

Summer school on Epitaxy MATEPI 2025 Porquerolles June 22-27 2025

Self-organization & surface nano-structuration

Noëlle Gogneau

Introduction

Definition of the self-organization and the nano-structuration

Self-organization

Nano-structuration methods, which impact on the epitaxial growth?

Examples of nano-structuration applications

Inspiration from the living world

Self-organization

The term self-organization refers to the process by which systems organize themselves to create global order by interactions

Our environment is a composite of numerous self-organized patterns

An interesting feature of self-organization is the appearance of patterns such as stripes, hexagons, spirals and other complex forms in very different natural systems



Patterns on the nest of social birds, the skin of animals, bacterial colonies and so on are examples of self-organized patterns in living world





Pattern formation is the rule also in the non-living world with the formation of galaxies, clouds, river systems, mountains..., all forms of erosion

At the materials (macro/millimeter) scales



Jusangjeolli Cliff















Lotus



\rightarrow Hydrophobic properties





Butterflies



\rightarrow Anti-reflection properties



Introduction: surface nano-structuration in our labs

At the materials (nano) scales



Self-organized growth and self-assembly of nanostructures on 2D materials (atomically flat surfaces without dangling bonds facilitating the well-organized assembly



Self-assembled NWs



Self-assembled MMs exhibiting long-range (A)–(C) and short-range order (D) – (G)



Self-assembled QDs



Textile

Nanostructuration of the fibers to induce the water repellency or to improve the mechanical resistance of dress

Nanostructuration of surface to study the human body such as the neurons or to develop nanoporous

Health

develop nanoporous materials and avoid the fixation of the bacteria.



6



Energy



Reduction of the energy consumption of microdevices, improvement of the efficiency of the energy conversion

Automobile



Synthesis of Plexiglass following a nano-motif induces an improvement of the resistance while keeping the transparence

The surface (volume) (nano)structuration opens the way towards a large range of applications





Aerospace Nanostructuration of the aircraft wings induces the inhibition of icing

Nanostructuration of Surfaces/materials

Electronic & Communication



Improvement of the devices performances, reduction of their dimensions

Introduction

Definition of the self-organization and the nano-structuration

Self-organization

Nano-structuration methods, which impact on the epitaxial growth ? Examples of nano-structuration applications

Combination of self-organization and nano-structuration towards applications

Surface self-organization

"A process where some form of overall order arises from local interactions"

The process can is spontaneous when sufficient energy is available, not needing control by any external agent.

In the case of growth at a surface:

"A growth process during which a spontaneous surface (nano)structuration occurs"

In heteroepitaxy, the growing film frequently undergoes a series of driving forces (surface/facete energies, potential barriers, strain...) that lead to self-organization mechanisms (that are not restricted to a specific growth system)

Self-organization includes:

surface reconstruction, step bunching, step meandering, faceting, relaxation with formation of misfit dislocations or islands...

Under certain conditions, these mechanisms and their interplay result in self-organized nanostructure arrays

Epitaxial Growth: a single crystal that grows with a particular orientation, a single crystal in its lattice structure and properties



Two type of epitaxy

Homo-epitaxy The film and substrate are the same material





Self-organization



Homo-epitaxy

The film and substrate are the same material



Different growth morphologies taking origin in the diffusion behavior of adatoms on singlecrystal surfaces, which is determined by the local potential energy surface for adatoms.

Steps are characterized by the Ehrlich–Schwoebel (ES) barrier making more difficult the diffusion for atoms to hop down over a descending step edge than to diffuse over the terrace.





At low-deposition fluxes, high-surface mobility, or small terrace, all depositing atoms find the ascending step edges during their 2D random diffusion over the terrace, where they get incorporated. Only a few atoms overcome the ES barrier and get incorporated in the descending step edge. This stabilizes the terrace widths during growth, resulting in equally spaced step–step distances characteristic.

At slightly higher deposition fluxes, lower mobility, or wider terraces, adatoms diffusing randomly on the terraces lead to the nucleation of islands. As the mean distance between islands is determined by the mean-free diffusion path of the arriving adatoms, most atoms overcome the ES barrier and get incorporated into the rim of the island. As a consequence, no second-layer islands nucleate before the original layer is completely filled.



At (very) higher deposition fluxes or lower mobility, island nucleation continuously occurs on top of the terrace leading to a rough growth front. No interlayer mass transport (very high or infinite ES barrier)

Epitaxial Growth: a single crystal that grows with a particular orientation, a single crystal in its lattice structure and properties



Two type of epitaxy

Homo-epitaxy

The film and substrate are the same material

Hetero-epitaxy

The film and substrate are different materials



Surface/facete energies & misfit strain: 2 driving forces affecting the surface self-organization

Epitaxial Growth modes 2D layer-by-layer growth (Frank-van der Merwe) Si/Si, TiN/MgO 3D island growth (Volmer-Weber) metals on SiO₂ Stranski-Krastanov In/Si, Ag/Si, Ge/Si, InP/GaAs, GaN/AIN Growth time (deposition) [19]





Surface energy (γ_S) Epitaxial layer energy (γ_D) Interfacial energy (γ_{int})

Frank-van der Merwe: each layer of deposited atoms is completed before the next layer starts to form. The surface at any instant will be flat or will contain a few monolayer steps.

Relaxation of strain via dislocations





Misfit dislocations





Volmer-Weber (island growth): each deposited atom attaches to an island (or incipient particle); islands grow appreciably before joining up to cover the substrate completely. The surface at any instant will not be flat, and the substrate may not be entirely covered.

Epitaxial Growth modes



Surface energy (γ_s)

Epitaxial layer energy (γ_D) Interfacial energy (γ_{int})





Stranski-Krastanov *(intermediate mode)*: initially the deposited atoms form one or more perfect layers (wetting layer) but this is followed by island growth. The surface is therefore initially flat but develops to become less flat.

Existence of a critical thickness defined as the limit of film thickness wherein the strain is still elastically accommodated.

Induced by lattice mismatch (a minimum is required) and can be delayed or suppressed by playing with surface energy

Surface energy (γ_S) Epitaxial layer energy (γ_D) Interfacial energy (γ_{int})

Epitaxial Growth modes





Surface energy (γ_S) Epitaxial layer energy (γ_D) Interfacial energy (γ_{int})

When barrier is sufficiently thick for presenting its proper lattice parameter: No correlation between QDs





DOI: 10.1016/j.jlumin.2017.06.030



When barrier is sufficiently thin, it remains locally affected : Vertical correlation between QDs



Self-organization: another growth mode













The mode by which epitaxial material grows depends on:

- The interface energy,
- The lattice mismatch between substrate and film/material,
- The growth temperature,
- The flux of the incoming species,
- The surface energy,
- ... and other effects that can be complicated by surface segregation and alloying

Surface self-organization

"A process where some form of overall order arises from local interactions" The process can is spontaneous when sufficient energy is available, not needing control by any external agent.

In the case of growth at a surface:

"A growth process during which a spontaneous surface (nano)structuration occurs"



Elegant approach and efficient route for fabricating large-scale arrays of nanostructures

Self-organized \rightarrow difficult control of the surface position, high-degree of uniformity...



Introduction

Definition of the self-organization and the nano-structuration

Self-organization

Nano-structuration methods, which impact on the epitaxial growth?

Combination of self-organization and nano-structuration towards applications

Surface Nano-structuration

Creation of well defined motif at nanometer scale

- \pm At the top of substrates or surface materials
- \pm Enside the material volume

A crucial issue for material science

- \checkmark Guide the growth
- \checkmark Control the nanomaterial dimensions and localization
- ✓ Understand the growth physics
- ✓ Modulate (enhance) the existent properties
- ✓ Favor the appearance of new properties
- ✓ A new alternative for characterizing properties of nano-objects, molecules or cells

Objectives

Direct nano-structuration of the surface/volume





Nanotechnology 2004







Nano-structuration through a deposited or self-assembled thin film on surface





SiO₂ patterned layer Nanotechnology 2011





HSQ patterned layer J. Cryst. Growth 2008



Si substrate

Photolithography

Process to transfer a pattern from a photomask to the surface of the substrate or of an underlying material.

For dimension > $1\mu m$

With this process, there is no limitations of substrate (Semiconductor, metal, glass, plastic...)

- > A **photosensitive polymer** is deposited (by spin-coating) directly on the substrate or on a masking layer.
- The photosensitive polymer is selectively exposed with \geq visible or UV light through a mask.
- To transfer the image of the mask in the polymer and \succ then providing patterned access to the underlying surface, the sample is developed
- If a masking layer covers the substrate, an etching step (via \succ chemical, plasma or physical process) is realized, then transferring the image of the mask in the underlying layer and then to the substrate



Photolithography

For dimension > $1\mu m$

Process to transfer a pattern from a photomask to the surface of the substrate or of an underlying material.With this process, there is no limitations of substrate (Semiconductor, metal, glass, plastic...)

Photolithography Process



Photoresist is organic compounds mixed with a solvent solution. Two type of resist:

- Positive Resist: the exposed regions of the photoresist become more soluble. They are left after development step. It is a direct transfer of the mask.
- Negative Resist: the exposed regions of the photoresist become harden. The non-exposed areas are left after development. It is an opposite (negative) transfer of the mask.

E-Beam lithography (EBL)

For dimension \rightarrow few nm

Process to transfer a pattern from an electron-sensitive mask to the surface of the substrate or of an underlying material.

With this process, there is not intermediate mask, it is a direct write technique

The EBL remains a tool of choice in application areas involving the writing of micro-and nanostructures on the wide variety of materials.

Some limitations of substrate due to the charge effects and the proximity effects



- A focused beam of electron is scanned across a substrate covered by an electron-sensitive resist.
- Due to the electron/material interaction, resist changes its solubility properties according to the energy deposited by the electron beam
- Depending of the resist (positive or negative) the mask will be revealed after development step.



24

E-Beam lithography (EBL)

Resolution \rightarrow few nm

or of an underlying material. The EBL remains a tool of choice in application areas involving the writing of micro-and

nanostructures on the wide variety of materials.

Process to transfer a pattern from an electron-sensitive mask to the surface of the substrate



E-beam Exposure



Nano-imprint lithography (NIL)



Process to create on the surface patterns by mechanical deformation of a thin imprint resist with a template (mold, stemp) .

NIL is a method of fabricating micro/nanometer scale patterns with low cost, high throughput and high resolution.

With NIL nanometer sized patterns can easily be formed on various substrates, e.g., silicon wafers, glass plates, flexible polymer films, and even nonplanar substrates

The principle of Nanoimprint lithography is a simple nanolithography

- The imprint resist, typically a monomer or polymer formulation, is deposited onto the surface.
- The mold is mechanically pressed with controlled pressure and temperature on a substrate.
- The thin polymer film, cured by heat or UV light during the imprinting, is modified.
- Then the mold is separated from the substrate
- A subsequent pattern transfer process (by using RIE) is used to transfer the pattern in the resist
- The underlying surface is etched, then transferring the pattern into the surface.



[14]

Focus Ion Beam (FIB)



Process to transfer a pattern from a mask to the substrate surface or an underlying material based on ions/material interaction

Like EBL, this process is a direct write technique, no required mask

FIB is characterized by a better resolution than EBL because secondary electrons have lower energy but it is easier to focus an electron beam "Classical" FIB used Ga⁺ ion beam to raster over the surface

The FIB working principle is similar to the EBL

- ✤ A sensitive layer is exposed to focused ion beam.
- ✤ A focused beam of electron is scanned across a substrate covered by an ion-sensitive material.
- Due to the ion/material interaction, the layer is depleted
- ✤ Resolution of few nm



[15]

27

Process to pattern the surface based on colloidal solution.

Colloidal nanolithography

This technique is an easy, fast and cheap process to implement [16]



- ✤ First, the colloidal solution is spin-coated on the substrate whose the surface has been previously chemically treated in order to allow the good adherence of the colloid.
- Commercial colloidal solution is formed by polyestirene nanobeads. Initially, the diameter of these nanobeads is around 100-200 nm and their density can be adjusted by a water dilution of the solution.
- Second, once the nanobeads are dispersed on the surface, a plasma oxygen treatment will be used to reduce the diameter of the nanobeads around 50-80 nm and thus to isolate them.
- Finally, a thin Ti layer is evaporated on the surface followed by a lift-off step. The process thus results in a substrate nanostructured with a Ti mask containing uniform circular nano-openings.

28

Block Copolymer	Nanometer-scale architectures in thin films of self-assembling block copolymers by hetero-epitaxy or grapho-epitaxy*
	self-assembled patterns are considered as nano-lithographic masks as well as templates for the further synthesis of
	inorganic or organic structures

Block copolymers consists of two or more polymeric chains (blocks), which are chemically different and covalently attached to each other. In the melt, they are driven to segregate into a variety of ordered structures by the repulsion of the immiscible blocks (according to a phase diagram).



[17] Fig. 1. Diblock copolymers are predicted to self-assemble according to a phase diagram predicted by self-consistent mean field theory (a) and proven experimentally (b). A variety of constant-radius geometries are observed as a function of relative lengths of the two blocks (c). Reproduced with permission from *Physics Today* [2].

* The growth of an aligned layer, from a seed, on the surface of a substrate

Nanometer-scale architectures in thin films of self-assembling

Block Copolymer

block copolymers by hetero-epitaxy or grapho-epitaxy*

self-assembled patterns are considered as nano-lithographic masks as well as templates for the further synthesis of inorganic or organic structures

Block copolymers consists of two or more polymeric chains (blocks), which are chemically different and covalently attached to each other. In the melt, they are driven to segregate into a variety of ordered structures by the repulsion of the immiscible blocks (according to a phase diagram).

if we consider the simple case of a blend of two homopolymers, A and B, the phase behavior may be controlled by three experimental parameters:

 \circ the degree of polymerization (N),

 \circ the composition (f),

 \circ the A–B Flory–Huggins interaction parameter (x)



* The growth of an aligned layer, from a seed, on the surface of a substrate

29

Inorganic layers Lithography

[19] **Self-assembled titanium calcium oxide nano-patterns**





Scanning probe lithography

Mechanical patterning technique based on the interaction between the surface and the AFM tip Voltage polarization of the conductive tip

AFM lithography – Scratching & Nano-indentation

- Material is removing from the substrate leaving deep trenches with characteristic shape of the tip
- A precise process (pattern wherever wanted) not requiring additional processing steps
- But a non clean process (debris on wafer).



AFM lithography – Anodic oxidation

- AFM Anodic Oxidation modifies the geometrical properties and also of the local electrophysical properties of the sample surface by applying voltage.
- In air or other humid atmosphere, the tip and the are covered by thin film of absorbed water. When the tip approaches sufficiently close to the surface, a water bridge is produced due to capillary effect. Because the surface is positively charged and the tip negatively, the application of an electric field induces the electrochemical reaction. The tip and the surface will interact as anode and cathode respectively.
- Oxide grows on the point right under the tip.





Introduction

Definition of the self-organization and the nano-structuration

Self-organization

Nano-structuration methods, which impact on the epitaxial growth?

Examples of nano-structuration applications

Combination of self-organization and nano-structuration towards applications

Surface Nano-structuration













2µm





Surface Nano-structuration Critical technological step which requires to take into account several criteria

→ Depend of the final objective, the targeted dimensions of the pattern, the patterned material/support, the epitaxial technique, epitaxial growth conditions...



Surface Nano-structuration Critical technological step which requires to take into account several criteria

Other impacts – *specific to your patterning process*

- The surface contaminants / Residuals
- Surface adhesion
- Over-etching in the case of wet etching,
- Oxidation in the case of RIE,
- Local induced strained (FIB),
- o Surface cleaning before and after the nano-patterning







All this parameters have to be identified and controlled in order to avoid/minimize "problems" of growth





Surface Nano-structuration



For each objective, its own surface nano-structuration

50 mm

0 hha

Numerous defects are generated in the hetero-epitaxy of GaN, with notably prevalent threading dislocations (TDs)



Substrate (Sapphire, Silicon Carbide, etc.)

Epitaxial Lateral Overgrowth (ELOG) technology for reducing the defect density

- Parts of the highly dislocated starting GaN is masked with a dielectric mask, and then the growth is restarted.
- The deposition initially occurs within the openings with no deposition on the mask. As the growth continuous, growth spreads increasingly onto the mask stripes while maintaining a 2D surface. At the end, a flat top surface is reached.
- The TDs are prevented from propagating into the overlayer by the dielectric mask, whereas GaN grown above the opening (coherent growth) keeps the same TDs density.
- This one-step-ELOG leads to a layer composed with highly dislocated GaN (above the openings) and low dislocation density GaN (over the masks).



Growth time

Numerous defects are generated in the hetero-epitaxy of GaN, with notably prevalent threading dislocations (TDs)



Epitaxial Lateral Overgrowth (ELOG) technology for reducing the defect density \rightarrow to about 10⁴ per cm²

- Parts of the highly dislocated starting GaN is masked with a dielectric mask, and then the growth is restarted.
- 2 steps ELOG process
 - \rightarrow In first step, the growth conditions are monitored to obtain triangular stripes.
 - → Inside these stripes, the threading dislocations arising from the templates are bent by 90° when they encounter the inclined lateral facet.
 - \rightarrow In a second step, the growth conditions are modified to achieve full coalescence.









[27] Selective area growth (SAG) attracts considerable interest as a powerful tool for the monolithic integration of semiconductor optical devices (InP-based photonic integrated circuits).







39

On substrate without mask

The pyrolysis reaction leading to the atomic In consists of three consecutive homolythis fission steps [28,29].

In the gas phase

$$(CH_3)_3 ln \rightarrow (CH_3)_2 ln + CH_3 (1)$$
$$(CH_3)_2 ln \rightarrow CH_3 ln + CH_3 (2)$$

At the surface

 $CH_3 In \rightarrow In + CH_3 (3)$



On substrate with mask Distribution of the active species is modified by the presence of the mask

Modulation of the epitaxial growth and compounds composition



3 mains species = 3 diffusion lengths

estimated from few hundreds of μm to few hundreds of nm



Plot of reactant concentration calculated for one example case.



Calculation of the macroscopic cross section of the concentration variation over the patterned surface Figure showing a magnified representation of the same calculation focusing on the region above the mask opening.

[34]

Low-dimensional nanostructures (QDs, NWs) are strongly interesting for fundamental research due to their unique structural and physical properties

Self-assembled nanostructures (QDs or NWs) are characterized by a dispersion of their size, shape, localization & composition in case of ternary/quaternary alloys



Not suitable for

high-efficient devices

Useful dispersion



To investigate the variation of the nanostructures properties as a function of their dimensions 1μm x 1μm (G)

(C







Selective area growth to

Control the position of the nanostructures

Control the dimension of the nanostructures

[33]

First solution : a dielectric mask with controlled nano-opening position and dimensions

Molecular beam epitaxy Sticking coefficient close to 1

(a) (c) SiO₂ mas Si(111) (f) Top-view HF 1% (d) (e) Patterned SiO₂ mask Si(111)



*If pitch of the nano-opening > 2*diffusion length of the adatoms*

Need to play with the difference in terms of sticking coefficient of the active layer between the mask and the surface \rightarrow Short range of growth parameters

41

First solution : a dielectric mask with controlled nano-opening position and dimensions

MOCVD epitaxy Sticking coefficient << 1



If pitch of the nano-opening > 2*diffusion length of the actives species diffusion in surface (MMx and x adatom)







Initial opening of few 10 nm



InAs/InP QDs

surface

Second solution : a direct pattern of the substrate with holes









Second solution : a direct pattern of the substrate with holes

MOCVD epitaxy Sticking coefficient << 1

GaAs(111)B $finite{f$



Chemical decomposition different on GaAs (111)A and GaAs (111) B

GaAs substrate

111)B

- Faster decomposition of actives species on 111A
- Capillarity effects are favorable to the QDs formation

Control of the DQ size and shape by adjusting the pattern dimensions and the growth condition



Introduction

Definition of the self-organization and the nano-structuration

Self-organization

Nano-structuration methods, which impact on the epitaxial growth ? Examples of nano-structuration applications

Combination of self-organization and nano-structuration towards applications

Use of vicinal substrate for localizing the self-assembled growth

Enhancement of self-assembly of SiGe QDs with superior PL



offcut misoriented substrate

QDs onSi

of SiGe

Growth

The misorientation of substrates modulate the surface energy and the surface diffusion length of adatoms leading to the formation of dense & small GeSi QDs on a miscut Si (001)/6° substrate with high confinement DOI/10.1063/1.4866356

Graphene surface self-organization on off-axis 4H-SiC(0001)

EFM characterization





The charge transfer between the substrate and graphene bilayer results in an asymmetric charge distribution between the top and the bottom graphene layers opening an energy gap.

Self-organized metal–semiconductor graphene reveals the appearance of permanent electronic band gaps in AB-stacked bilayer graphene on (112–0) SiC nanofacets of 150 meV.



Use of nano- micro- structured surface to organize the growth

Orientation-patterned gallium phosphide for photonic integrated circuit

Nonlinear crystals are dispersive

 \rightarrow need to eliminate the phase mismatch between the different waves contributing to the wave-mixing process





https://doi.org/10.1051/photon/202312264

Phase matching within the nonlinear crystals can be achieved through the periodical reversal of the crystal orientation

References and sources

- 1. <u>https://blog.itil.org</u>
- 2. Sohrab Ahmadi-Kandjani, Thesis 2007
- 3. World meteorological organization; <u>www.hbrfrance.fr</u>; <u>www.nature.org</u>; <u>www.americanrivers.org</u>
- 4. Unesco.org
- 5. Wikipedia
- 6. <u>www.matierevolution.fr</u>;
- 7. www.ft.com
- 8. <u>https://doi.org/10.1515/nanoph-2012-0036</u>; FlatChem 5 (2017) 50–68; small 2006, 2, No. 6, 700 717; <u>https://doi.org/10.1063/1.1381102</u>
- 9. nanoscale.unl.edu
- 10. DOI: <u>10.1116/1.4799662</u>
- 11. <u>www.osapublishing.org</u>
- 12. electricianworldnews.com
- 13. doi:10.1016/j.jcrysgro.2008.04.019
- 14. Ag Nanohole Arrays with Silica Shells for Surface Plasmon Resonance Biosensing, ACS Nano 2011
- 15. SiGe NWs/Si(111), Beilstein J. Nanotechnology 2014
- 16. J. Cryst. Growth, 353, 1 (2012)
- 17. Materials Science and Engineering R 48 (2005) 191–226
- 18. To construct more diverse and complex nanostructures, Scientific Reports 2013
- 19. Self-assembled titanium calcium oxide nano-patterns, Nanoscale 2013
- 20. www.ntmdt-si.com
- 21. https://doi.org/10.1088/2399-1984/ab8450
- 22. DOI: 10.1088/0034-4885/73/3/036501
- 23. DOI: <u>https://doi.org/10.1557/S1092578300000788</u>
- 24. DOI: 10.1109/JSTQE.2004.837735
- 25. Phys. Chem. Chem. Phys., 2012,14, 9558–9573
- 26. https://doi.org/10.1016/j.mssp.2006.01.002
- 27. Jean Decobert Teams III-V Lab
- 28. DOI: 10.14279/depositonce-1618
- 29. J. Crystal Growth 92 (1988) 605.
- 30. https://doi.org/10.1038/s43586-020-00005-y
- 31. DOI: 10.1109/ICIPRM.2013.6562576
- 32. Progress in Quantum Electronics 75 (2021) 100304
- 33. C2N, Materials Dpt
- 34. DOI 10.1002/pssa.201228367
- 35. These R. De Lepinau, Thesis 2020
- 36. https://doi.org/10.1021/acs.nanolett.0c02236
- 37. M. Morassi Thesis 2018
- 38. Phys. Rev. B 65, 205306 (2002)

Thank you!