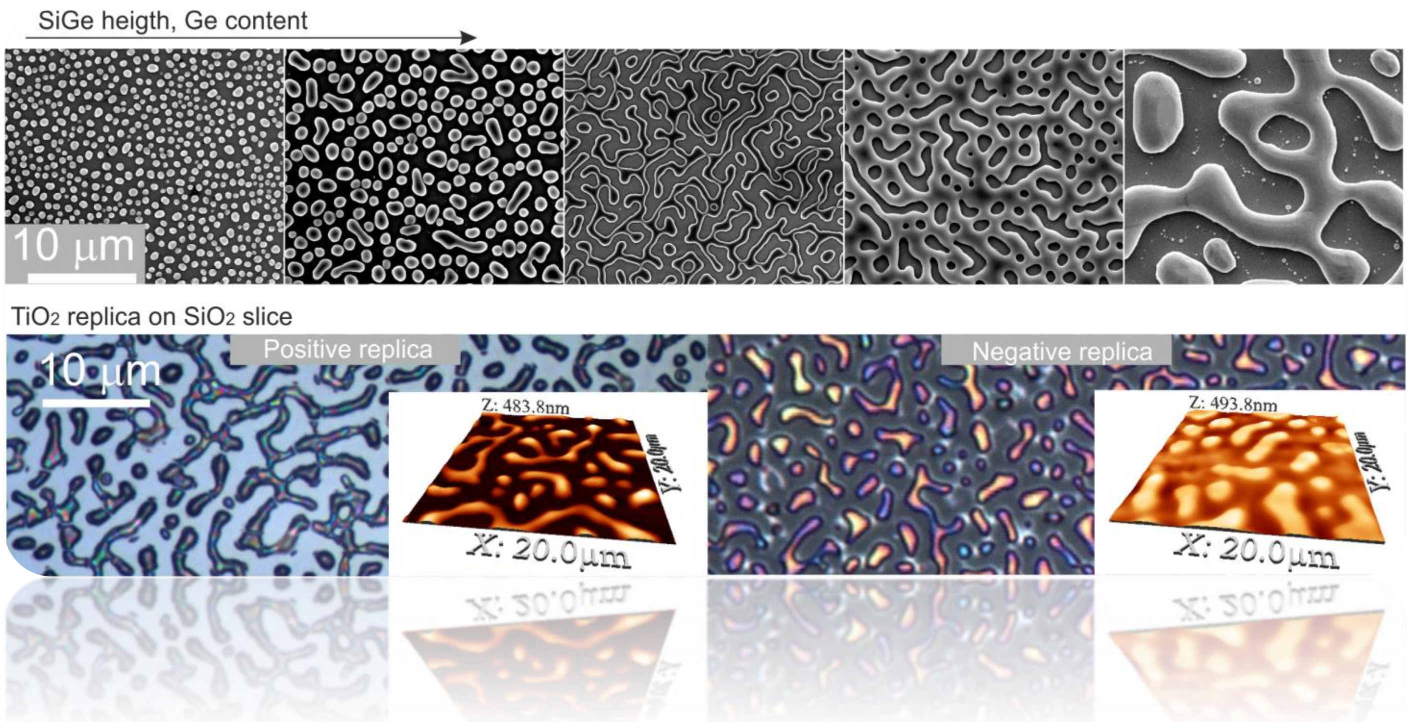
SOLID STATE DEWETTING IN SEMICONDUCTOR THIN FILMS



L-NESS

NARCISO

IFN
Institute for Photonics and Nanotechnologies

Monica Bollani

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M.BOLLANI'S BACKGROUND

Master degree in physical chemistry in Milan (Nov 1997)

European phD in physics of materials in Marseille (Nov 2000)

Post doc in Zurich on SiGe epitaxial growth (2001 - 2004)

CNR researcher since 2004 studying the growth and nanofabrication of IV group semiconductors (Como, LNESS laboratory)

L-NESS: Laboratory for nanostructure Epitaxy and Spintronics on Silicon

In 2008, I worked at Physics Univ. of Linz (Austria) and then at Berkeley (California) to learn how to use electronic nanolithography (EBL), photolithography and dual beam systems, keeping -as research material- semiconductors of group IV.

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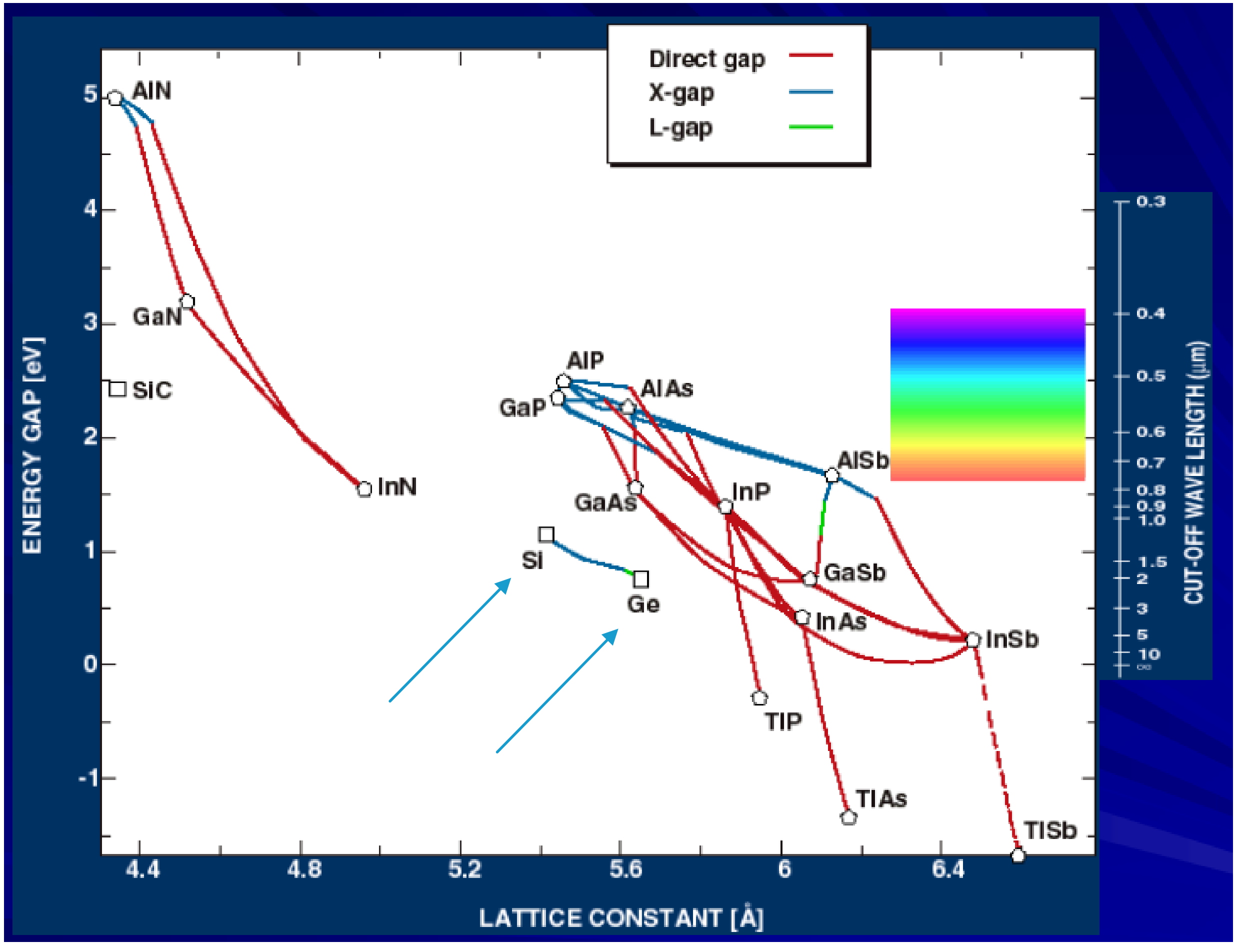
M.BOLLANI'S BACKGROUND



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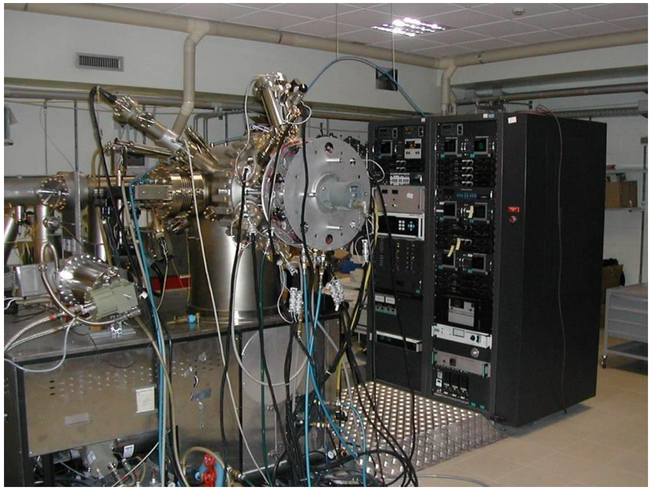
Laboratory for
Nanostructures
Epitaxial growth
and Spintronics on
Silicon

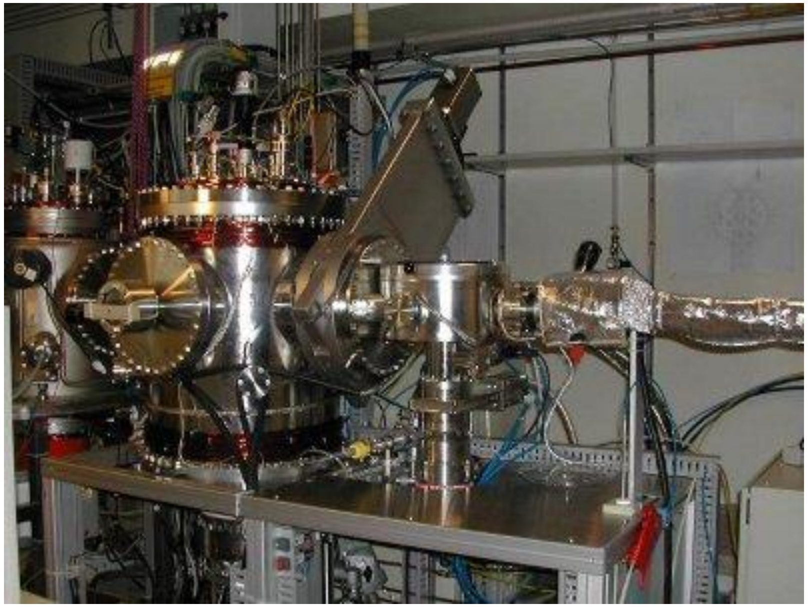
L-NESS = POLITECNICO DI MILANO DIPARTIMENTO DI FISICA + UNIVERSITA' DEGLI STUDI DI MILANO BICOCCA + IFN

1: EPITAXIAL GROWTH OF SEMICONDUCTOR HETEROSTRUCTURES

- ❑ low-energy plasma-enhanced CVD of SiGe heterostructures
- ❑ MBE growth of GaAs AlGaAs hetero/nanostructures



Molecular Beam Epitaxy (MBE) Gen II (III/As)



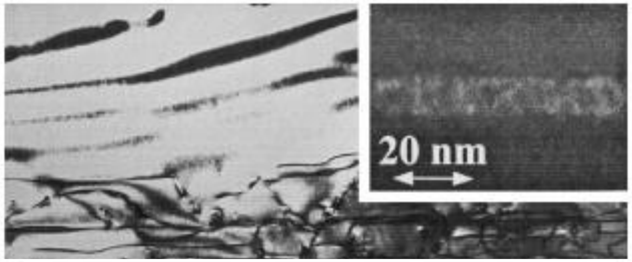
Low-energy plasma-enhanced CVD

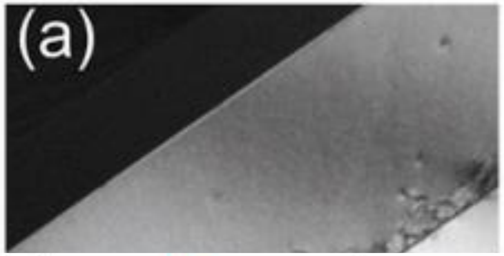
1: INTEGRATION ON SI OF SIGE AND III-VS

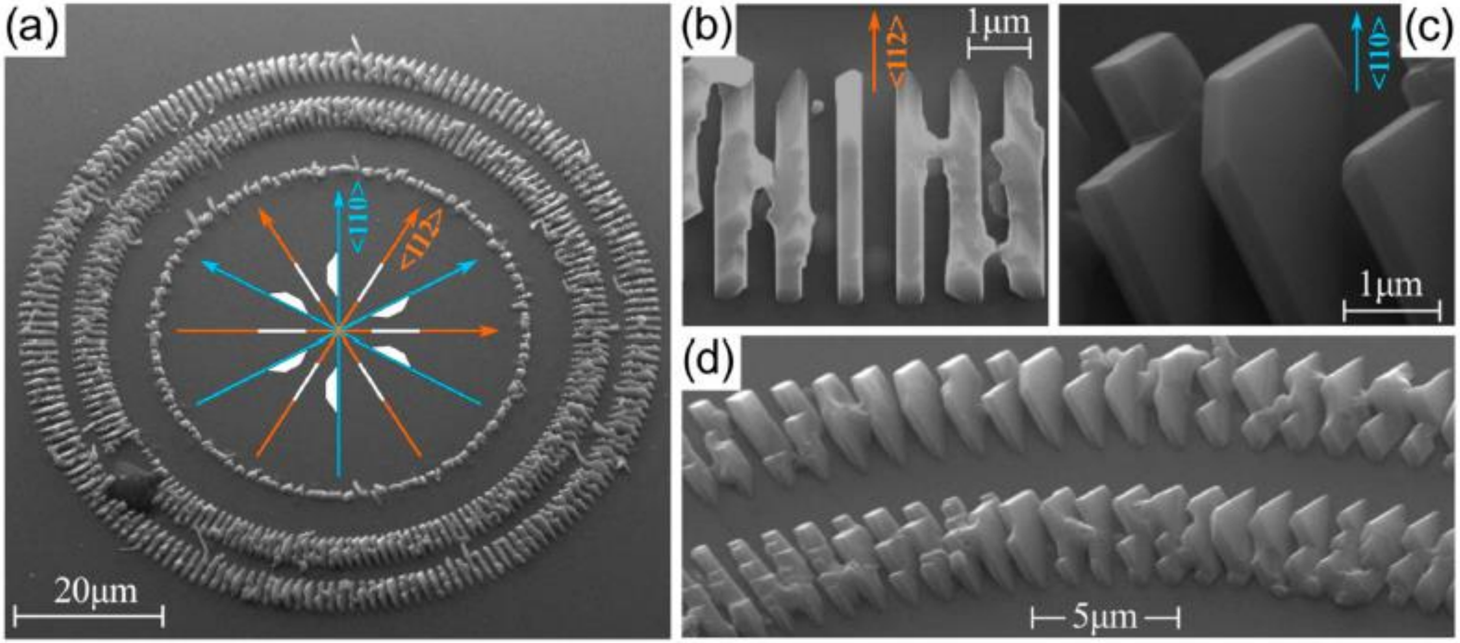
linearly graded buffers

Ge-on-Si

III-V on Si

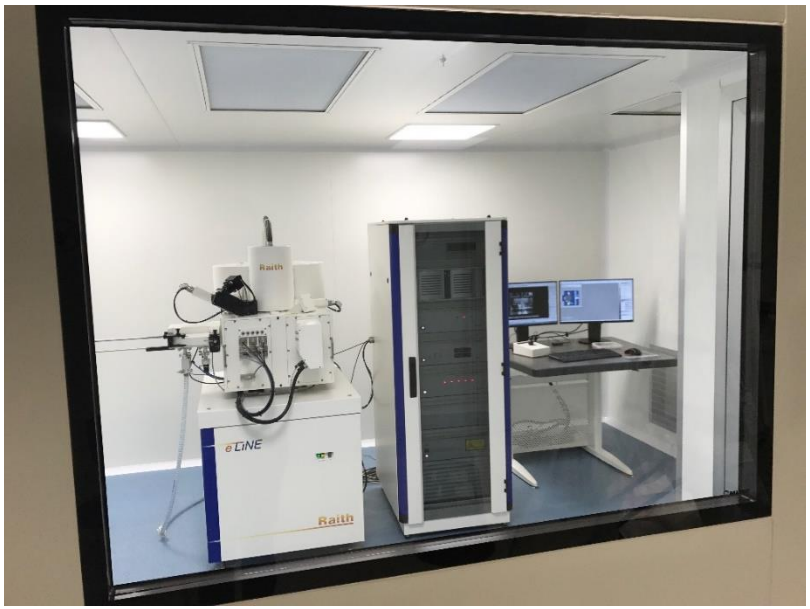






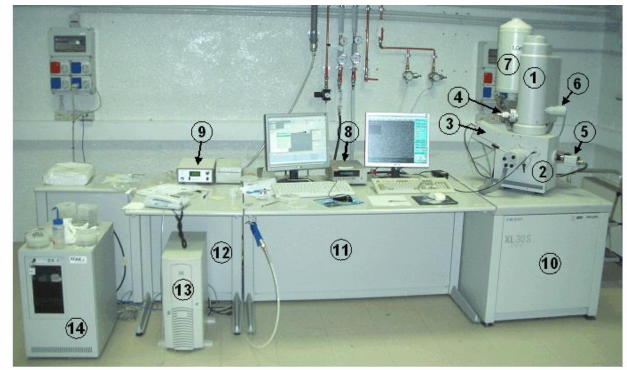
2: MICRO- NANO-FABRICATION

Raith eLINE 4” e-beam lithography system



- High-speed pattern generator (20 MHz)
- Laser interferometer stage with a stitching error < 20 nmand 100 x 100 mm horizontal and 30 mm vertical travel range under full interferometric control

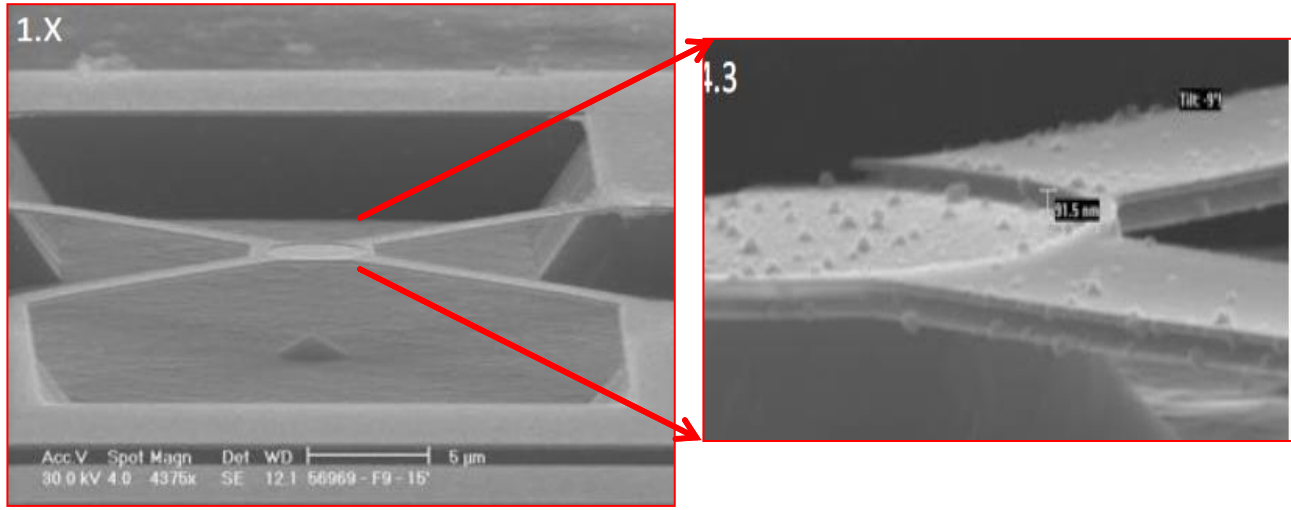
SEM e-beam system

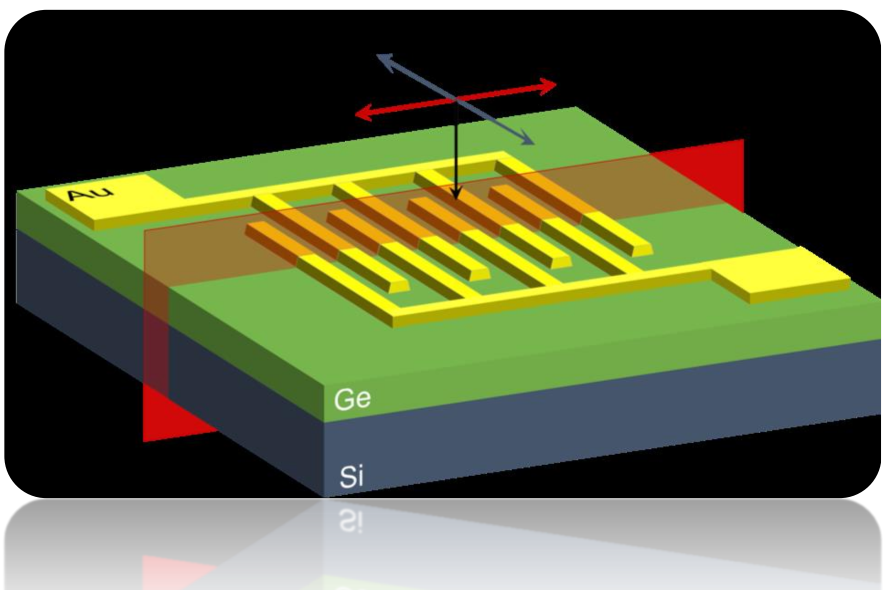


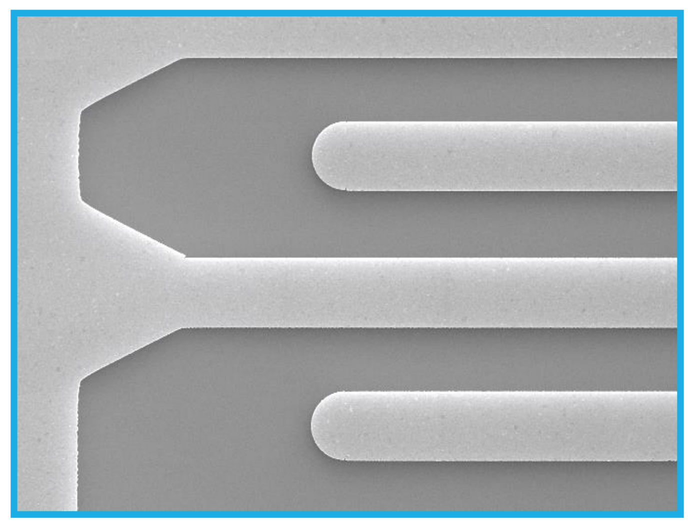
Optical lithography

2: STRAIN-ENGINEERING AND SUBSTRATE PATTERNING

- ❑ Strained suspended membranes
- ❑ Plasmon enhanced photodetectors





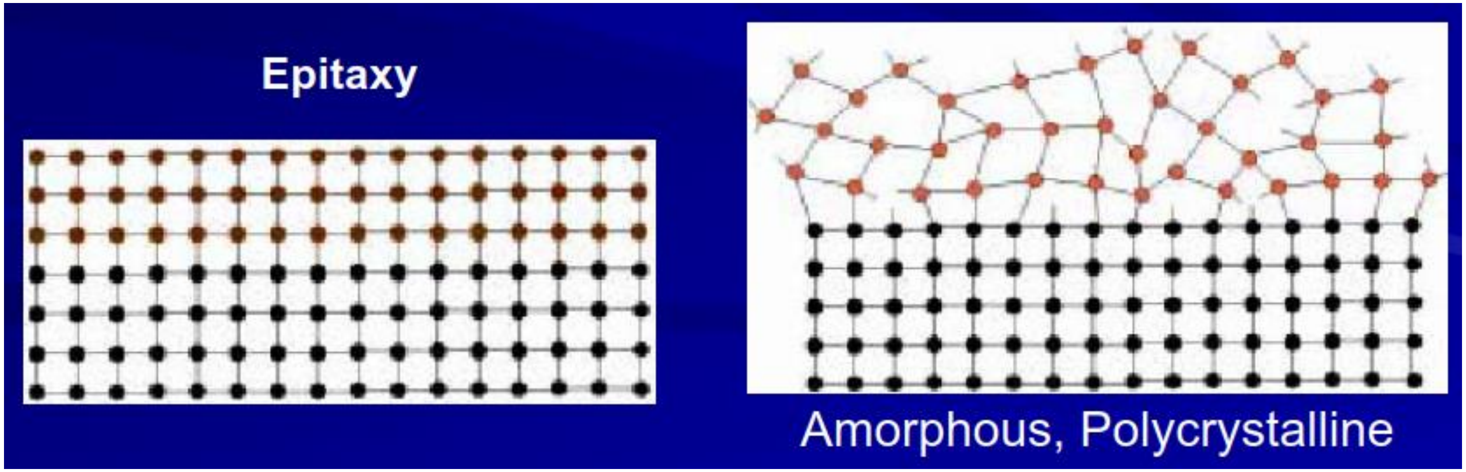


GROWTH PROCESSES

- **Epitaxy**: the film grows following the same lattice of the substrate

Film and substrate of the same material: **homoepitaxy**
Film and substrate are of different materials: **heteroepitaxy**

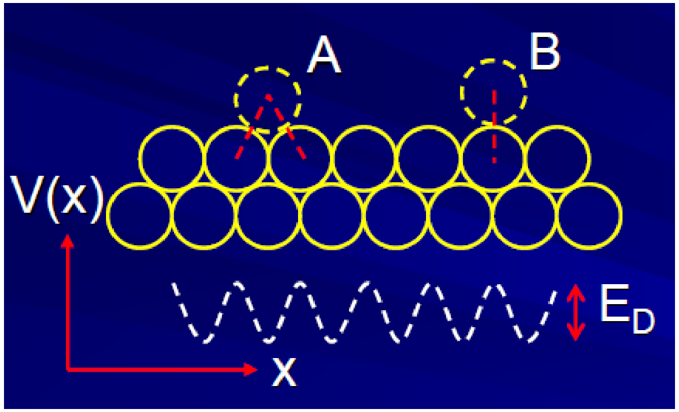
- Accurate structure and composition control;
- Growth takes place on planar, single-crystal substrates, atomic layer- by – atomic layer.



BASIC CONCEPTS IN EPITAXY

Surface diffusion

1) An atom on the crystal surface can diffuse to reach the energetically most favourable position!
2) The diffusion length depends on the T and the binding energy



$$\text{Rate} \propto \nu_D \exp\left(-\frac{E_D}{kT}\right)$$

ν_D Characteristic diffusion frequency $\sim 10^{14}\ s^{-1}$

$E_D < E_0$ diffusion is more likely than desorption

E_D depends on the substrate orientation and the nature of the diffusion atom!

BASIC CONCEPTS IN EPITAXY

Diffusion coefficient, diffusion length

Diffusion coefficient (*mean square displacement of the random walker per unit time*):

$$D = \nu_D a^2 \exp\left(-\frac{E_D}{kT}\right)$$

a= lattice constant

Adatom lifetime before desorption: $\tau = \tau_0 \exp\left(\frac{E_0}{kT}\right)$

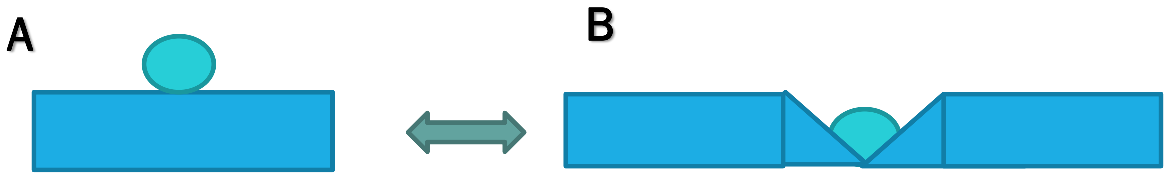
Diffusion length (characteristic length within which the adatom ca move):

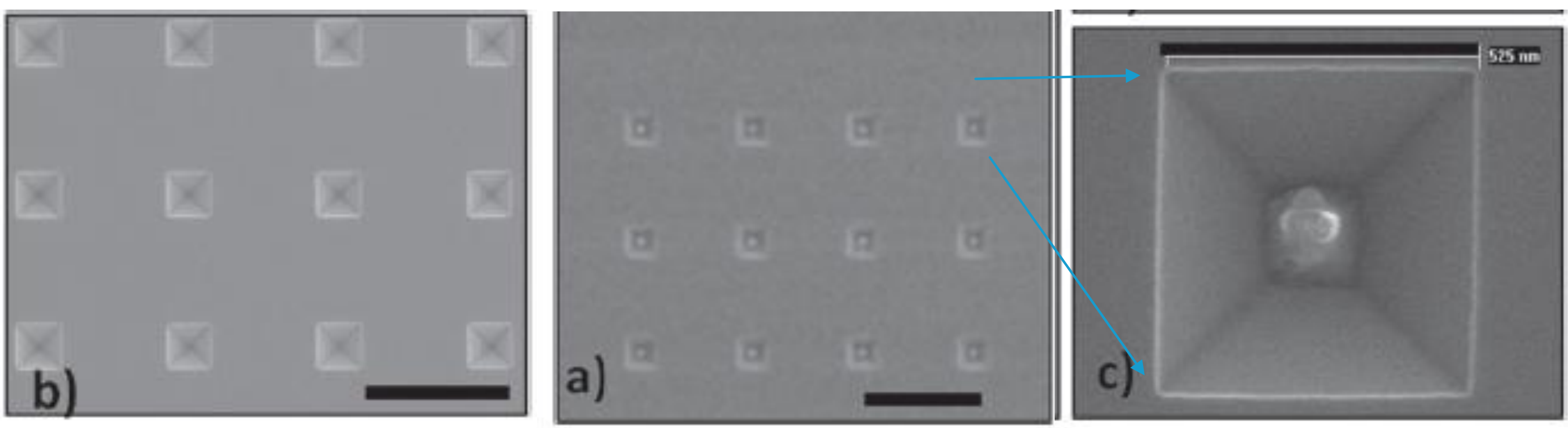
$$\lambda = \sqrt{D\tau} = a\sqrt{\nu_D \tau_0}\ \exp\left(\frac{E_0 - E_D}{kT}\right)$$

Measurable quantity!

BASIC CONCEPTS IN EPITAXY

Surface diffusion& capillarity forces



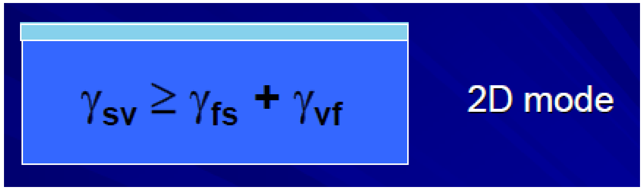


M.Bollani et al, Nanotechnology 25 (2014) 205301

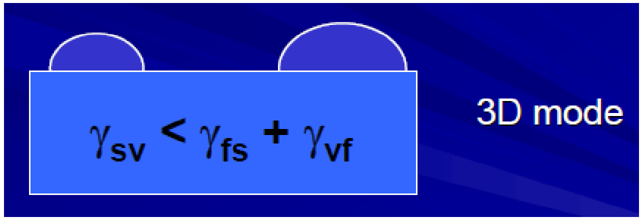
BASIC CONCEPTS IN EPITAXY

Nucleation

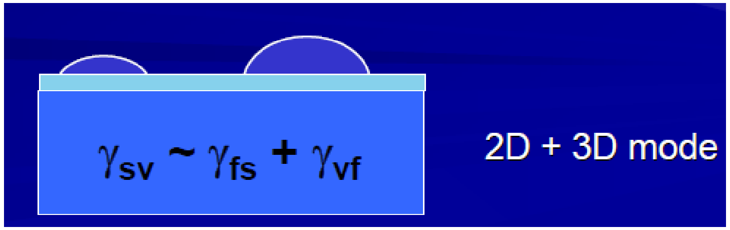
Franck-Van der Merwe: *the interatomic interactions between substrate and film are stronger than those between the different atomic species within the film*



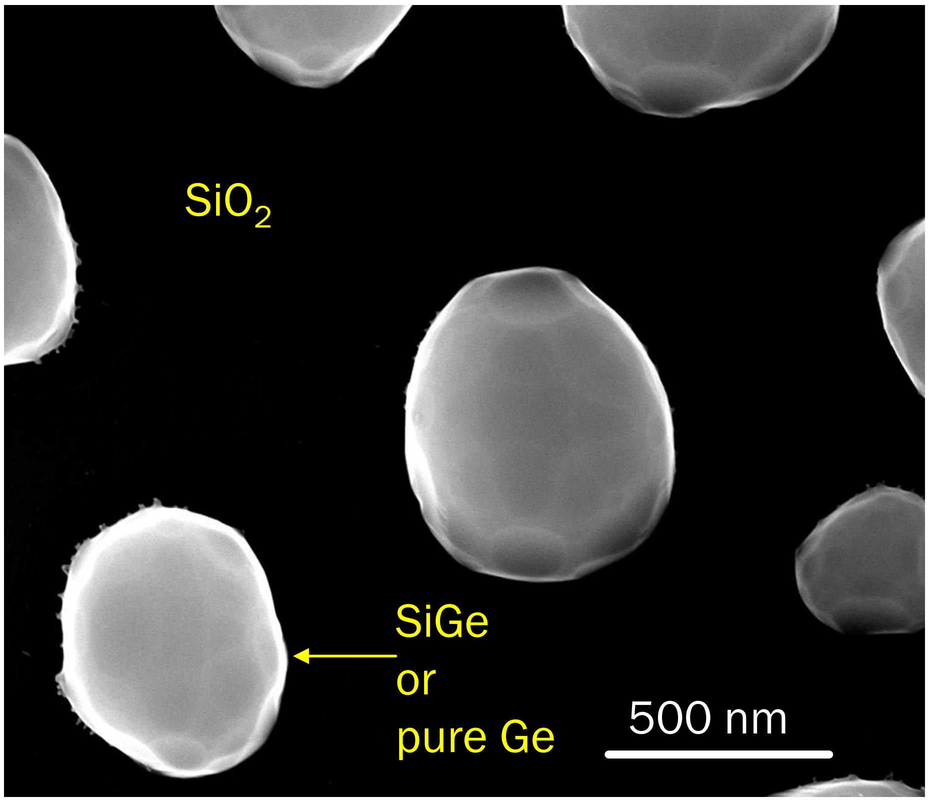
Volmer-Weber: *opposite situation*

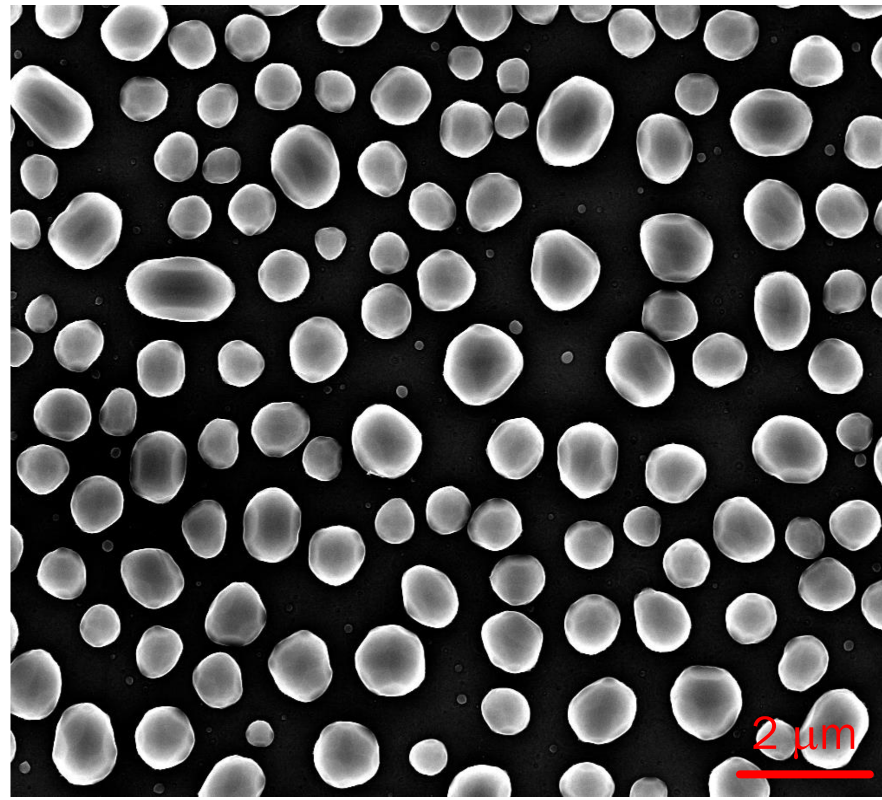


Stranski-Krastanov: *occurs for interaction strengths somewhere in the middle*.

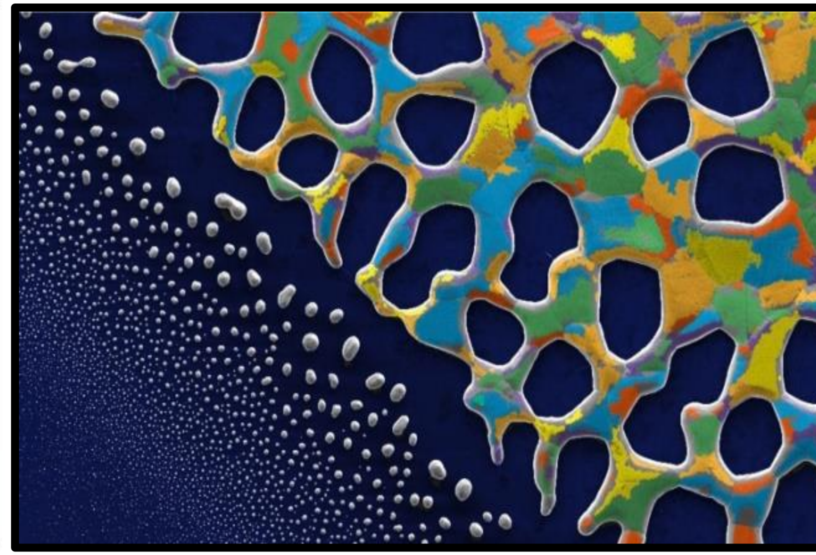


NEW APPROACH TO OBTAIN SINGLE ISLANDS OR MORE COMPLEX SYSTEMS: DEWETTING INSTABILITY IN SEMICONDUCTOR THIN FILMS

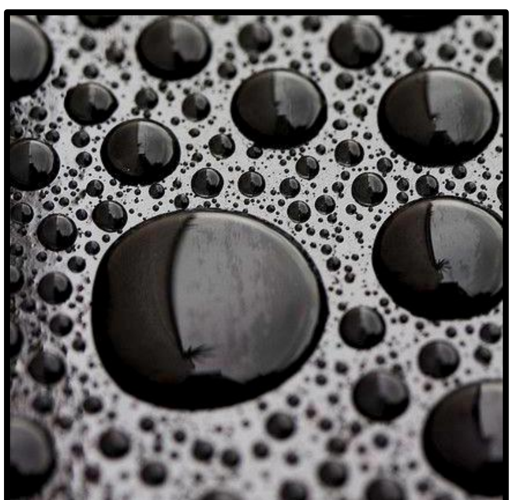




DEWETTING, UBIQUITOUS PHENOMENON IN NATURE:



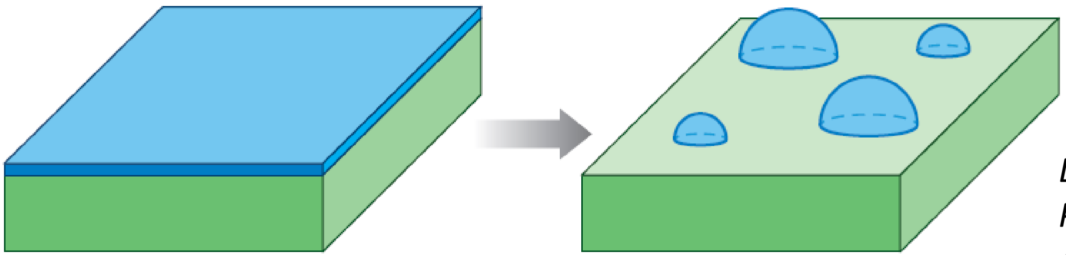
Cu dewetting on SOI



- ❑ Ultra –thin layers are not stable under perturbation
- ❑ It exists a critical thickness below which surface tension dominates and film breaks.

OVERVIEW OF PHENOMENOLOGY

Thin films will spontaneously dewet to form islands when heated to temperatures at which the mobility of the constituent atoms is sufficiently high.



*C. V. Thompson, Ann. Rev. Mat. Res. **42**, 399 (2012)*

Danielson JOURN. APPL. PHYS 2006
Pierre-Louis PHYS. REV LETT 2007, 2009
Jiang, ACTA MAT. 2012
Wang, PHYS. REV B 2015

- Because dewetting requires atomic transport, the rate of dewetting is strongly temperature dependent.

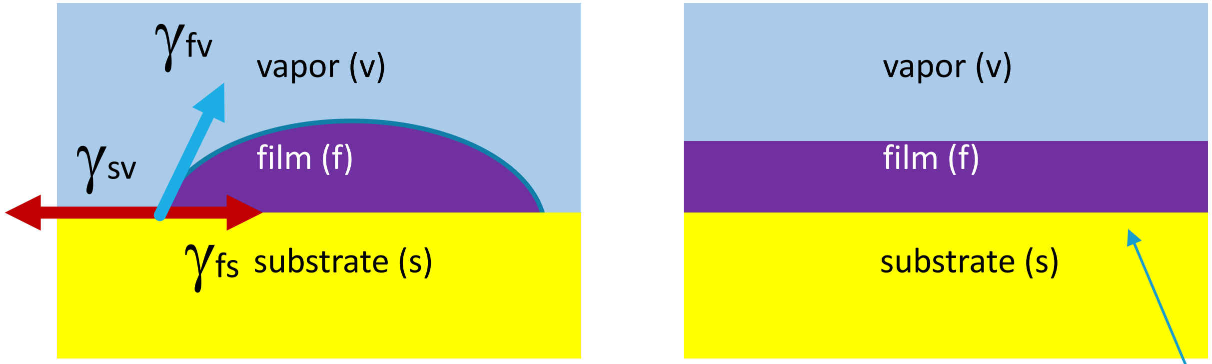
- The size and spacing of the islands that form through dewetting also decrease with h.

- While these trends generally hold, there are many factors that control the specific relationships among T_{dewet}, $R_{islands}$, and h.

CAPILLARY ENERGIES

The surface tension (γ) is an energy per unit area and thus a force per unit length. It applies along the interfaces and minimizes the corresponding (positive) surface energy. The energy minimization for a fixed volume gives the Young-Laplace equation:

$$\gamma_{sv} = \gamma_{fs} + \gamma_{fv} \cos \vartheta$$



-droplets if:

$$\gamma_{sv} \leq \gamma_{fs} + \gamma_{fv}$$

-flat film if:

$$\gamma_{sv} \geq \gamma_{fs} + \gamma_{fv}$$

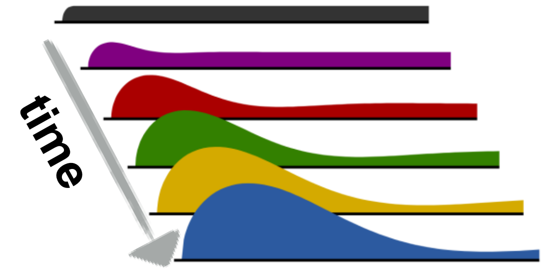
the film will dewet when the rates of the necessary kinetic processes are sufficiently high.

Young equation of the equilibrium contact angle for thin film:

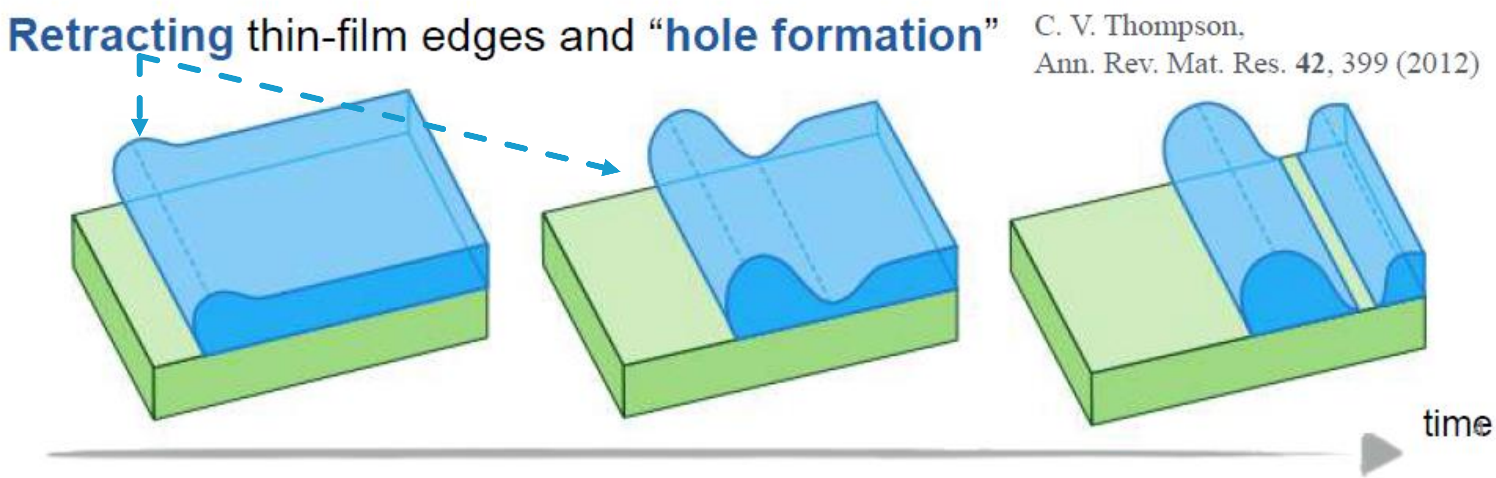
$$\Theta_c = \cos^{-1}\left[\frac{\gamma_{sv} - \gamma_{fs}}{\gamma_{fv}}\right]$$

γ = surface energy density
s = substrate
v = vapour
f = film

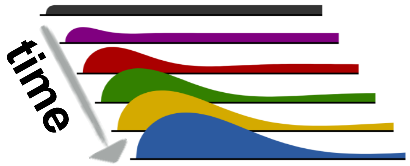
PHENOMENOLOGY OF DEWETTING (I)



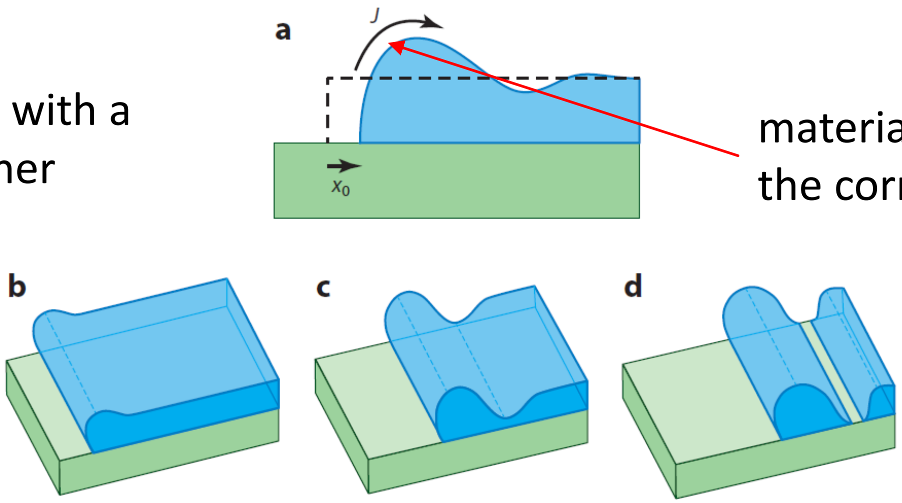
Dewetting generally progresses through at least three distinct stages: hole formation, hole growth and impingement, and ligament breakup.



PHENOMENOLOGY OF DEWETTING (II)



hole edge with a sharp corner

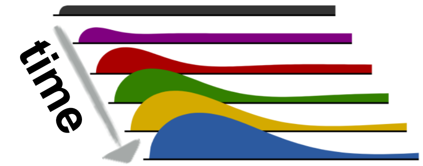


material will be transported from the corner to reduce its curvature.

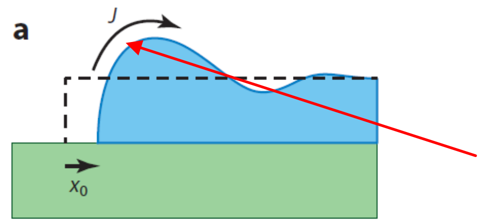
- The curvature of the edge of the film will always be higher than that of the flat surface → a continuing net flux of material from the triple line over the rim of the hole, and out into the flat area surrounding the hole.

- This flux leads to retraction of the edge and to corresponding hole growth!

PHENOMENOLOGY OF DEWETTING (II)



hole edge with a sharp corner



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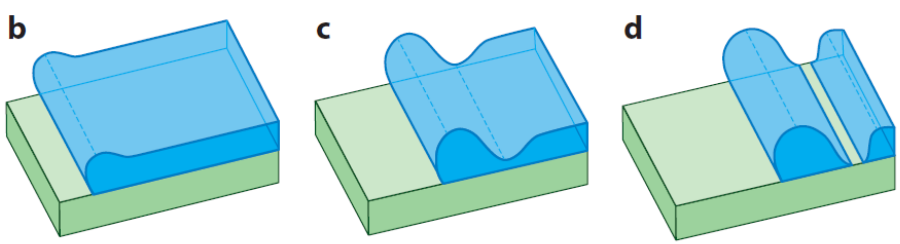
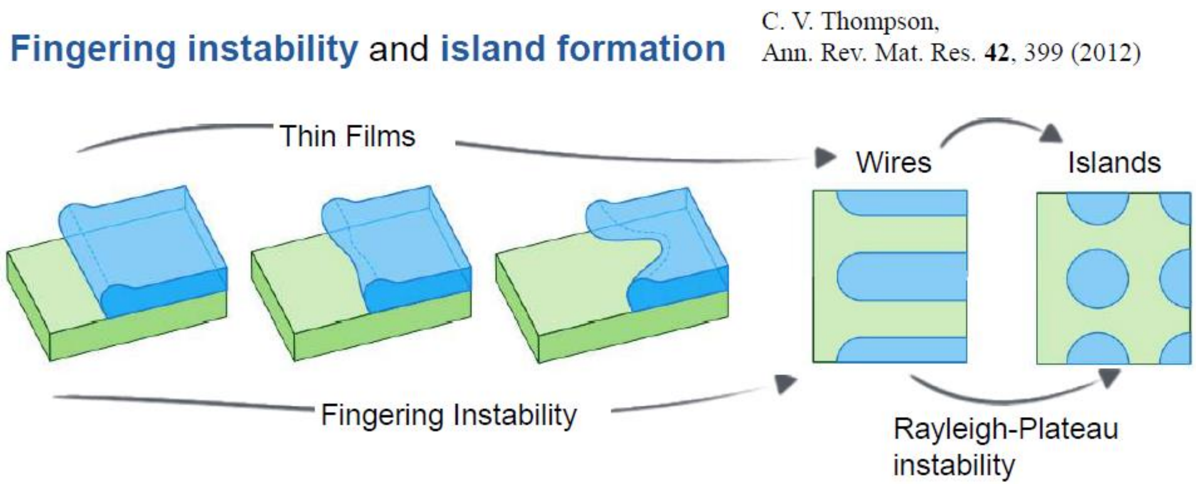


Once a hole of critical size has formed, capillary energies will drive retraction of its edge and the hole will grow. The rate of hole growth is therefore governed by the rate at which the edge retracts and on how the shape of the edge evolves.

PHENOMENOLOGY OF DEWETTING (III)



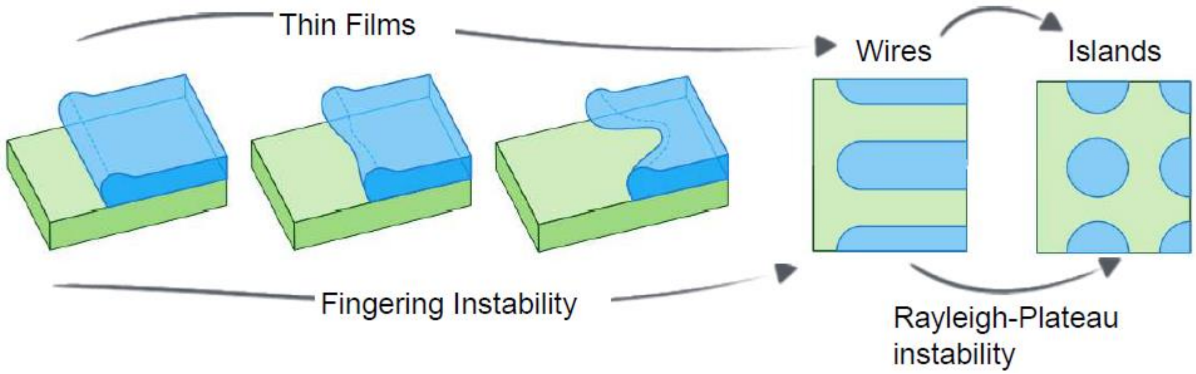
These shapes are unstable

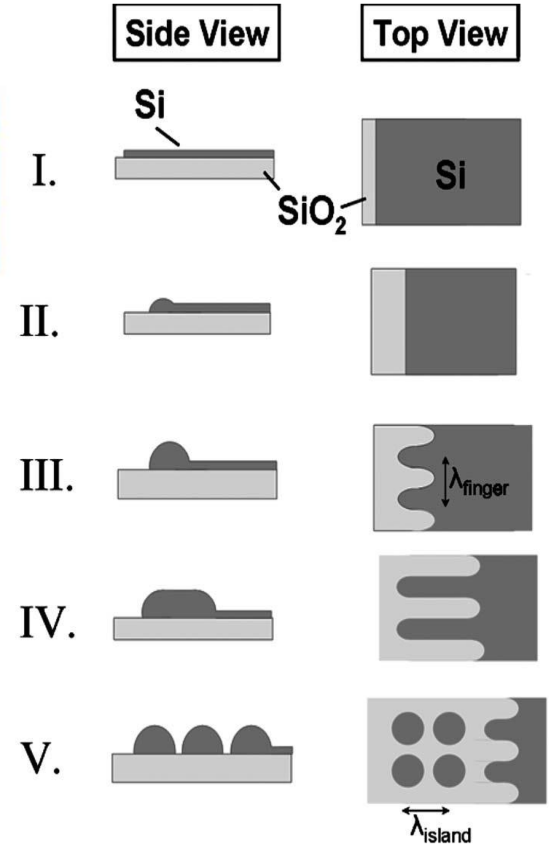
Sphere formation, the free energy decreases

PHENOMENOLOGY OF DEWETTING (III)

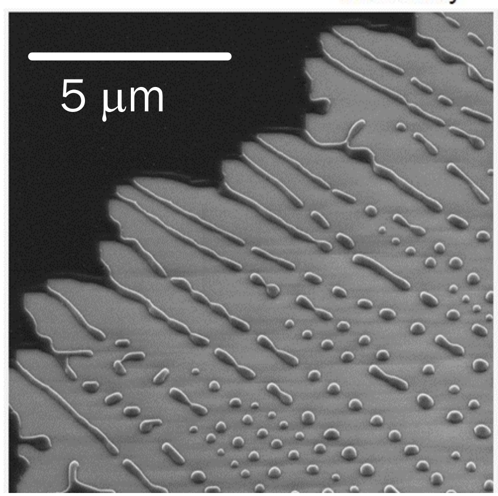
Fingering instability and **island formation**

C. V. Thompson,
Ann. Rev. Mat. Res. **42**, 399 (2012)





The rims of holes tend to remain circular if they interact with neighboring holes at an early stage.
If the holes are sparse, the rims of growing holes may break up into fingers and then into islands.

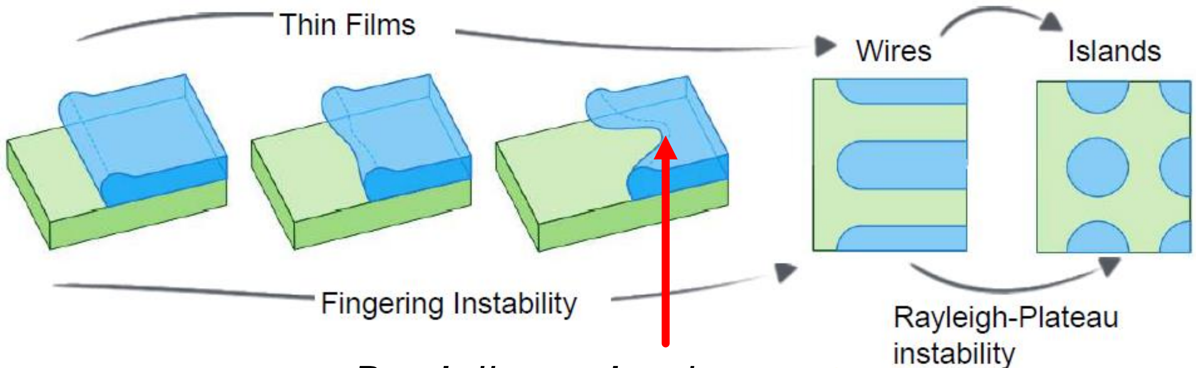


hole growth leads to the development of rims that can break down into wire-like strands through pinch-off or fingering

PHENOMENOLOGY OF DEWETTING (IV)

Fingering instability and **island formation**

C. V. Thompson, Ann. Rev. Mat. Res. **42**, 399 (2012)



Partially strained area

A hole is formed

strain in the material closed to the hole can partially relax

the strain energy decreases

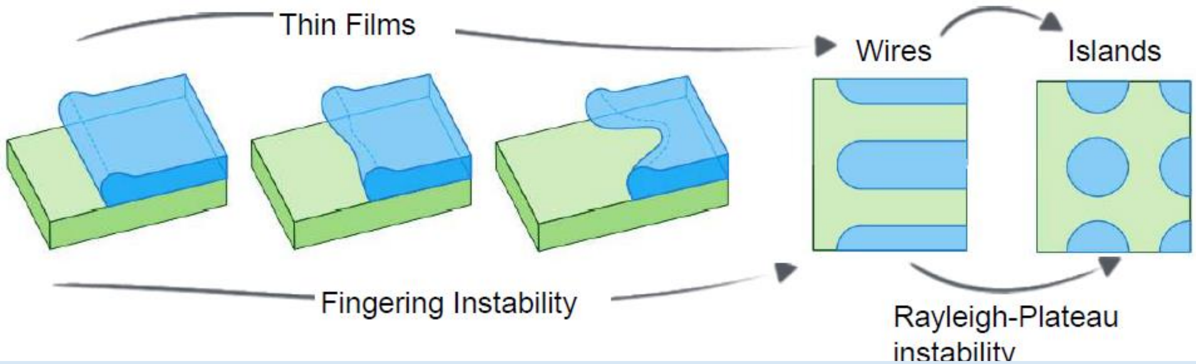
the critical radius values is reduced!

The hole formation is more likely!

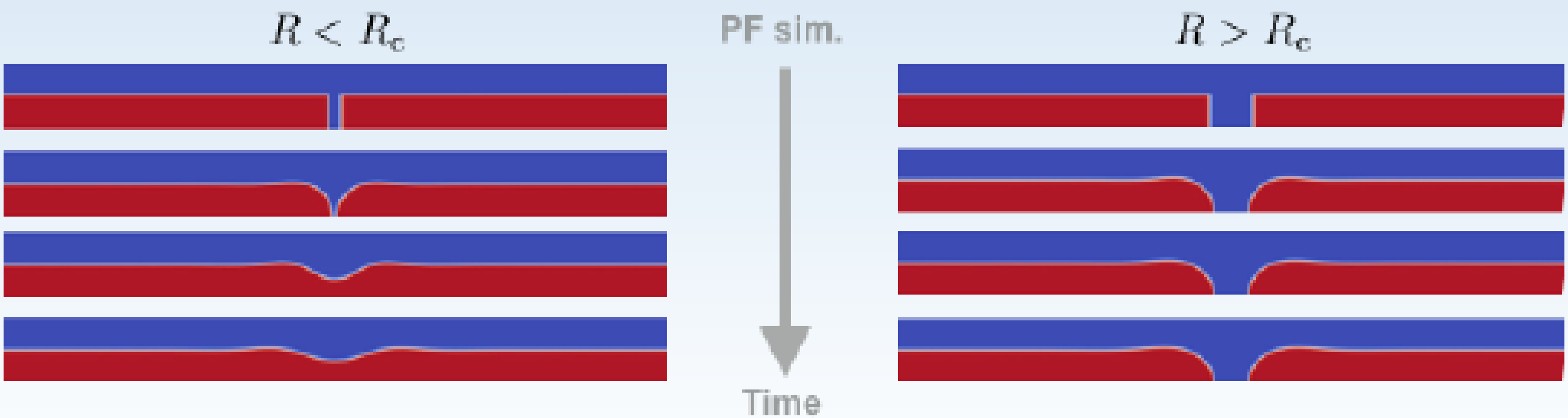
PHENOMENOLOGY OF DEWETTING (IV)

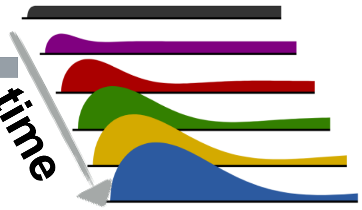
Fingering instability and **island formation**

C. V. Thompson, Ann. Rev. Mat. Res. **42**, 399 (2012)



- Critical Void Radius





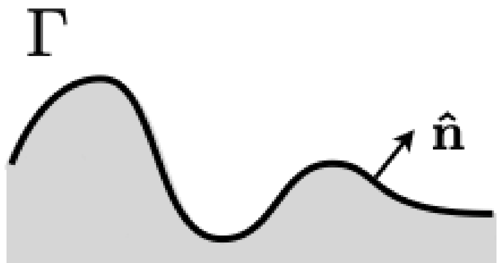
PHENOMENOLOGY OF DEWETTING (II)

The dominant transport mechanism for solid films is surface self-diffusion. For surfaces with **isotropic** energies, the flux due to curvature-driven surface self-diffusion is described by:

$$J = -\left(\frac{D_s \gamma_f N_s \Omega}{kT}\right) \nabla_s \kappa ,$$

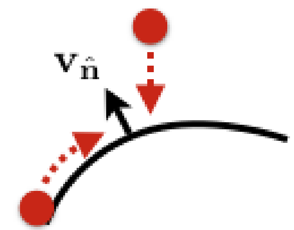
Ds is the surface diffusivity,
γ f is the surface energy,
Ns is the number of surface atoms per area,
Ω is the atomic volume,
k is Boltzmann's constant,
T is temperature,
κ is the local surface curvature.

PHENOMENOLOGY OF DEWETTING (II)



normal-velocity field

$$\mathbf{v}_{\hat{\mathbf{n}}} = \hat{\mathbf{n}} \left[\frac{d\mathbf{x}}{dt} \cdot \hat{\mathbf{n}} \right]$$



$$J = -\left(\frac{D_s \gamma_f N_s \Omega}{kT} \right) \nabla_s \kappa ,$$

Ds is the surface diffusivity,
γ f is the surface energy,
Ns is the number of surface atoms per area,
Ω is the atomic volume,
k is Boltzmann's constant,
T is temperature,
κ is the local surface curvature.

$$\mu \propto \kappa$$

$$v_{\hat{\mathbf{n}}} = -\nabla_\Gamma \cdot \mathbf{j} \qquad \mathbf{j} = -M \nabla_\Gamma \mu$$

Continuity equation — Onsager's linear law

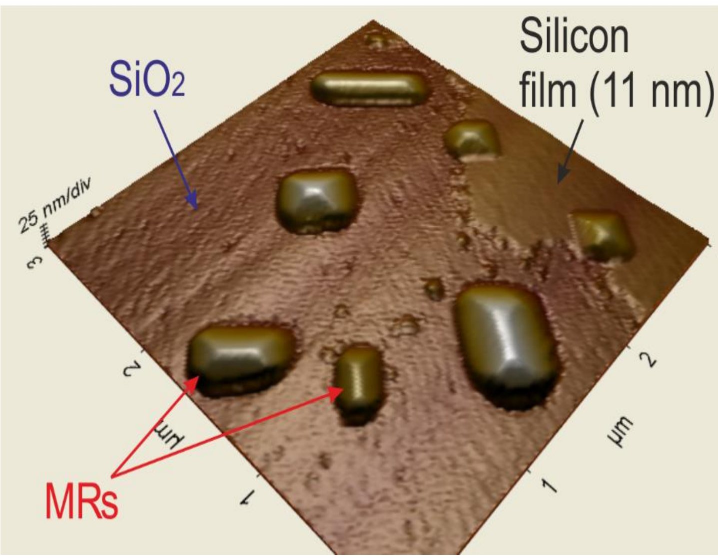
$$v_{\hat{\mathbf{n}}} = \nabla_\Gamma \cdot [M \nabla_\Gamma \mu]$$

- Mass is conserved
- Evolution towards the minimization of the surface energy

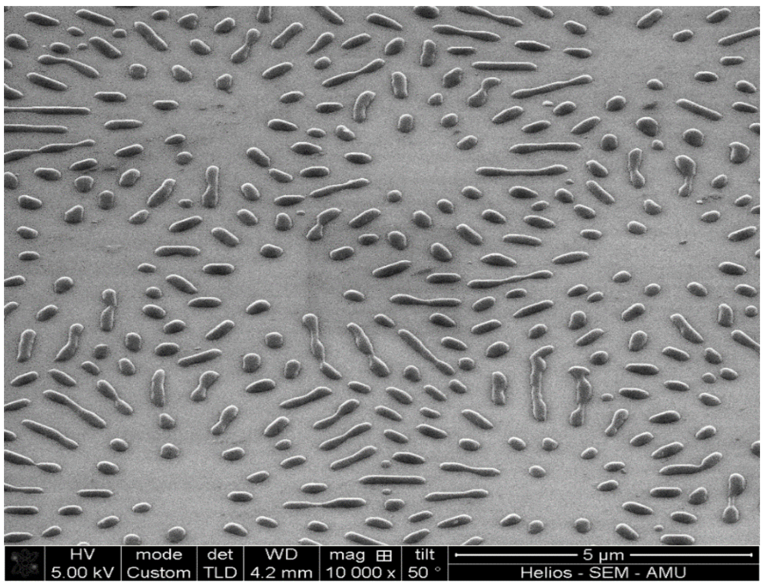
Mullin's equation $\quad v_{\hat{\mathbf{n}}} \propto \nabla_\Gamma^2 \kappa$

INSTABILITY OF THIN FILMS: SOI CASE

-ULTRA-THIN SOI (~ 10 nm, CYSTALLINE)
-ANNEALED AT HIGH TEMPETARURES (700-750 C)
-IN ULTRA-HIGH VACUUM (< 10^{-9} torr)



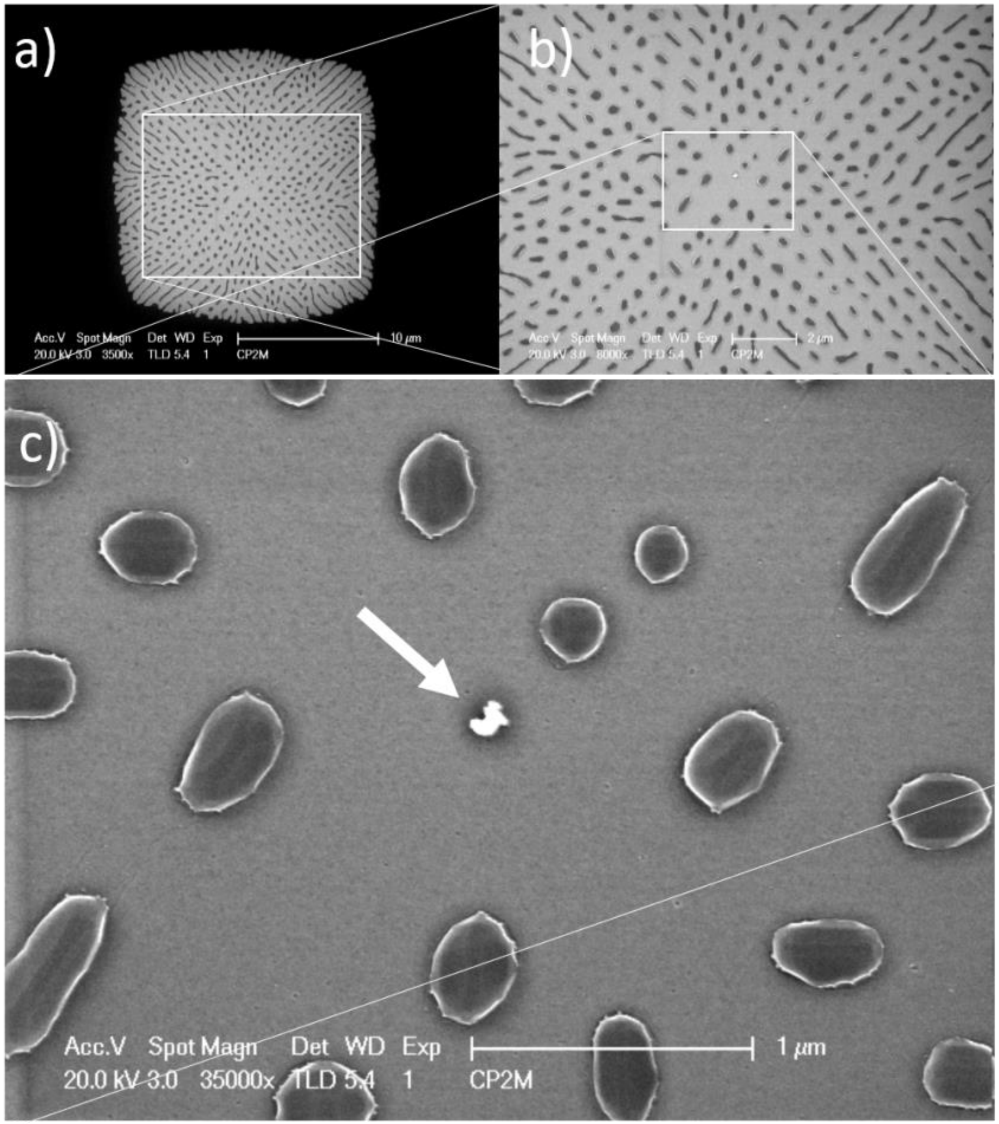
BUSSMAN , New Journal of Physics 2011

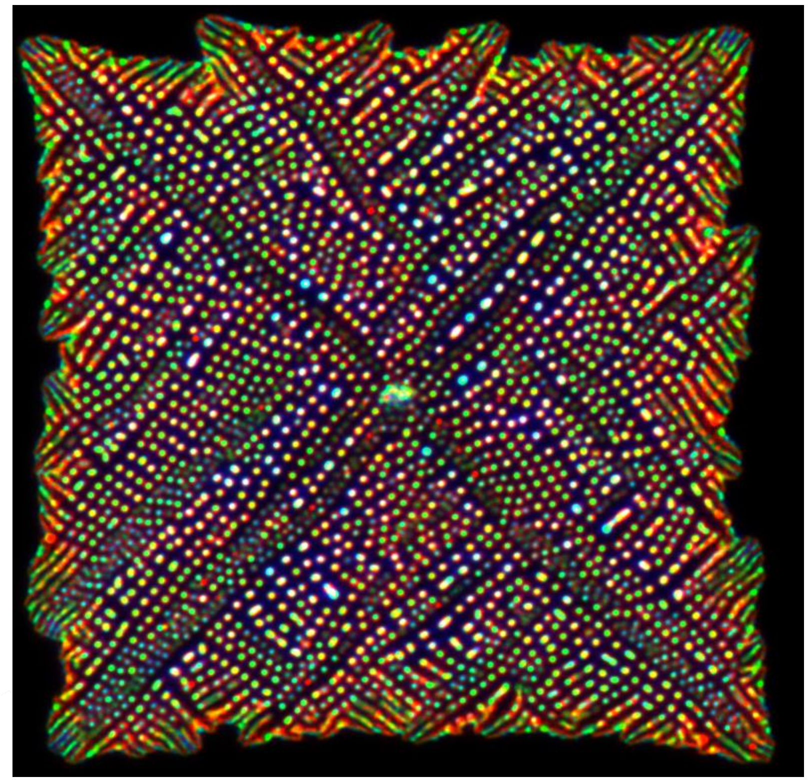


ABBARCHI ,ACS nano 2014

In real systems thermal fluctuation and non-idealities actually make dewetting a rather disordered phenomenon

DEFECT AS A STARTING POINTS OF MASS TRANSPORT

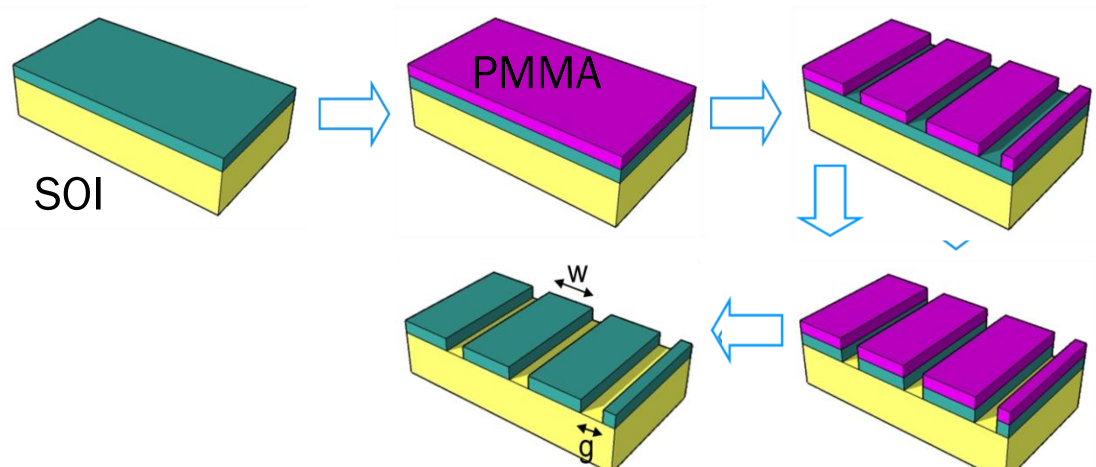


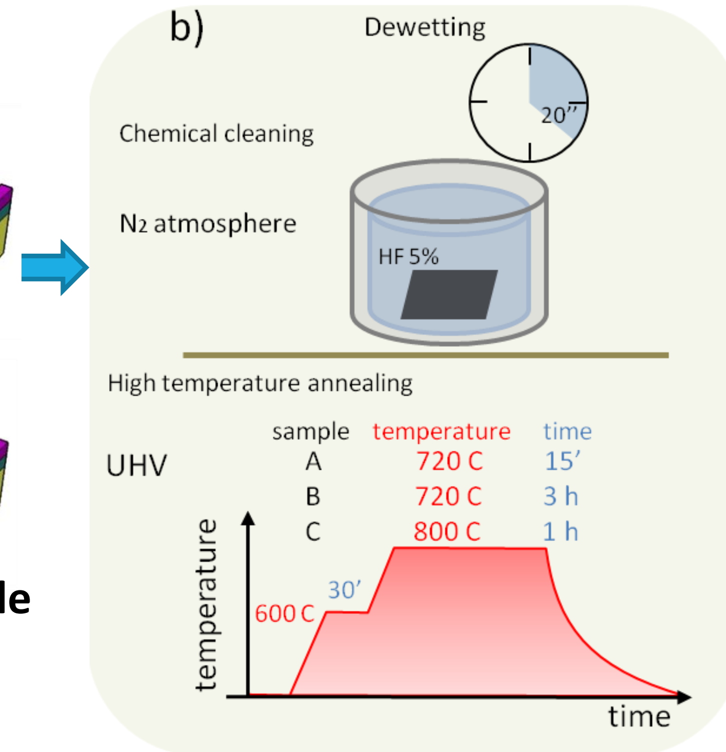


HOW TO CONTROL THE ULTRA-THIN FILM DEWETTING?

Pattern assisted dewetting

12nm of Si on 25nm of SiO_2

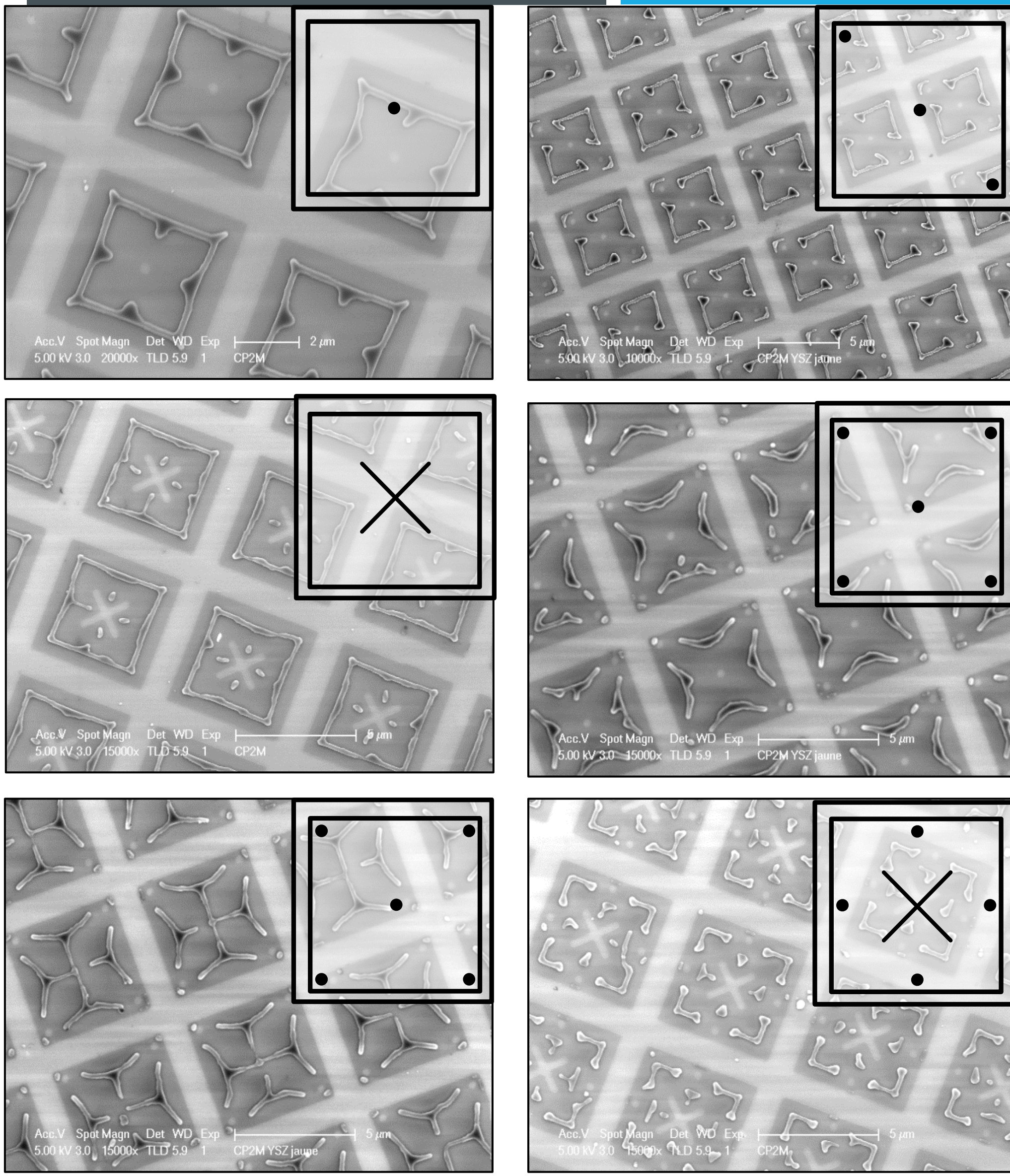


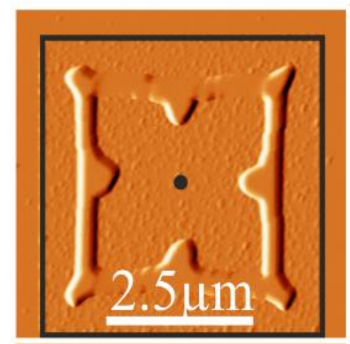


All patches are etched along the [110] direction (= stable dewetting front)

M. Abbarchi, M.Naffouti, M.Lodari, M.Salvalaglio, A.Voigt, M.Bouabdellaoui, Abdelmalek Benkouider, L.Favrè, I.Berbezier, David Grosso, M.Bollani, Microelectronic Engineering, Volume 190, Pages 1-6 (2018)

Complex dewetting scenario

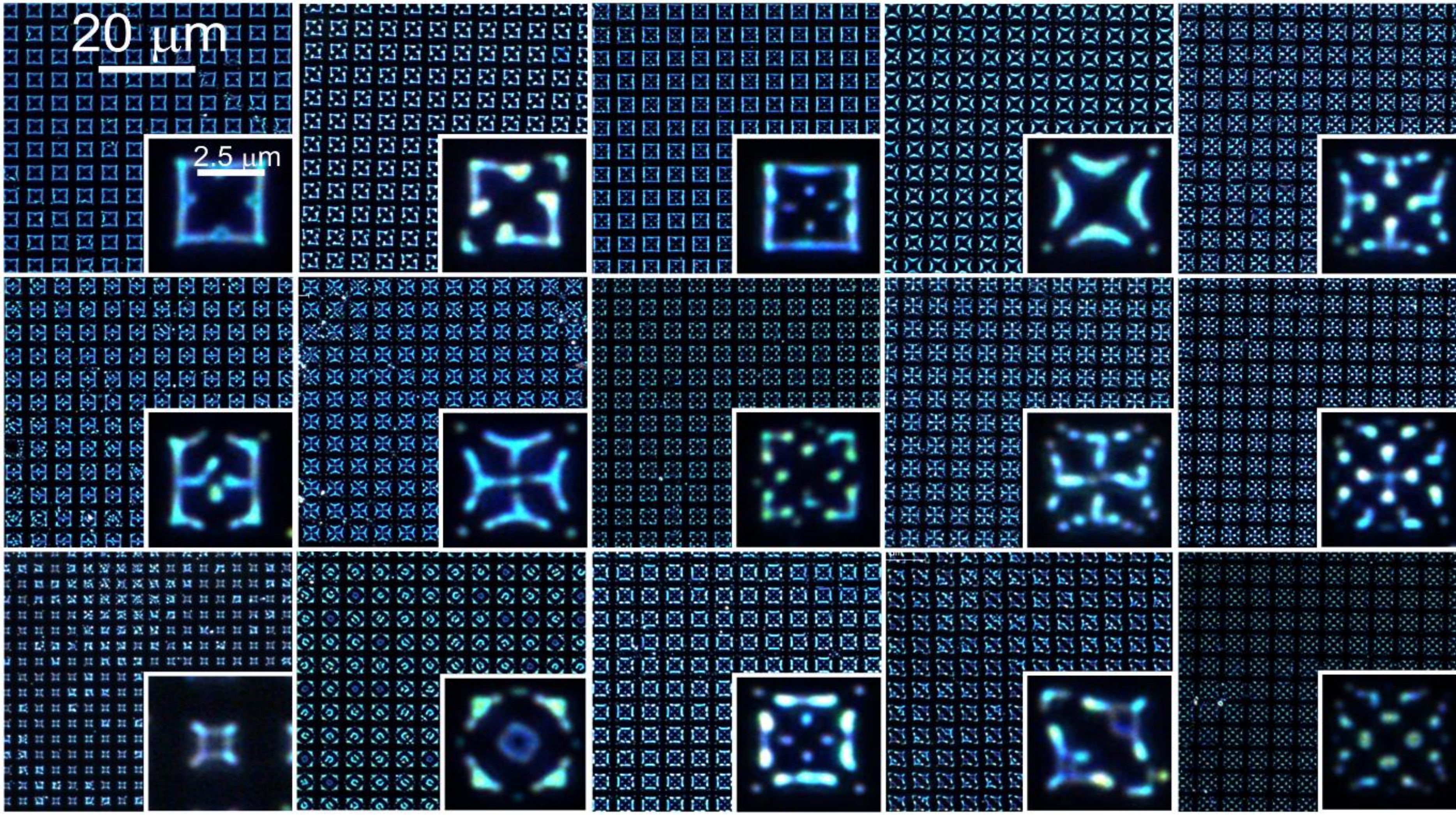




Solid state dewetting forms monocrystalline and facetted structures, free from defects and from the typical roughness produced by conventional etching methods;

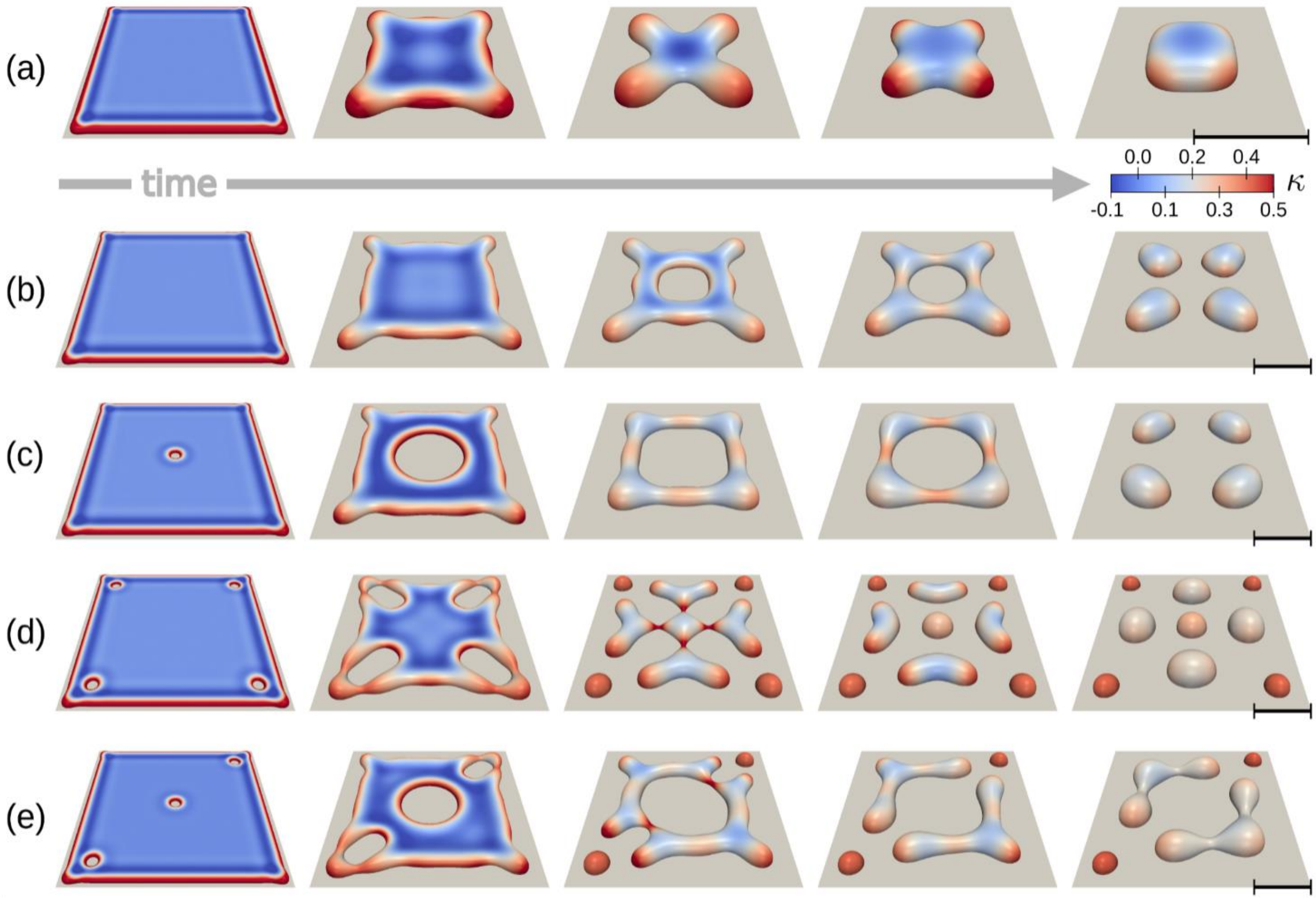
M. Naffouti, R. Backofen, M. Salvalaglio, M. Lodari, A. Voigt, T. David, L. Favre, I. Berbezier, D. Grosso, M. Abbarchi, M. Bollani, Science Advance, 10 Nov 2017, Vol. 3, no. 11, eaao1472

Versatility and stability of the method:



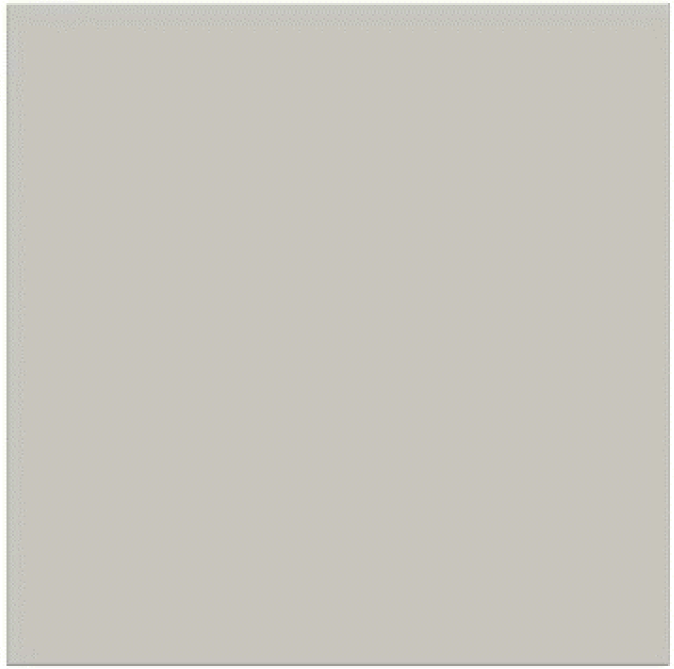
M. Naffouti, R. Backofen, M. Salvalaglio, M. Lodari, A. Voigt, T. David,L. Favre, I. Berbezier, D. Grosso, M. Abbarchi, M. Bollani, Science Advance, 10 Nov 2017, Vol. 3, no. 11, eaao1472

3D numerical simulation: phase –field model

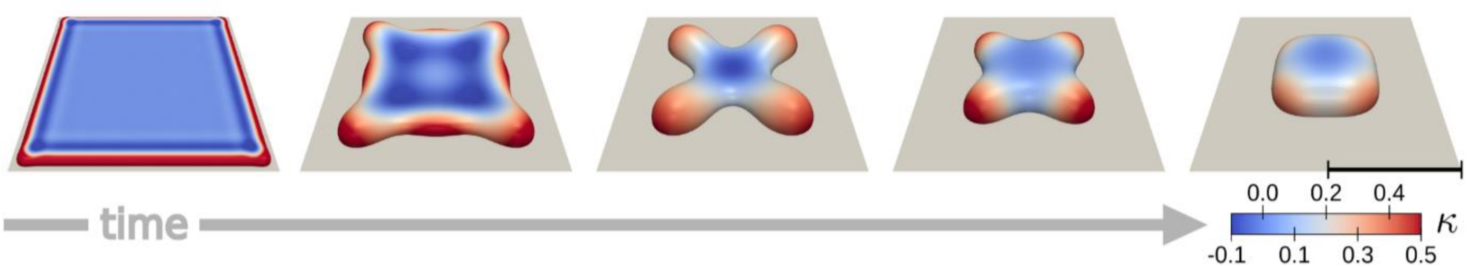


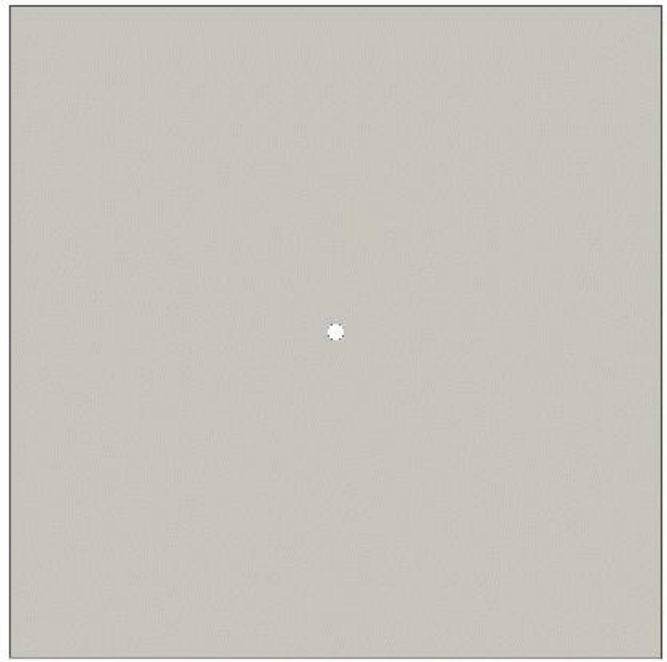
by Institute of Scientific Computing, Technische Universität Dresden, Germany

M. Naffouti, et al., PHYSICAL REVIEW MATERIALS 3, 103402 (2019)

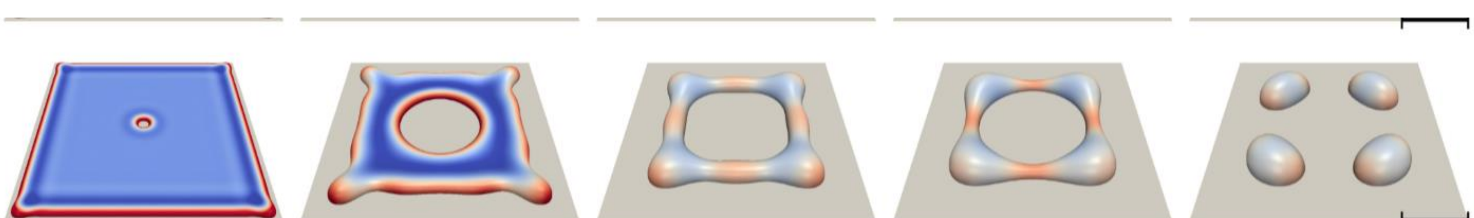


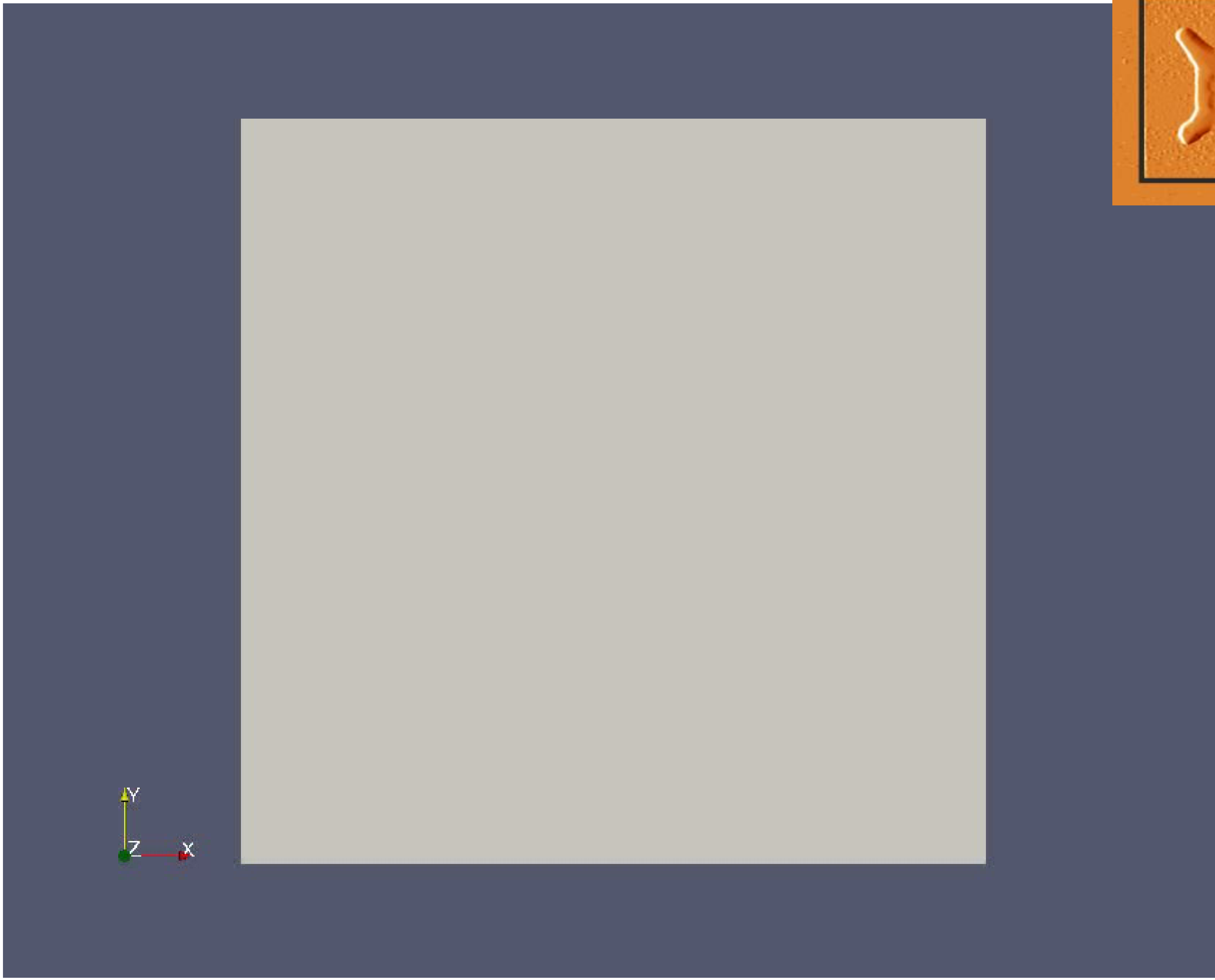
(a)





(c)




Y
Z
X


RESEARCH AND INNOVATION, *DILEMMA* ON NANOTECHNOLOGY

The Horizon Europe program represents a paradigm shift with respect to the past introducing a strong focus on innovation.

- Two pillars of the European program and numerous instruments are aimed to promote and develop innovation processes.

- The effects on society and the productive system are many cases below expectations

RESEARCH AND INNOVATION, *DILEMMA* ON NANOTECHNOLOGY

Research:
A method of discovering knowledge about the natural world based in making falsifiable predictions (*hypotheses*), testing them empirically, and developing *theories* that match known data from repeatable physical experimentation.

- A creation process
- Well-defined actors for training and working fields
- Linear and simple process
- Even in case of failure an useful result is obtained
- The destination field of the final product is always, in first approximation, in research scope
- Use money to produce knowledge

RESEARCH AND INNOVATION, *DILEMMA* ON NANOTECHNOLOGY

Innovation is a discontinuity in knowledge, and in know-how, which generates a significant increase in productivity: a parity of resources is doing more things (**development**) or doing the same with fewer resources (**sustainability**)

- A creative/disruptive process
- Actors with many and different competences and skills
- Not linear process with many driven forces
- A failure is total defeat
- The final scope is the society/market
- Use knowledge to produce money

To unlock potential benefits at the most, it is necessary to enhance the track record in transforming breakthroughs into commercially valuable innovations.

RESEARCH AND INNOVATION, *DILEMMA* ON NANOTECHNOLOGY

- *A creation process*
- *Well-defined actors for training and working fields*
- *Linear and simple process*
- *Even in case of failure an useful result is obtained*
- *The destination field of the final product is always, in first approximation, in research scope*
- *Use money to produce knowledge*

- *A creative/disruptive process*
- *Actors with many and different competences and skills*
- *Not linear process with many driven forces*
- *A failure is total defeat*
- *The final scope is the society/market*
- *Use knowledge to produce money*

To unlock potential benefits at the most, it is necessary to enhance the track record in transforming breakthroughs into commercially valuable innovations.

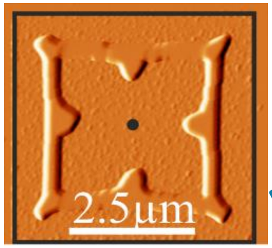
RED QUEEN EFFECT

“Well, in our country," said Alice, still panting a little, "you'd generally get to somewhere else— if you run very fast for a long time, as we've been doing”

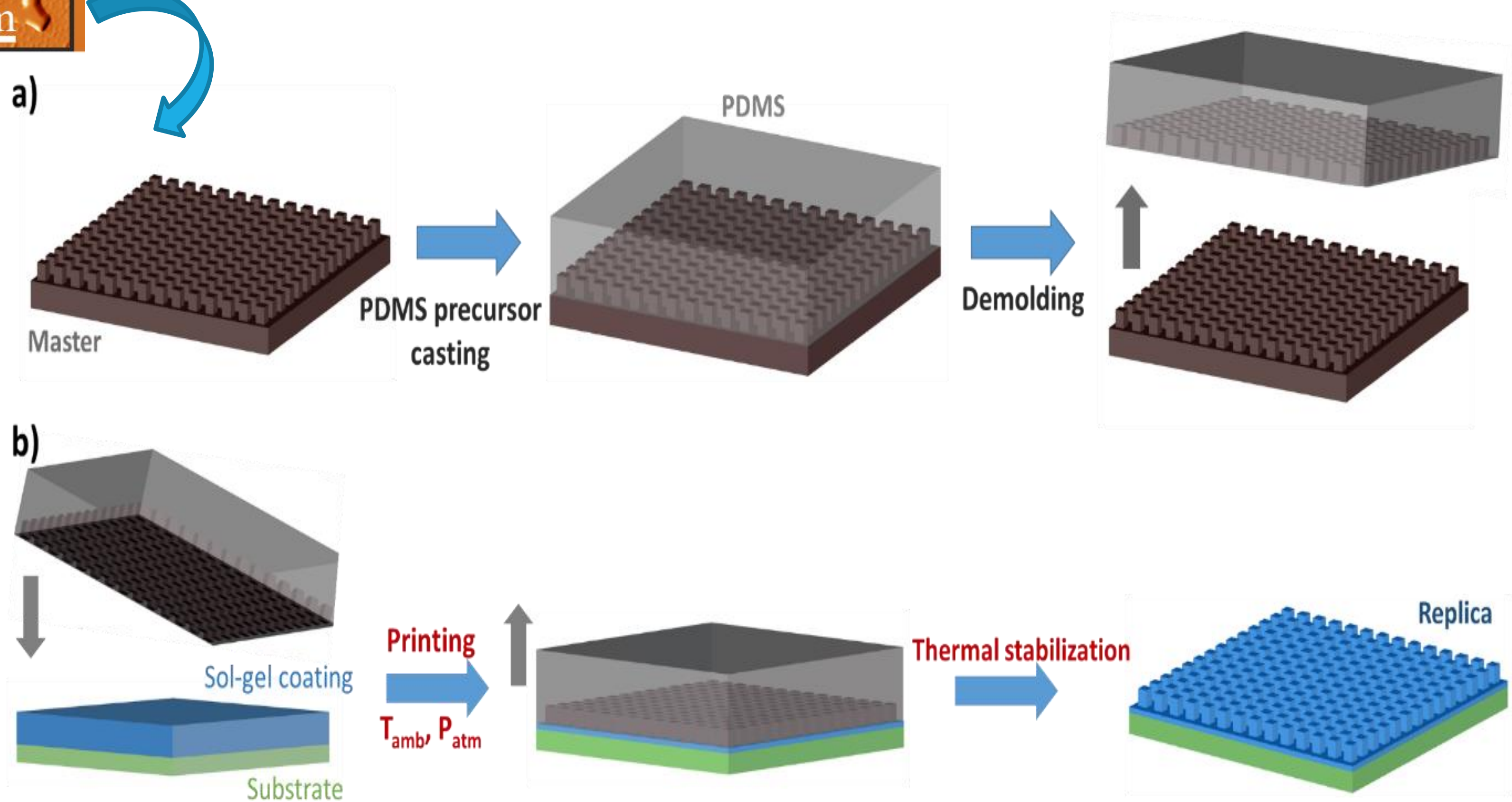
“My dear, here we must run as fast as we can, just to stay in place. And if you wish to go anywhere you must run twice as fast as that”

Lewis Carroll, 1865
«Alice in Wonderland»

Application : Soft Nanoimprint lithography process:



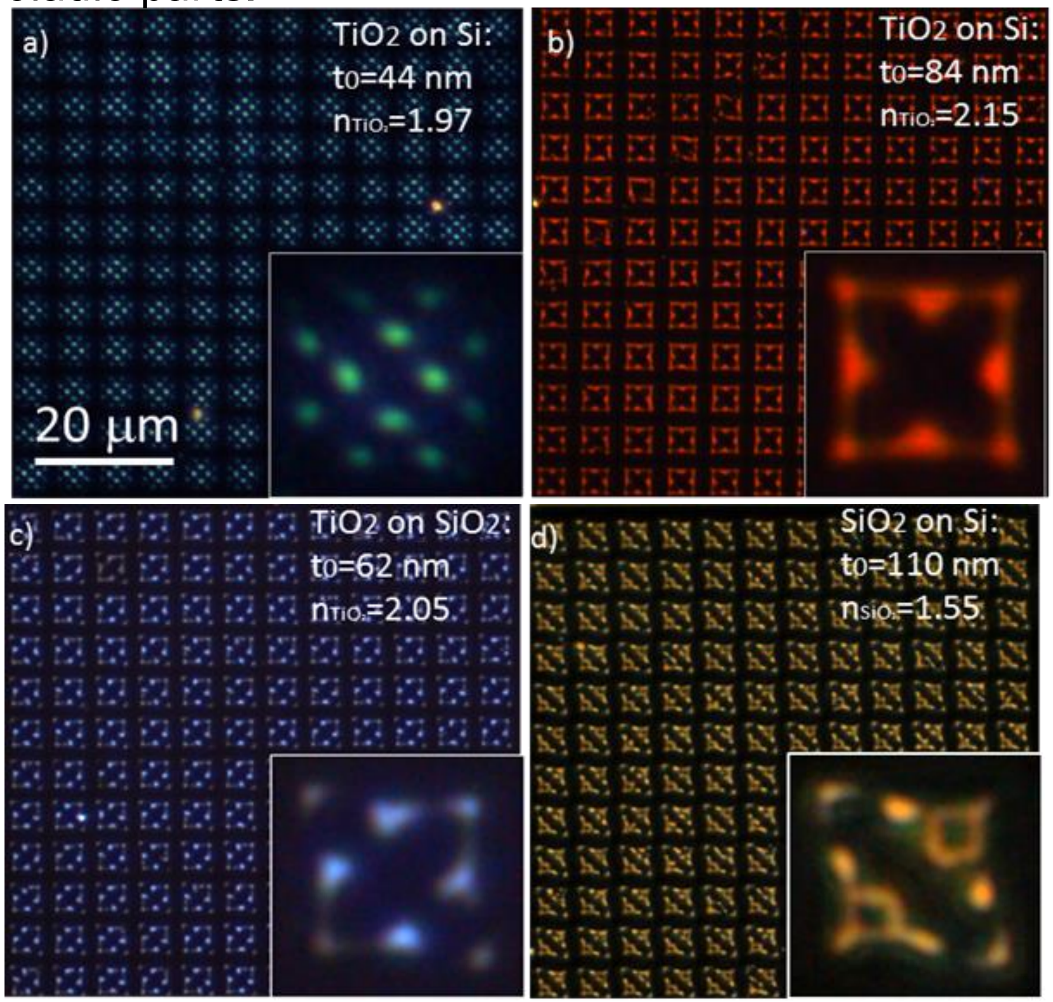
a) *Fabrication of the mold from the master.*
b) *Soft-NIL printing process.*



Materials which do not usually undergo dewetting

Soft Nanoimprint lithography process:

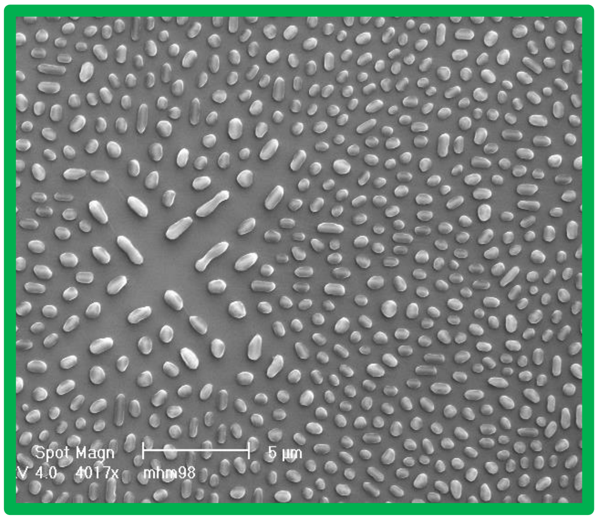
Dark field image of a SiO_2 motif nanoimprinted on a 110 nm thick xerogel: on each figure are reported the material of the nano-imprinted motif, the substrate in use, the initial thickness of the xerogel t_0, and the refractive index of the material after evaporation of the volatile parts.

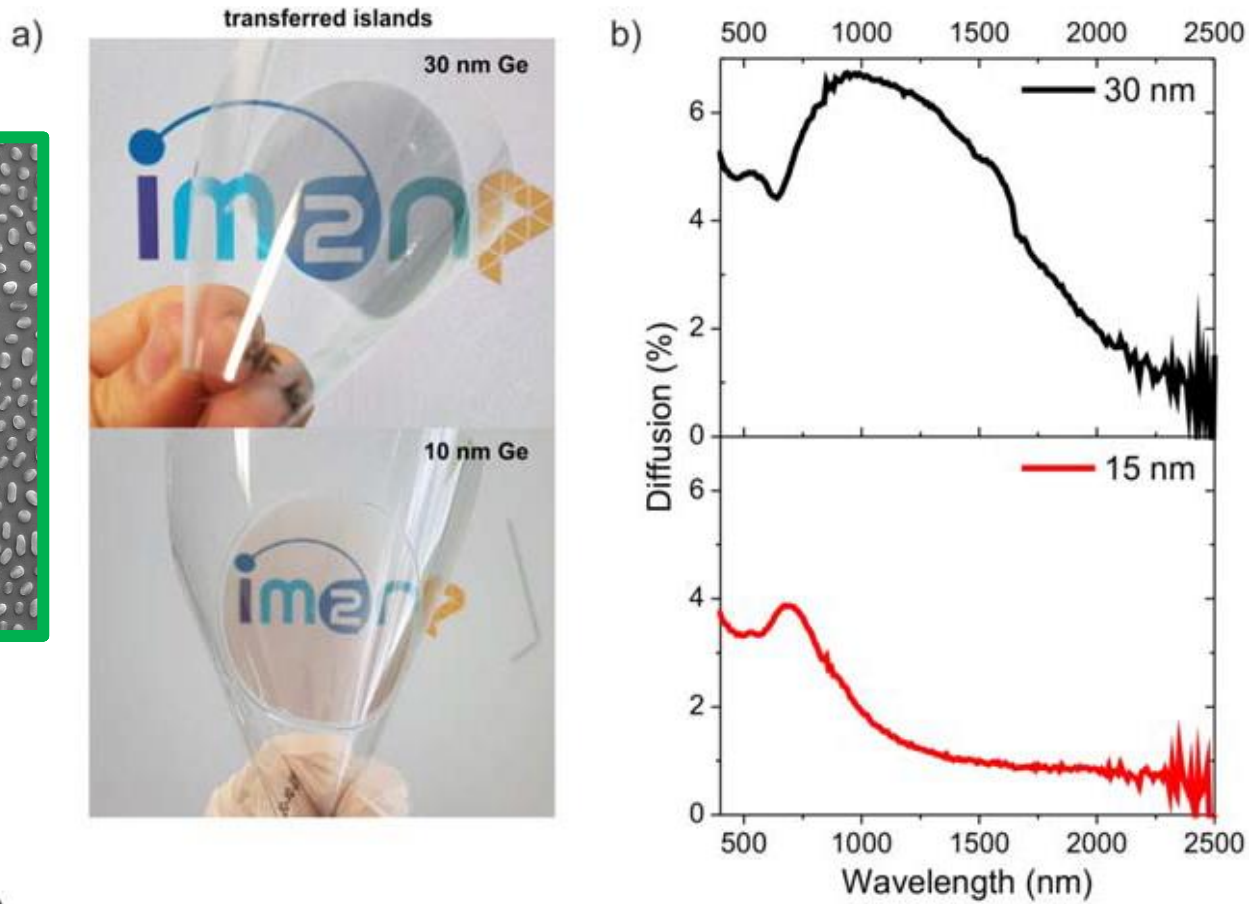


M. Naffouti, R. Backofen, M. Salvalaglio, M. Lodari, A. Voigt, T. David,L. Favre, I. Berbezier, D. Grosso, M. Abbarchi, M. Bollani, Science Advance, 2017, Vol. 3, no. 11, eaao1472

Flexible photonic devices based on dielectric antennas

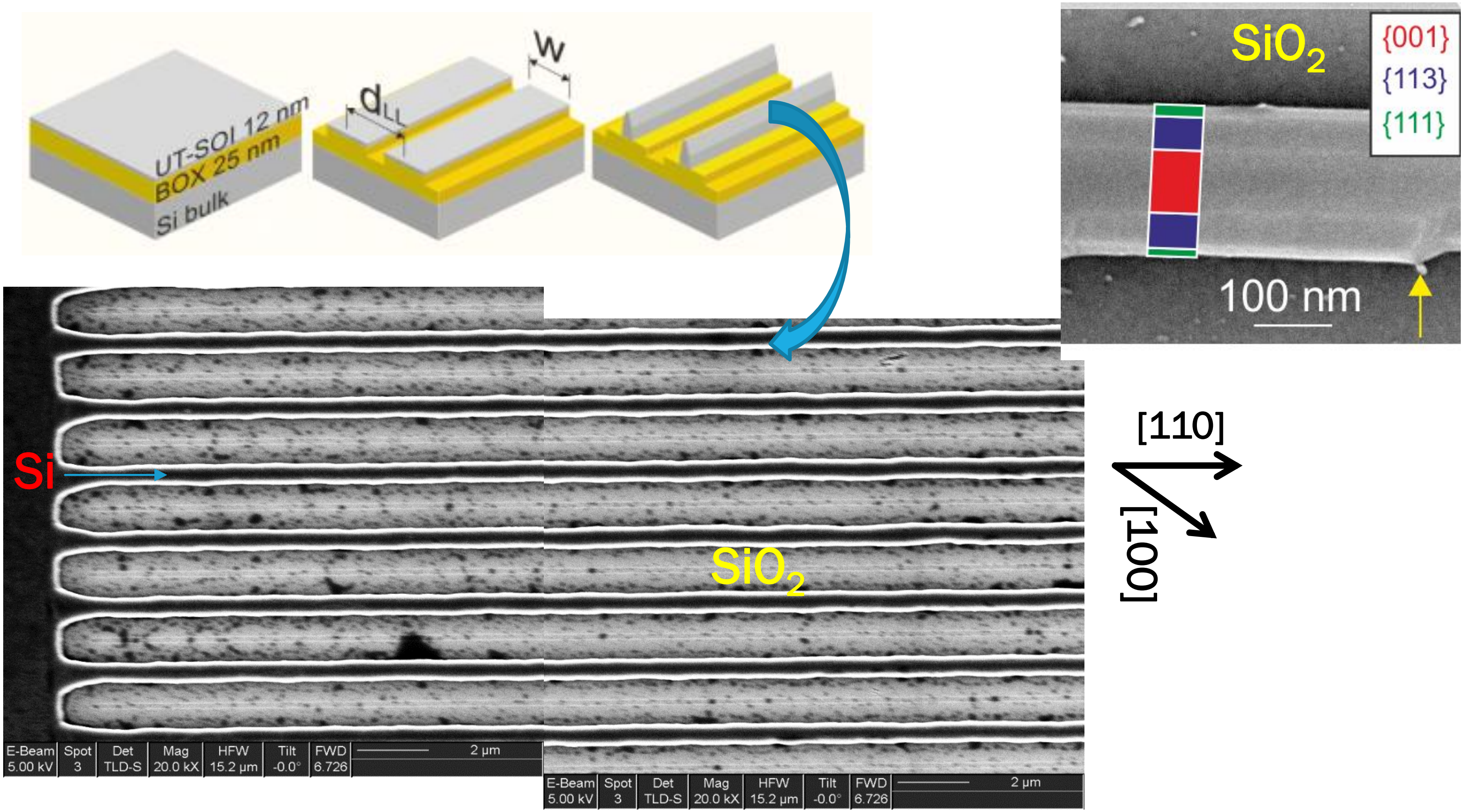
Simple, low cost and efficient protocols for fabricating $Si_{1-x}Ge_x$-based, sub-micrometric dielectric antennas over record scales (50mmwafers) with ensuing hybrid integration into different plastic supports.





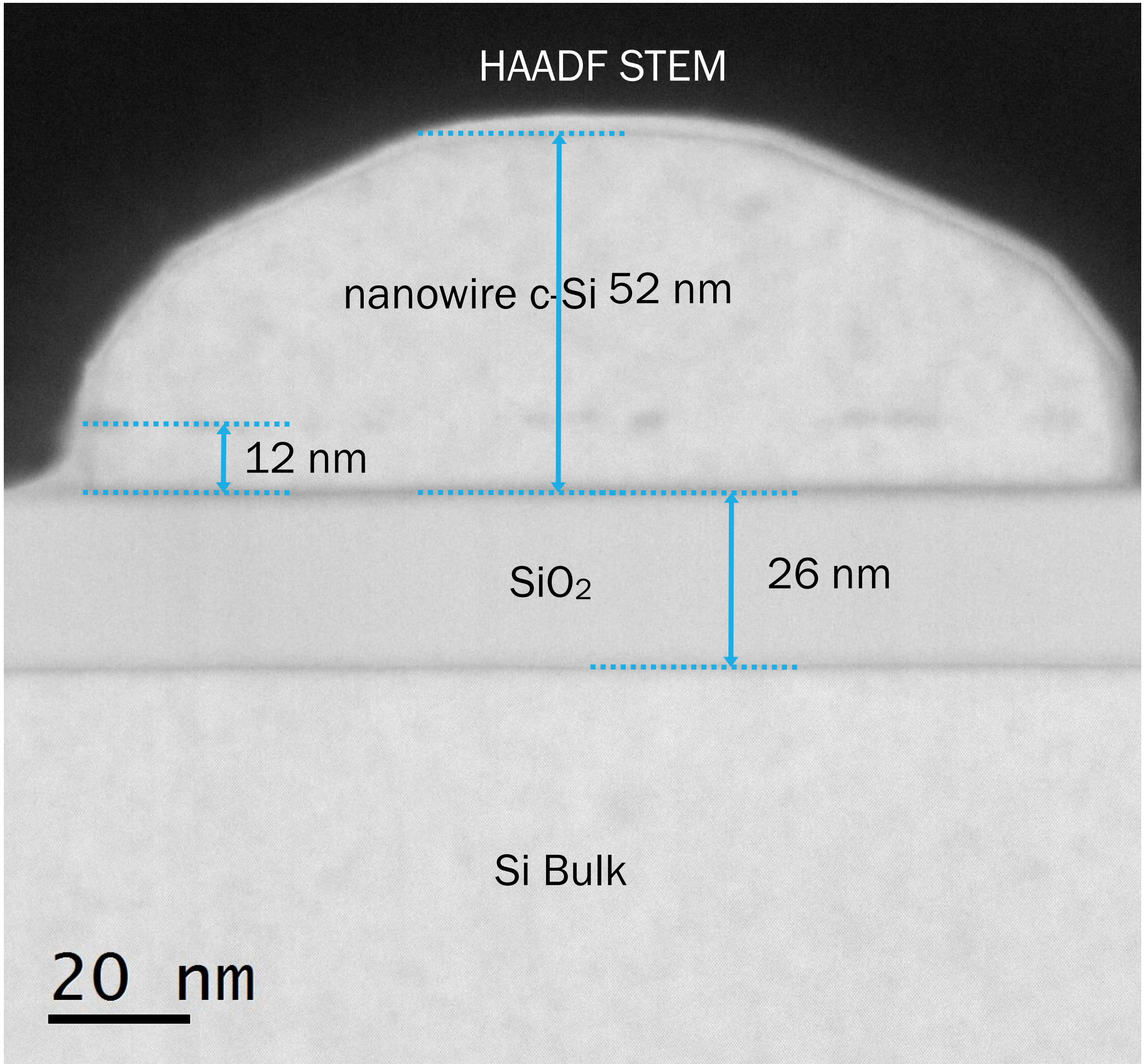
Abdennacer Benali *et al* 2020 *J. Phys. Photonics* **2** 015002

Ultra-long dewetted nano-wires



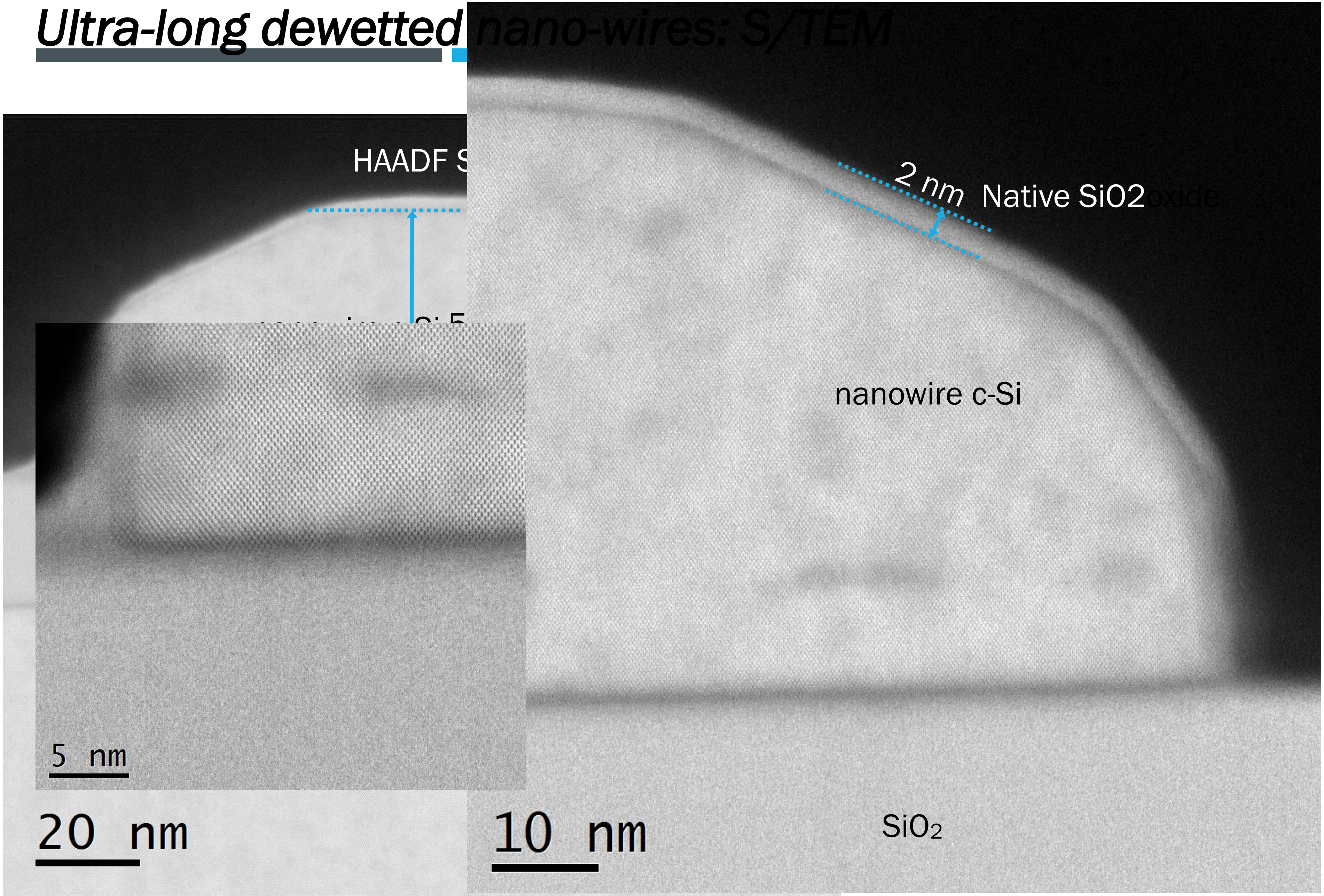
M.Bollani,M.Salvalaglio,A.Benali,M.Bouabdellaoui,M. Naffouti,M.Lodari, S.Di Corato, A.Fedorov, A.Voigt,L. Favré, D.Grosso,G.Nicotra,A.Mio,I.Berbezier,M.Abbarchi, Nat Commun 10, 5632 (2019)

Ultra-long dewetted nano-wires: S/TEM



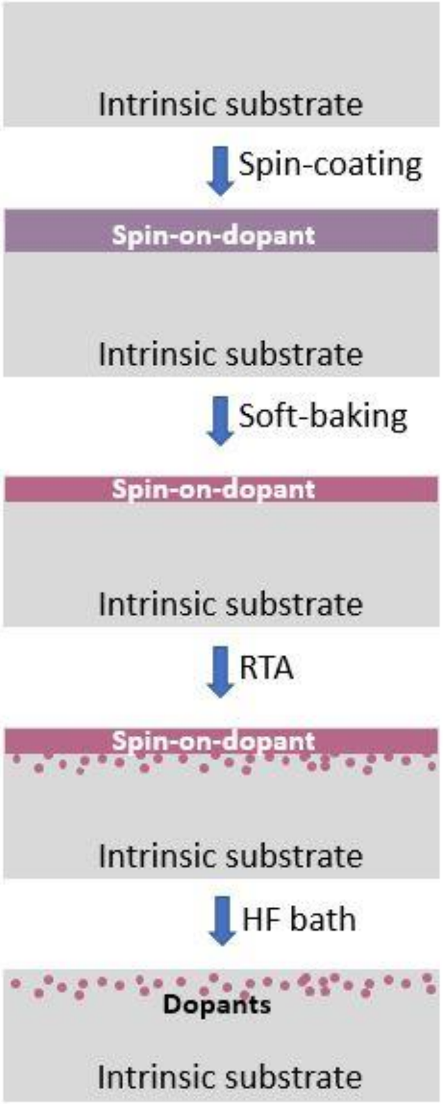
M.Bollani,M.Salvalaglio,A.Benali,M.Bouabdellaoui,M. Naffouti,M.Lodari, S.Di Corato, A.Fedorov, A.Voigt,L. Favré, D.Grosso,G.Nicotra,A.Mio,I.Berbezier,M.Abbarchi, *Nature Comm*. 10, 5632 (2019)

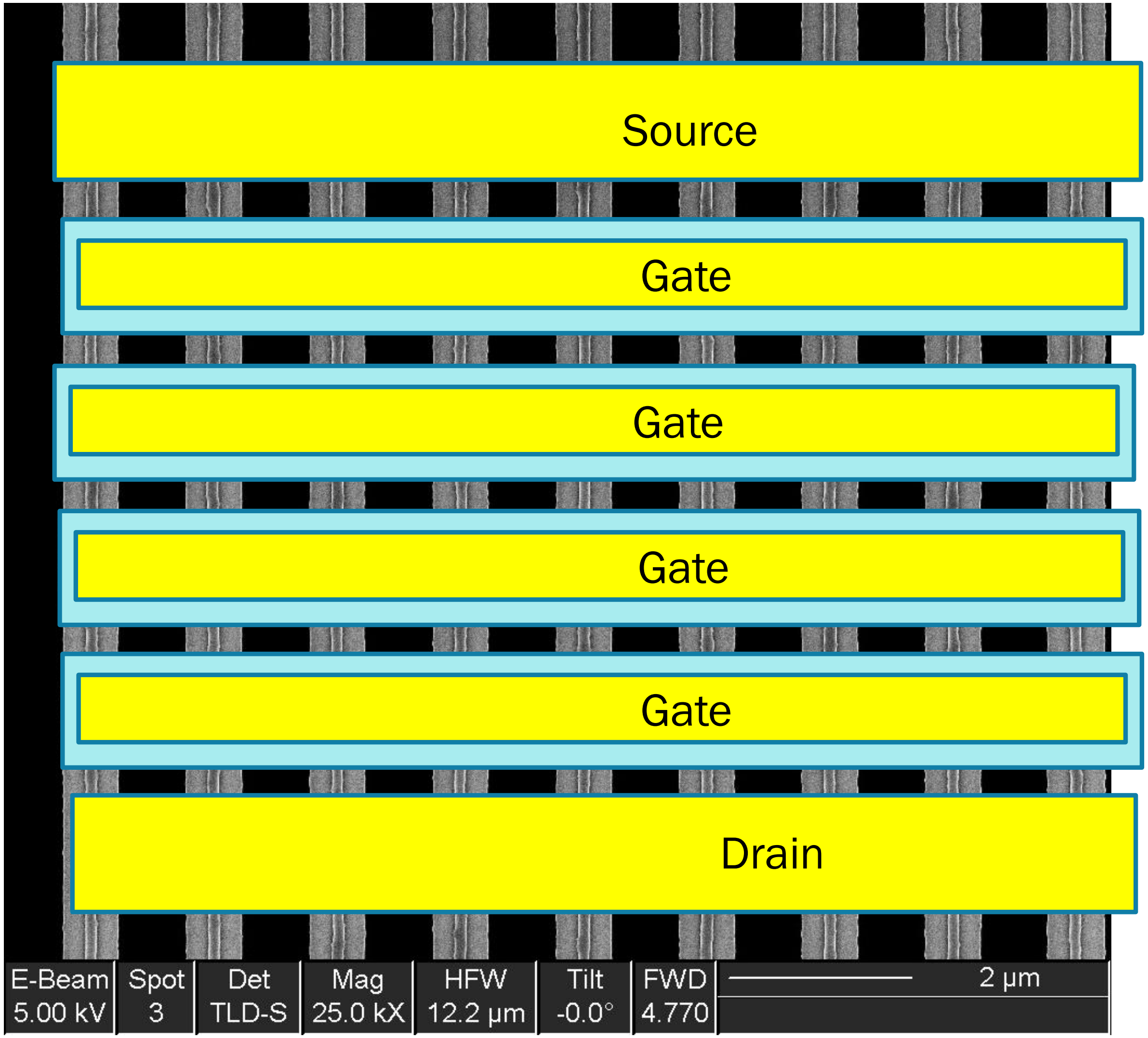
Ultra-long dewetted nano-wires: S/TEM



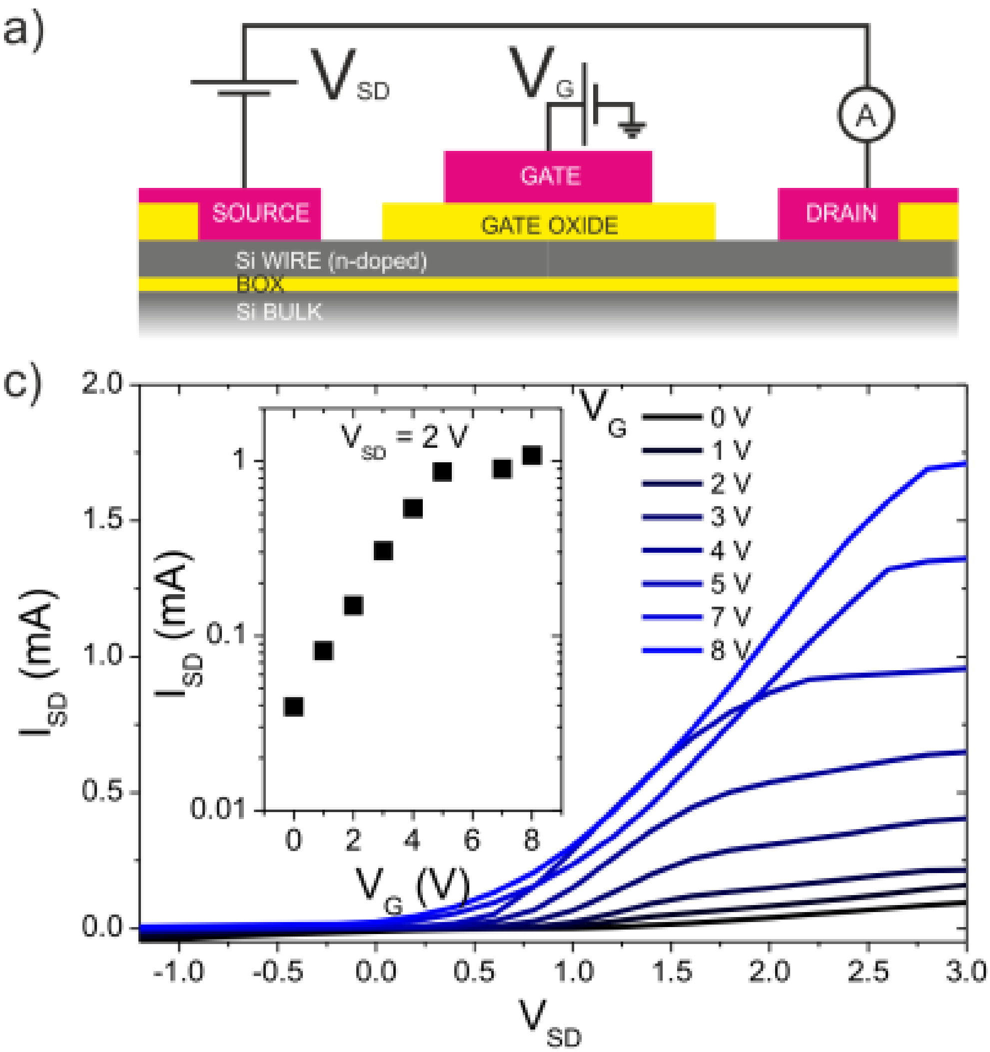
M.Bollani,M.Salvalaglio,A.Benali,M.Bouabdellaoui,M. Naffouti,M.Lodari, S.Di Corato, A.Fedorov, A.Voigt,L. Favré, D.Grosso,G.Nicotra,A.Mio,I.Berbezier,M.Abbarchi, *Nature Comm*. 10, 5632 (2019)

n-channel FET based on dewetted material





n-channel FET based on dewetted material



- **Transconductance:**
  $G_{NW} = \Delta I_{SD}/\Delta_{VG}$
  ~ μS per wire (**1-9 μS**)

- Leakage current: ~ ten pA

- **Mobility :**
  $\mu_e = L^2 G_{NW}/V_{SD}C_{NW}$
  0.5 and 5^10³ cm²/Vs

- **Gate capacitance:**
  $C_{NW} = 2\pi\varepsilon_0\varepsilon_r L/\cosh^{-1}(t/R)$
  C_{NW} ~ 5 fF

(t = t_{ox} + R distance between wire center and metallic contact, where t_{ox} is the oxide thickness ad R the wire radius).

M.Bollani,M.Salvalaglio,A.Benali,M.Bouabdellaoui,M. Naffouti,M.Lodari, S.Di Corato, A.Fedorov, A.Voigt,L. Favré, D.Grosso,G.Nicotra,A.Mio,I.Berbezier,M.Abbarchi, *Nature Comm*. 10, 5632 (2019)

SOLID STATE DEWETTING *vs* SPINODAL DEWETTING

The dewetting mechanism is determined by the thickness dependence of the **excess interaction free energy per unit area (ΔG)** of the interfaces associated with the thin film.

SSD

$$\partial^2 \Delta G / \partial h^2 > 0$$

the small surface perturbation decays to reduce the surface area by capillary force.

SD

$$\partial^2 \Delta G / \partial h^2 < 0$$

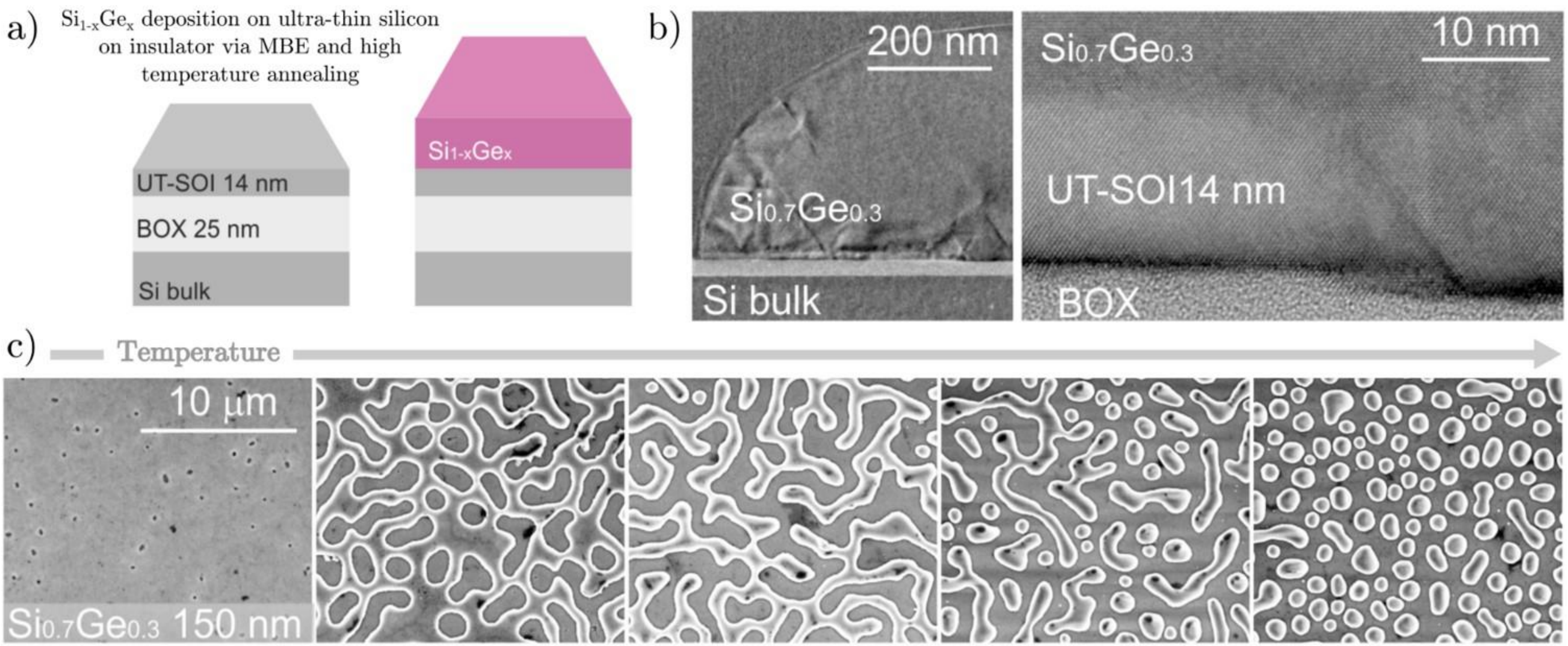
the film is thermodynamically unstable against thickness perturbation, such that the perturbation spontaneously grows and its minimal points eventually reach the substrate surface

Mullins WW. Flattening of a nearly plane solid surface due to capillarity. J Appl Phys. 1959;30: 77–83

SPONTANEOUS SPINODAL DEWETTING

By using a strained bilayer (SiGe on Si), the onset of an Asaro-Tiller-Grinfeld instability sets-in: surface corrugation. When the trenches touch the BOX dewetting starts all over the sample surface.

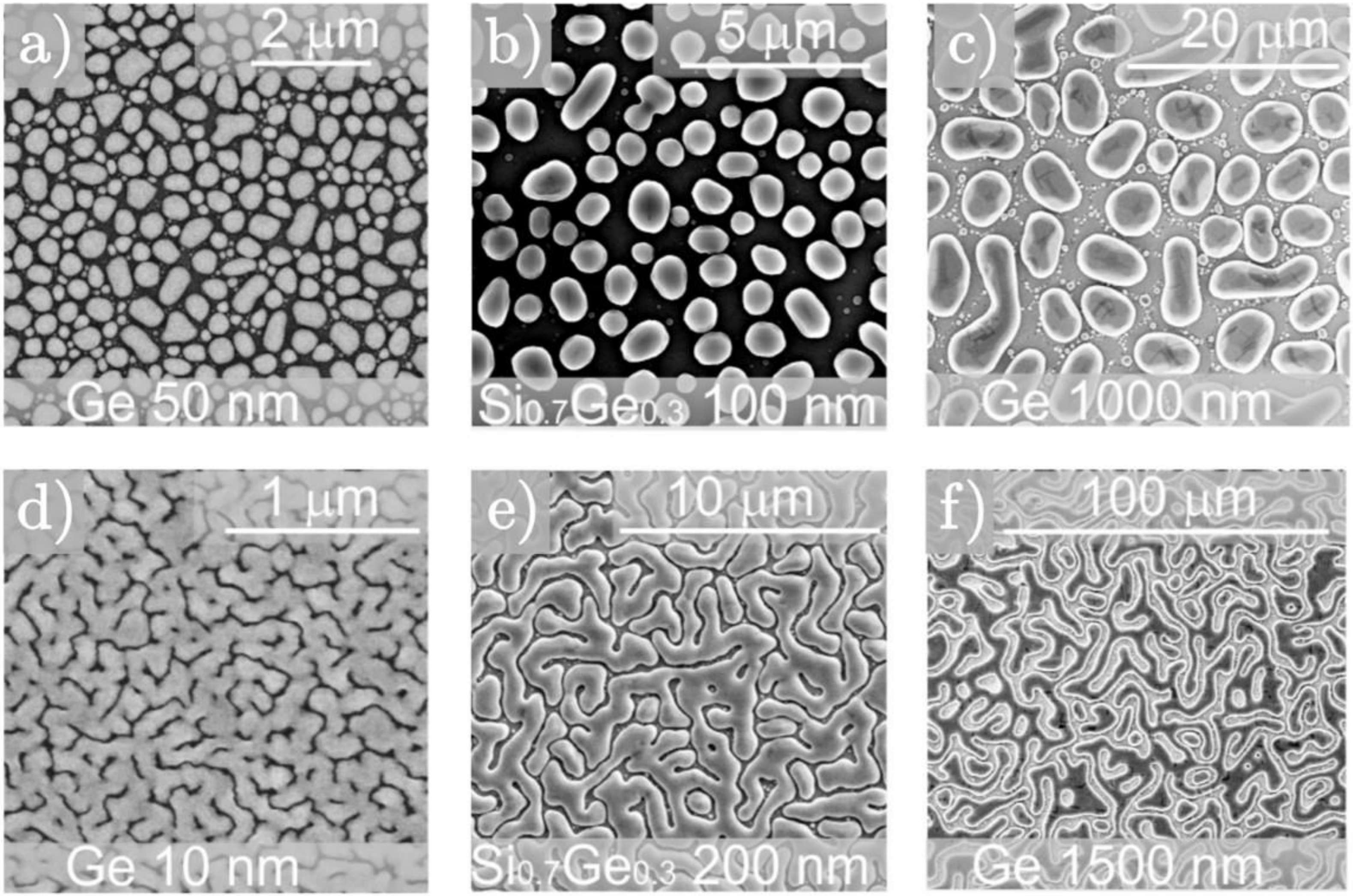
Due to the similarities of the final morphologies observed in thin films dewetting to those observed in phase separation via spinodal decomposition, this process is commonly termed spinodal dewetting.



M.Salvalaglio et al, PHYSICAL REVIEW LETTERS 125, 126101 (2020)

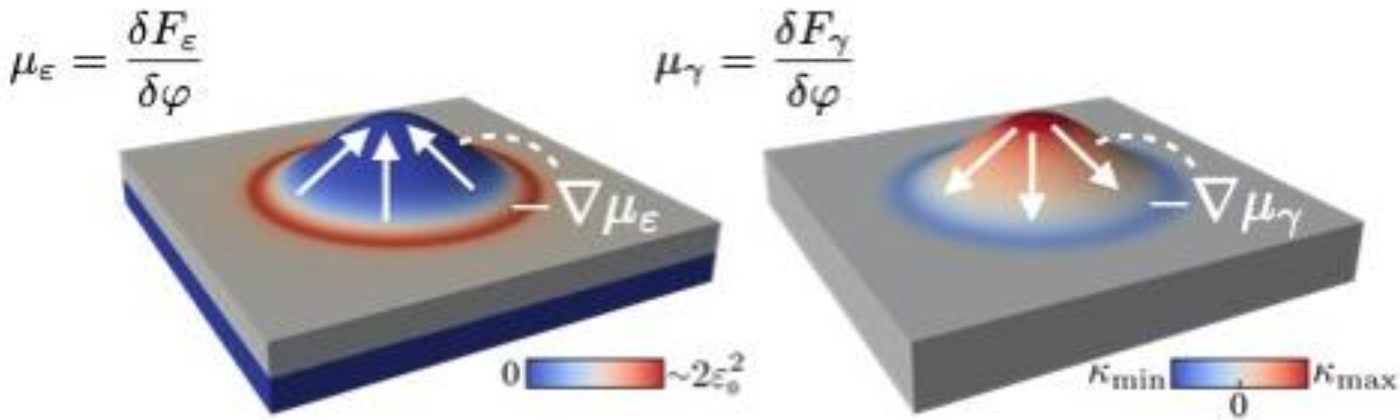
SPONTANEOUS SPINODAL DEWETTING

The morphology (e.g. islands, connected structures), size and composition can be tuned in a very large range of values



SPINODAL SOLID-STATE DEWETTING

- **Elastic energy** tends to flatten surface corrugation
- **Surface energy** tends to form high aspect reatio structures

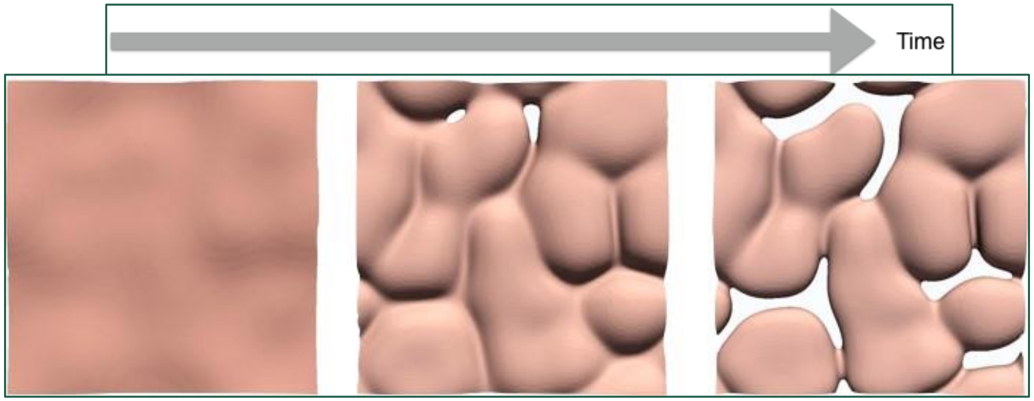


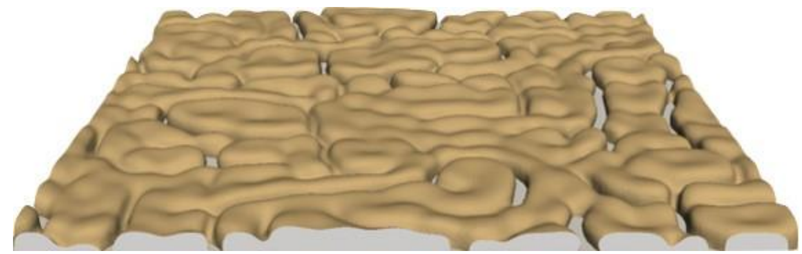
(phase field simulation)

M.Salvalaglio et al, PRL 125, 126101 (2020)

SPINODAL SOLID-STATE DEWETTING

- Simultaneous onset of the instability “everywhere”
- Characteristic length scales (competition between surface and elastic energy)





➢ The thickness perturbation can be continuously amplified during spinodal dewetting, leading to the formation of bi-continuous patterns with a characteristic λ

➢ Increasing the thickness perturbation→ holes formation, each of which corresponds to the valley of the perturbation.

➢ Front **retraction instability** since the retraction velocity of a front varies as E_S/h^3 so that the thinner parts of a front recede faster than the thicker ones (*E_S dewetting driving forces*).

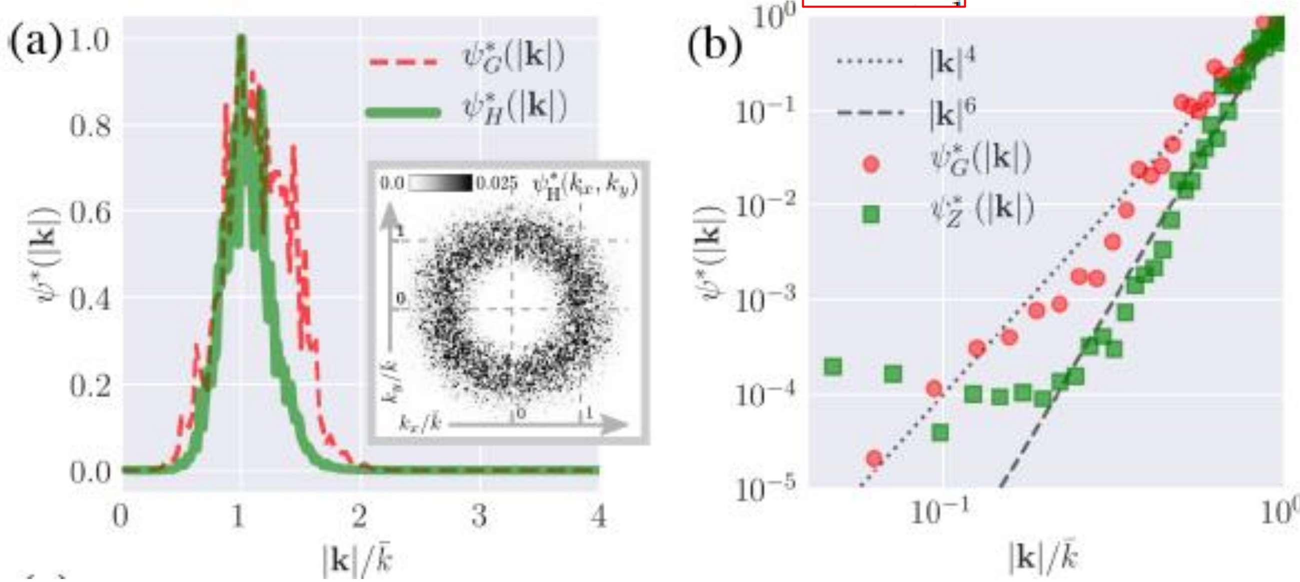
M.Salvalaglio et al, PRL 125, 126101 (2020); 26L. Rayleigh, Proc. London Math. Soc. s1–10, 4 (1878). 27E. Jiran and C. Thompson, J. Electron. Mater. 19, 1153 (1990).28W. W. Mullins and R. F. Sekerka, J. Appl. Phys. 35, 444 (1964). International Materials Reviews DOI: 10.1080/09506608.2018.1543832

SPINODAL SOLID-STATE DEWETTING

Disordered hyperuniform systems are characterized by an anomalous suppression of density fluctuations over large length scales:
while not presenting any Bragg peak in diffraction (as a liquid), they have strongly suppressed density fluctuations at long distances (as an ordered crystal).

possibility to build photonic devices exploiting a full photonic band-gap for light propagation and for carrier management with topologically protected electronic states.

$\boxed{\psi^*(|\mathbf{k}|)}$ Radial spectral density

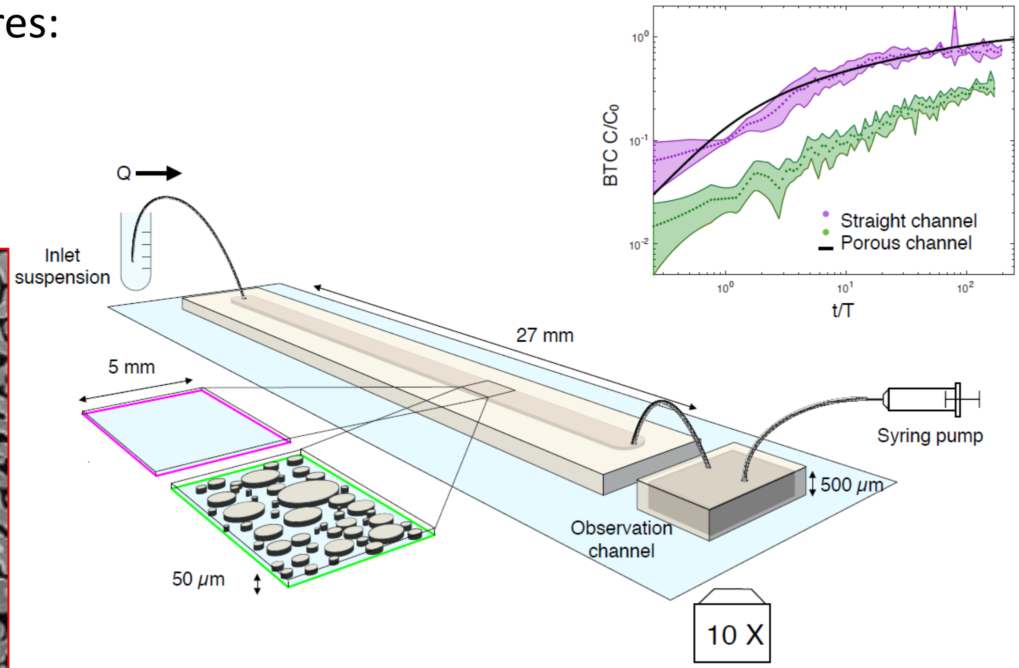


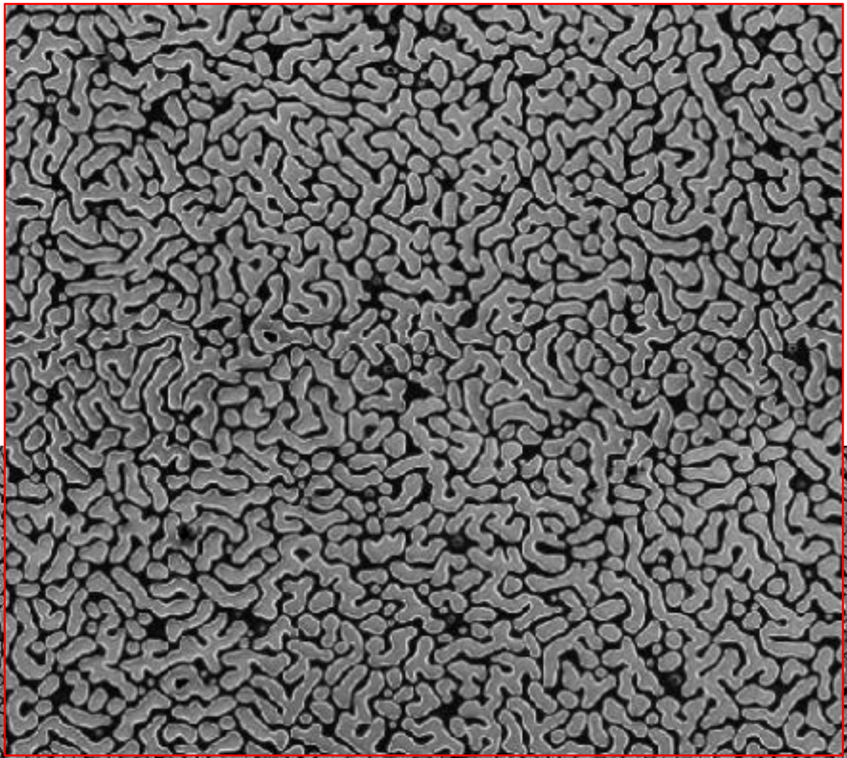
L. S. Froufe-Perez, et al. Sci. Rep. 6, 19325 (2016); R. Lin, Laser & Photonics Reviews 14, 1800296 (2020); S. Yu, *PRL. 117, 053902 (2016) ; Z. Ma and S. Torquato, J. Appl. Phys. 121, 244904 (2017); M.Salvalaglio et al, PRL 125, 126101 (2020)*

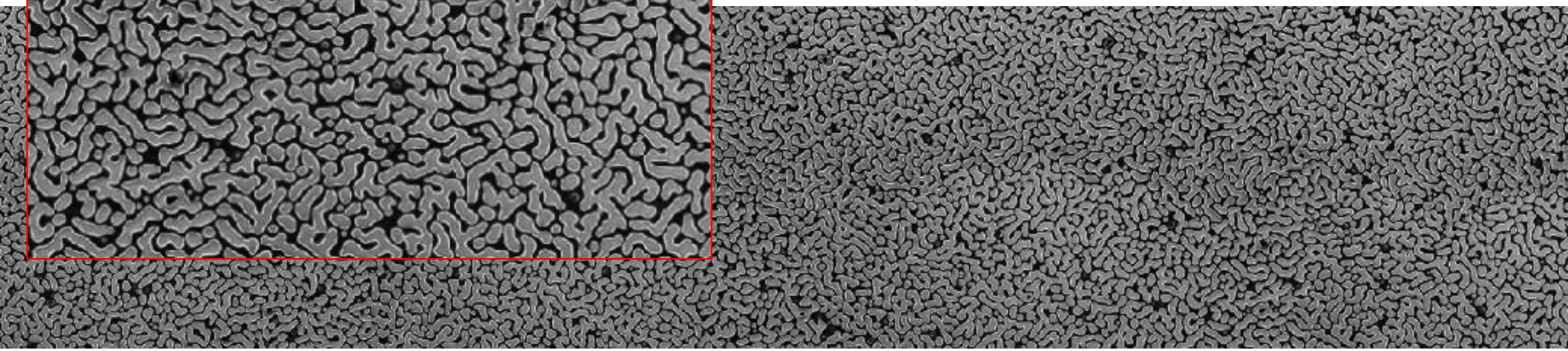
NEW MICROFLUIDIC DEVICES

Use PDMS to print new geometries with long range correlation properties.
Statistical characterization of these pictures:

- Black phase percolates.
- Statistical distribution of “pore” sizes.
- Define correlation properties.

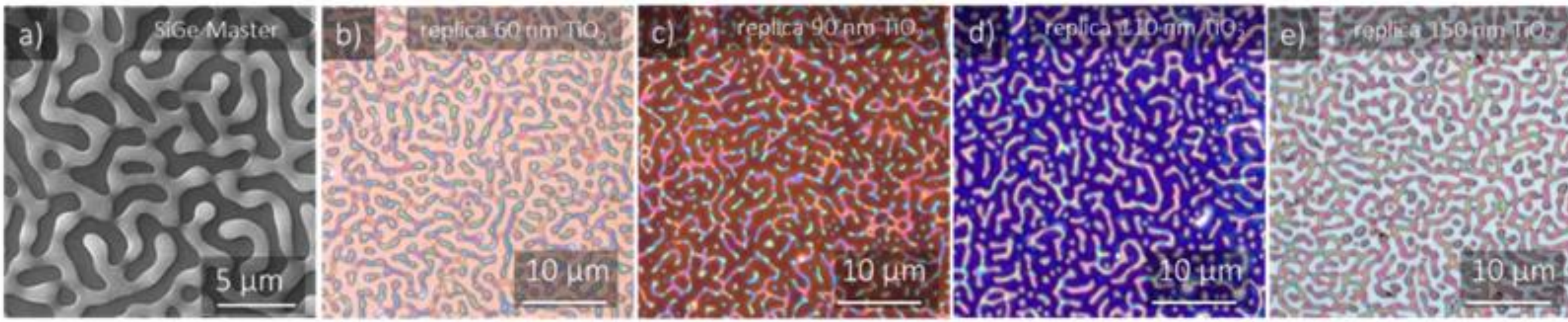






ANTI-REFLECTIVE CHARACTER OF TITANIA STRUCTURES ON SILICON

Reproduction of disordered hyperuniform metasurfaces in metal oxides



- ✓ Flexibility of sol-gel chemistry & dewetted masters to print a plethora of Mox;
- ✓ The refractive index of the silica and titania (respectively a low and high refractive index) can by tuned (e.g by mixing them, introduce nano-particles or organic moieties;
- ✓ Metasurfaces are scalable to large surfaces.

“That’s all Folks!”