

Ion-induced nanopatterning of semiconductor surfaces

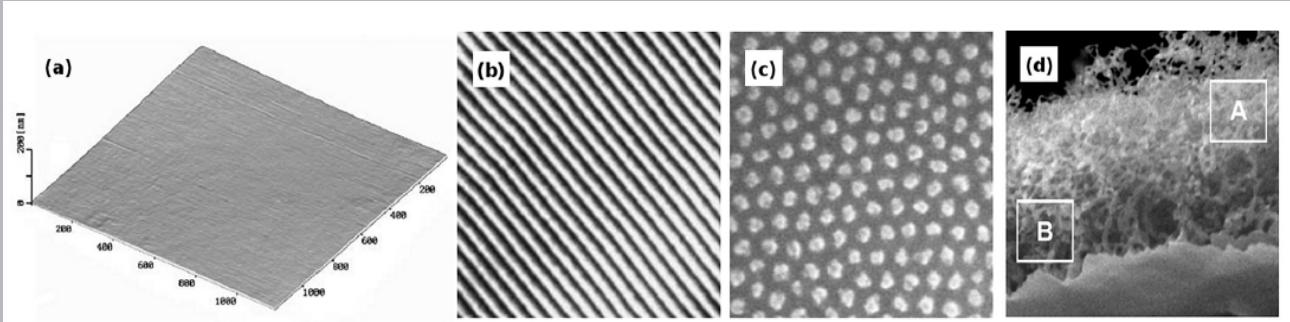
A short link between basic research and applications

Rossana Dell'Anna

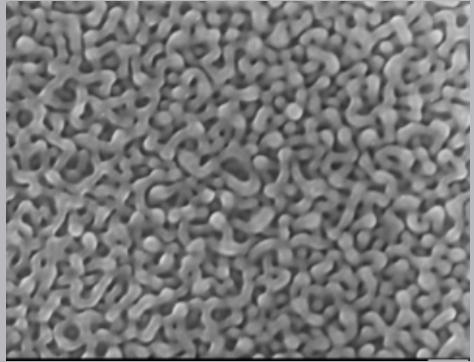
MNF - FBK

It-fab

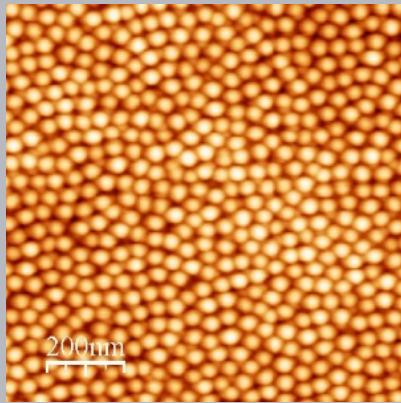
Italian Network for
Micro and Nano Fabrication



S. Norris et al., *Appl. Phys. Rev.* 2019, 6, 011311



R. Dell'Anna et al., *JPCM* 30 (32), 324001

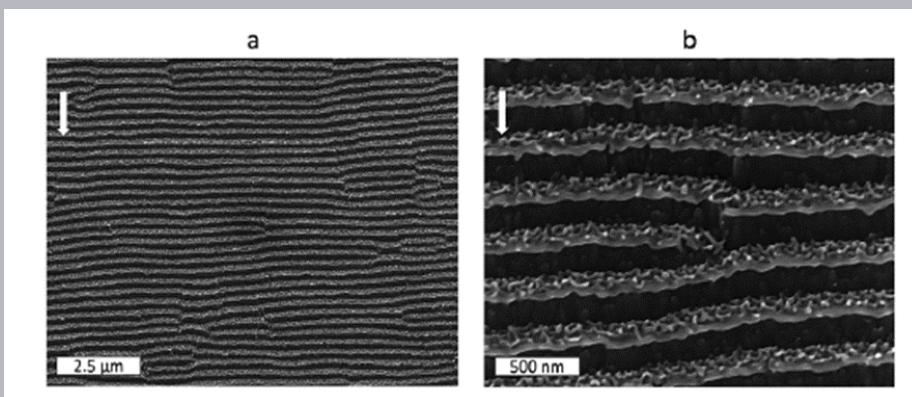


S. Facsko et al. *APL*, 2002, 80, 130

**Taniguchi et al,
1974**

Erosion of solid targets through ion beam irradiation as a promising technique to nanostructure the surface of a wide range of materials.

“Nanotechnology”

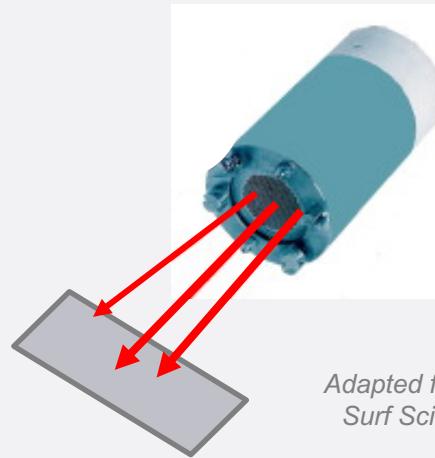


R. Dell'Anna, C. Masciullo et al., *RSC Adv.*, 2017, 7, 9024

Experimental pattern control

Variation in the induced nanostructures by changing:

- Incident ion species
- Angle of ion incidence ϑ
- Energy of incident ions E
- Ion fluence Φ
- Substrate temperature T
- Target material



Adapted from Lloyd et al.
Surf Sci 2016, 653, 334

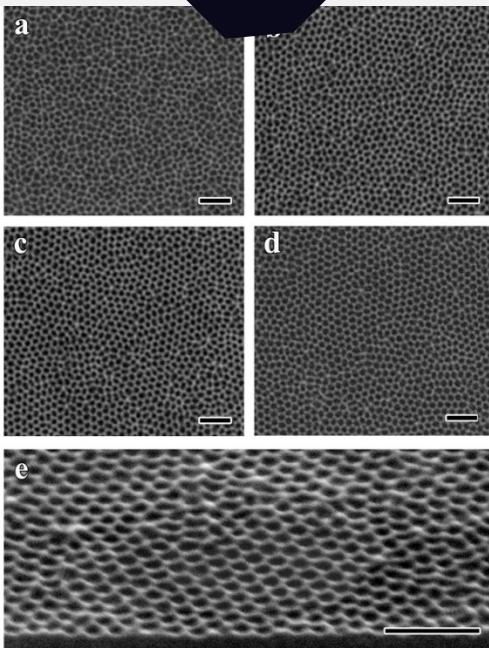
nanopatterning by IBI in brief

Q. Wei et al., *Adv. Mater.* 2009, 21 2865

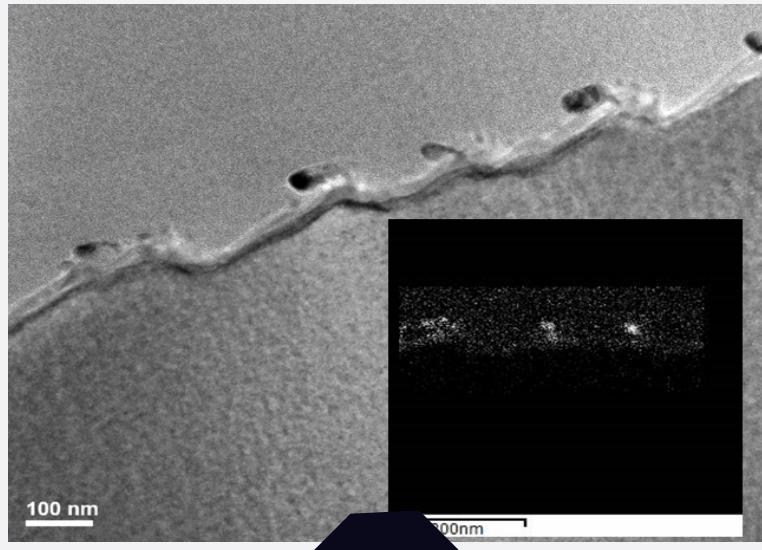
R. Dell'Anna et al., *JPCM* 30 (32), 324001

Implicit characteristics:

- self-organizing phenomenon
- one step process
- short time
- large surface area (high output)
- sub-micrometer and nanometer length scales



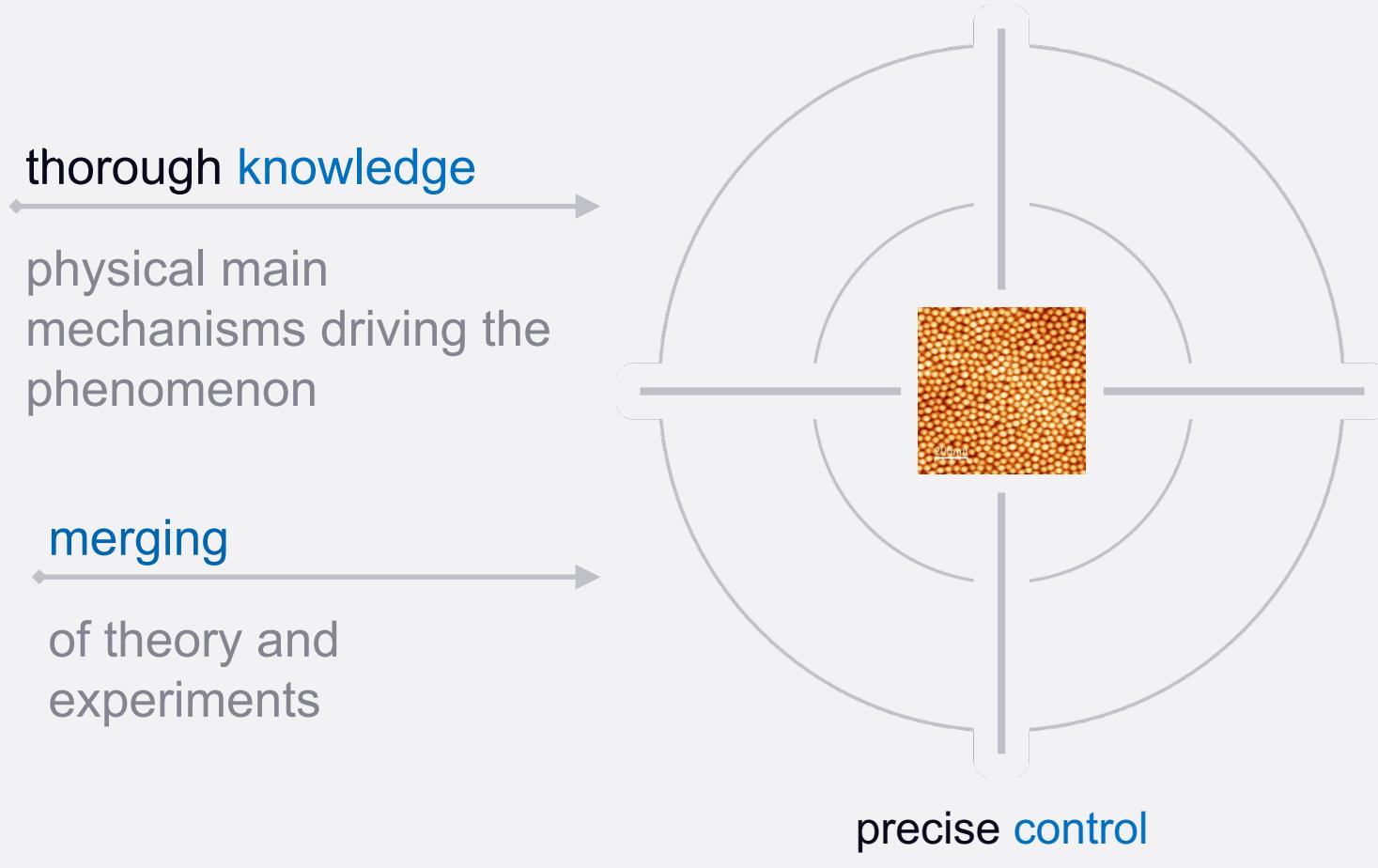
Complementary with respect
to lithographic techniques



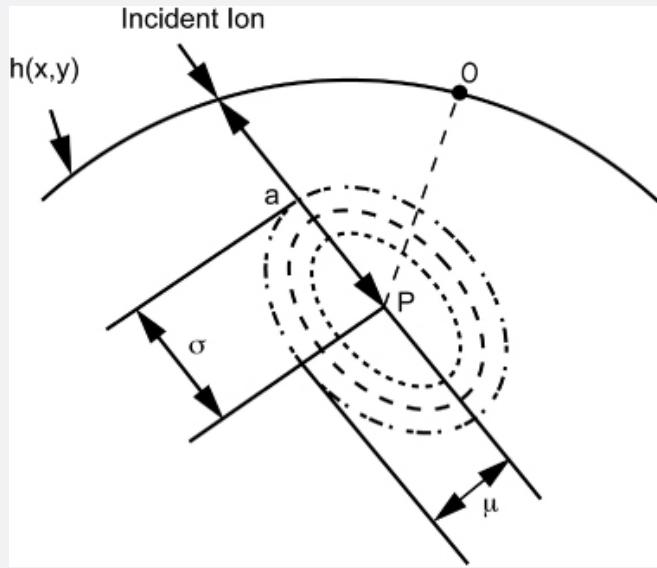
- Fabrication of different possible nanostructures
- on different materials (semiconductors, metals, insulators)
- Through the ion species, chemical engineering of the surface

Different possible application fields

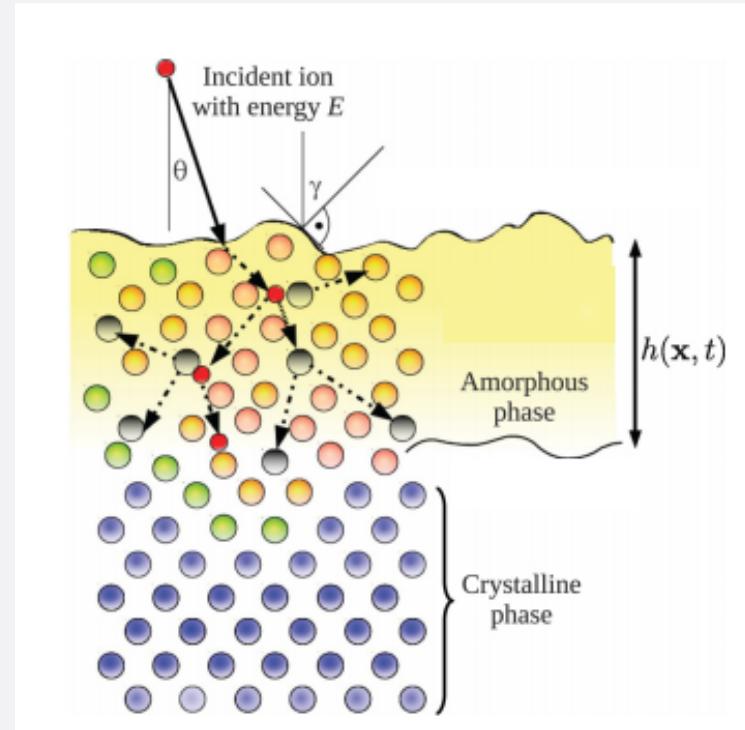
pattern production in a controlled & reproducible fashion



Cascades of atomic displacements by energetic ion impacts



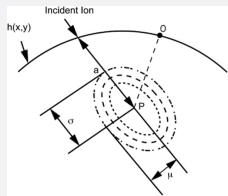
Headrick et al, J. Phys.: Condens. Matter, 2009, 21, 224005



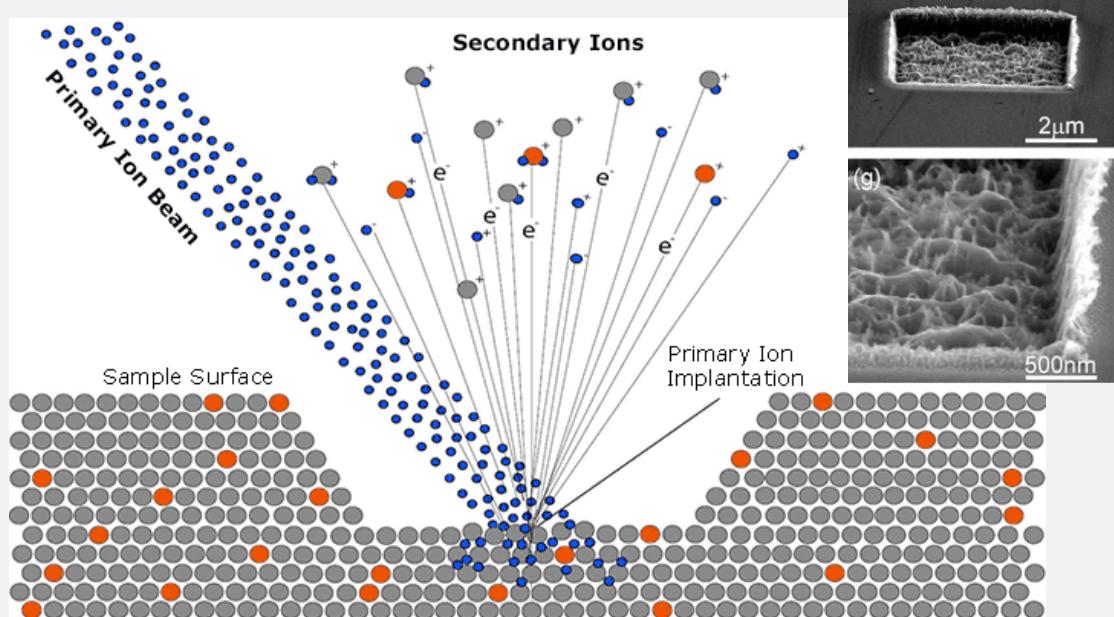
Adapted from Castro et al, PRB, 2012, 86, 214107

Sputtering

P. Sigmund (1969)

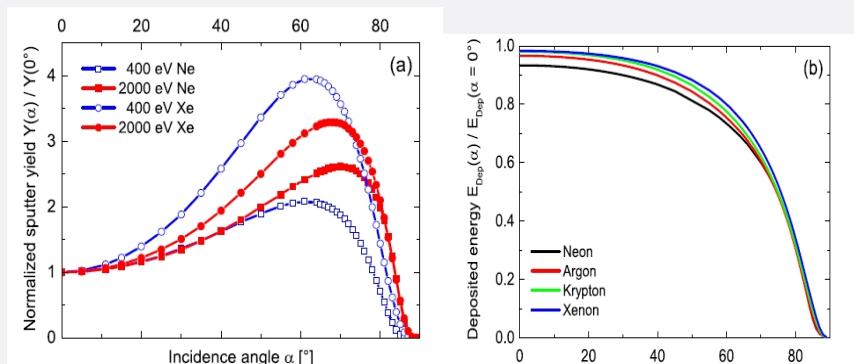


The sputtering yield Y (atoms/ion) is proportional to the energy deposited by the ion at the surface



<https://www.cameca.com>

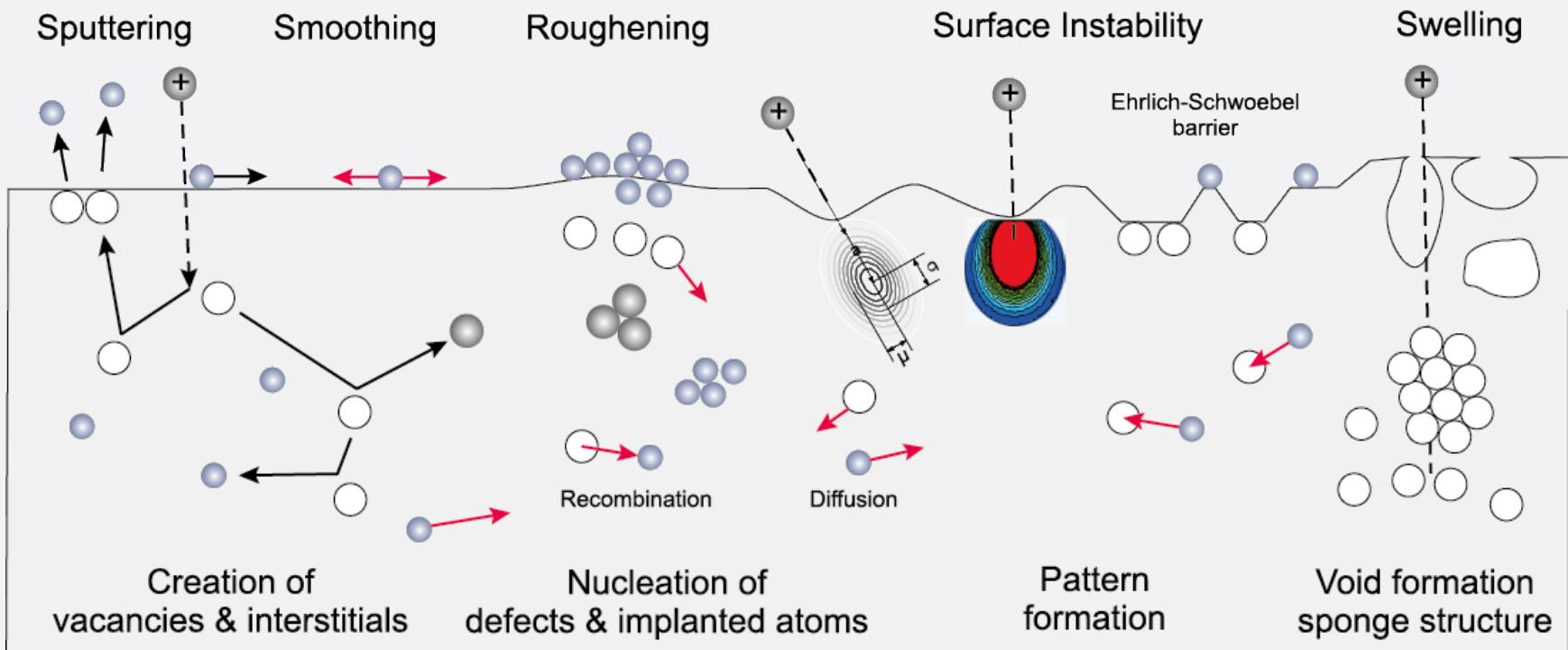
Angular dependence of the sputtering yield $Y(\theta)$ and of the deposited Energy $E(\theta)$:



M. Teichmann et al., New Jour of Phys 2013 15 103029

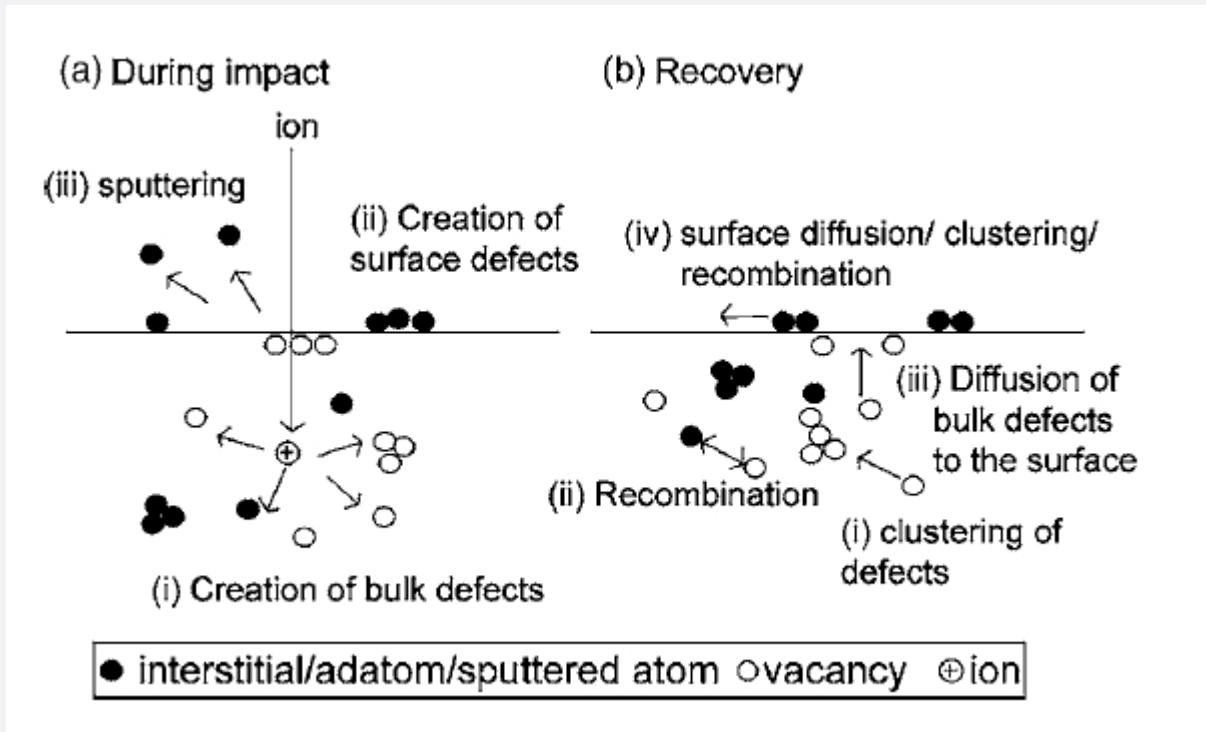
Ion induced nanostructures: physical mechanisms

Credits: <https://www.hzdr.de>



Ion induced nanostructures: physical mechanisms

W Chan et al., JAP 2007 101 121301



related to the ion damage

- Cascades of atomic displacements by energetic ion impacts:
 - Thin layer amorphized and stressed
 - Crater → surface redistribution effects
 - Sputtered atoms

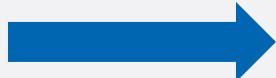
counteracting relaxations

- Thermal diffusion
- Ion-induced viscous flow
- Defect recombination
- Athermal diffusion

pattern production in a controlled & reproducible fashion

T, θ ,Φ, E...

Experimental parameters



Theories and Models

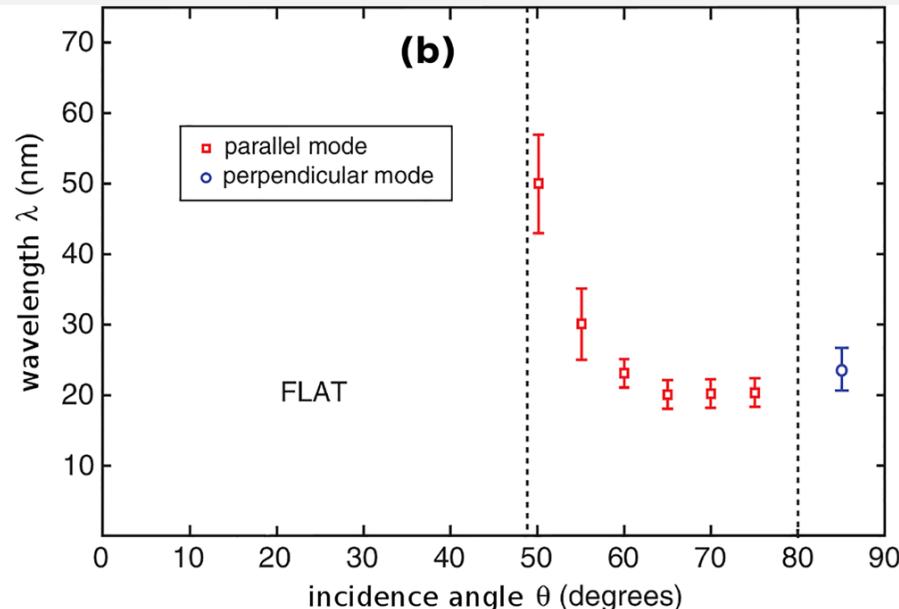
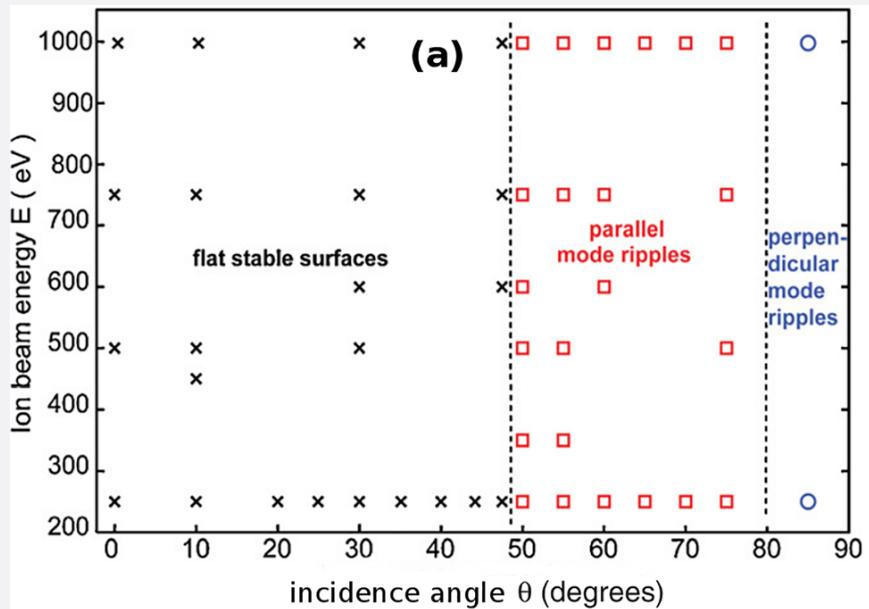
$$\frac{\partial h}{\partial t} = -v_0 + \frac{\partial v_0}{\partial \vartheta} \frac{\partial h}{\partial x} + A_x \frac{\partial^2 h}{\partial x^2} + A_y \frac{\partial^2 h}{\partial y^2} - B \nabla^4 h,$$



Nanopatterns

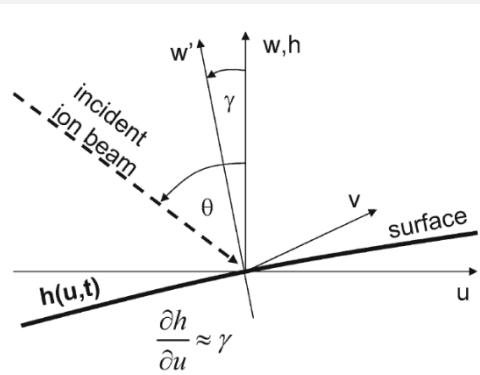


Understanding a **subset** of mechanisms for a **subset** of experimental parameters



S. Norris et al., Appl. Phys. Rev. 2019 6 011311

Understanding a subset of mechanisms for a subset of experimental parameters



H. Hofsaess, Appl. Phys. A 2014 14 401

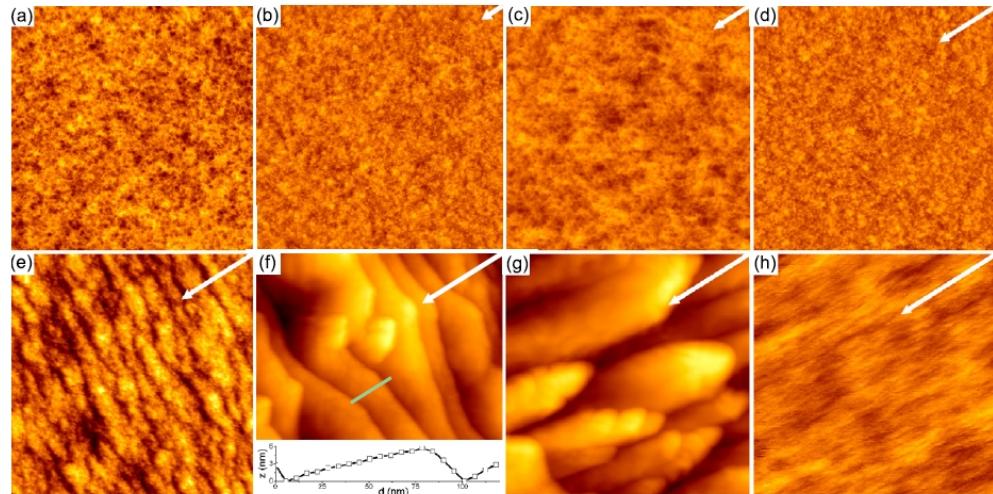
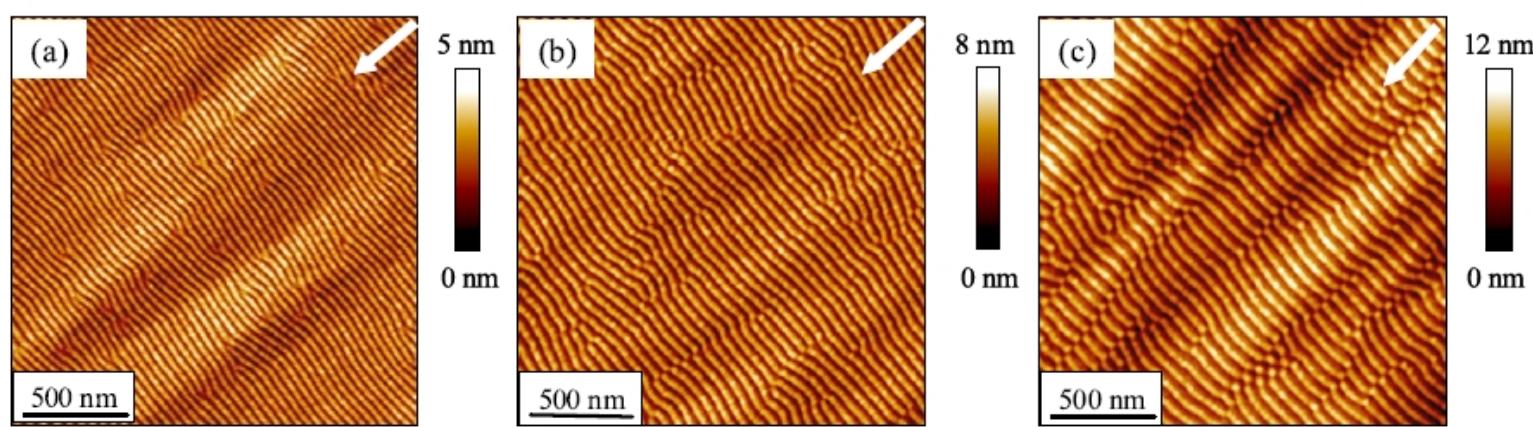


Figure 1. STM topographs of Si(100) after a fluence of $2 \approx 10^{22}$ ions m^{-2} 2 keV Kr^+ at 300 K. The angle of incidence ϑ with respect to the surface normal is (a) 0°, (b) 15°, (c) 26°, (d) 45°, (e) 60°, (f) 75°, (g) 79° and (h) 83°. The image size is for (a)–(d) and (h) $316 \text{ nm} \times 316 \text{ nm}$ and in (e)–(g) $625 \text{ nm} \times 625 \text{ nm}$. The white arrows in (b)–(h) indicate the ion beam azimuth. The corrugation Δz is 3 nm in (a)–(e) and (h) and 30 nm in (f) and (g). Inset in (f): height profile along line indicated in (f).

Si surfaces irradiated by Kr^+ $E = 2000 \text{ eV}$, $\Phi = 2 \times 10^{18} \text{ ions/cm}^2$

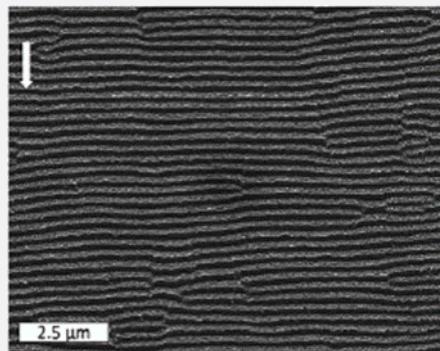
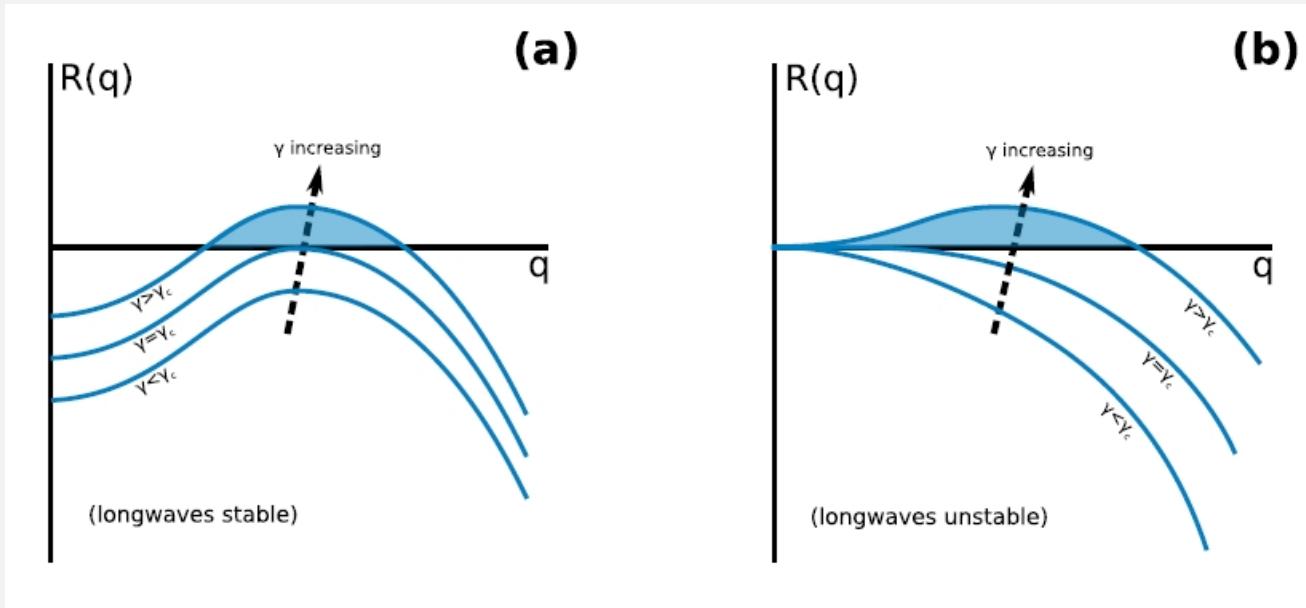


Si surfaces irradiated by Ar^+ at 15°, $E=800 \text{ eV}$, 1200 eV , 2000 eV , $\Phi = 6.7 \times 10^{18} \text{ cm}^{-2}$

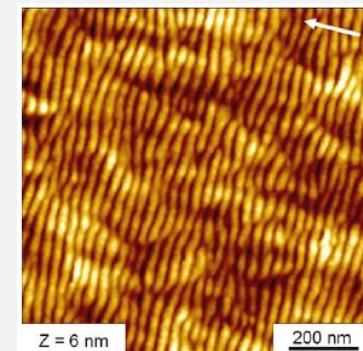
Type I and Type II instabilities

$$h_1 = h_{11} \exp \left[R(\mathbf{q})t + i\mathbf{q} \cdot \left(\mathbf{x} + \frac{\psi(\mathbf{q})\mathbf{q}}{|\mathbf{q}|^2} t \right) \right]$$

S. Norris et al., *Appl. Phys. Rev.* 2019, 6, 011311



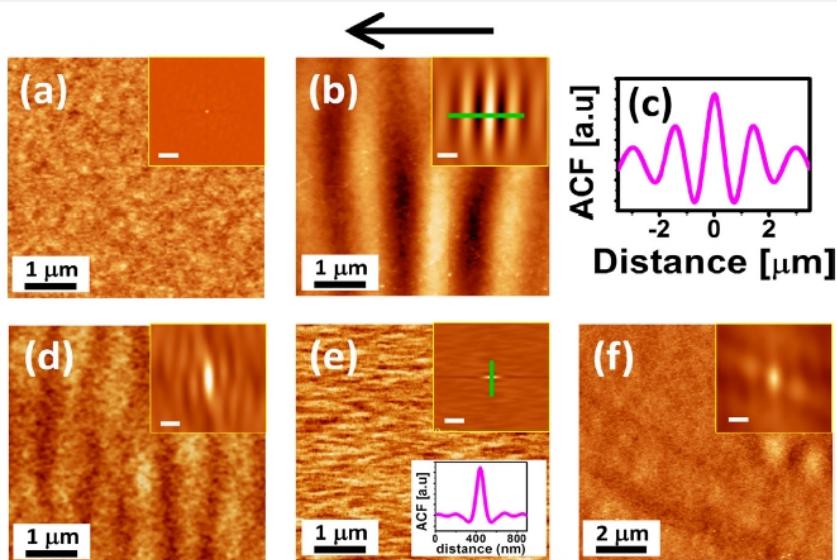
R. Dell'Anna et al,
RSC Advances 2017 7 9024



M. Teichmann et al.,
New Jour of Phys 2013 15 103029

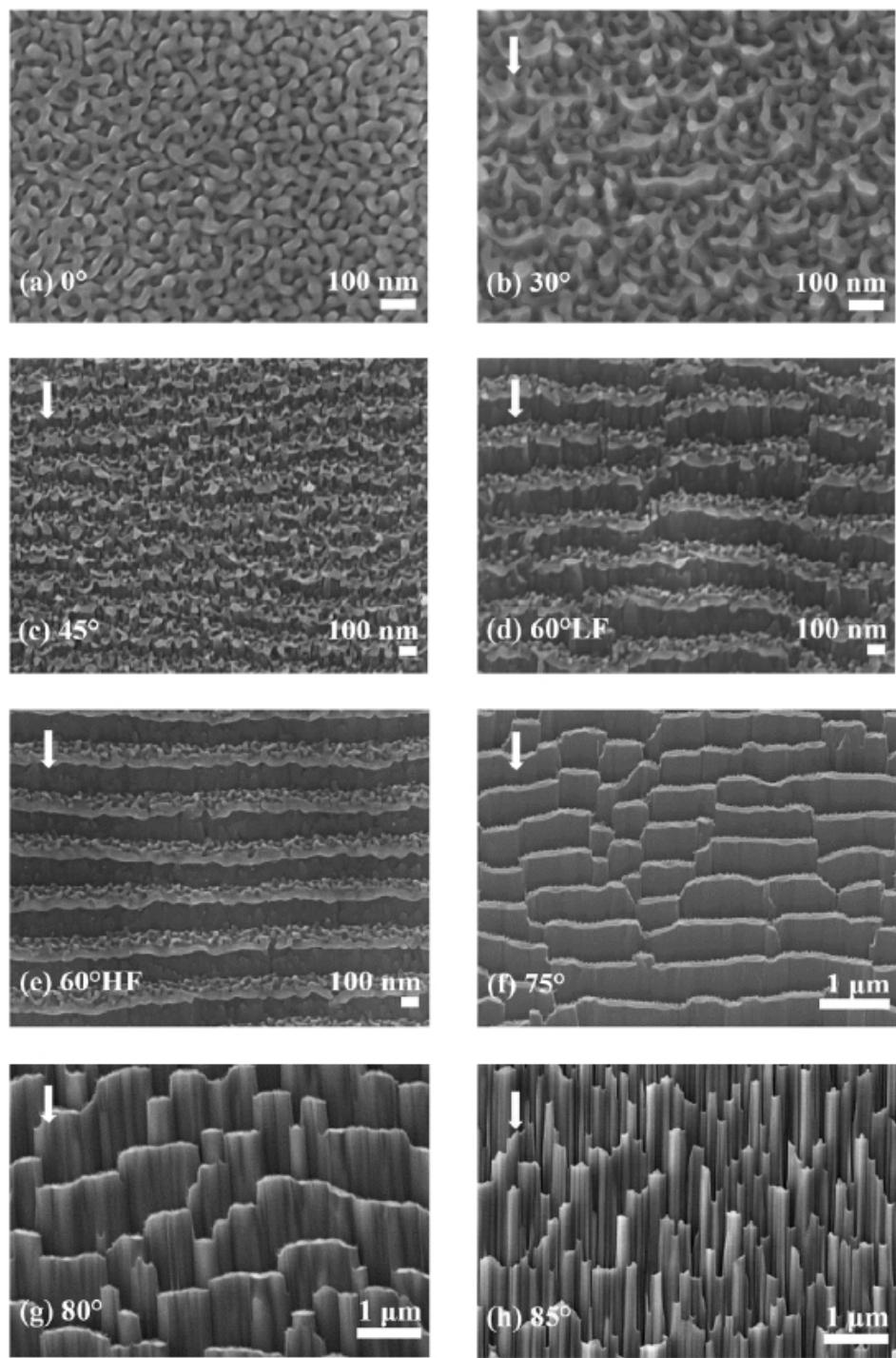
Understanding a subset of mechanisms for a subset of experimental parameters

D. Datta et al, Appl Surf Sci 2016 360 131



Ge surfaces irradiated by 100 keV Kr⁺ to the fluence of
 3×10^{18} ions cm⁻²

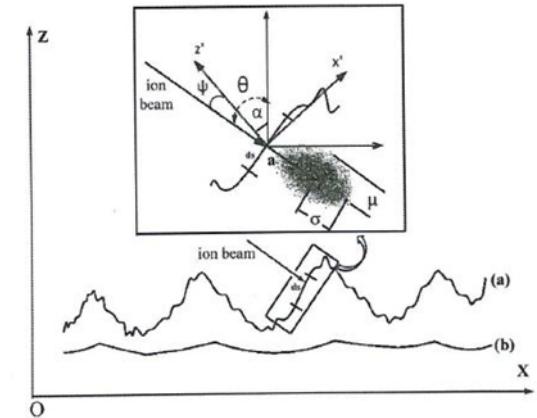
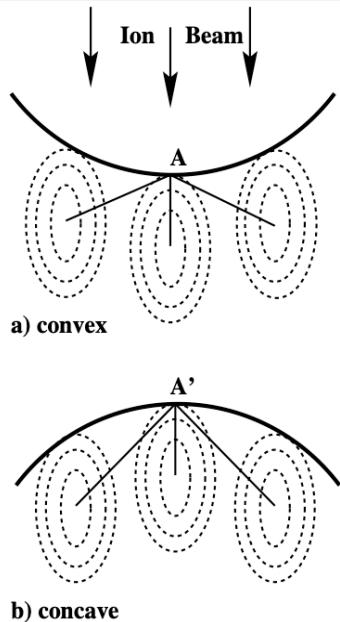
Ge surfaces irradiated by
 Au+ E= 26 keV,
 $\Phi = 5 \times 10^{16}$ ions cm⁻²



continuum models

T. Som & D. Kanjilal Eds,
Nanofabrication by ion beam sputtering, 2013

M A Makeev et al., Nucl. Instruments Methods Phys. Res. B 2002 197 185



Linear continuum theory of
Bradley & Harper for pattern
formation

$$\frac{\partial h}{\partial t} = -v_0 + \frac{\partial v_0}{\partial \vartheta} \frac{\partial h}{\partial x} + A_x \frac{\partial^2 h}{\partial x^2} + A_y \frac{\partial^2 h}{\partial y^2} - B \nabla^4 h,$$

small slope approximation

competition between a roughening process by surface sputtering and smoothening process by surface diffusion

continuum models

Credits: <https://www.hzdr.de>

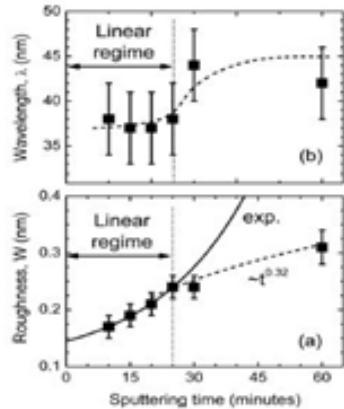
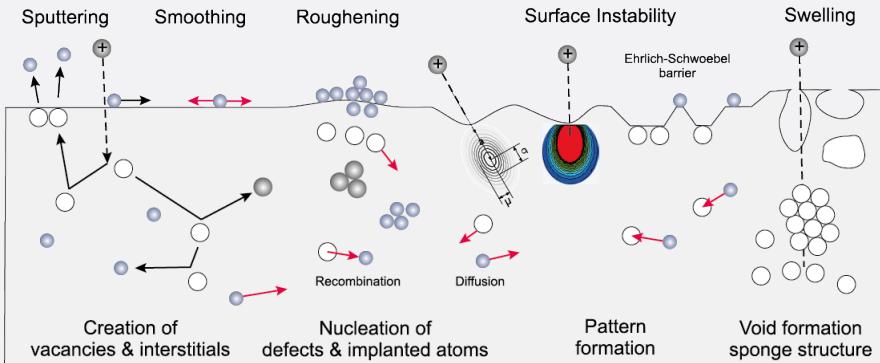


FIG. 5. Time evolution of the (a) surface roughness and (b) ripple wavelength for $E = 700$ eV, $J_0 = 30 \mu\text{A cm}^{-2}$ and $\theta = 55^\circ$. The solid line in (a) is an exponential fit in the linear regime, while the dashed line is a power-law fit in the nonlinear regime with exponent 0.32. The dashed line in (b) is a guide to the eye. The time regime in which the wavelength grows with time (coarsening) starts at $t \approx 25$ min, as indicated by the vertical dotted line; this is a signature of the onset of nonlinear effects. At shorter times the wavelength is almost constant. The same crossover time separates exponential from power-law behavior for the roughness.

M. Castro et al, PRB, 2012, 86, 214107



The (noisy) anisotropic Kuramoto-Sivashinsky equation

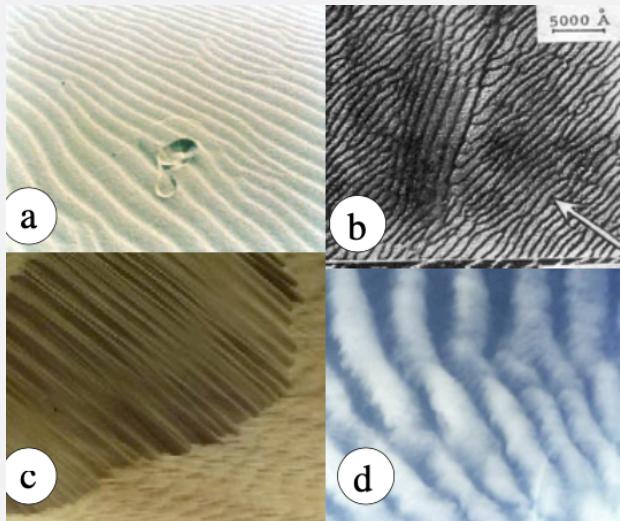
$$\frac{\partial h}{\partial t} = -v_0 + \frac{\partial v_0}{\partial \vartheta} \frac{\partial h}{\partial x} + A_x \frac{\partial^2 h}{\partial x^2} + A_y \frac{\partial^2 h}{\partial y^2} - B \nabla^4 h - B_{I,x} \frac{\partial^4 h}{\partial x^4} - B_{I,xy} \frac{\partial^4 h}{\partial x^2 \partial y^2} - B_{I,y} \frac{\partial^4 h}{\partial y^4} + \frac{\lambda}{2} (\nabla h)^2 + \eta(x, y, t).$$

-ah

BH

Kinetic roughening

aeolian sand dunes

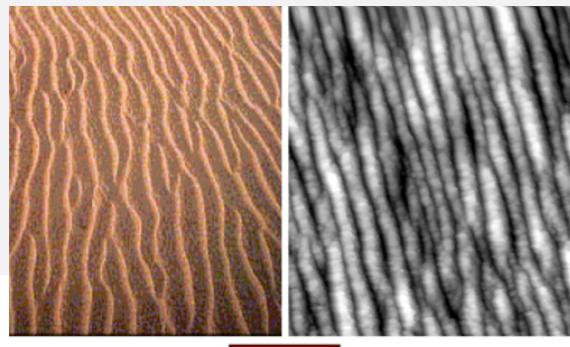


$$\partial_t h = \sum_{i=x,y} \left[-v_i \partial_i^2 h + \lambda_i^{(1)} (\partial_i h)^2 \right] + \sum_{i,j=x,y} \left[-K_{ij} \partial_i^2 \partial_j^2 h + \lambda_{ij}^{(2)} \partial_i^2 (\partial_j h)^2 \right].$$

The hydrodynamic model

Generalization of continuum theory: it retrieves all the features of the BH theory in the linear and nonlinear regimes;

T. Aste et al. *New J Phys*, 2005, 7, 122



Diversity of materials and similarities in morphologies → some kind of universality



Dependence on irradiation parameters



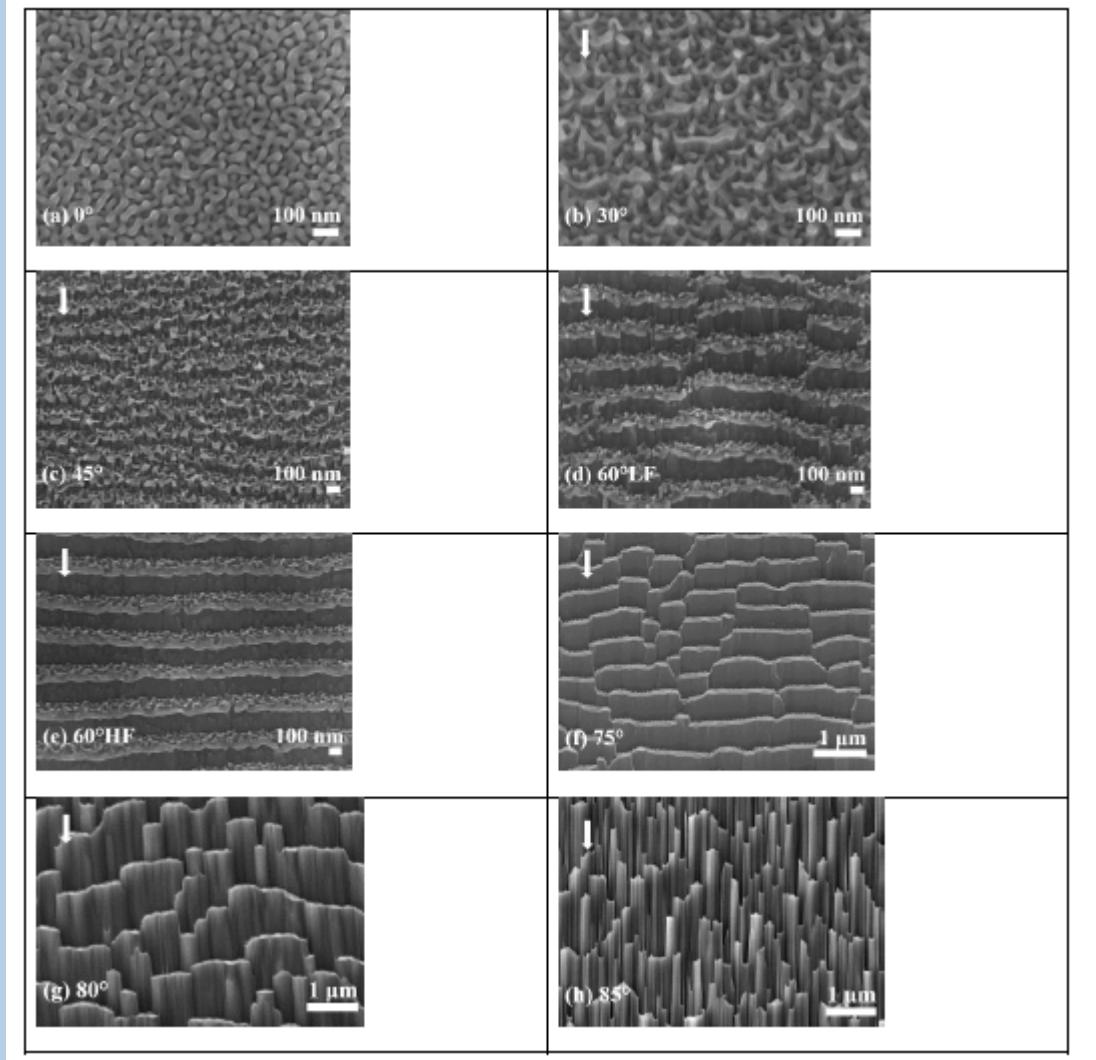
Nano-porous Ge and rippled Ge by ion irradiation



MNF-FBK, Trento

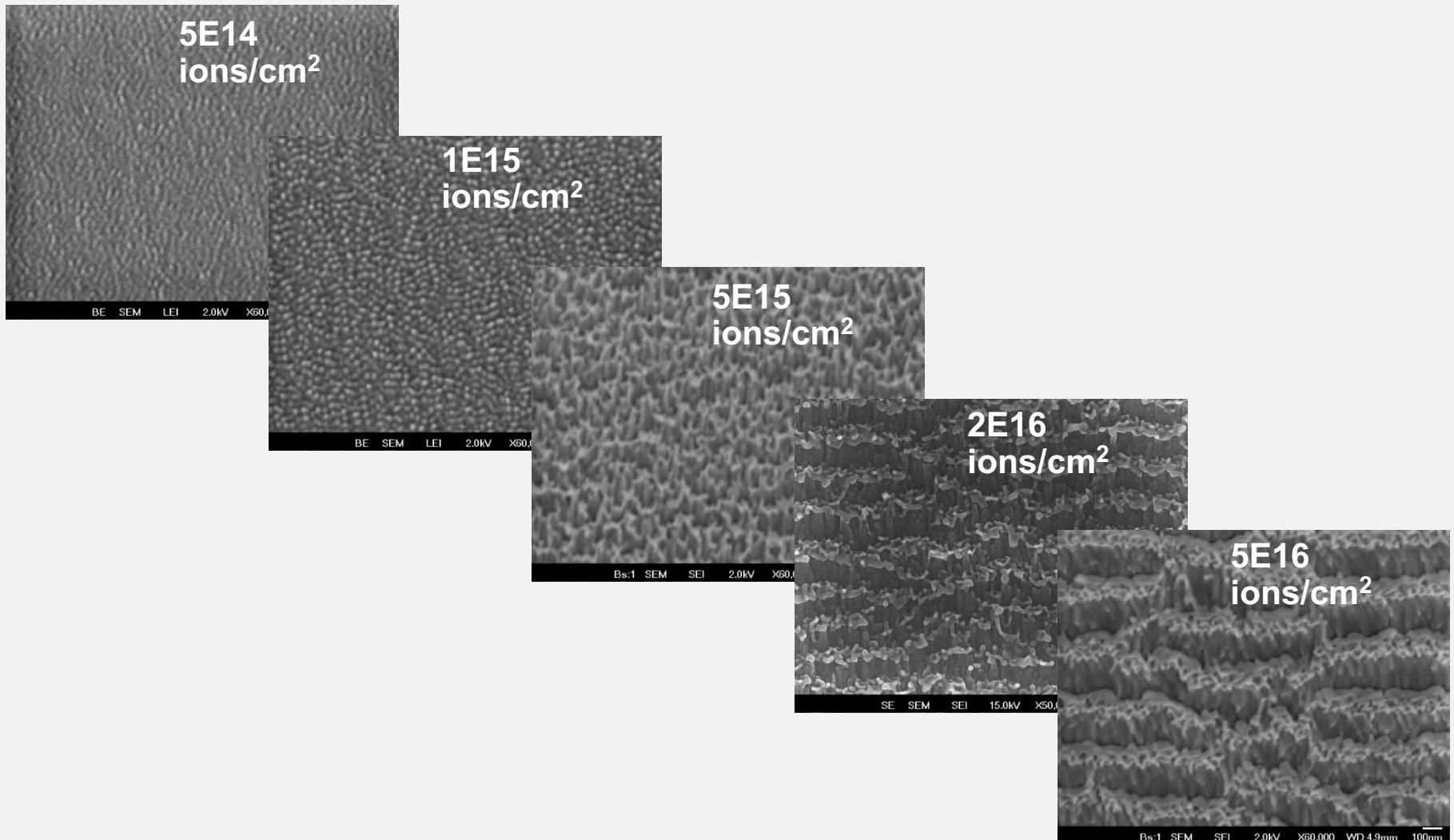
HZDR, Dresden

**Ge surfaces irradiated with
26 keV Au ions at
 $5 \times 10^{16} \text{ cm}^{-2}$ fluence
and varying angles**

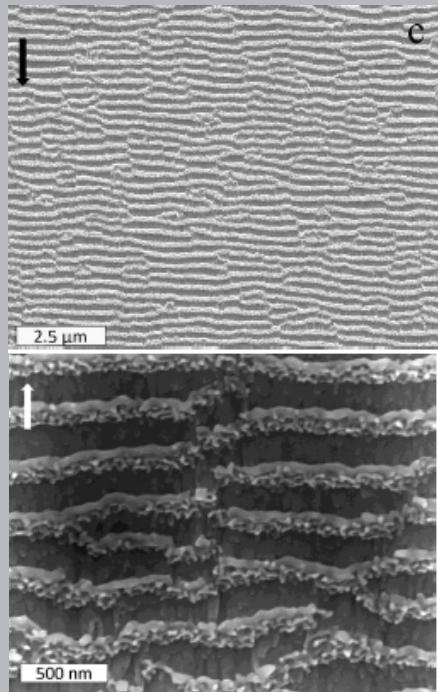


Au low energy/ oblique incidence of Germanium

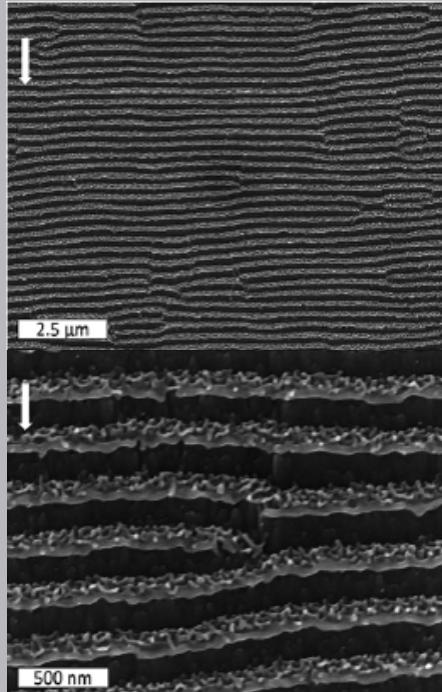
Au⁺ 26 keV – 60° - vs. ion fluence



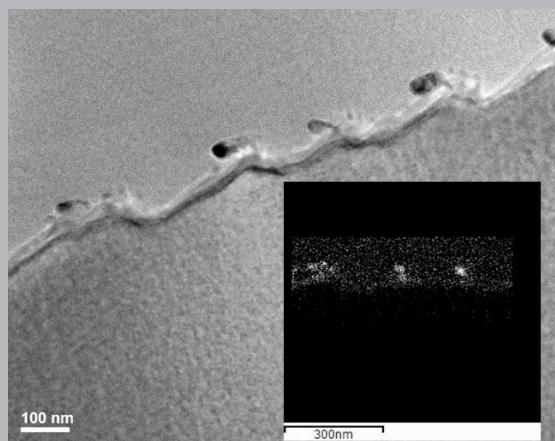
Nanoripples produced on Ge substrates by Au ion beam irradiation



$\Psi = 1.0 \times 10^{17} \text{ ions}\cdot\text{cm}^{-2}$

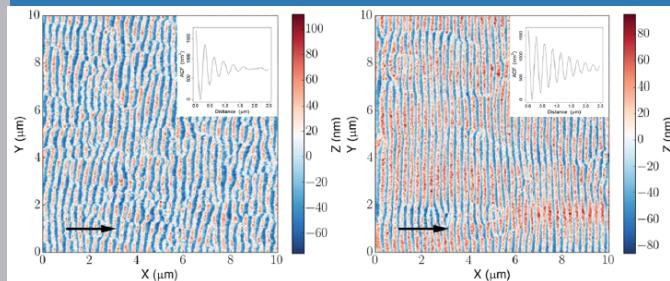


$\Psi = 4.3 \times 10^{17} \text{ ions}\cdot\text{cm}^{-2}$



$\Psi = 5.0 \times 10^{16} \text{ ions}\cdot\text{cm}^{-2}$
2D EDX map of Au
Lb2 emission line,
at 11.5847 keV

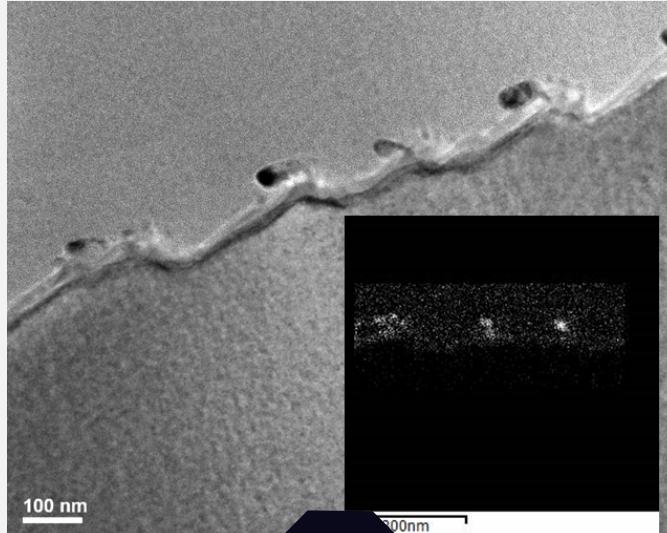
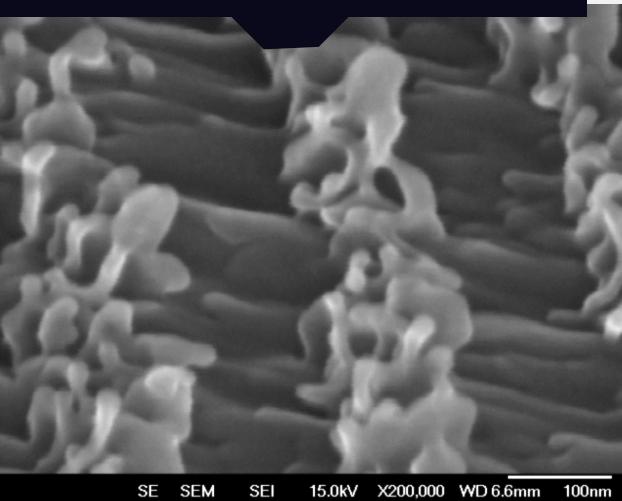
R. Dell'Anna et al, J. Phys.:
Condens. Matter 30 324001
2018



Au low energy/ oblique incidence of Germanium

Au⁺ 5E16 cm⁻²/ 26 keV – 60° - CROSS SECTIONS

SEM,
tilted view

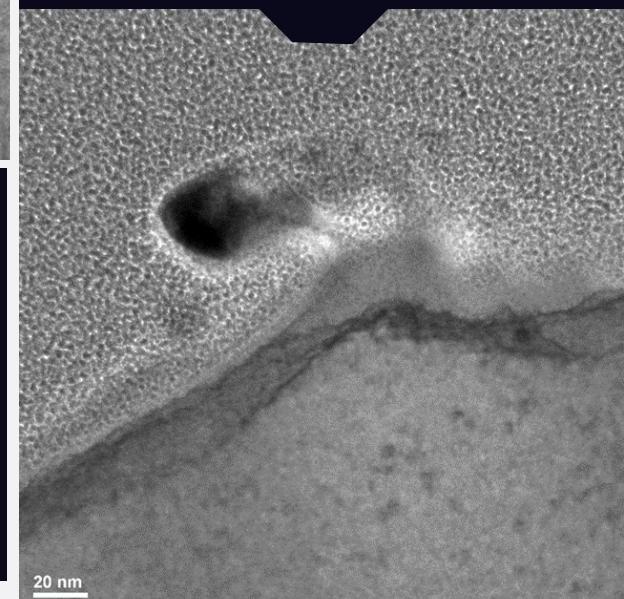


X-TEM

- Cross sections confirm the presence of nanowires on top of the ripple-crests.
- Nanowires are curled, in the opposite direction with respect to the ion beam.
- On top of the nanowires, there are particles very rich in Au (EDX image, Au L2b2 line, ~11600 eV, left).

X-TEM

An amorphous thick layer is present on the side of the ripple facing the beam, whereas it is much thinner on the other side.





Hierarchical Ge nanoripples as templates for bioactive surfaces

MNF-FBK, Trento

NEST, Pisa

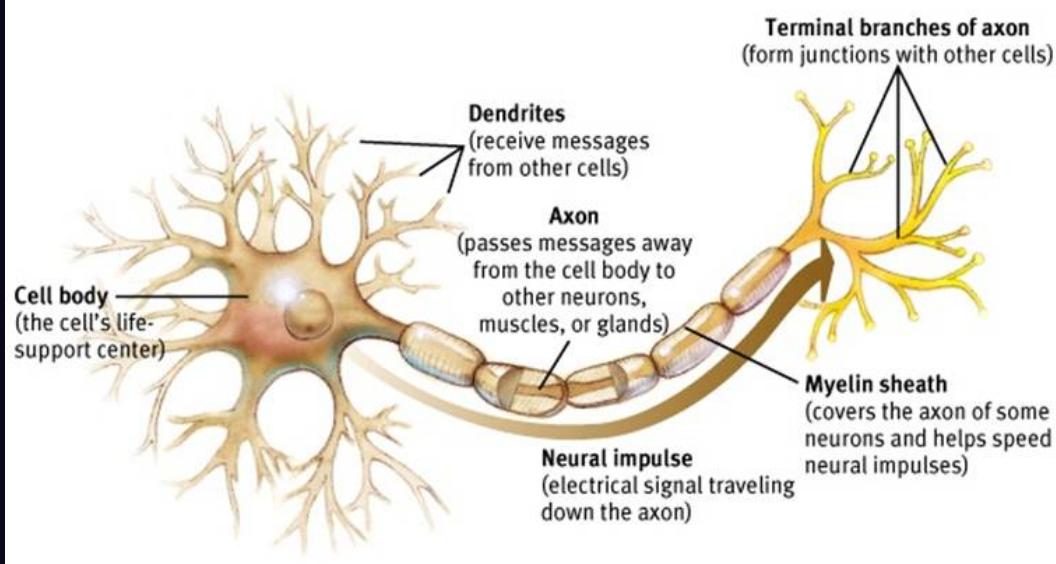
HZDR, Dresden

R. Dell'Anna, C. Masciullo et al., RSC Adv., 2017, 7, 9024

C. Masciullo, R. Dell'Anna et al., Nanoscale, 2017, 9, 14861

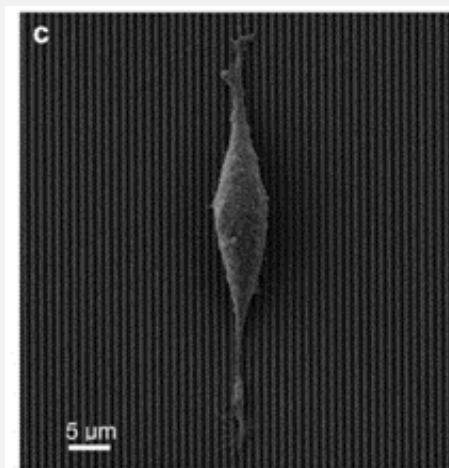
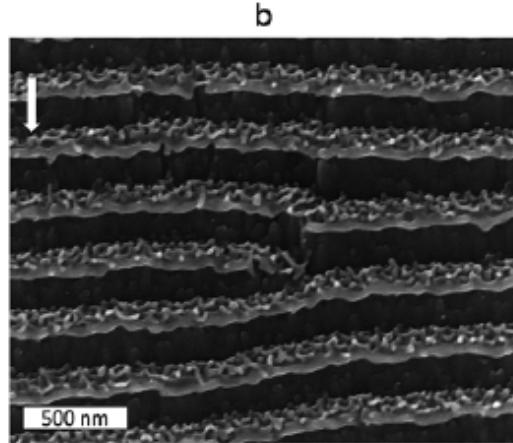
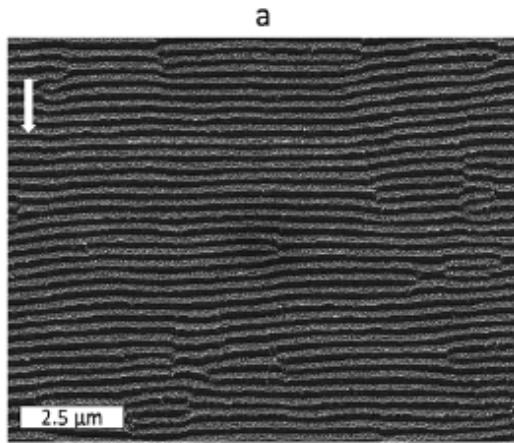
the rationale behind

development of artificial neuronal interfaces for nerve-regeneration devices



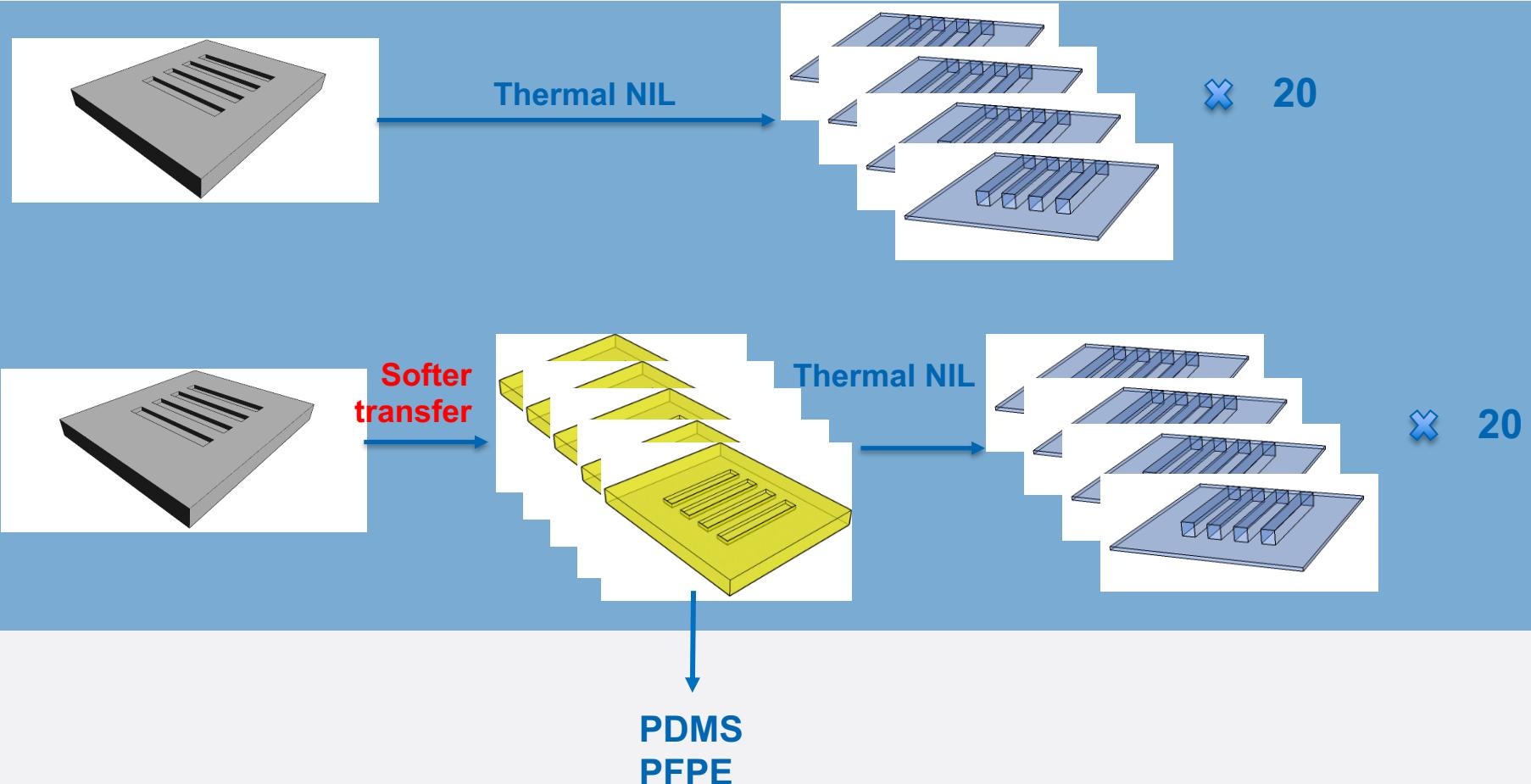
[www.csun.edu/~cmm14283/PSY%20150/
handouts/NeuronDiagram.doc](http://www.csun.edu/~cmm14283/PSY%20150/handouts/NeuronDiagram.doc)

The substrate



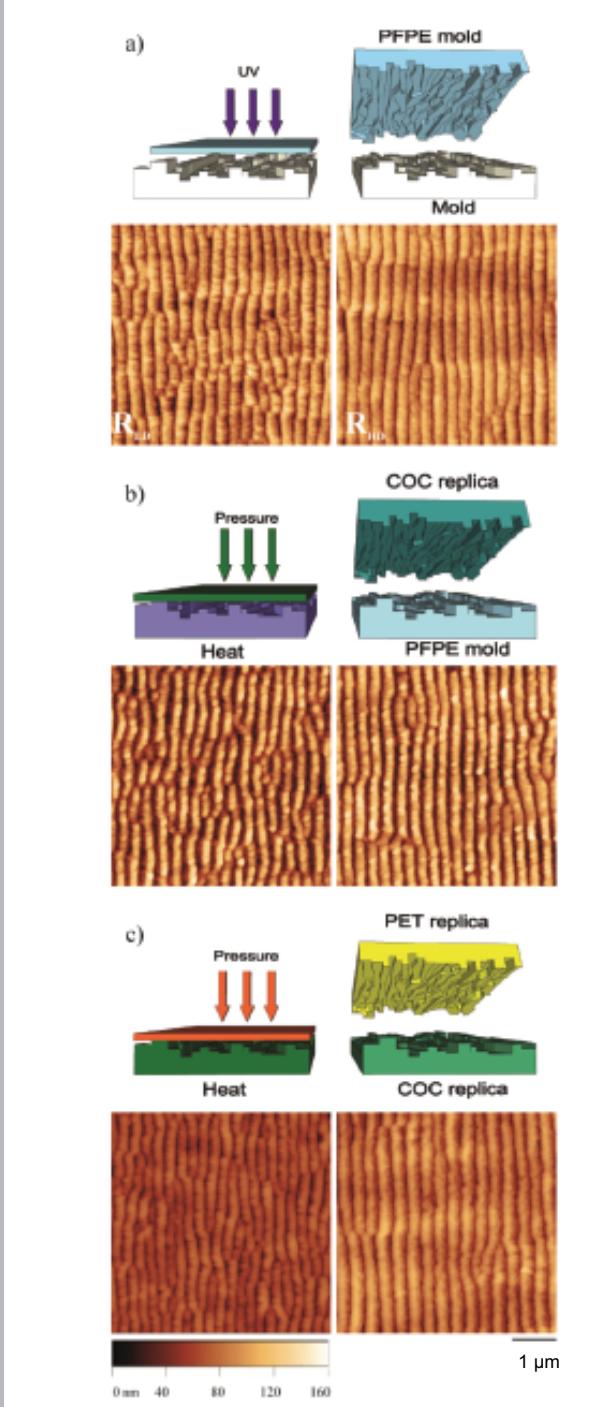
Ge surface irradiated with
26 keV Au ions
at $4.3 \times 10^{17} \text{ cm}^{-2}$ fluence and
60° incidence angle

the intermediate mold



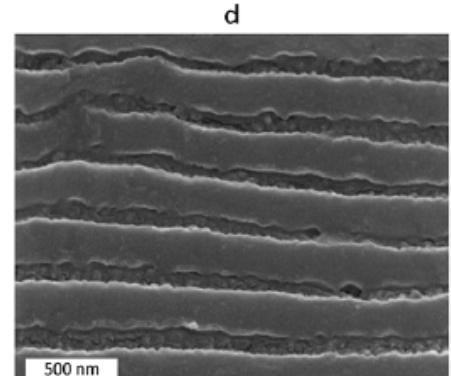
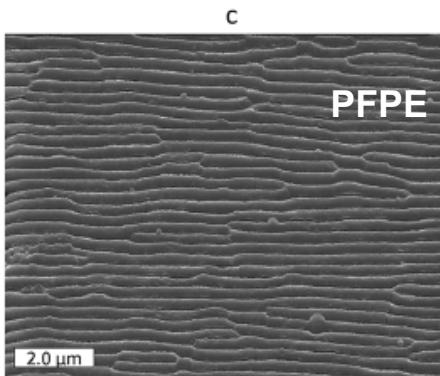
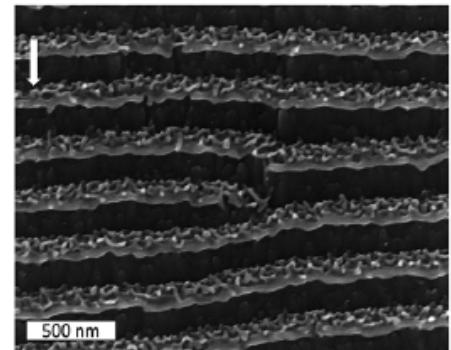
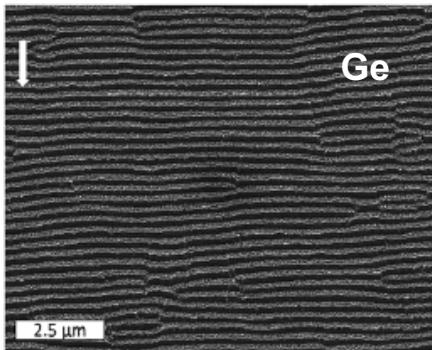
「The 3-step embossing process」

From Ge molds
to
polyethylene terephthalate
(PET) substrates

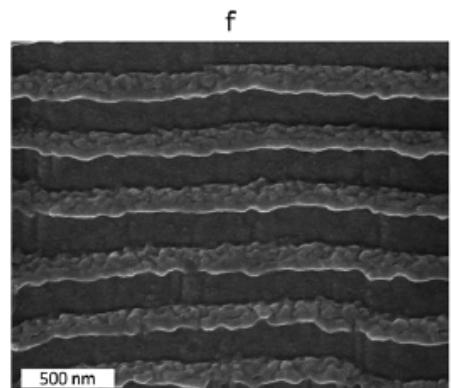
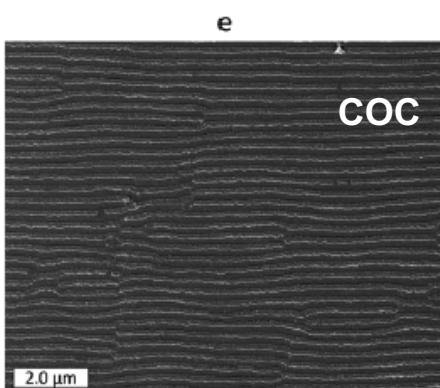
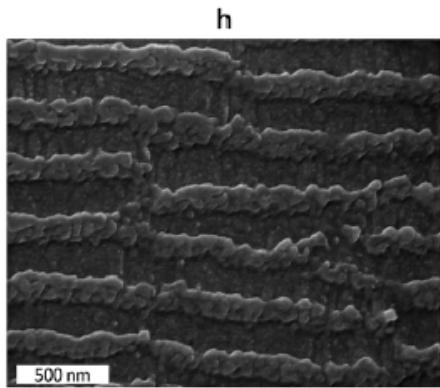
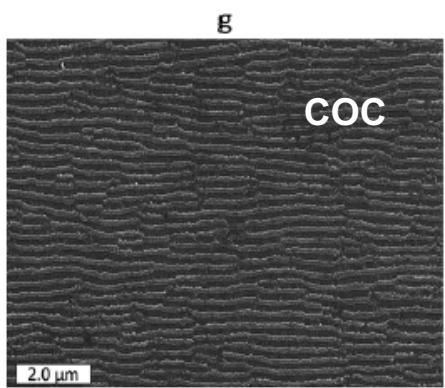


output

$$\Psi = 4.3 \times 10^{17} \text{ ions} \cdot \text{cm}^{-2}$$



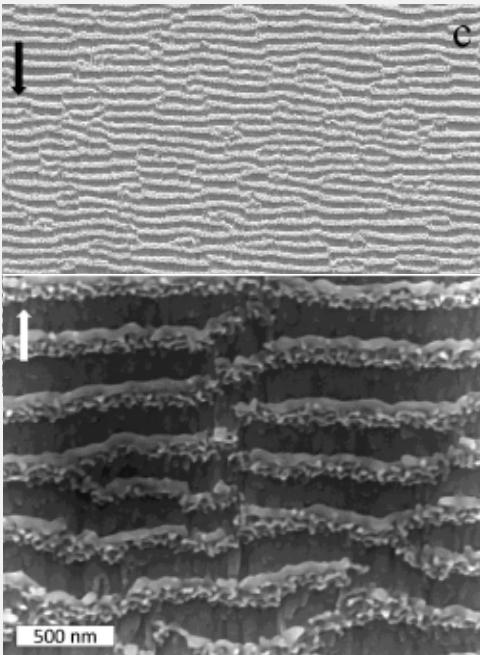
$$\Psi = 1.0 \times 10^{17} \text{ ions} \cdot \text{cm}^{-2}$$



R. Dell'Anna, C. Masciullo et al, RSC Adv 7 9024 2017

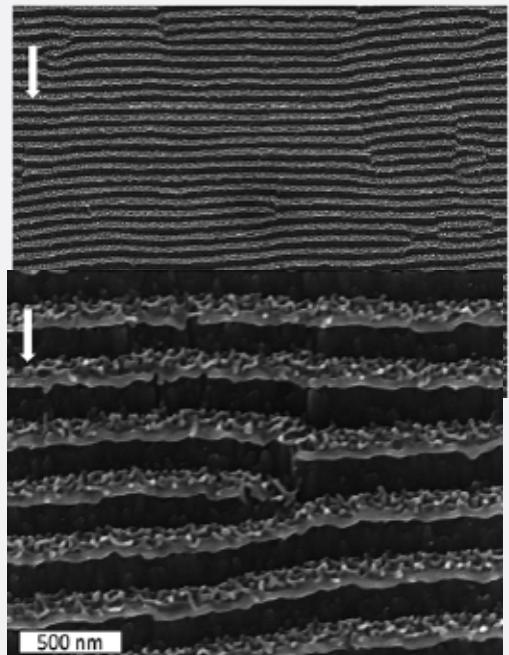
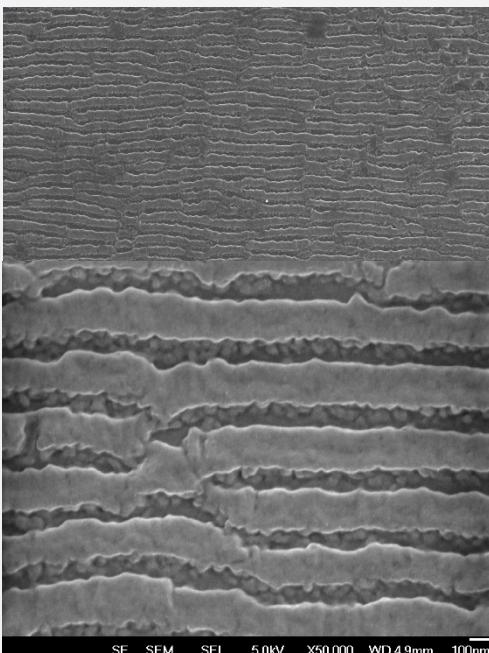
the 3-step embossing process

Ge

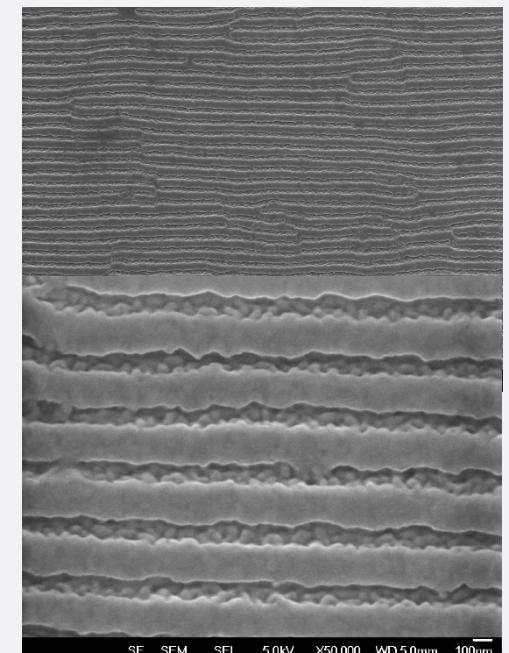


1.0×10¹⁷ ions·cm⁻²

PET



4.3×10¹⁷ ions·cm⁻²

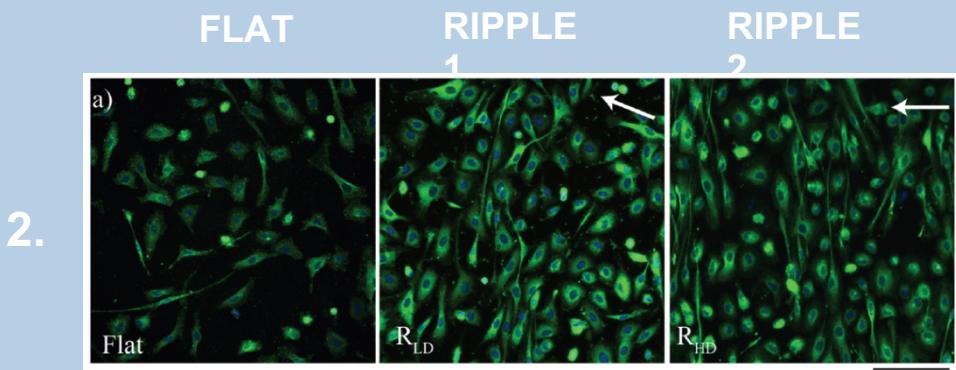
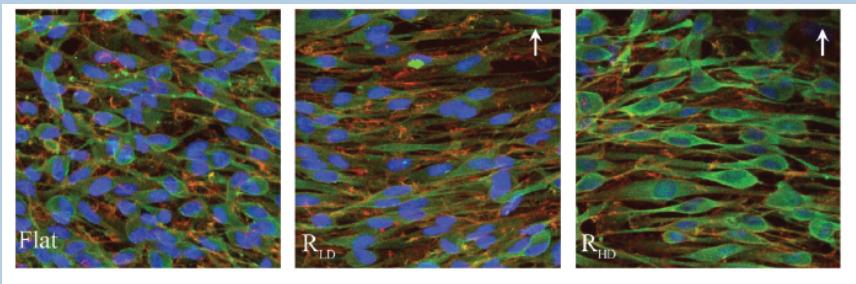
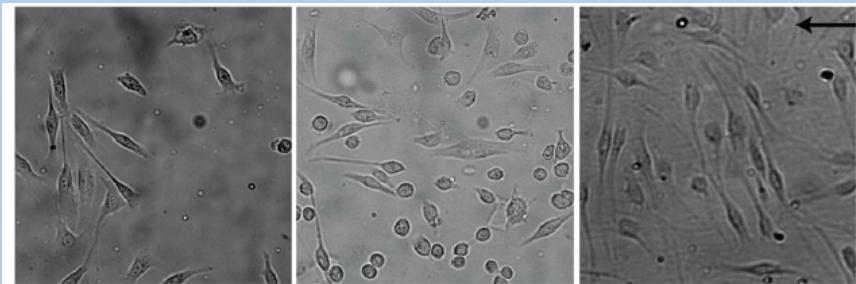


C Masciullo, R Dell'Anna et al,
Nanoscale 9 14861 2017

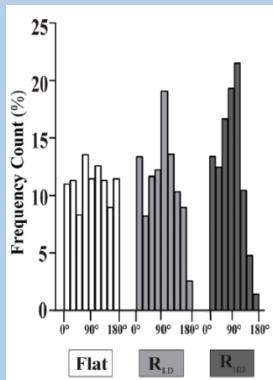
Cellular behavior

Schwann cells

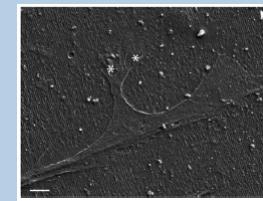
1. adhesion and viability
2. spatial organization
3. filopodia orientation



Cell angular distribution



3.



Filopodia



AFM and Raman study of graphene deposited on silicon surfaces nanostructured by ion beam irradiation



MNF-FBK, Trento

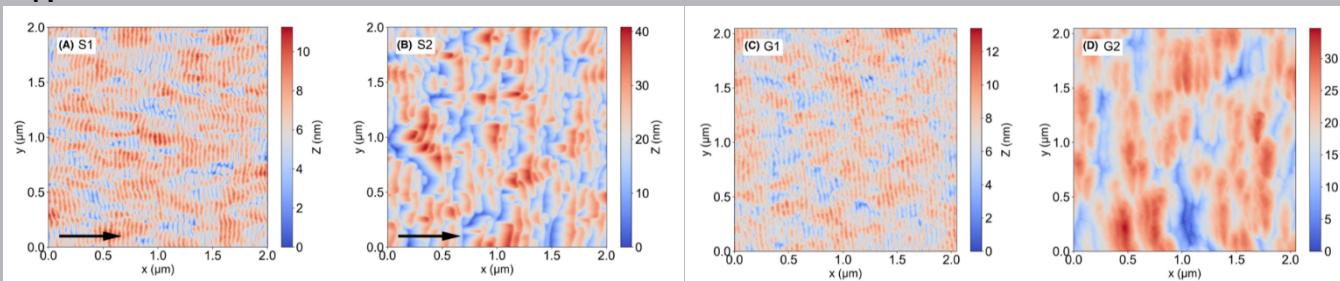
University of Sussex, Brighton

HZDR, Dresden

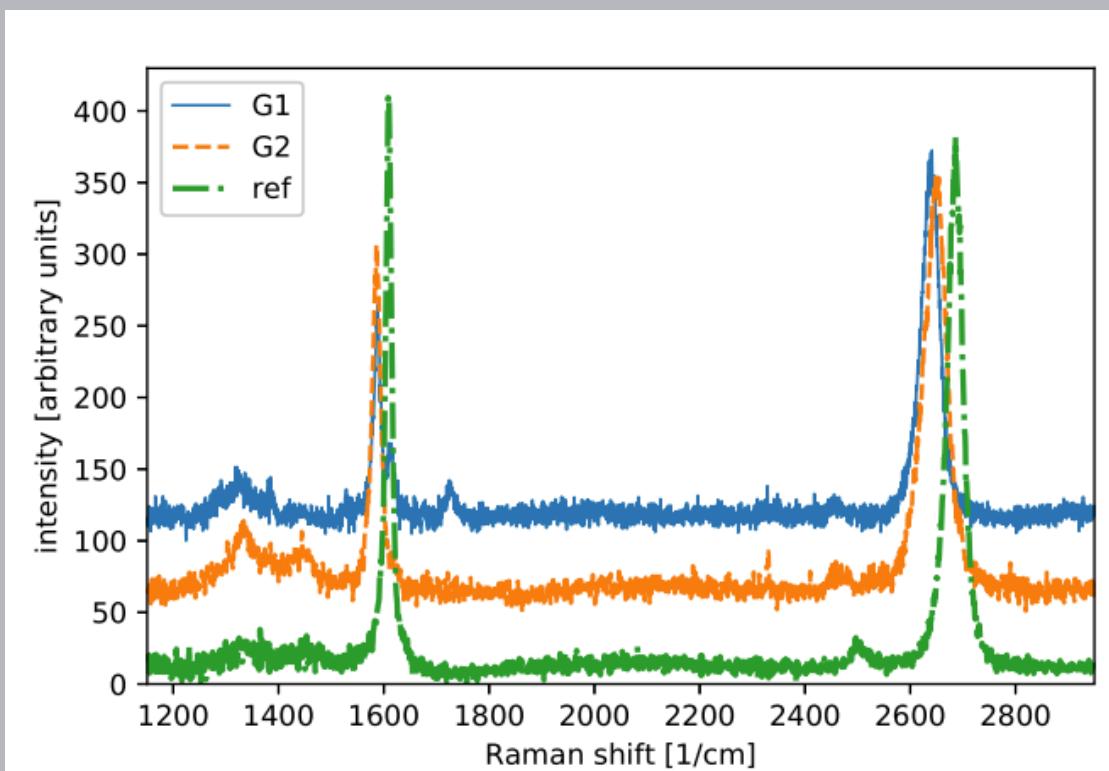
Raman from graphene deposited on Si nanostructured surfaces

Bare Si samples	After graphene deposition	Implanted ion species	Energy (keV)	Fluence 10^{18} (ions/cm $^{-2}$)	Incidence angle (°)
S1	G1	O+	1	1.0	50
S2	G2	O+	1	2.0	55
S3	G3	O+	1	2.0	50

1.



2.



1. AFM topography of the O+ irradiated Si surface and subsequent graphene deposition;
2. Raman spectra from graphene covered samples G1 and G2 and from CVD-grown graphene deposited onto a flat Si surface (reference)

uniaxial strain
in the
more conformal
graphene sheet



*Fondazione Bruno Kessler,
Micro Nano Facility, Trento*



thank you



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Materials Research,*



*NEST, Scuola Normale Superiore,
Istituto Nanoscienze-CNR, Pisa*



Department of Physics and Astronomy