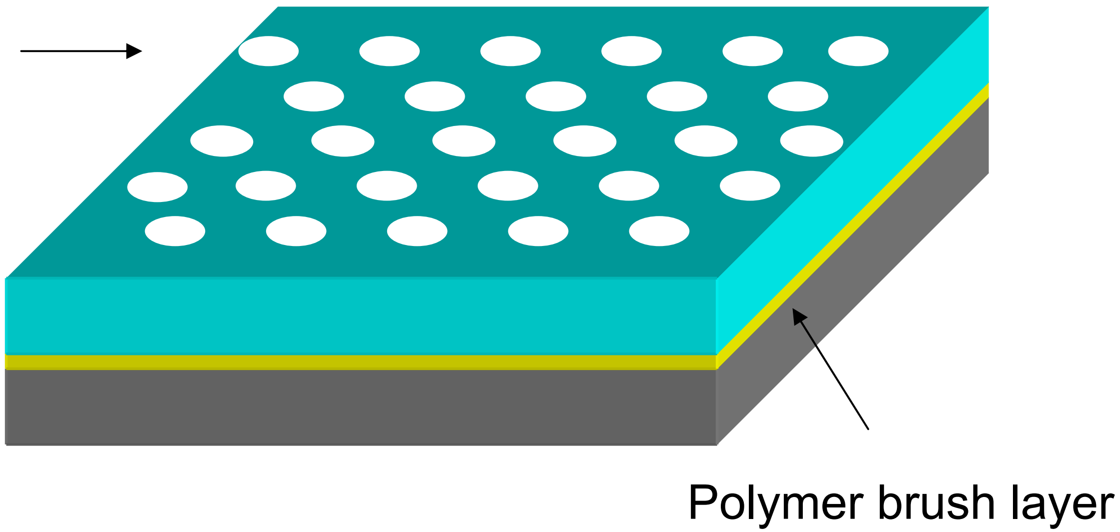
Up to now the only lithography technique used to pattern HSQ films in the nm range is electron beam lithography.

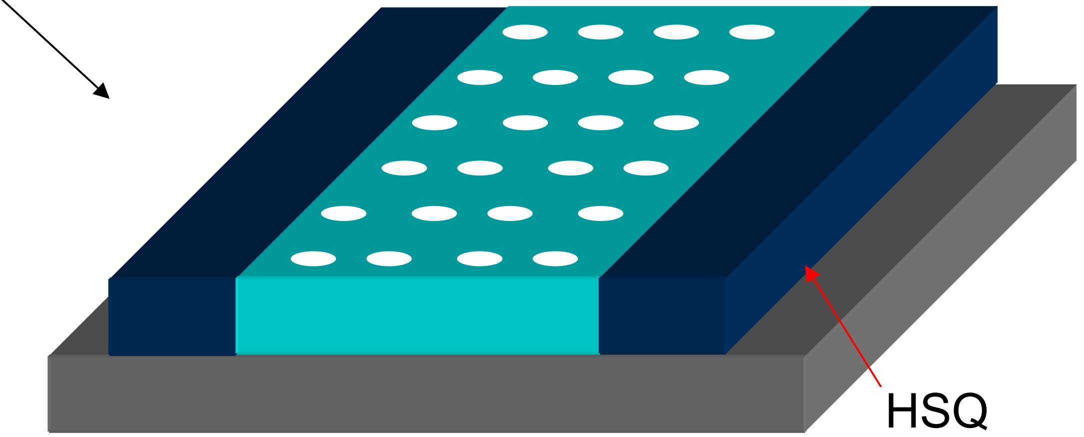
A NIL- based technique, eg, reverse nanoimprint lithography RNIL, to pattern/transfer HSQ films on a hard substrate

Advantages of RNIL technique:
- Low cost
- High throughput
- Flexible
- Reliable

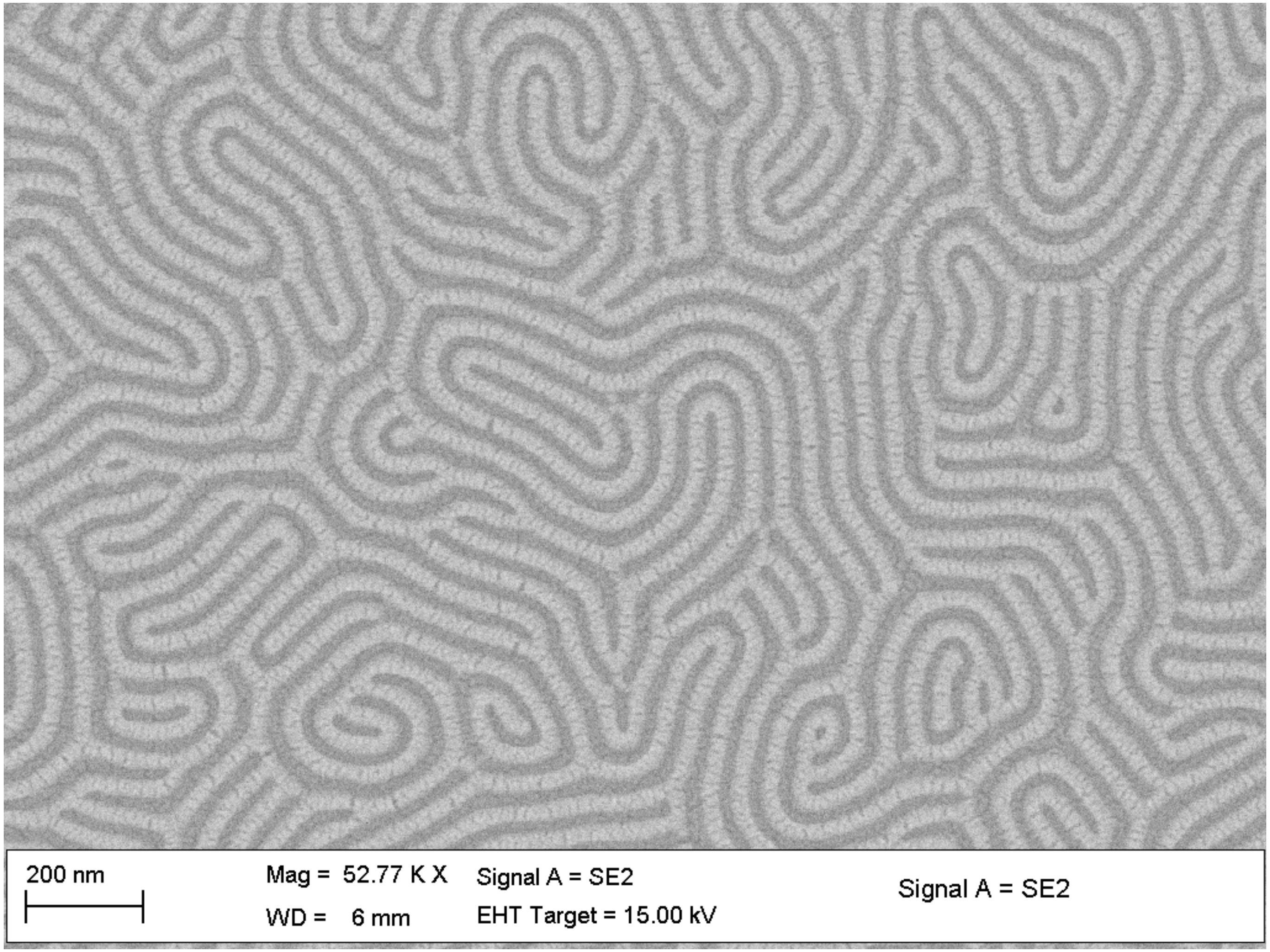
Target: deposit block copolymers in voids of a hexagonal array avoiding the use of a brush layer





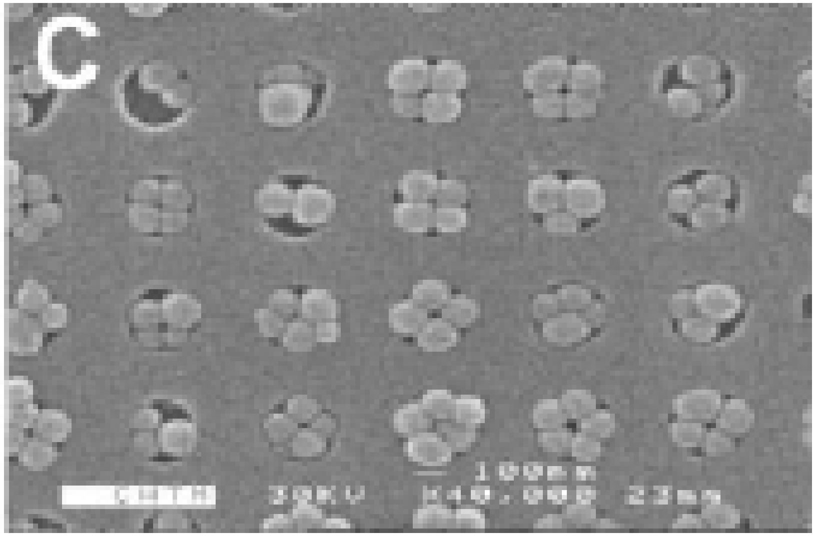


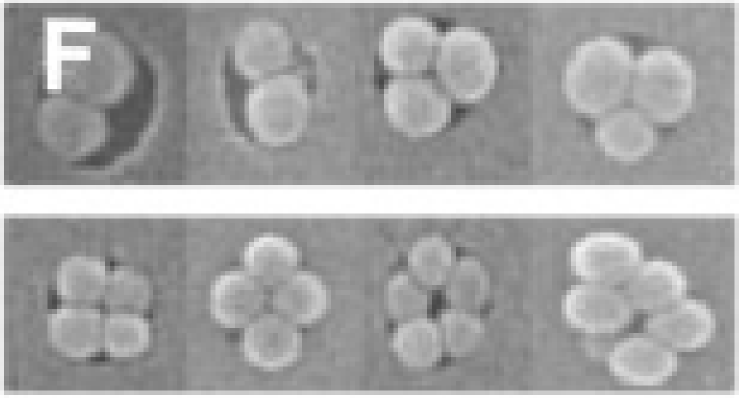
Evidence of morphology-induced phase separation on a nanoimprinted polymer substrate



N Kehagias et al, to be published

Substrates for ordering particles



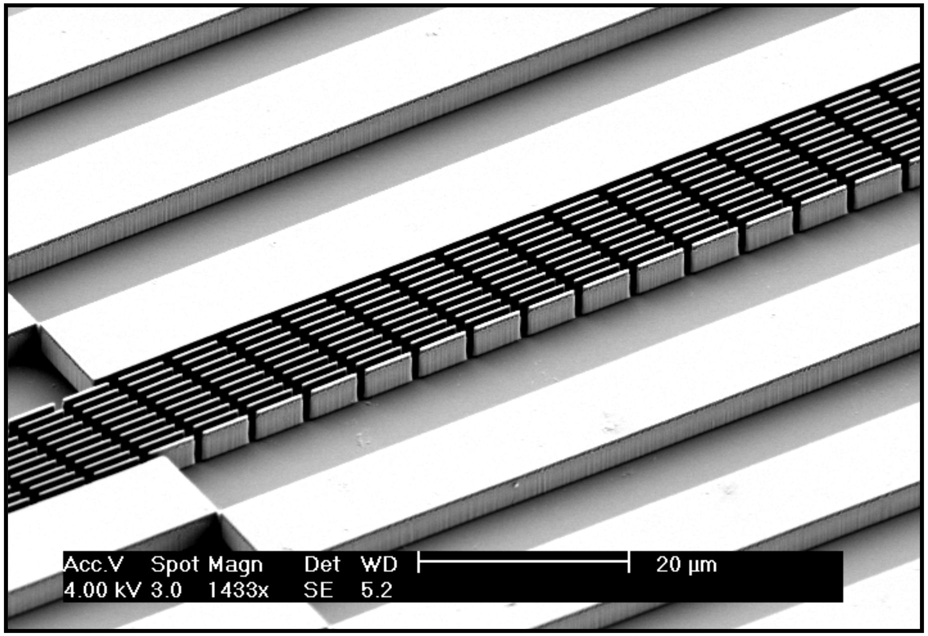


Silica particles (200-230 nm) spin coated on silicon substrates patterned with cylindrical holes by interference lithography, lift off and dry etching.

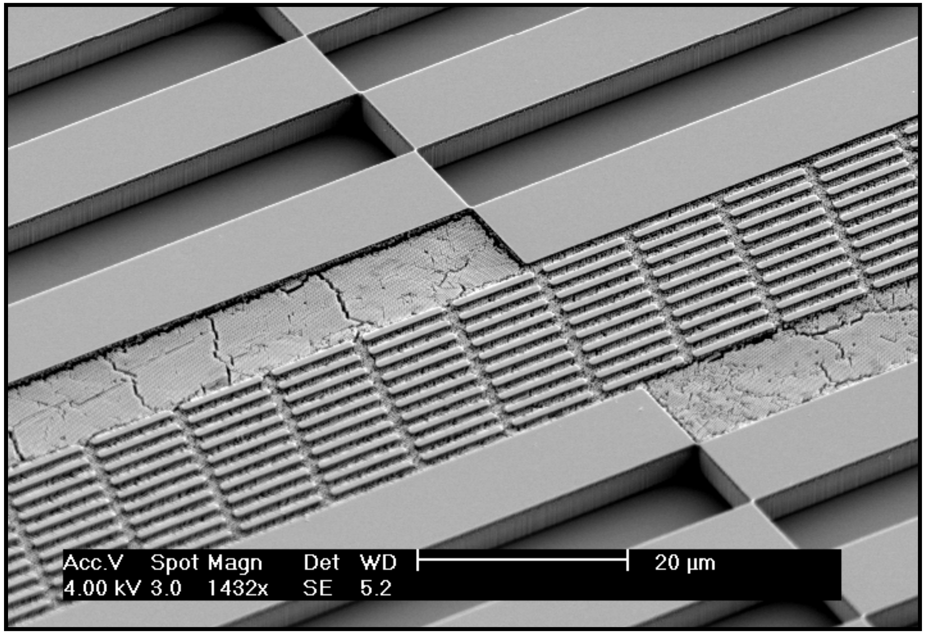
Patterning could also be done with NIL for flexible designs.

Deying Zia et al Adv Mat **76** 1427 (2004)

Particles deposited on patterned substrates



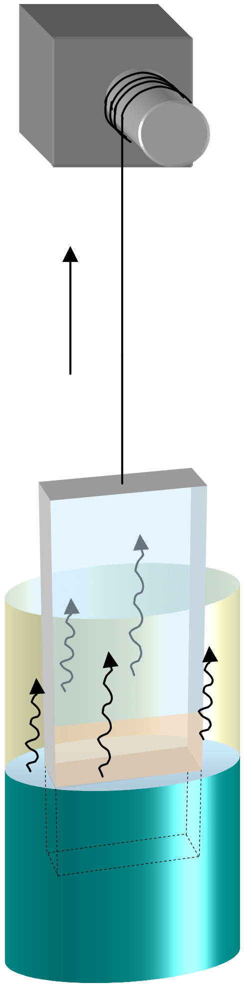
a) Etched silicon substrate supplied by VTT (ET97 pattern)



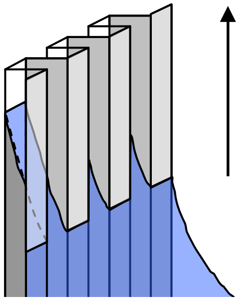
b) PMMA opal self-assembled in basins in etched silicon substrate (PMMA beads supplied by JOGU)

Joint patent 2007, S Arpianen, J Ahopelto, F Jonsson and C M Sotomayor Torres.

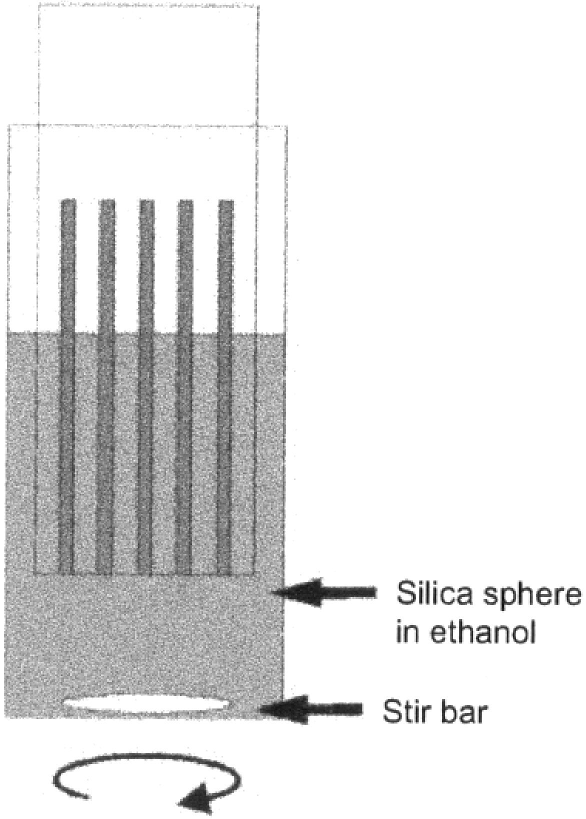
Lifting with stirring



v ≈ 200 nm/s



Stirring to control better sedimentation



J H Ye et al, Langmuir 2006

Capillary force-induced growth

Filling rate $dz/dt = R\,\gamma\,\cos\theta / 4\eta z$

η= viscosity of liquid

R= radius of capillary (lateral trench size)

γ = liquid-vapour interfacial energy (substrate preparation)

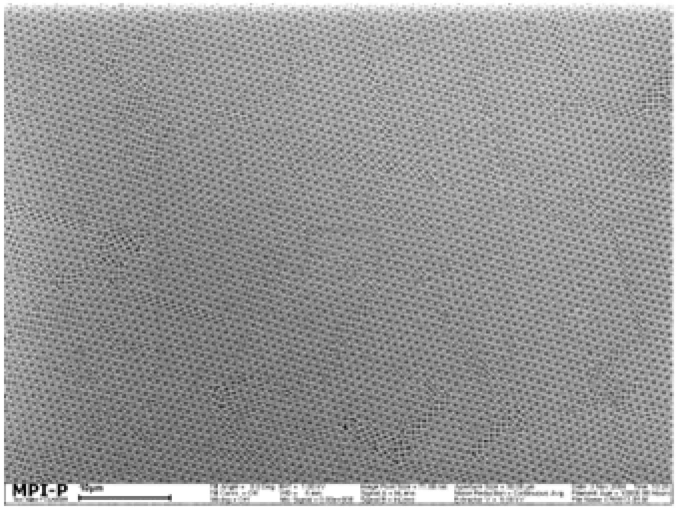
θ= contact angle between liquid and surface of capillary

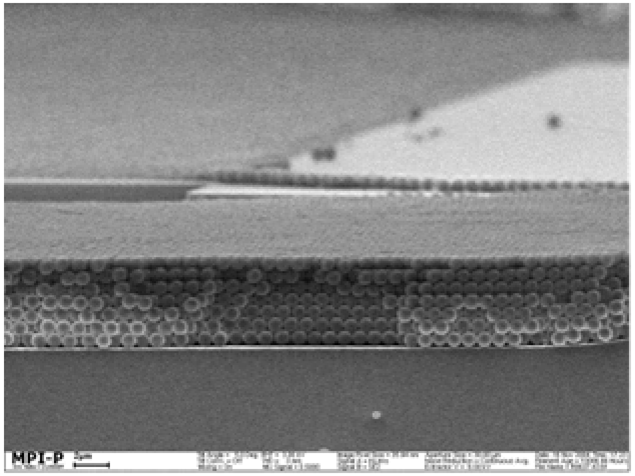
All can be optimised

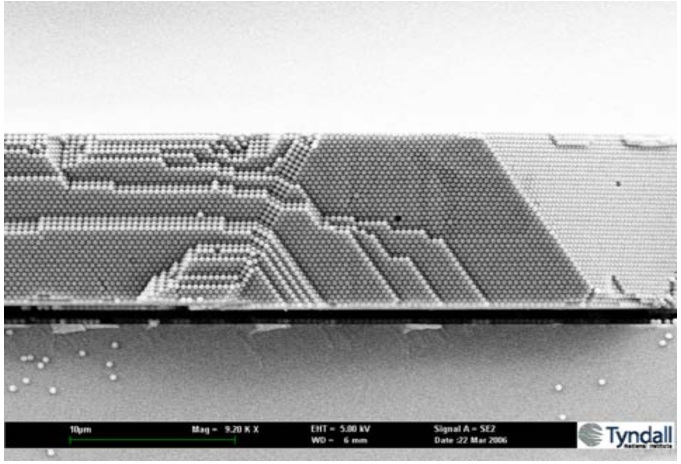
Rate of growth and … crystal quality after growth and sintering?

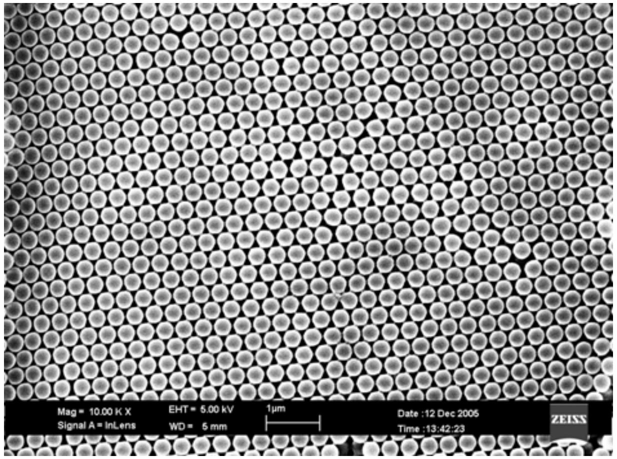
E Kim et al, Nature **376**, 58 (1995), JACS **118** 5722 (1996)

Self-assembled photonic crystals

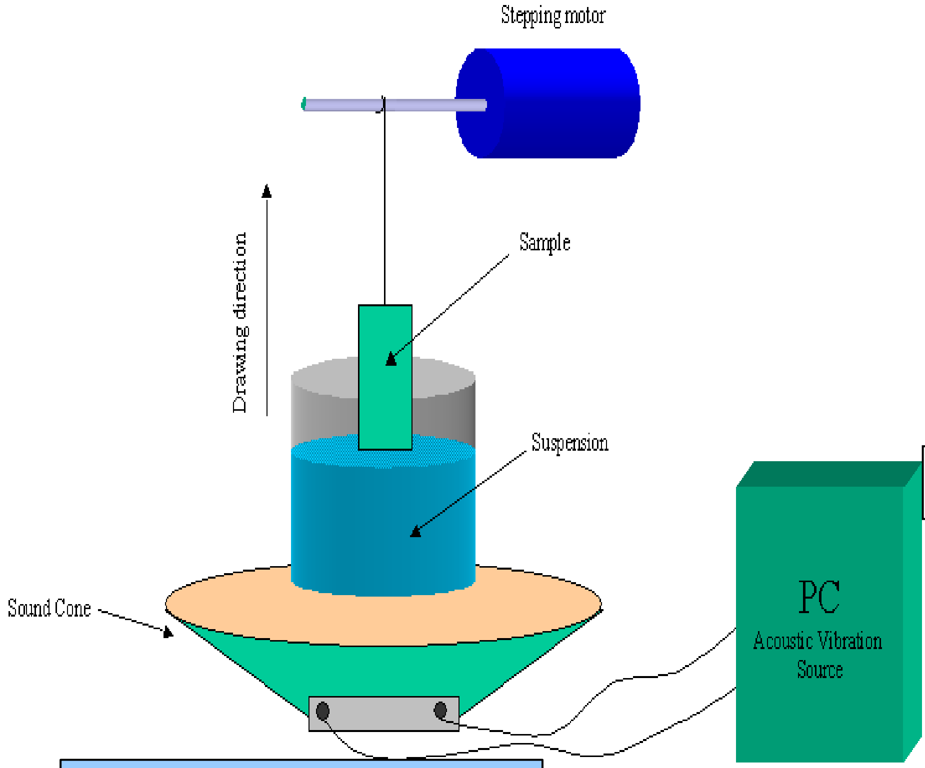




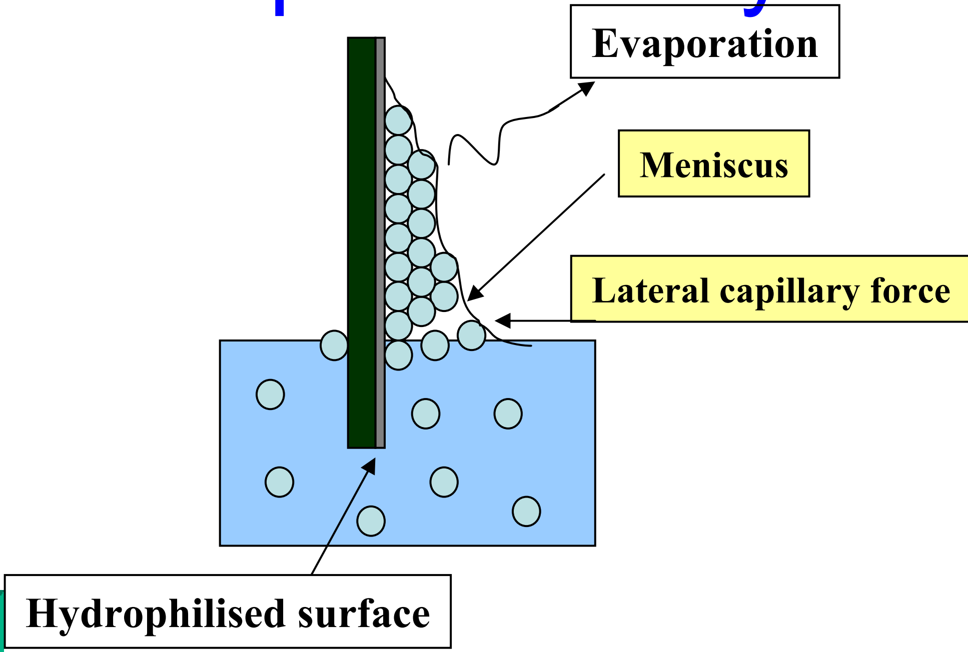


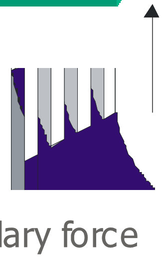


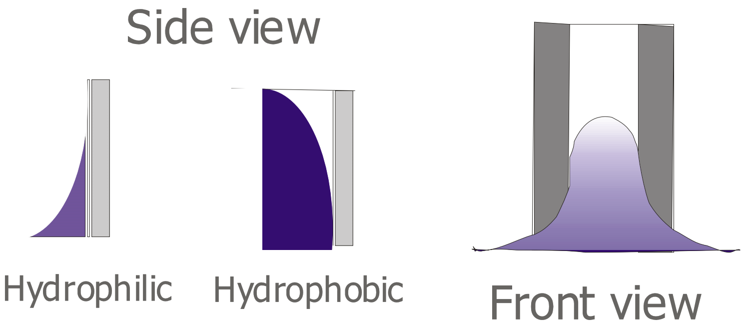
Field-assisted growth of 3D photonic crystal



$$Noise = \sum_{n} \mathrm{Im}(e^{i2\pi f_n})$$





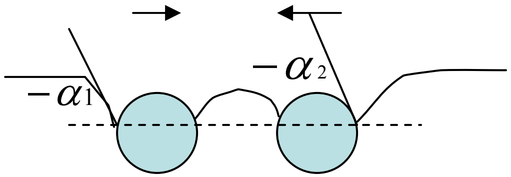


G Kocher, W Khunsin et al in preparation

Formation mechanism

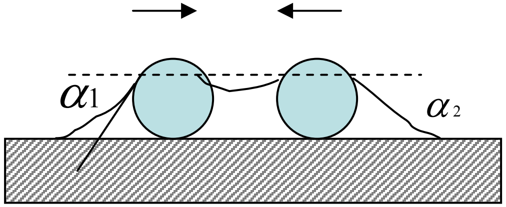
I – Lateral capillary force (floating force)

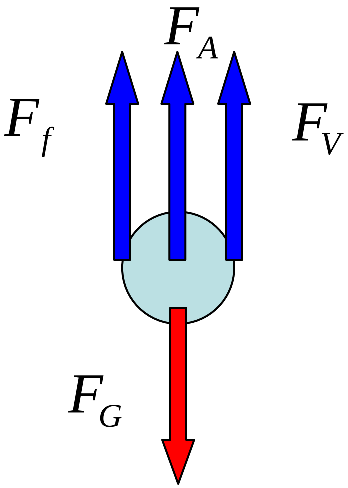
$$\boxed{\alpha \;\; R^{6}, 1/\gamma}$$



II – Vertical capillary force (immersion force)

$$\boxed{\alpha \;\; R^{2}, \gamma}$$

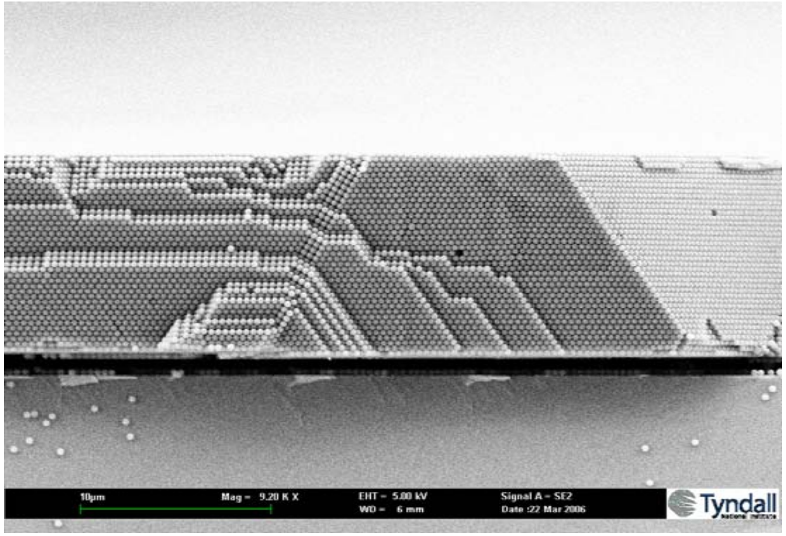




Stoke's Law

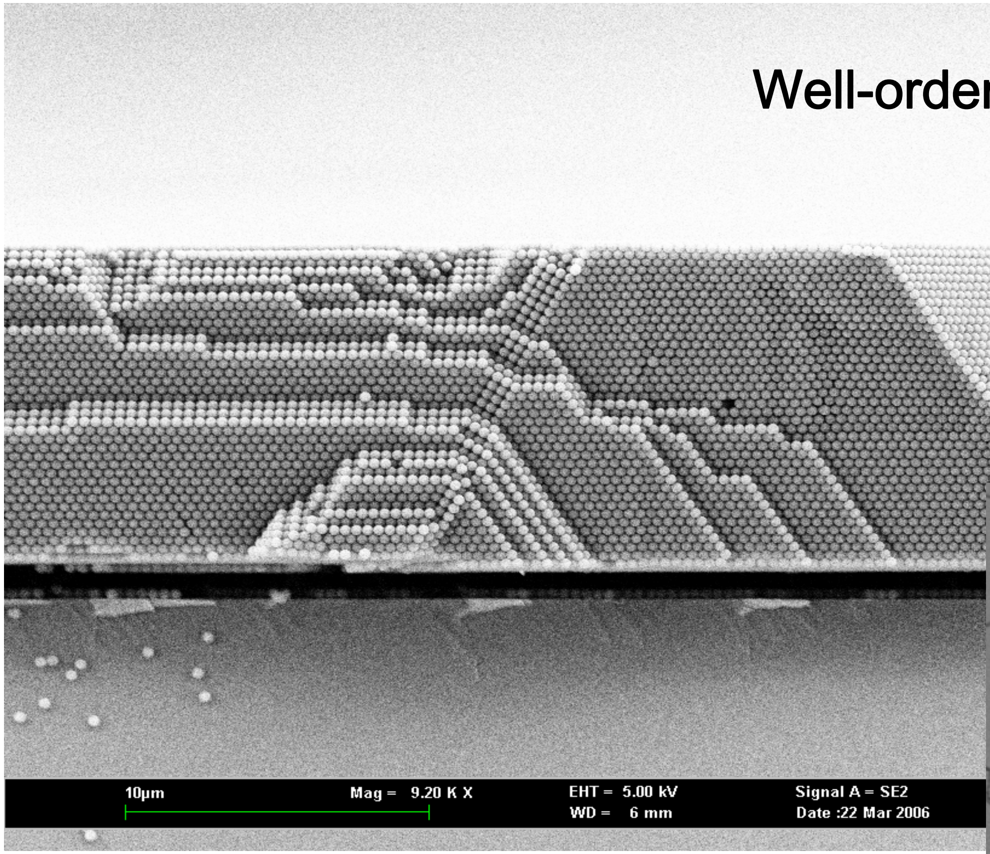
$$\boxed{v = \frac{d^{2}(\rho_s - \rho_w)}{18\eta} + C_{ac}}$$

- Counteract Gravity
- Deformation of meniscus
- Stochastic Resonance
  - •Long term ordering

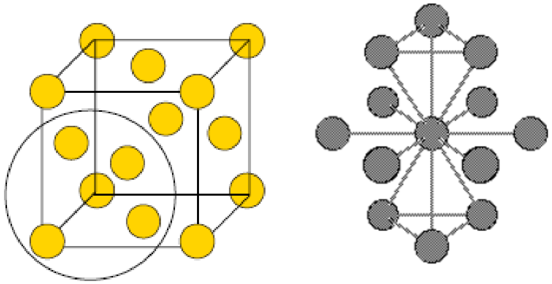


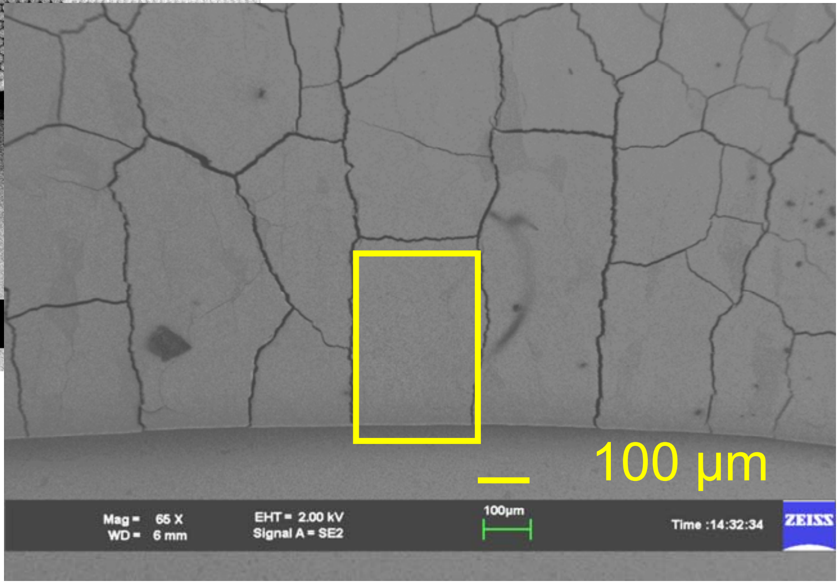
Gravitational
Archimedes
Friction

Crystal quality improvement



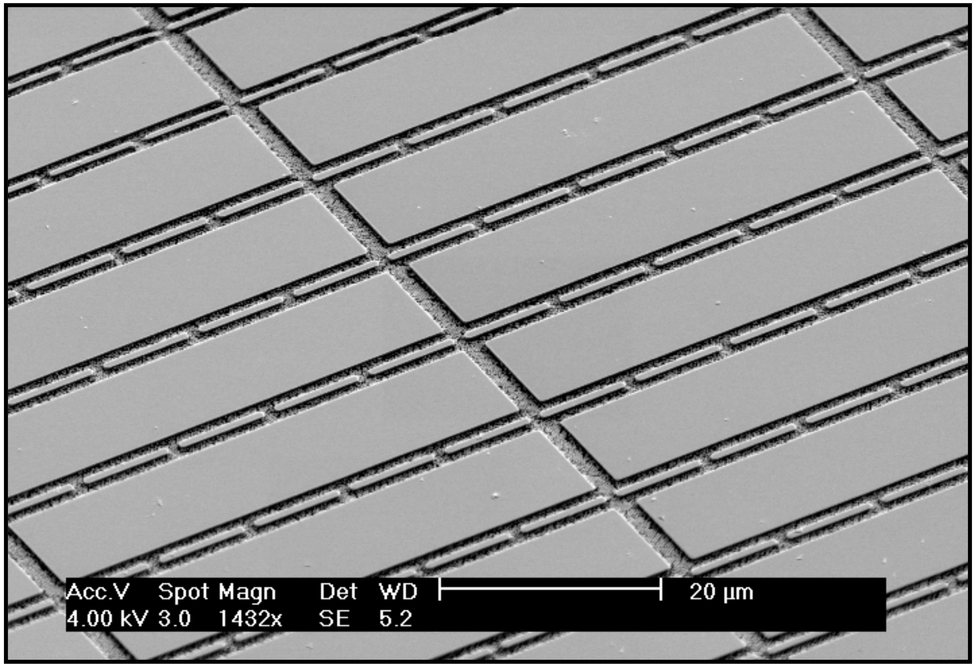
Well-ordered structures with uniform thickness





- Cracks align along growth direction
- Large area without crack ~200um

Emission from opals in rectangular channels

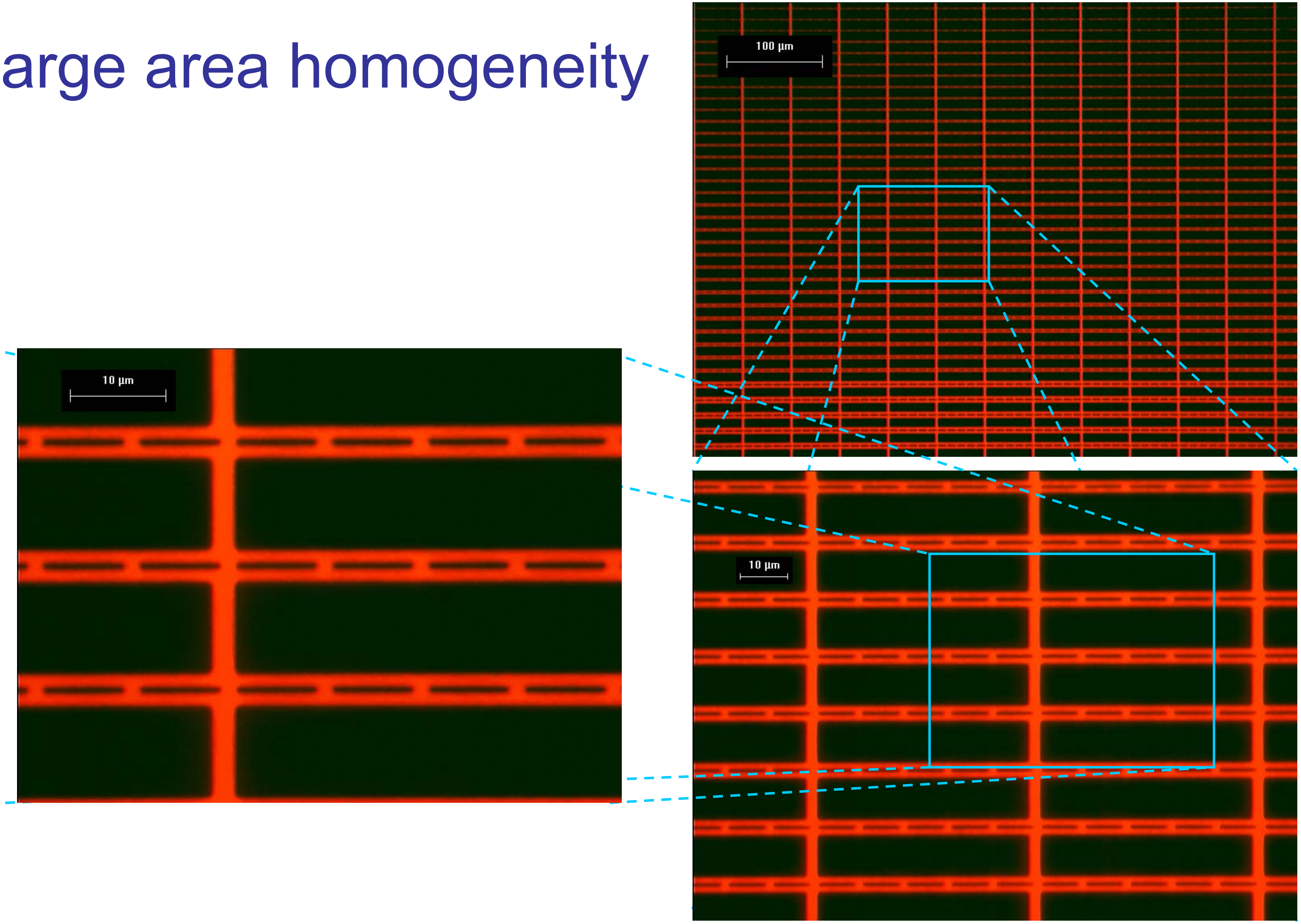


Fluorescence images of 369 nm beads with R6G

The PHAT project

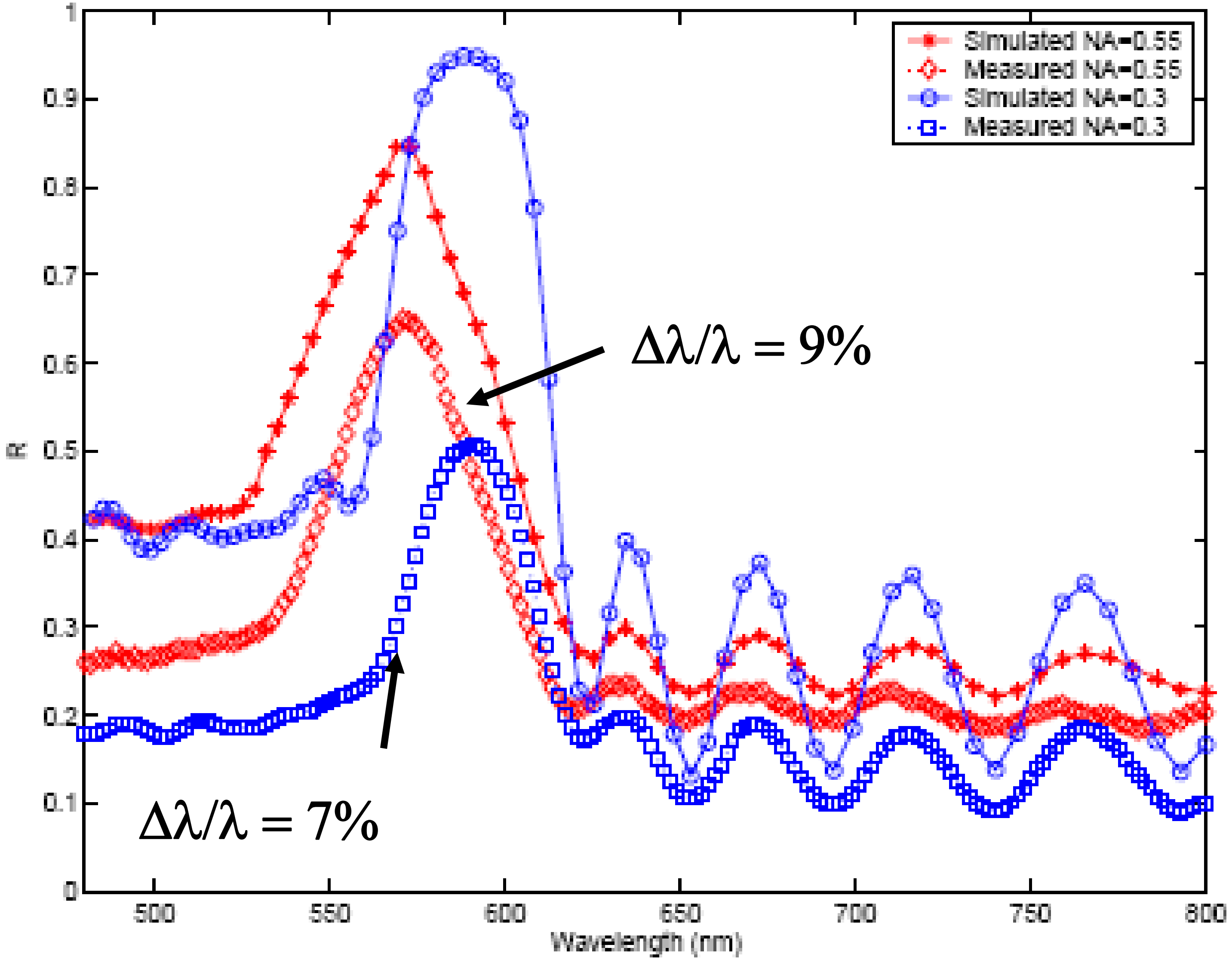
G Koccher et al, in preparation

Large area homogeneity



F Jonsson et al, in preparation

Measured and simulated reflection spectra



Δλ/λ = 9%

Δλ/λ = 7%

NA 0.55
X 50
→3 μm

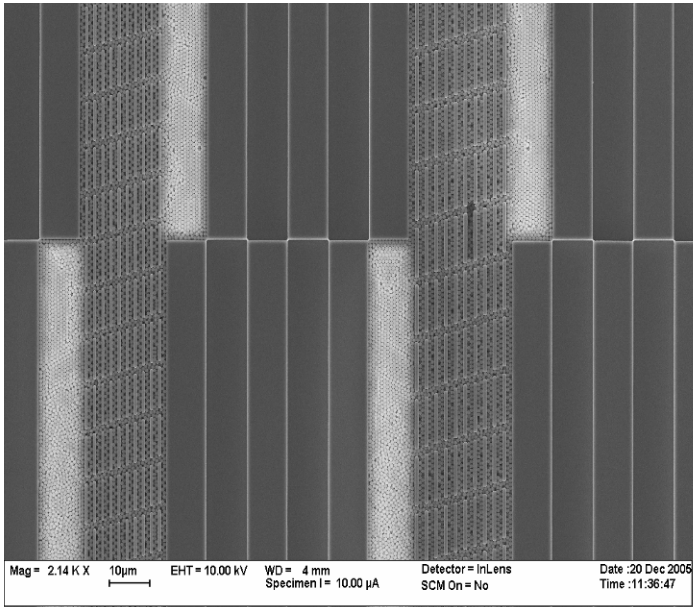
and

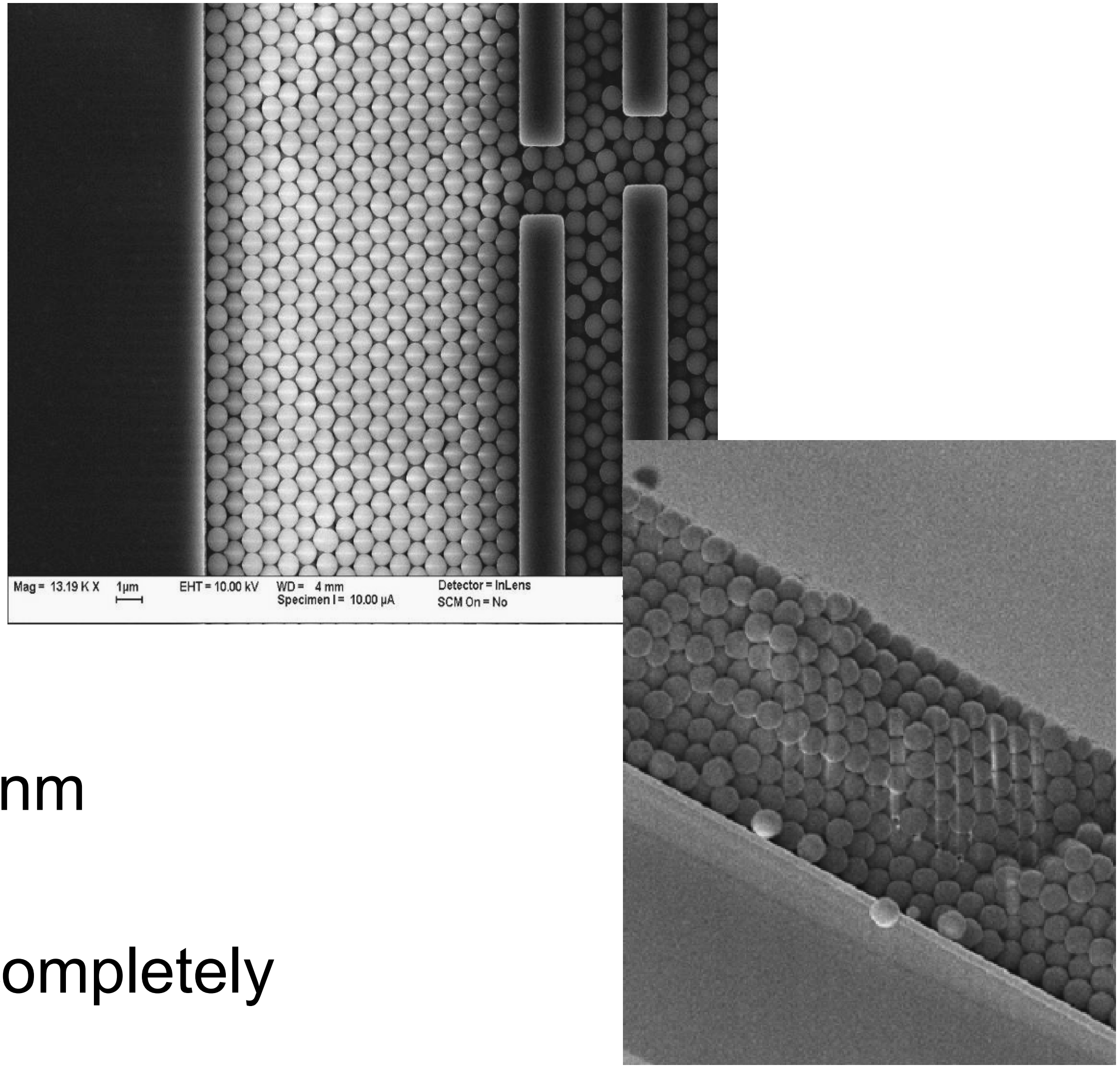
NA=0.3
x10
→15 μm

K Varis et al, Opt Exp **13** (7) 2653 (2005)

The PHAT project

3D PhCs on SOI-substrates - Now





- SOI – Silica beads
  - As etched; ∅ = 890 nm
  - Ordering
  - Capillary channels completely filled
  - No cracks

The PHAT project

Conclusions and prospects

- The combination of NIL and modification of printed polymer surfaces is a promising mix-and-match approach for new nanofabrication concepts.

  - growth of polymer brushes for further functionalisation

  -a variation of NIL (reverse NIL) was used to patttern HSQ without a residual layer. HSQ promising for graphoepitaxy

- Nanometrology research is a corner stone for standards.

- For use in heterogeneous integration need also studies of reliability, throughput and cost.

- **Rosy future and more so at systems level**

Happy birthday LAAS!!!