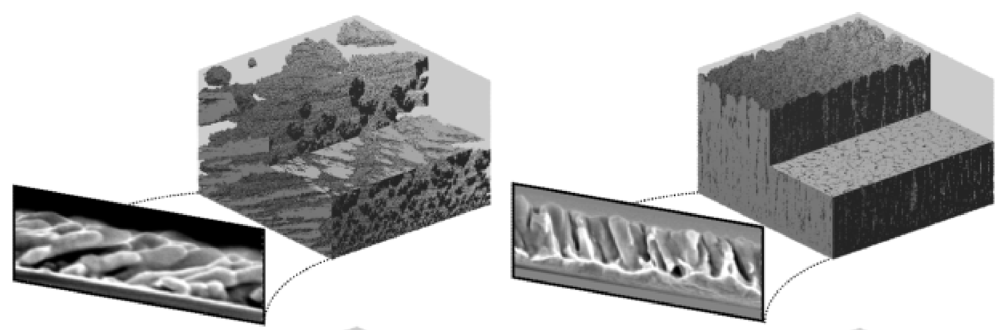
Fundamentals and Process-Control in Physical Vapor Deposition of Thin Films

Is it possible to design nanomaterials by computer?



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Outline

- Introduction to atomistic processes in thin films grown by vacuum and plasma-assisted PVD techniques
- Fundamentals of Physical Vapor Deposition
  - Without Plasma: electron beam-assisted physical vapor deposition
  - With Plasma: Magnetron sputtering depositions
- Is it possible to design nanomaterials by computer?

Introduction to atomistic processes in thin films grown by vacuum and plasma-assisted PVD techniques

Human technological evolución has been divided in ages

Stone Age
(-2500 AC)
First Tools

Copper Age
(2500-1800 AC)
Metals

Bronze Age
(1800-1600 AC)
Alloys

Iron Age
(1600 AC-)

What about now?

Nanotechnology and Plasma Technologies "in the kitchen"

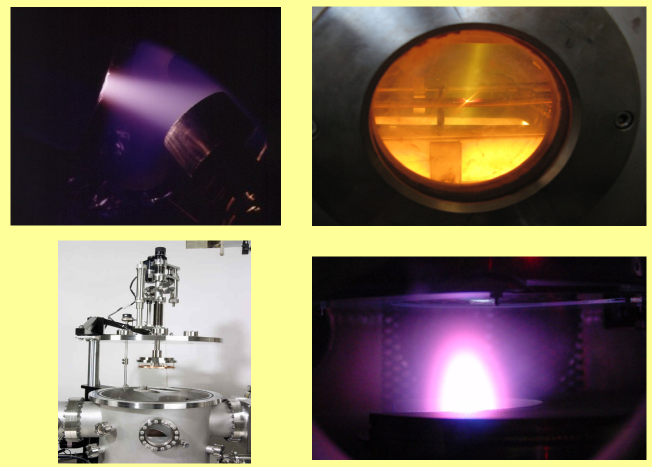
01.- Plasma TV
02.- Coated jet turbine blades
03- Manufactured LEDs in panels
04.- Diamond-like CVD eyeglass coating
05.- Ion-implanted artificial hip
06.- Plasma laser-cut cloth
07.- Plasma HID headlamps
08.- H_2 in fuel cell
09.- Plasma-aided combustion
10.- Plasma muffler
11.- Plasma ozone water purification
12.- Plasma-deposited LCD screen
13.- Silicon thin films for solar cells
14.- Microelectronics components
15.- Plasma sterilization in pharmaceutical production
16.- Treated Polymers
17.- Treated textiles
18.- Plasma-treated heart stent
19.- Diffusion barriers for containers
20.- Coated window
21.- Compact fluorescent plasma lamp

Processing Techniques in Nanotechnology

E-beam Assisted Physical Vapor Deposition

Thermal Evaporation

Laser ablation



Cathodic Arc Deposition

Others

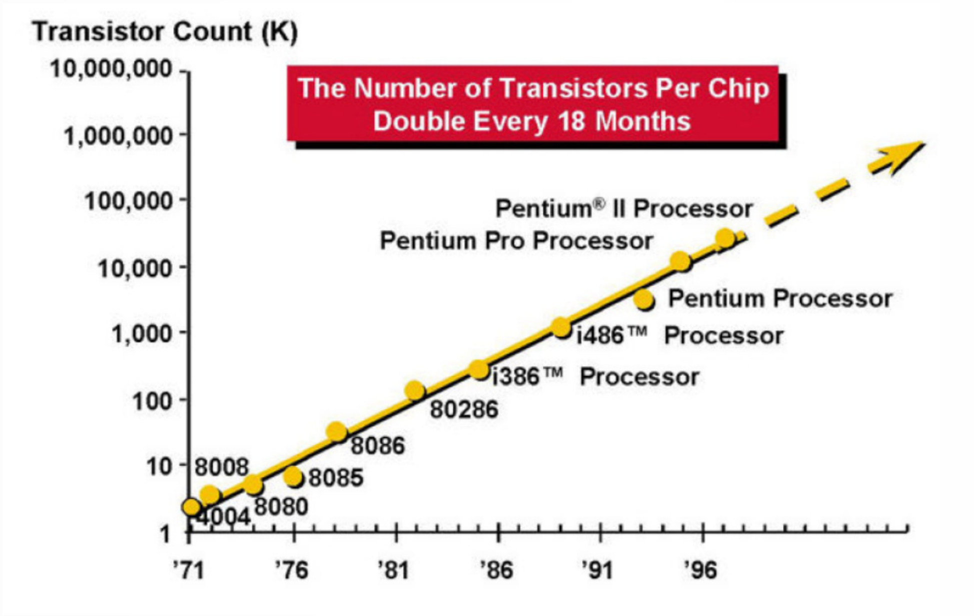
Plasma-Assisted deposition Techniques

Properties of the films are not only determined by the chemical composition but also by **the physical structure**!

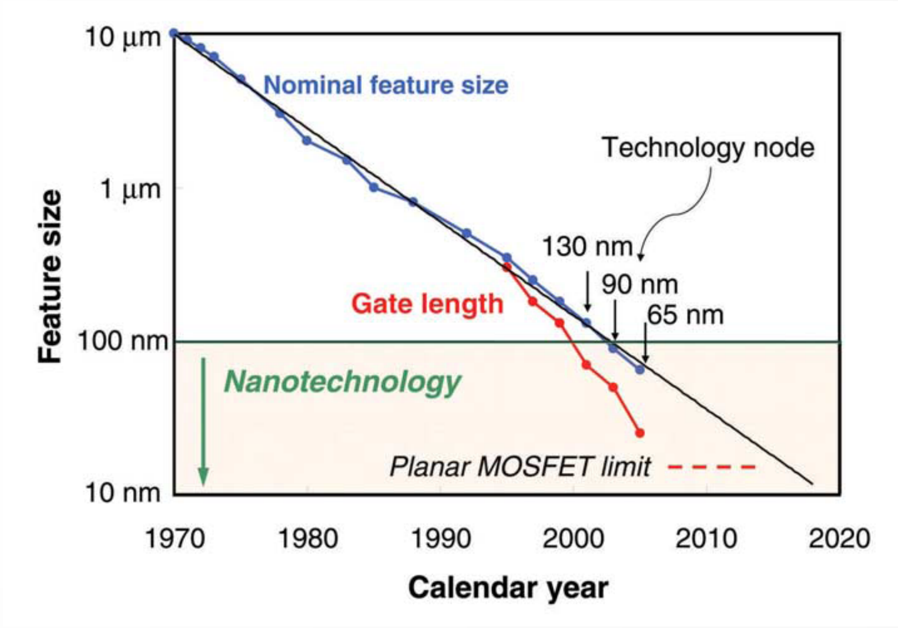
We need **far from equilibrium situations** to grow materials with metastable structures. We do not want **EQUILIBRIUM**

Control of the film nanostructure in smaller scales

Microelectronics: Moore's Law



Number of Transistor versus years



Transistor gate length versus calendar year

We need to tailor thin film structures in smaller scales

How do we approach the problem? (I)

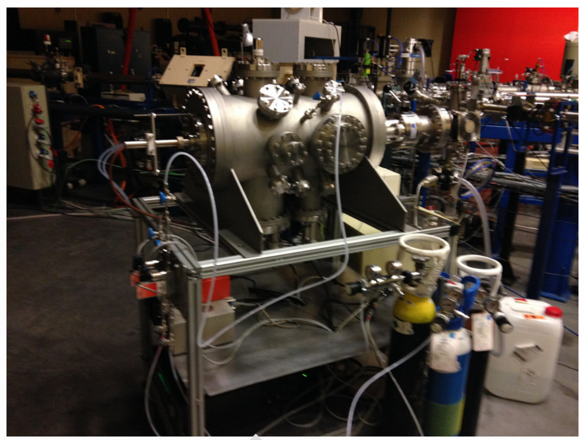
Top-Down Strategy

- An **overview** of the system is formulated.
- Often specified with the assistance of "**black boxes**“.
- Top-down approach starts with the **big picture.**
- **Trial and error**.

$$\begin{pmatrix} x_1 \\ \vdots \\ x_N \end{pmatrix}_0$$

Reasonable values of experimental parameters

→ Synthesis of coatings



→ Characterization for a given application (efficiency)

→ Correlation between efficiency and experimental parameters.

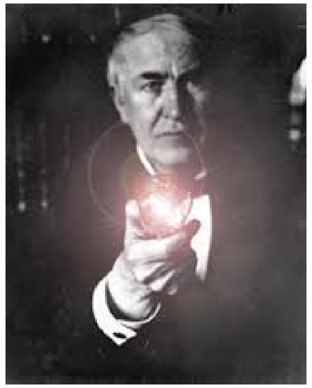
$$\begin{pmatrix} x_1 \\ \vdots \\ x_N \end{pmatrix}_i$$

Heuristic search of parameters for optimum efficiency

Top-Down Strategy

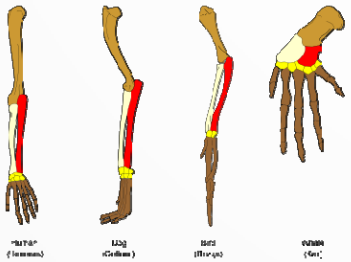
Pros:

- It leads towards fast results.
- A setup is tuned for maximum efficiency for a given application
- Economically viable
- Good examples that it works in history.



Thomas Edison failed more than 1,000 times when trying to create the light bulb, by trial and error

Edison allegedly said, "**I have not failed 1,000 times. I have successfully discovered 1,000 ways to NOT make a light bulb**."



Biological evolution: Random mutations and sexual genetic variations can be viewed as trials and poor reproductive fitness as the error. After a long time 'knowledge' of well-adapted genomes accumulates simply by virtue of them being *able* to reproduce

Cons: *System-dependent results*

- What if we add another element, thus another variable?
- What element do we need to introduce to improve results?
- No causal correlation between input and output
- Do we really control all the variables?
- Protocols at the laboratory could not be straightforwardly up-scaled to mass production.

Look out when correlating data using black boxes!!

It is proved that **butter production in Bangladesh, U.S. cheese production, and sheep population in Bangladesh and the U.S.** together "explained" 99% of the annual movements in the **stock market in U.S. between 1983 and 1993**.[1]


FREE SUMMER FLOWERING CLEMATIS
The Mail ON SUNDAY
ANITA HARRIS
I'm homeless and penniless
MI6 CHIEF BLOWS HIS COVER ON FACEBOOK
Andy's secret

Cows really can predict the rain. A theory says that cows can sense increasing air moisture **and will plop down to preserve a dry patch of grass**. Another theory states that cows lie down to **ease their stomachs, which are supposedly sensitive to changes in atmospheric pressure** brought on by rainfall. (Daily Mail March 14th 2007)

Cows can´t really predict the weather. Cows may lie down before it rains, **but they do that a lot**. Cows lying down in a field more often means **they're chewing their cud**, rather than preparing for raindrops. (NBC News August 20th, 2012)

[1]David J . Leinweber, Journal of Investing , "Stupid Data Miner Tricks" 16(1), 15-22 (2007)

How do we approach the problem? (II)

Bottom-Up Strategy

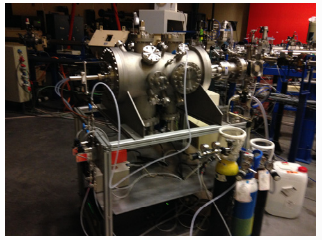
- A **bottom-up** approach is the piecing together of systems to give rise to more complex systems.
- Results analyzed as a function of **fundamental processes** and interaction among subsystems
- **Hypotheses and predictions** are made: a model is built

Hipotheses on fundamental processes

Experiment in wisely chosen conditions to prove or disprove them

$$\begin{pmatrix} x_1 \\ \vdots \\ x_N \end{pmatrix}$$

Experiment



Development of a model

$$\begin{pmatrix} x_1 \\ \vdots \\ x_N \end{pmatrix}$$

Solution of the model

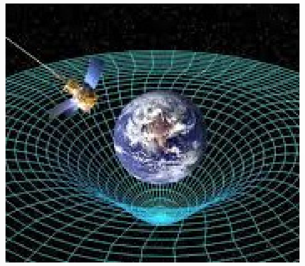
?

Once processes are understood: - Reactor design/modification for desired structures
- Open the door to computer design of nanomaterials

Bottom-up Strategy

Pros:

- It gives relevant information from fundamental level
- Allows indentifying the atomistic processes responsable for the nanostructuration
- Permits to design a deposition system to deposit "a la carte" thin films
- Enables computer design of thin films
- Permits process-control and upscaling of laboratory results to industry



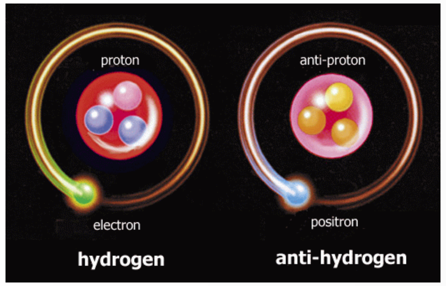
Laws of physics (Gravity)

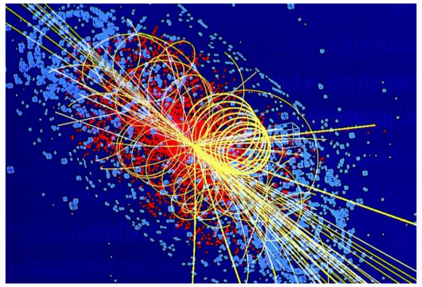
Higgs Boson

Theory of Relativity

Existence of antimatter

…

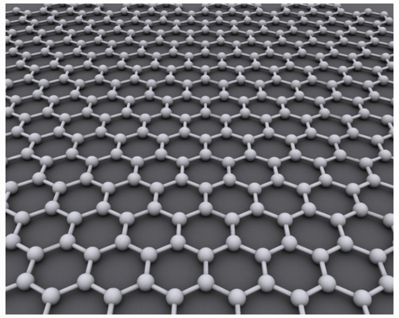




Cons: *Complex systems!*

- Far from equilibrium
- Non-lineal processes
- Not all processes are known
- Theories are also based on approximations: search of simple conditions

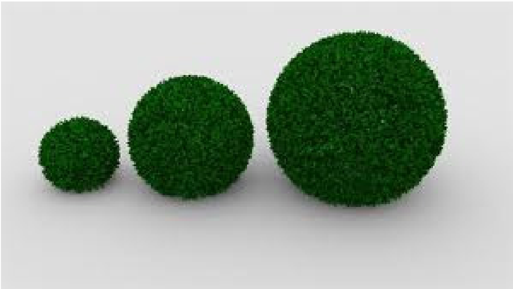
It has also failed in many cases



Graphene does not to exist in the free state, and believed to be unstable with respect to the formation of curved structures.[1]

[1]Fradkin, E. Critical behavior of disordered degenerate semiconductors, *Phys. Rev.* B **33**, 3263-3268 (1986).

Light propagates in ether

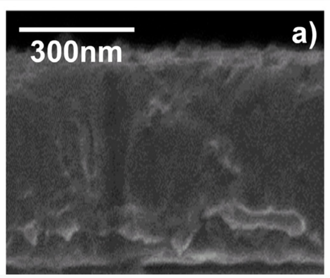


What is a thin film?

Thin Films are **very thin layers of materials** used to manipulate various surface properties.

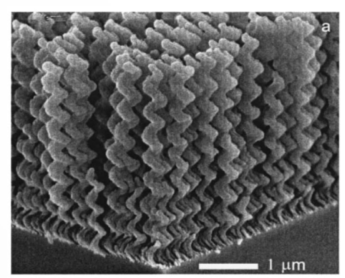
- **Optical thin films** (Filters, Anti-reflection, Cosmetic, security devices, architectural)
- **Surface chemical modification**(hydrophobic, bio & chemical sensors)
- **Barrier coatings** (packaging films, ultra-barriers)
- **Electrical coatings** (anti-static, shielding, displays)
- **Hard and wear resistant coatings** (cutting tools, bearings, engine parts, plastic optics)
- **Decorative coatings** (watch cases, bathroom furniture, door furniture, plastic mouldings, metallic yarns

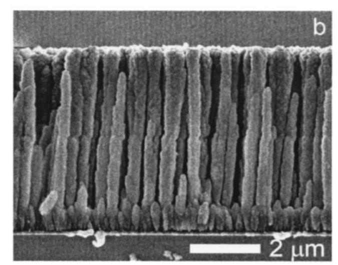
Compact Thin Films

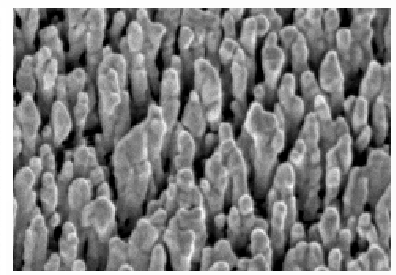


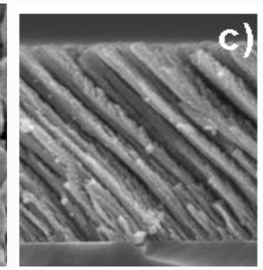
Highly Dense
High Refractive Index
Low Surface

Porous Thin Films





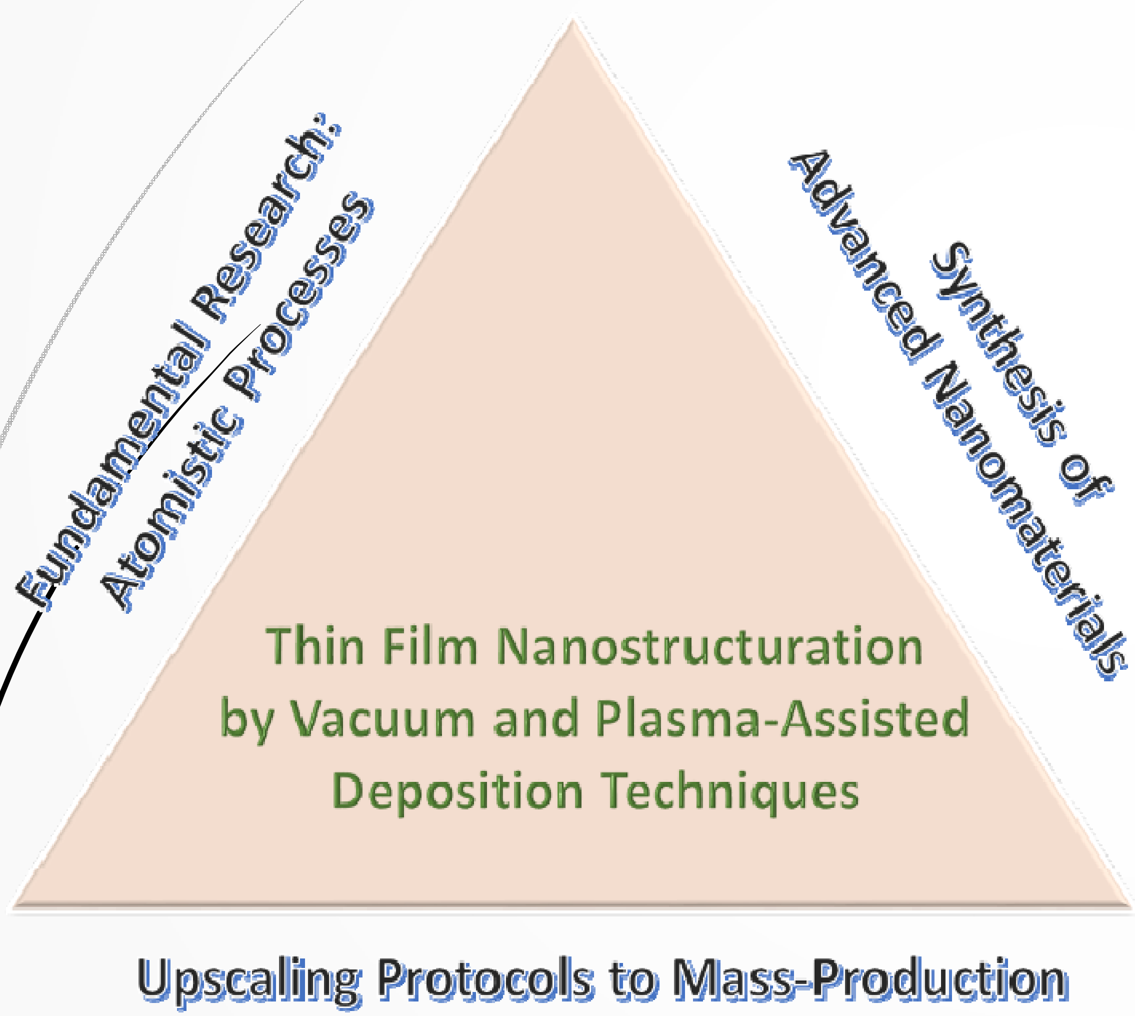




Low Density
Low Refractive Index
High Surface
Percolation

Control of the structure in smaller scales

Fundamentals of Thin Film Growth (Bottom-Up)



Scientific Scopes

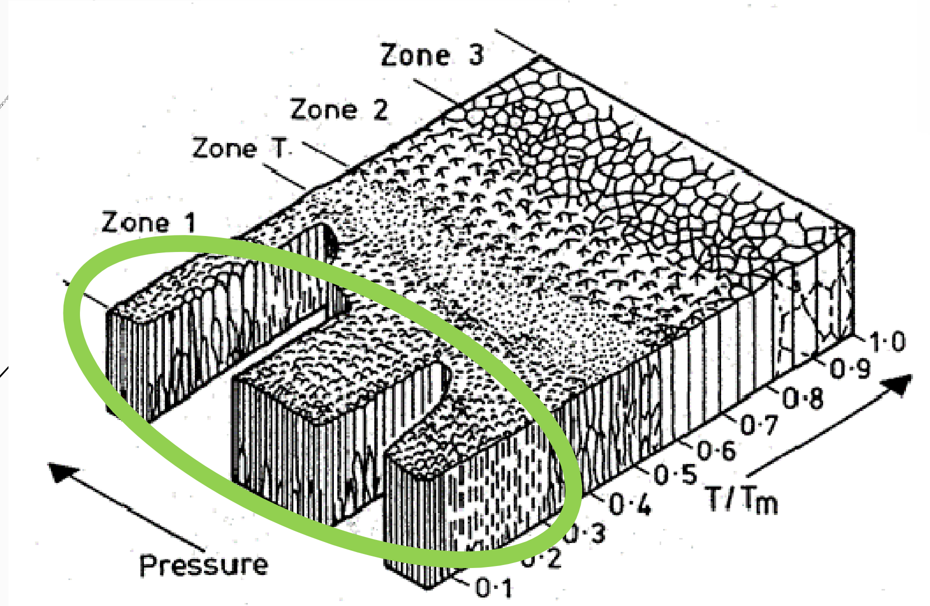
- General understanding of the physical-chemical processes responsible for film nanostructuration
- Relation between experimentally controllable quantities and film structure
- Connection between structure and properties
- Search of key non-dimensional quantities

Applied scopes

- Development of industrially scalable techniques
- Computer design of materials
- Patents

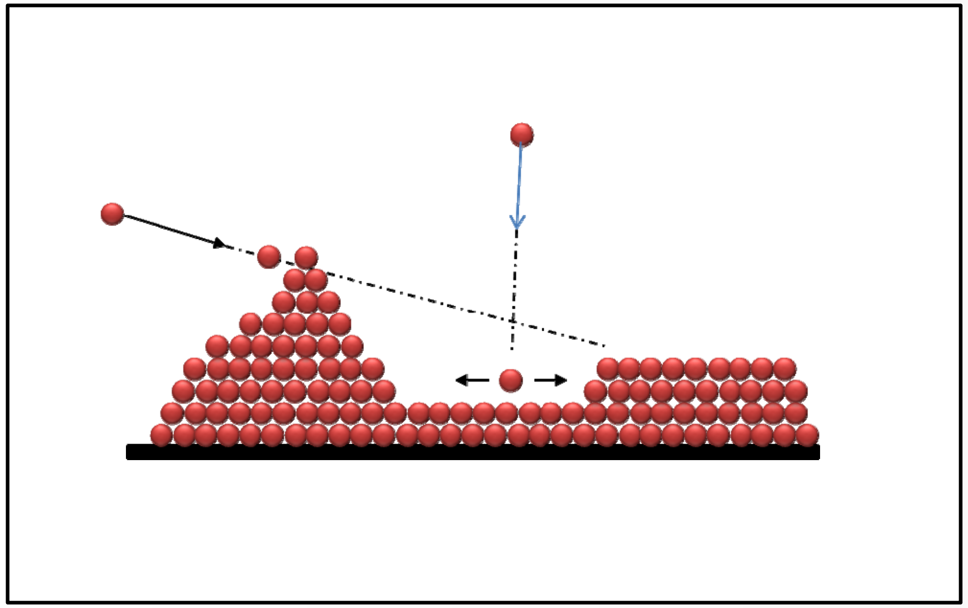
Fundamentals of physical vapor deposition

Thornton Structure Zone Model



When **T/T_m<0.3**, the film growth is dominated by the surface shadowing mechanism

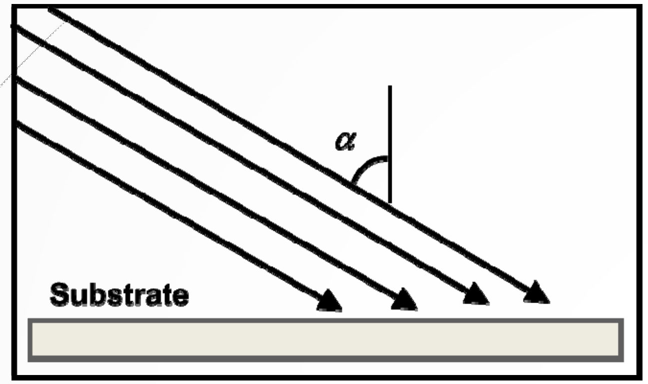
When **0.3<T/T_m<0.5**, the film growth is dominated by surface shadowing and thermally activated surface mobility processes



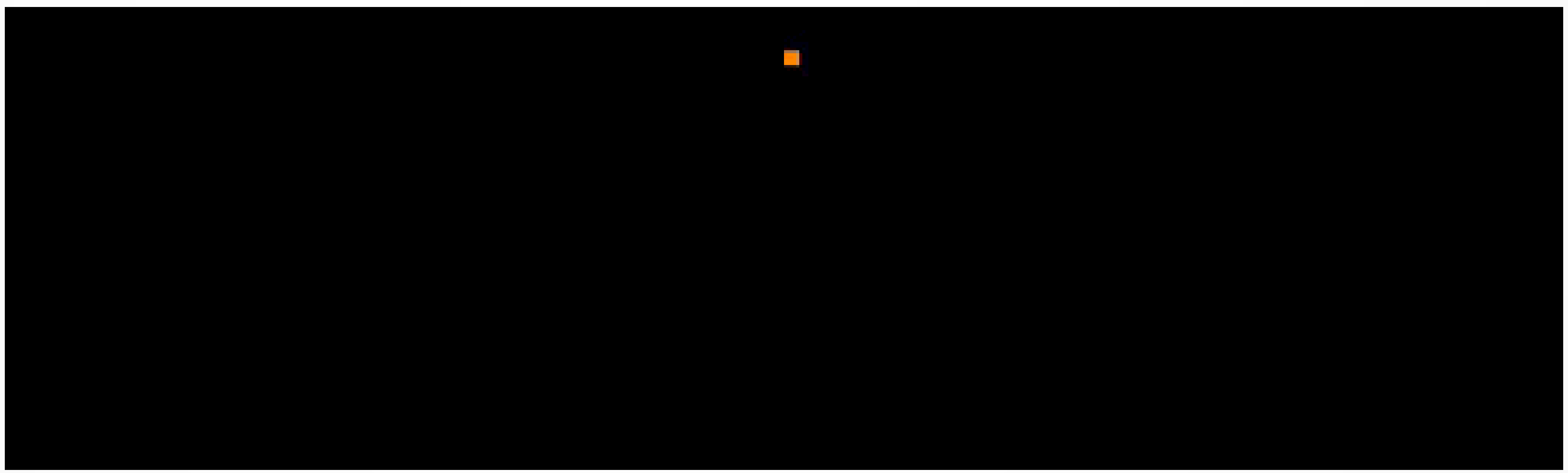
Surface Shadowing

- Non-local process
- Depends on the incidence of atoms
- Taller surface features receive more atoms
- Competitive Surface Growth

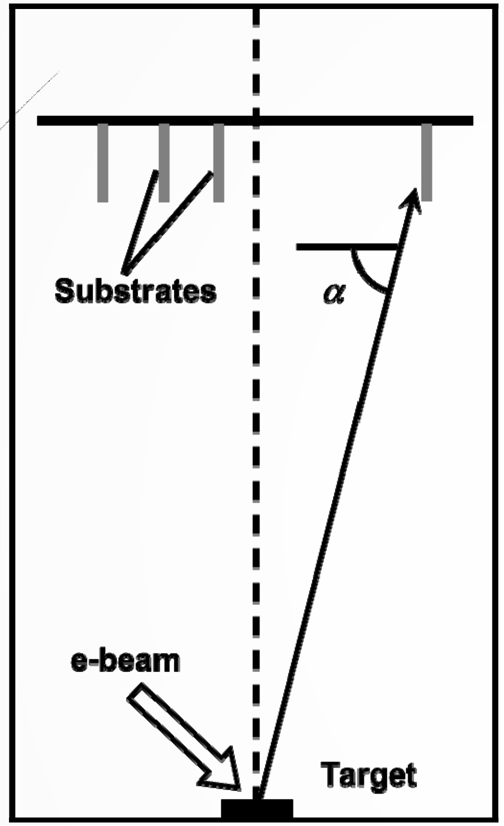
Competitive Surface Growth



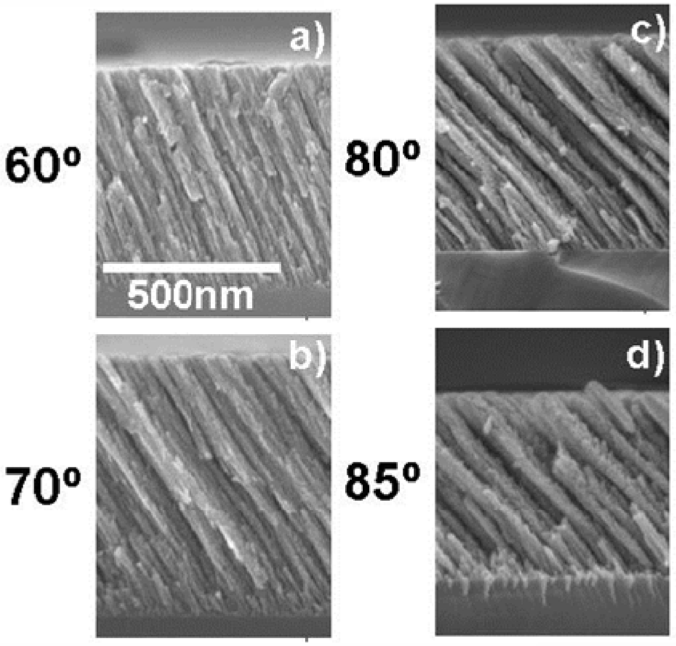
Assume a 2 dimensional problem
Particles arriving with incident angle α

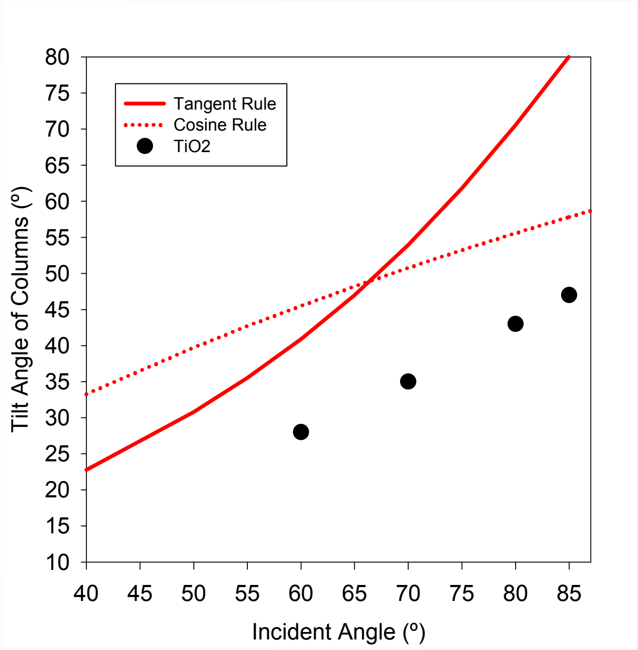


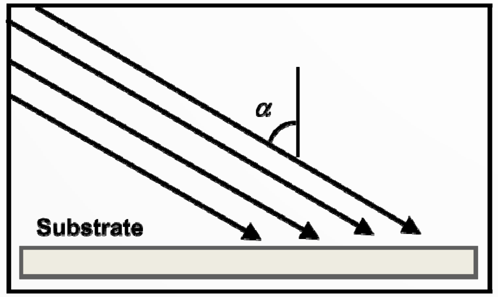
E-beam assisted PVD



Atoms arrive along a preferential direction
Low kinetic energy of vapor atoms (~0.2 eV)







Tangent Rule

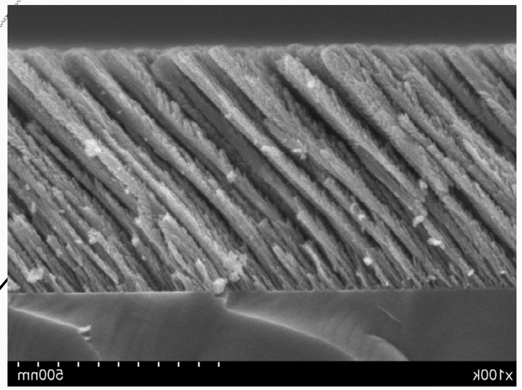
$$\tan \alpha = 2 \tan \beta$$

Cosine Rule

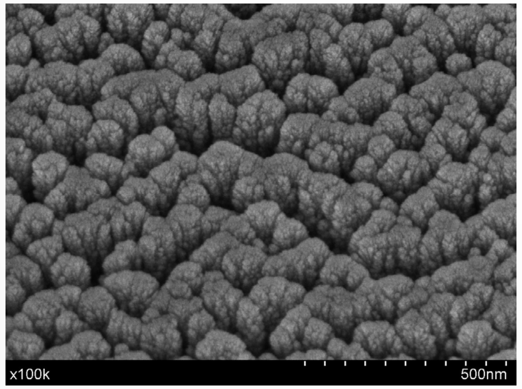
$$\beta = \alpha - \arcsin\left(\frac{1-\cos\alpha}{2}\right)$$

Development of a model for E-beam assisted PVD

Cross-sectional view
Tilted Columnar Structures



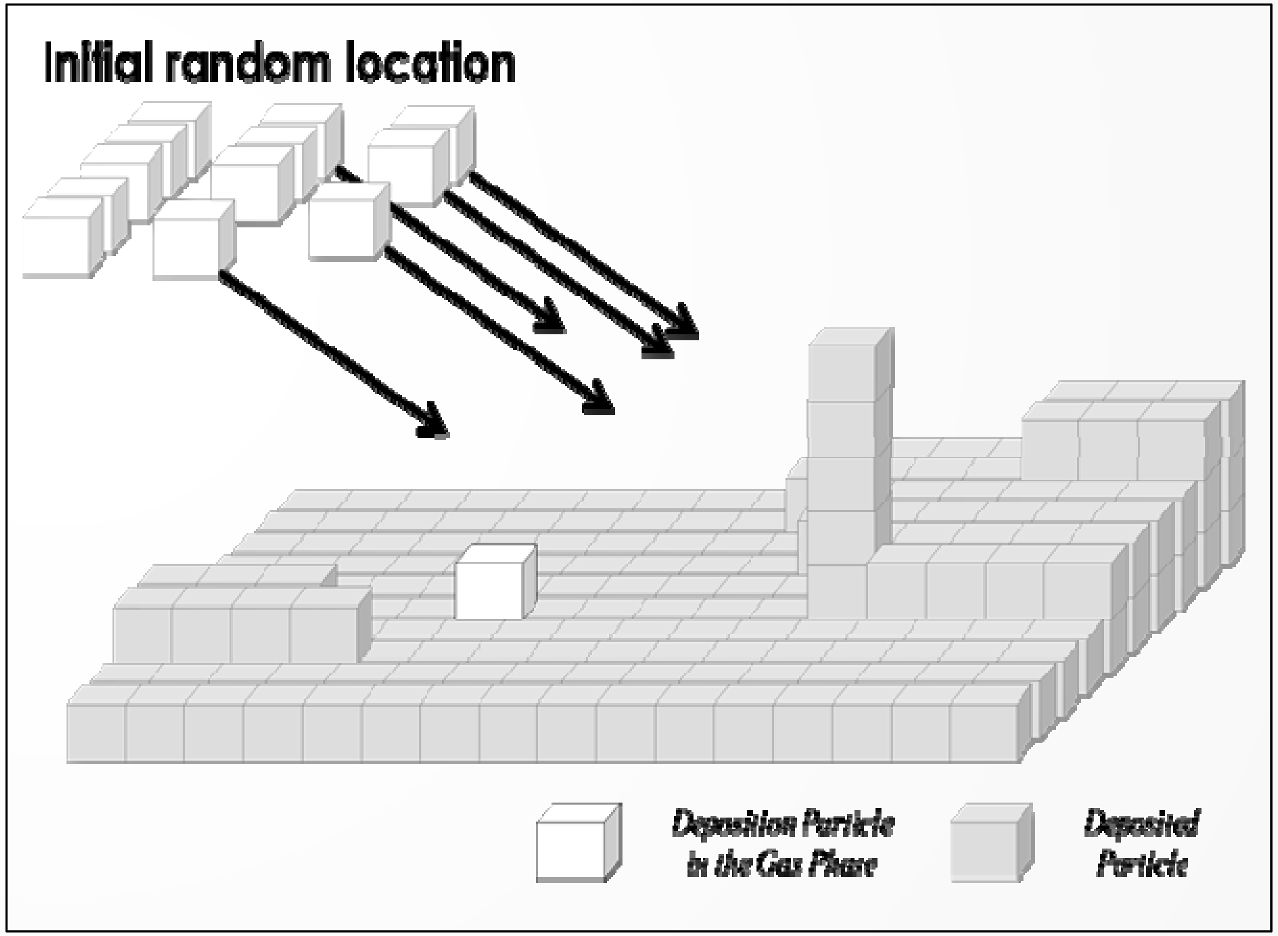
Top view
Fan-like structures



$\alpha = 80°$

TiO_2

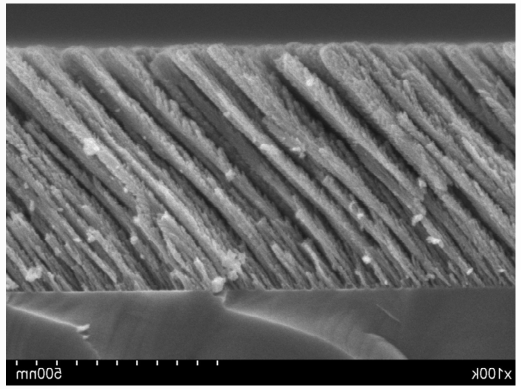
What are the key fundamental quantities?
Hypothesis on Growth Model



Results of the Model (I)

$\alpha = 80°$

TiO_2

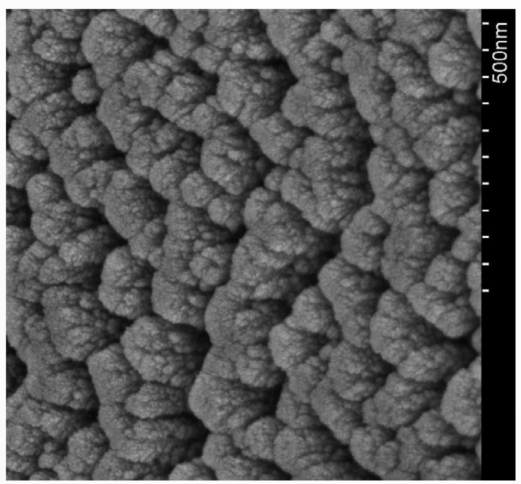


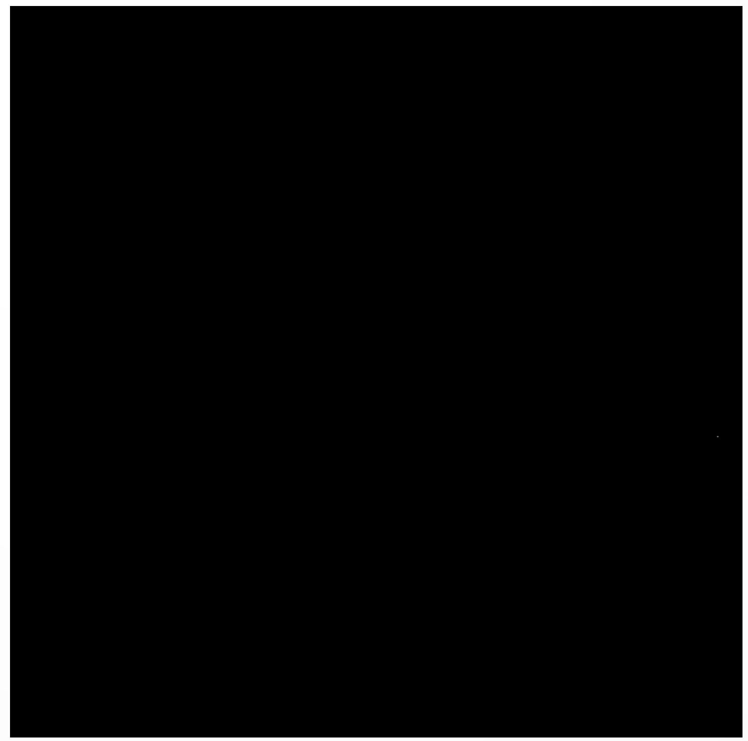
Cross-sectional view

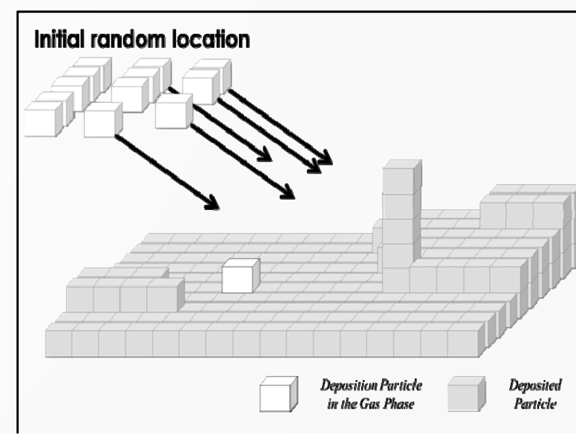
Tilted Columnar Structures

Top view

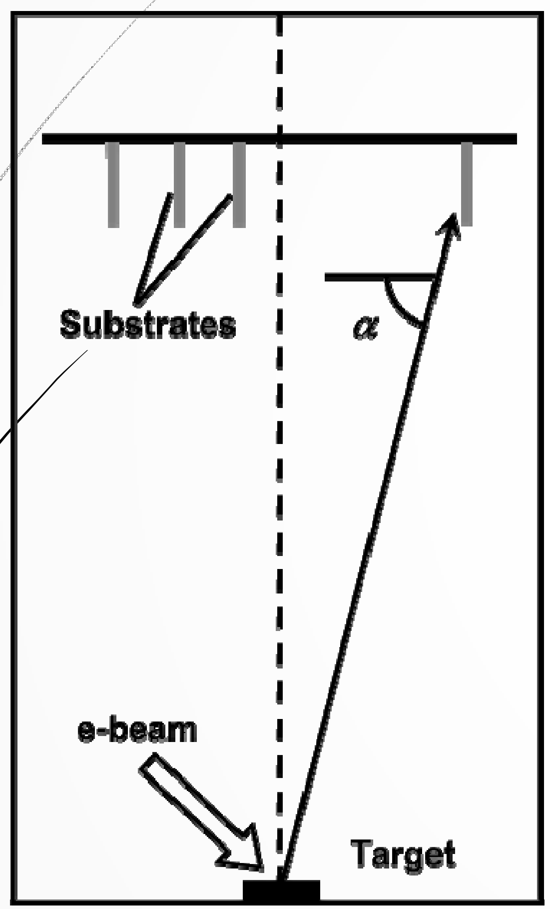
Fan-like structures

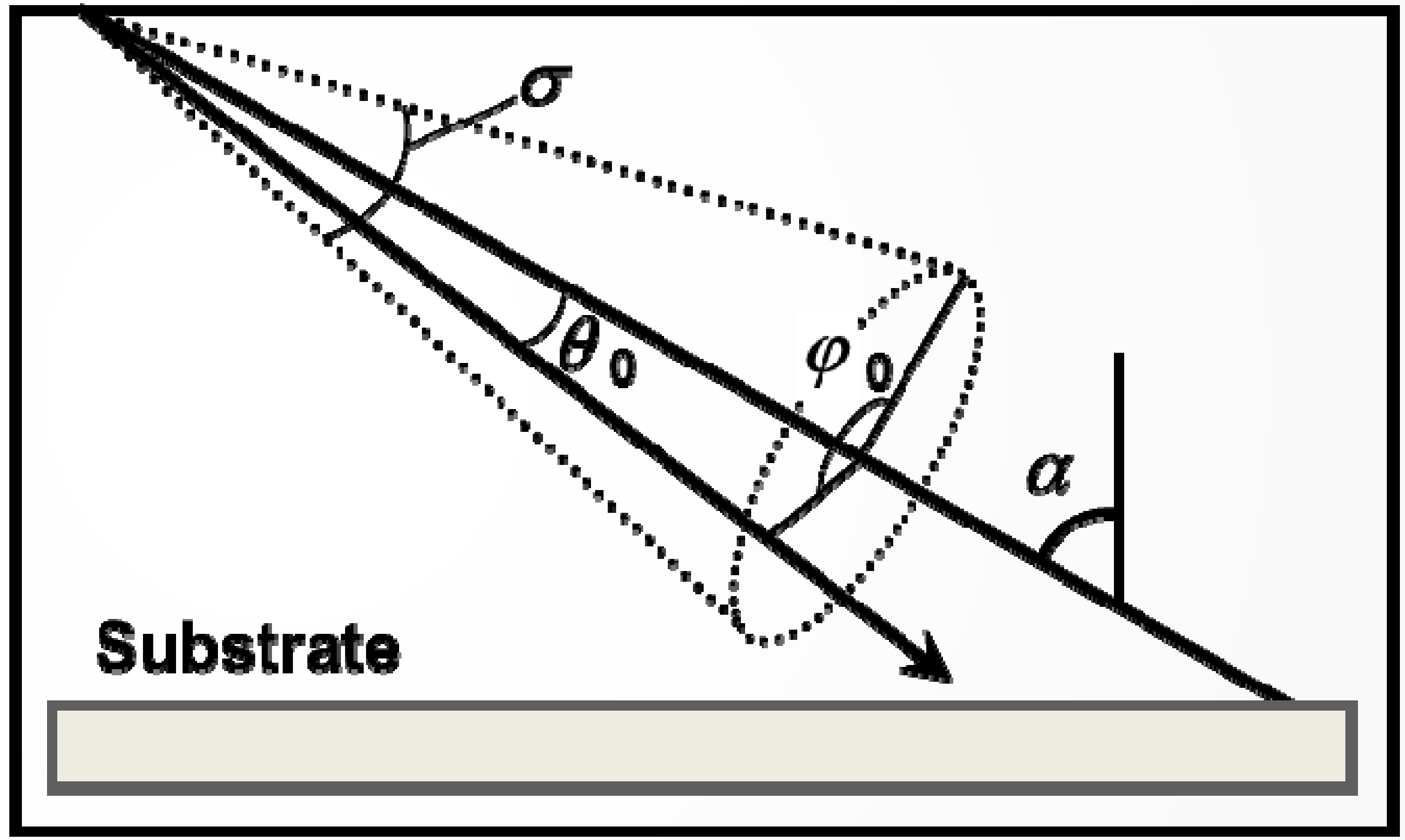






Hypothesis: Angular Broadening



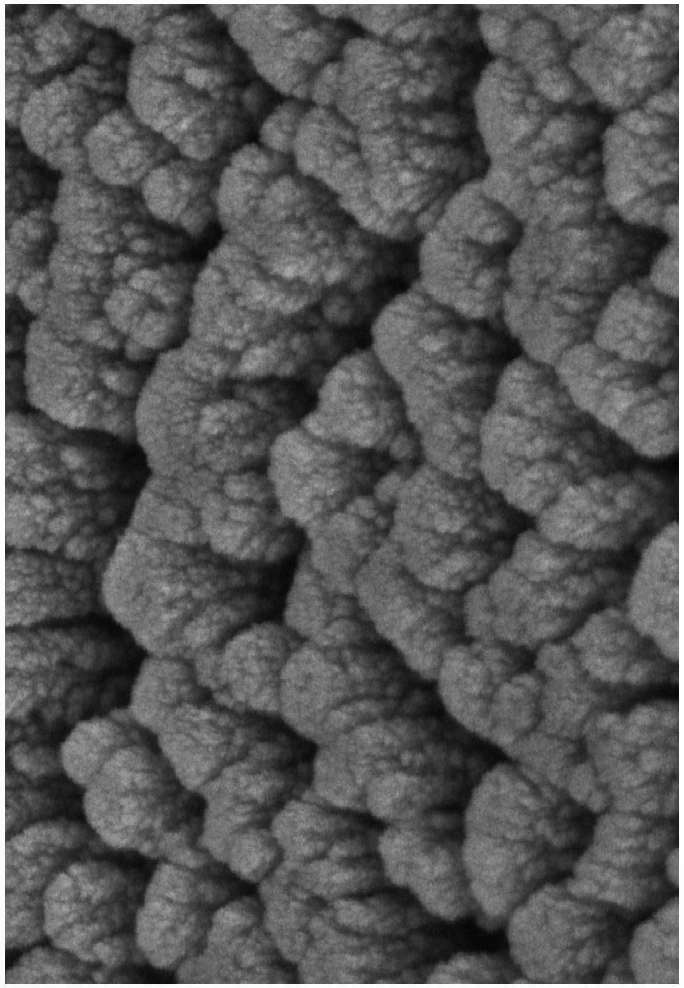


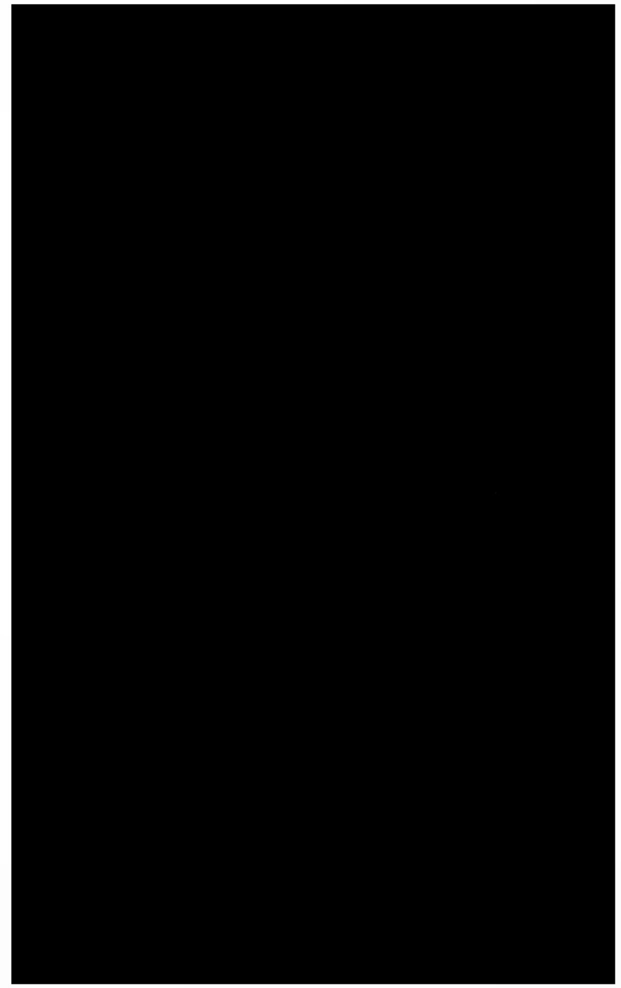
σ is a system-dependent parameter

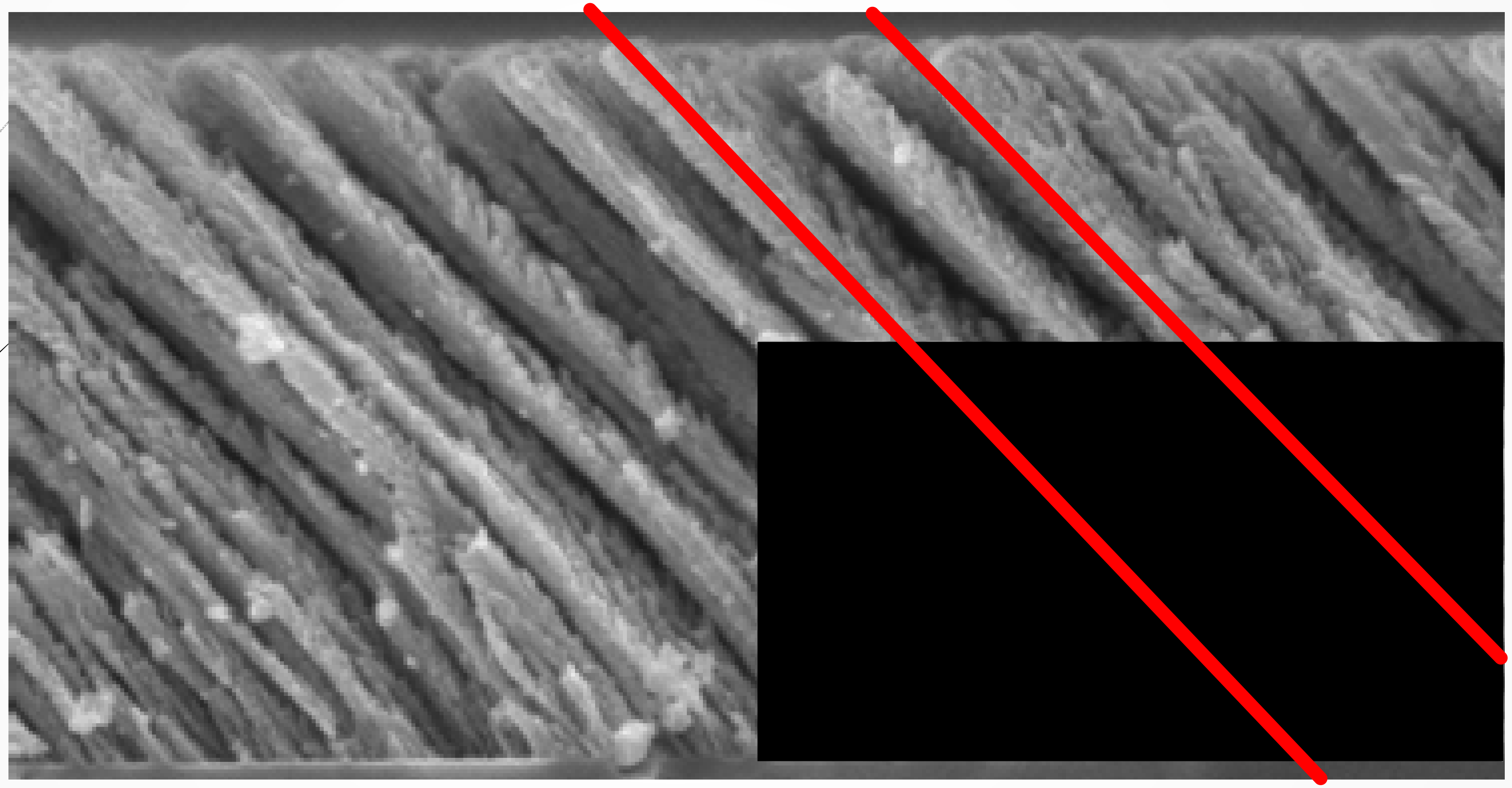
Top view

Fan-like structures

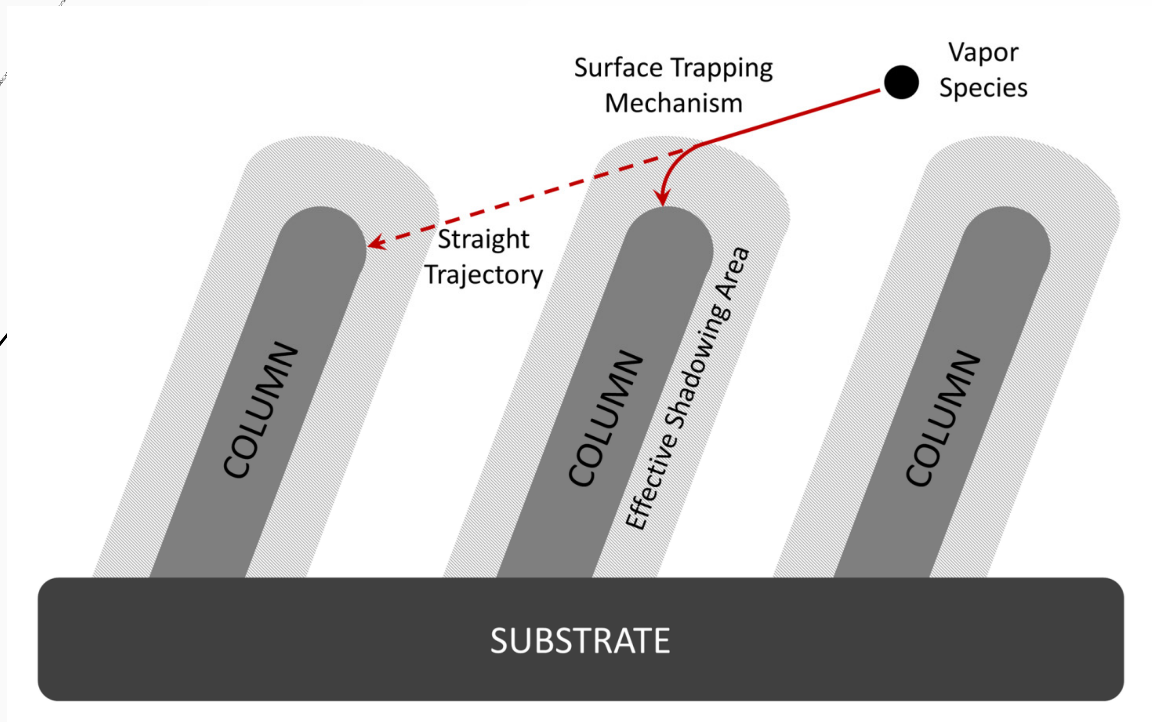
σ=10°

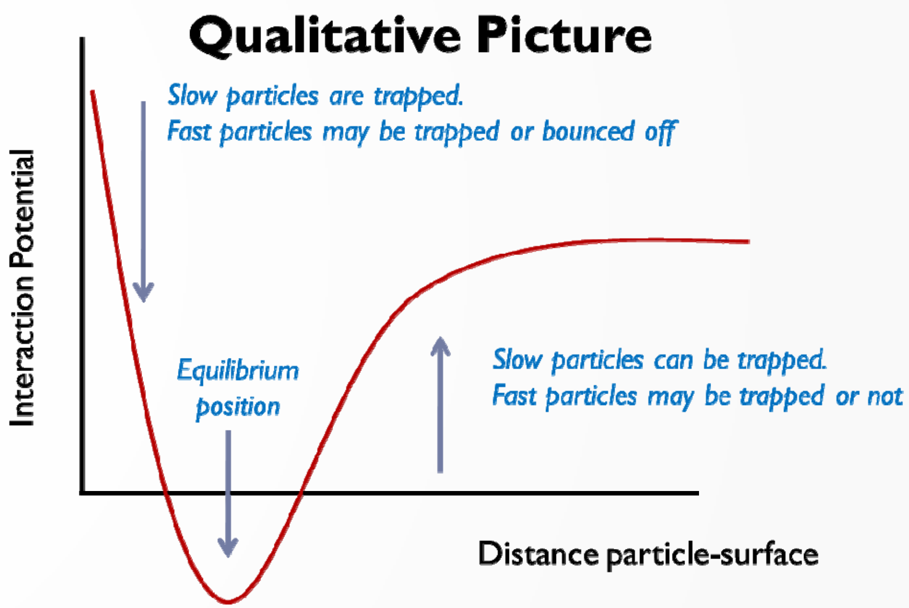




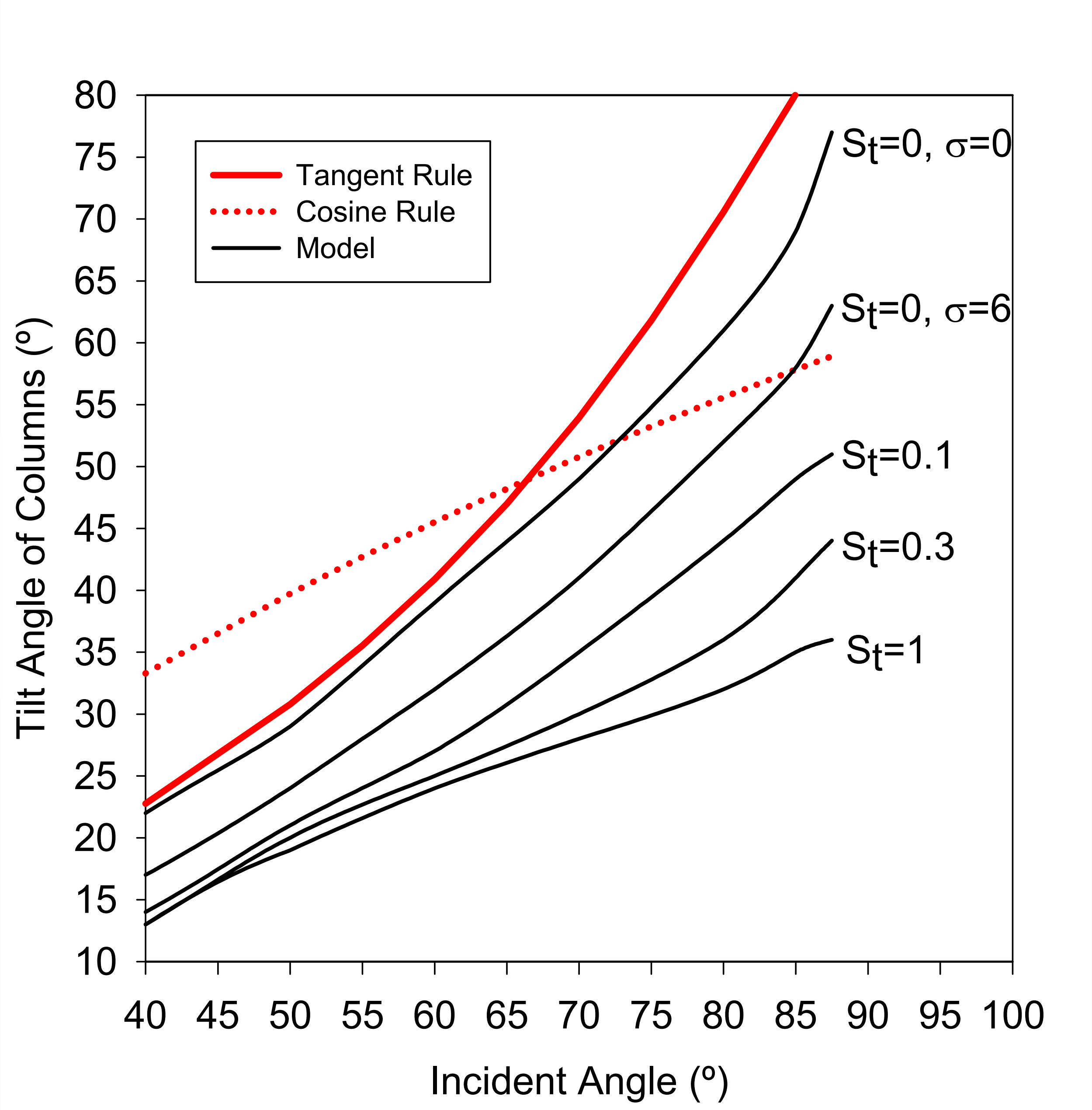


Surface Trapping Mechanism

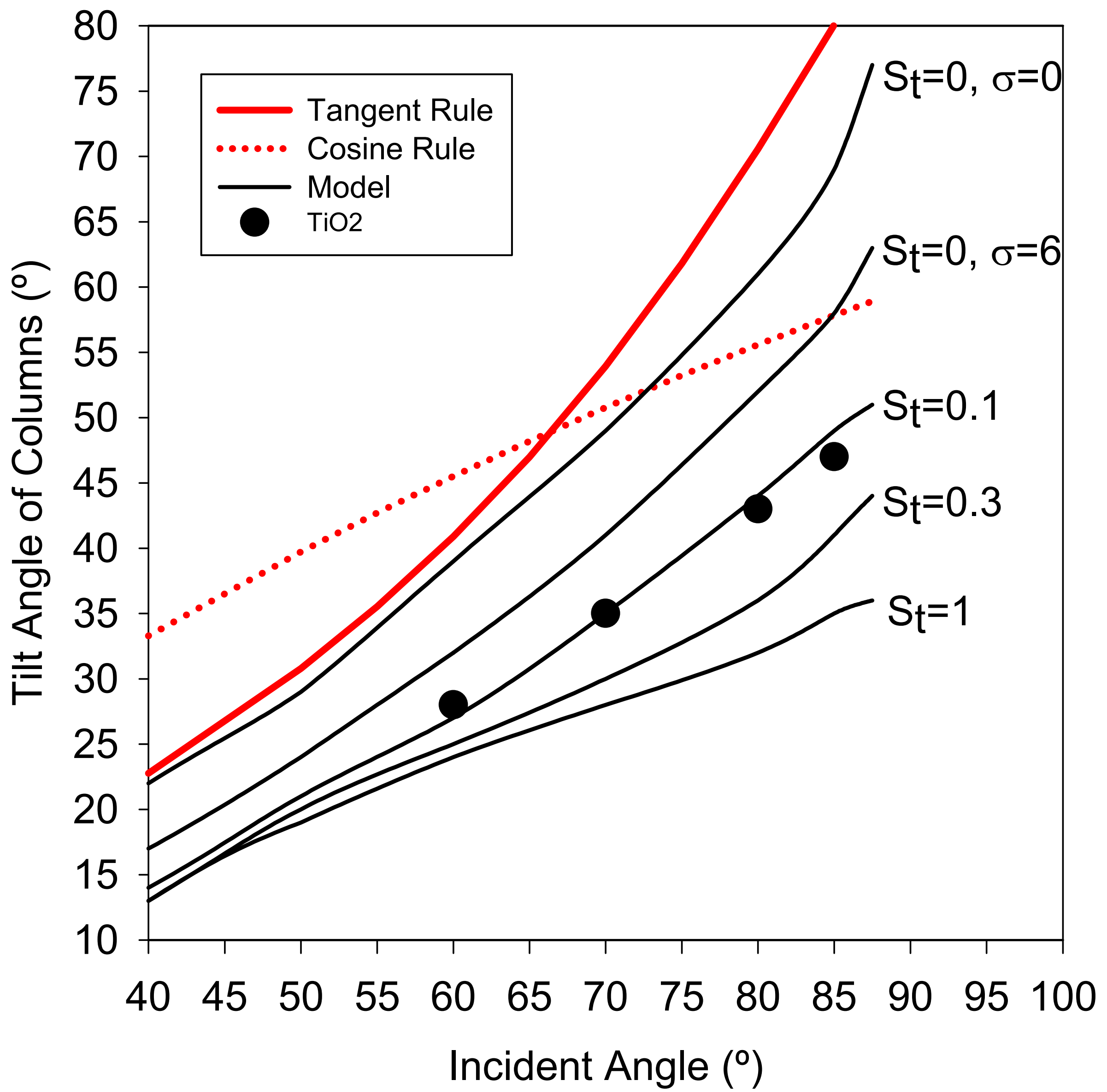




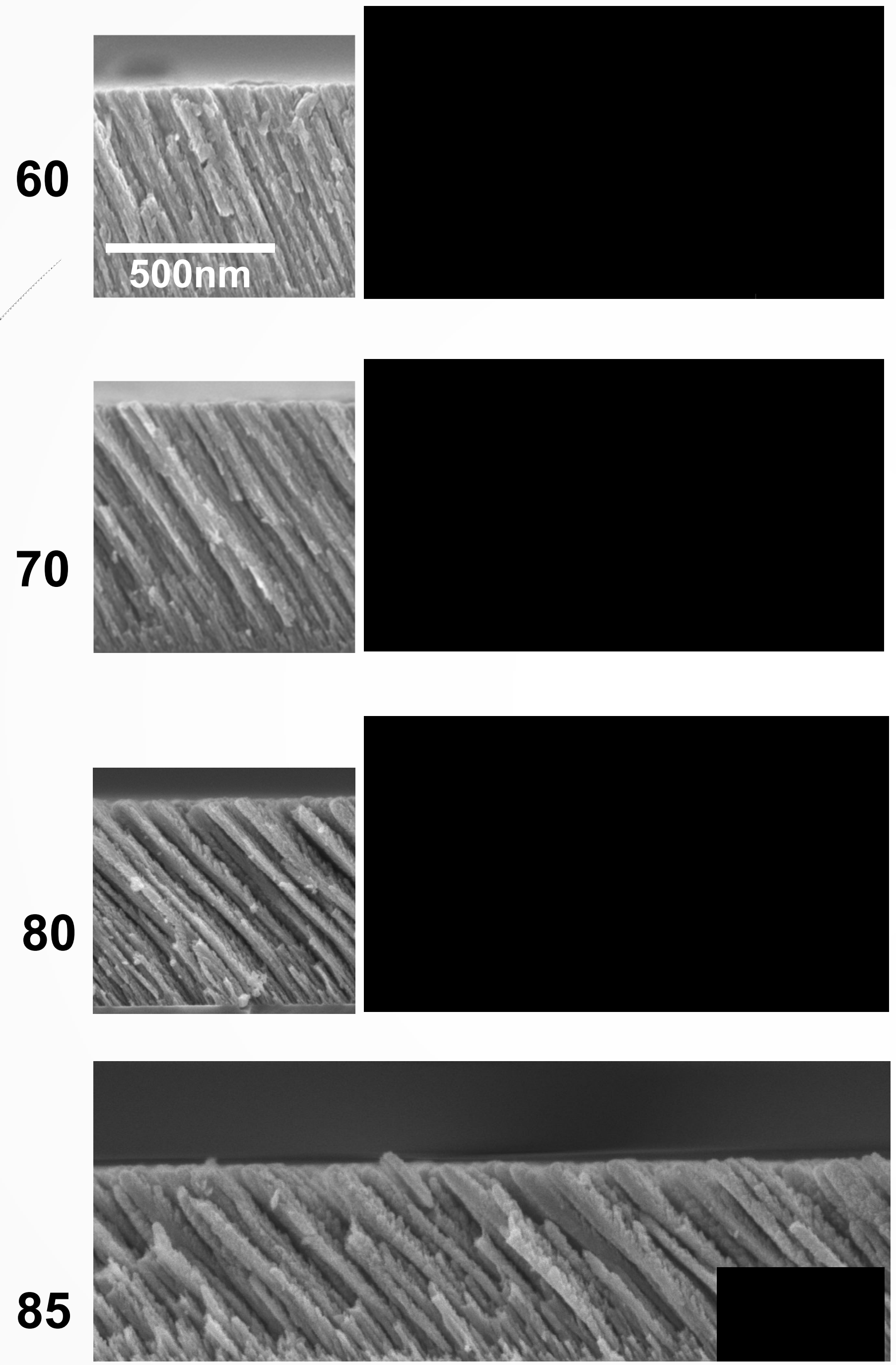
S_t trapping probability



Tangent Rule
Cosine Rule
Model
St=0, σ=0
St=0, σ=6
St=0.1
St=0.3
St=1
Tilt Angle of Columns (º)
Incident Angle (º)
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
40
45
50
55
60
65
70
75
80
85
90
95
100



Tangent Rule
Cosine Rule
Model
TiO2
St=0, σ=0
St=0, σ=6
St=0.1
St=0.3
St=1
Tilt Angle of Columns (º)
Incident Angle (º)
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
40 45 50 55 60 65 70 75 80 85 90 95 100



Results of the model

S_t=0.1

σ=6°

Results are good for TiO2 but,

are S_t and σ physical parameters?

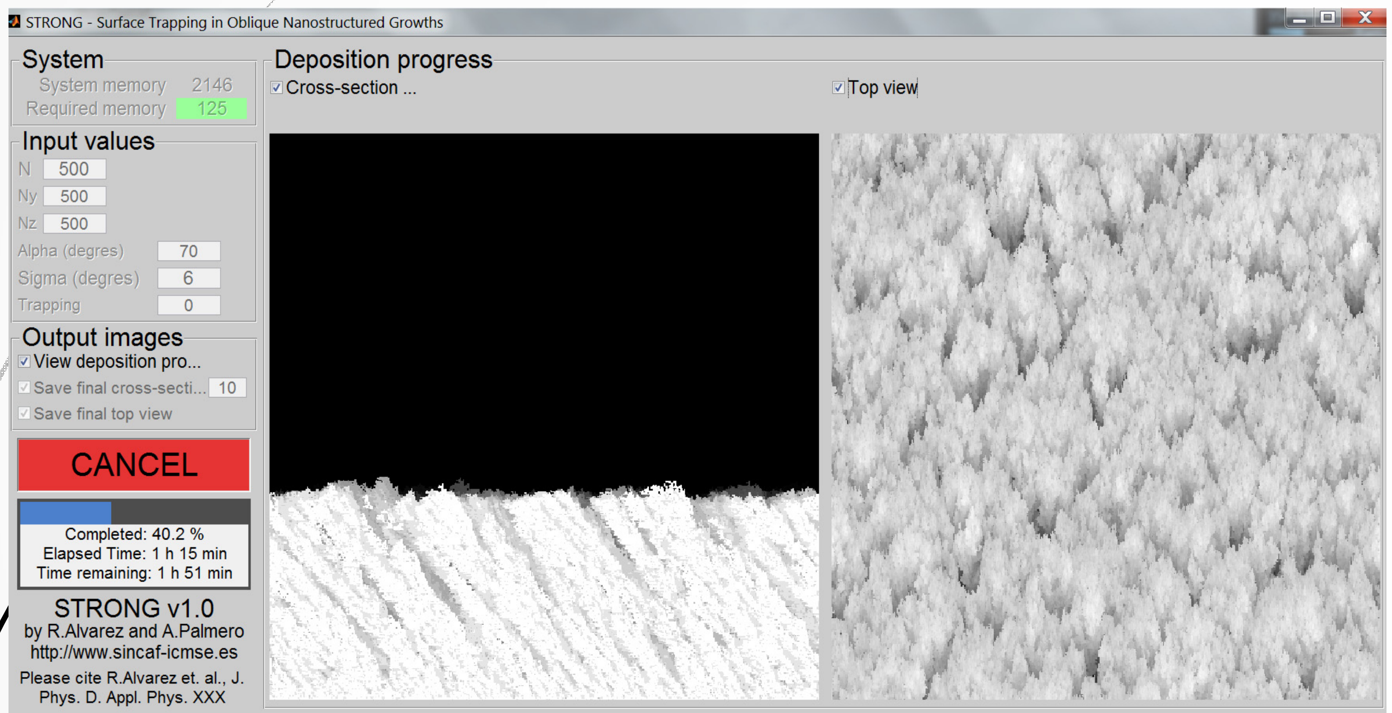
Is this model good for other materials?

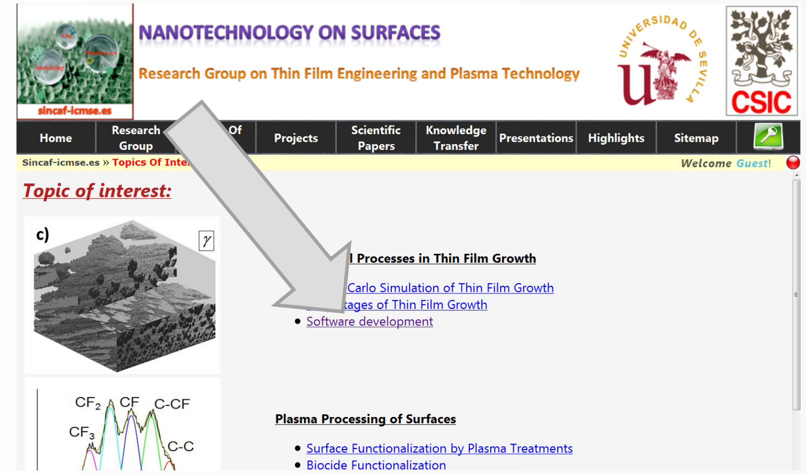
<u>Hypotheses of the model</u>

S_t dependent on the sublimated and deposited material

σ dependent on the deposition system

STRONG (Surface Trapping in Oblique Nanostructured Growths)





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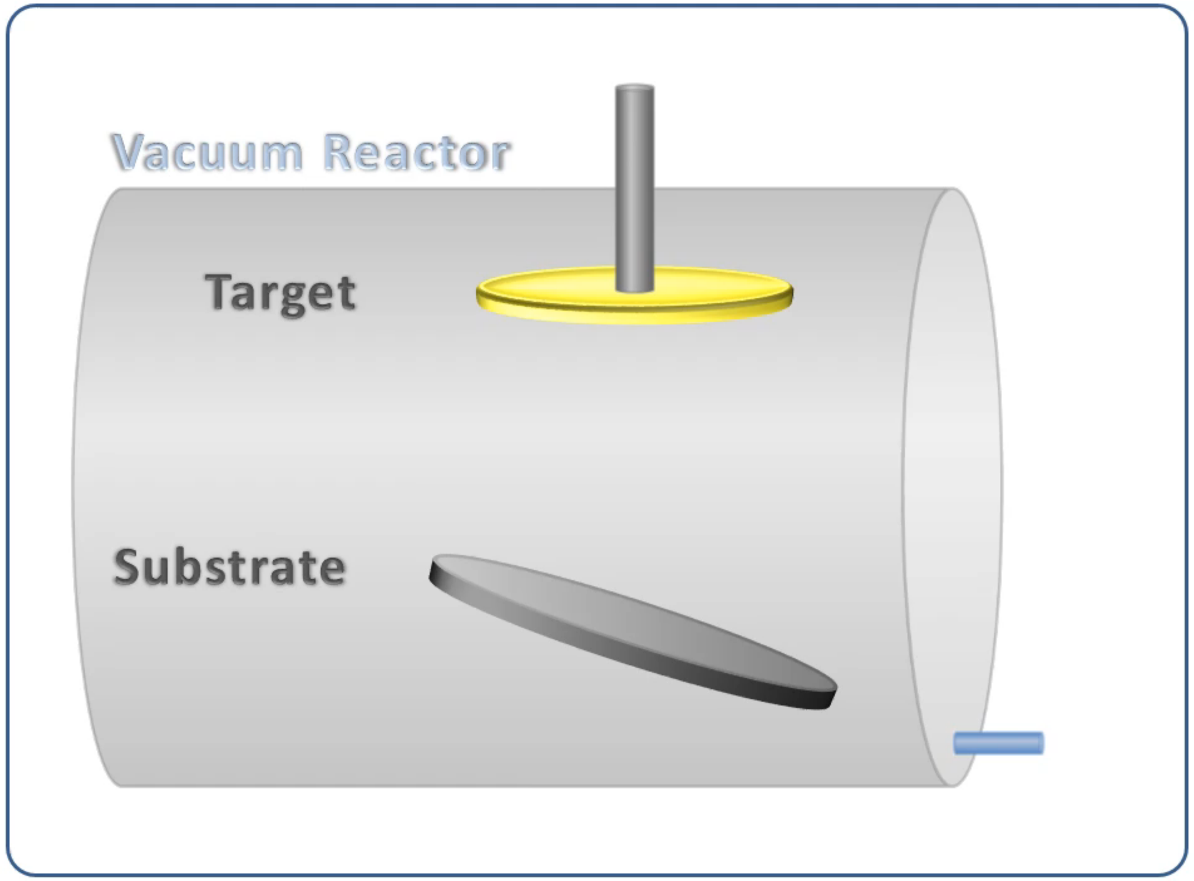
Magnetron Sputtering Deposition

- Well-known plasma-assisted deposition technique
- High deposition rates
- Possibility to work on large areas
- Room Temperature
- In classical configurations: compact thin films
- Oblique angle configurations: porous structures



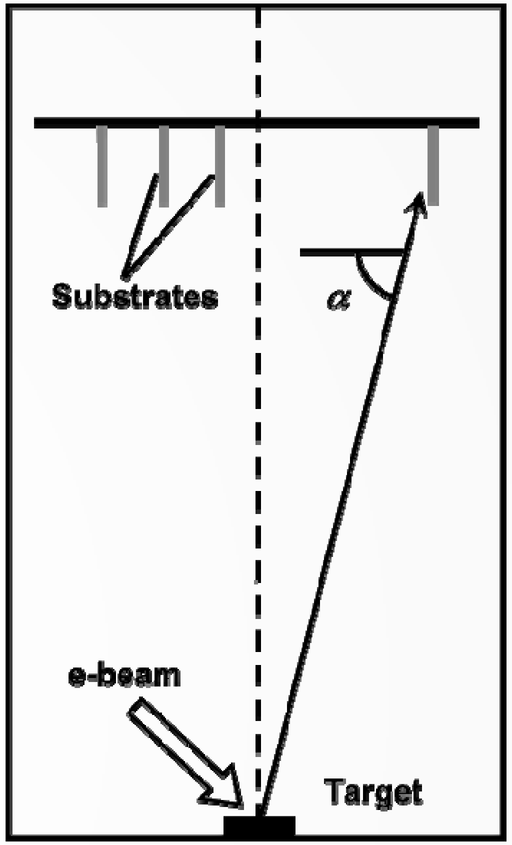
Difference with e-beam PVD

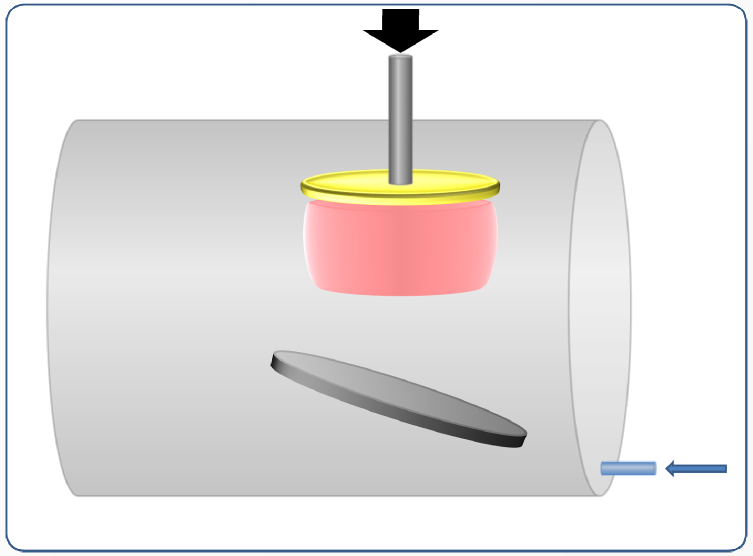
Sputtered atoms leave the target with energies around 10 eV

Plasma pressure can be tuned, thus sputtered particles may undergo collisions

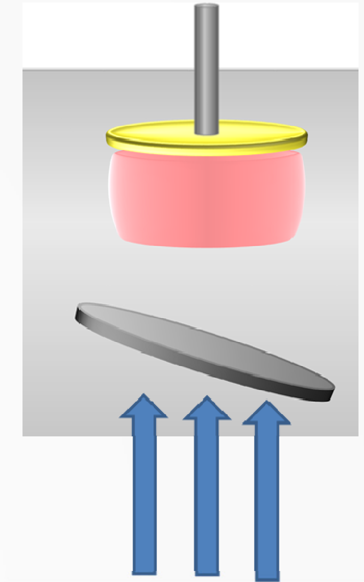
Momentum distribution of sputtered particles may vary

- Very directed and along a preferential direction (low collisions in the plasma)
- Isotropic distribution nearly thermalized (high amount of collisions in the plasma)



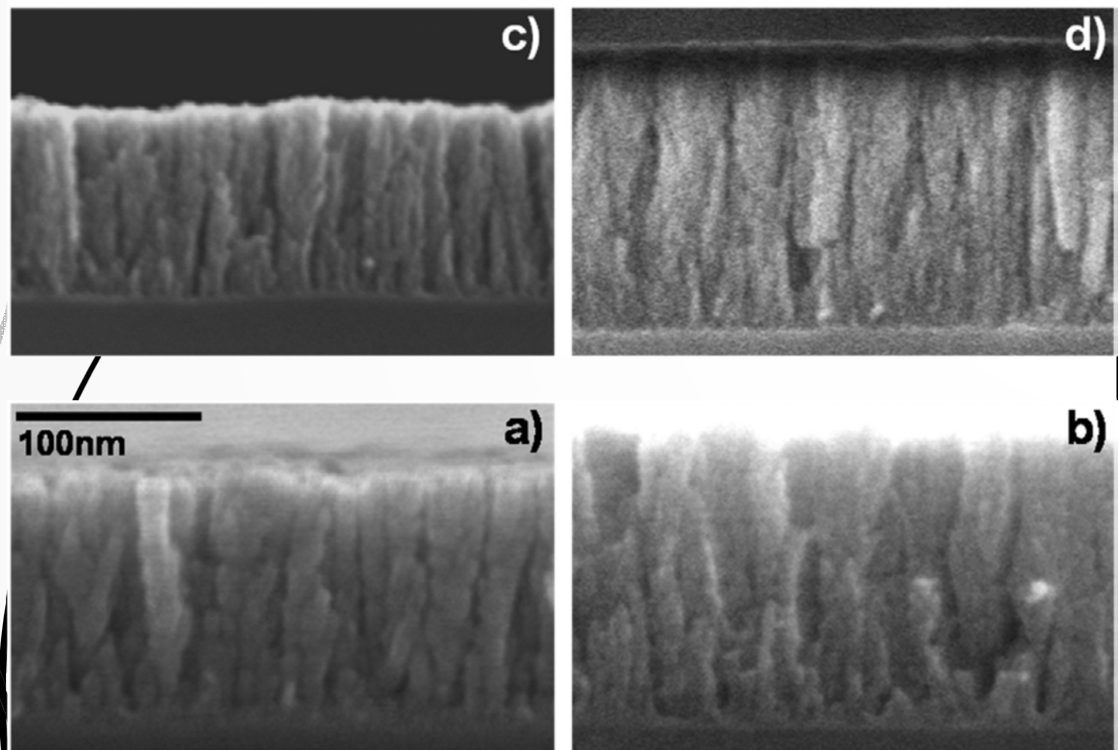


What happens on the dark side?
Cross-Section View



TiO_2
i-MS

SiO_2
i-MS



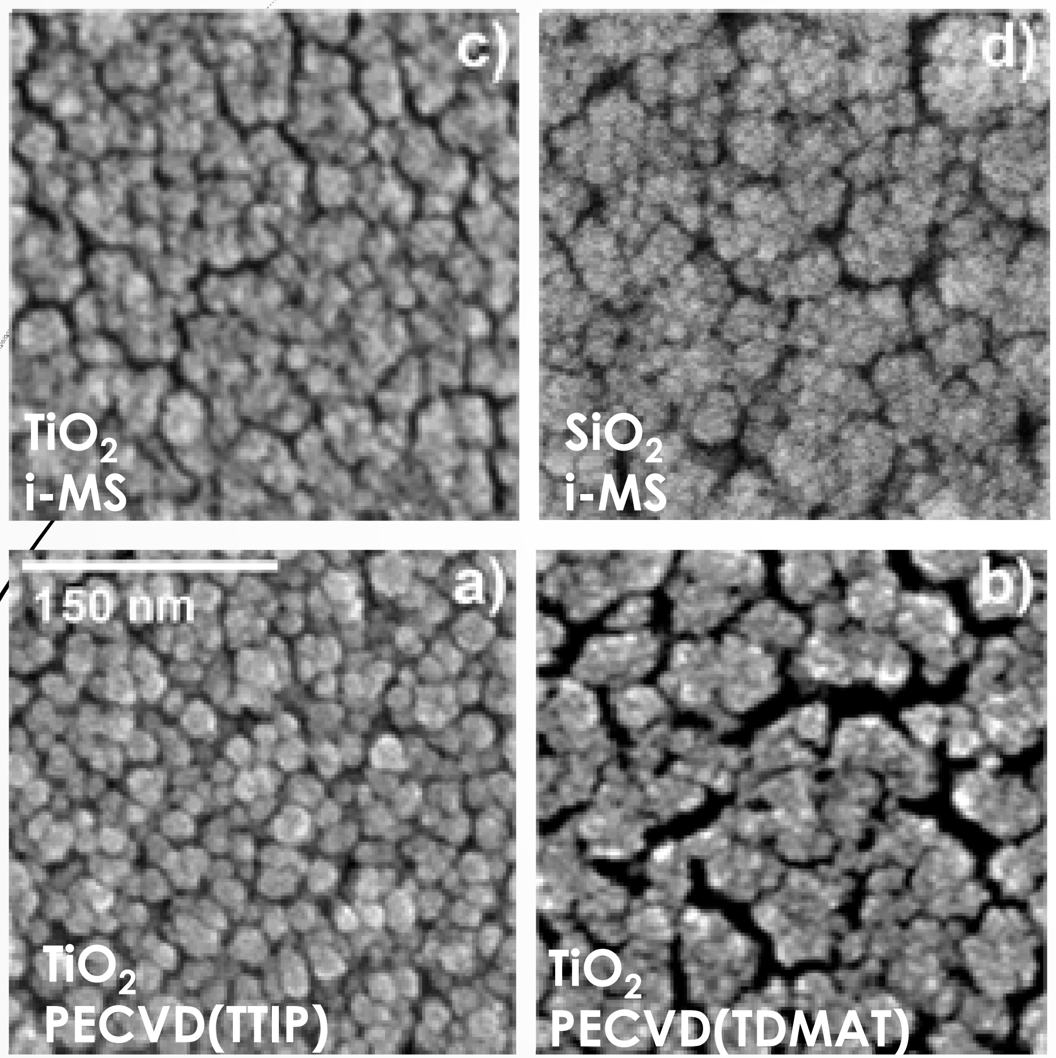
TiO_2
PECVD(TTIP)

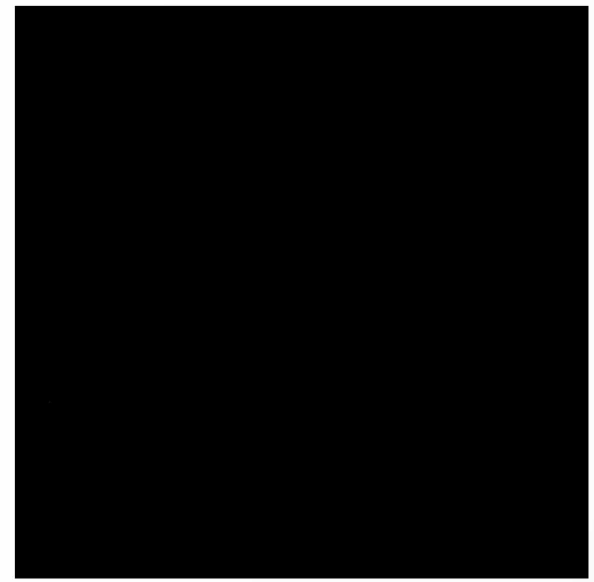
TiO_2
PECVD(TDMAT)

Isotropic Deposition Growth Mode

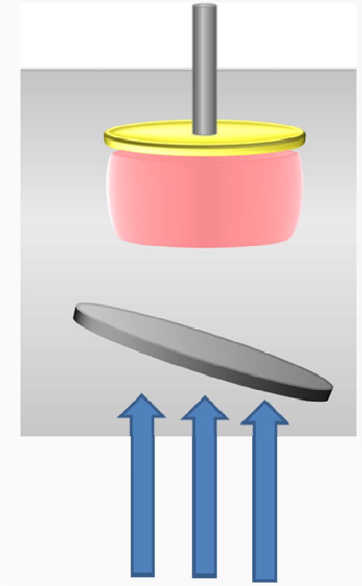
What happens on the dark side?

Top View





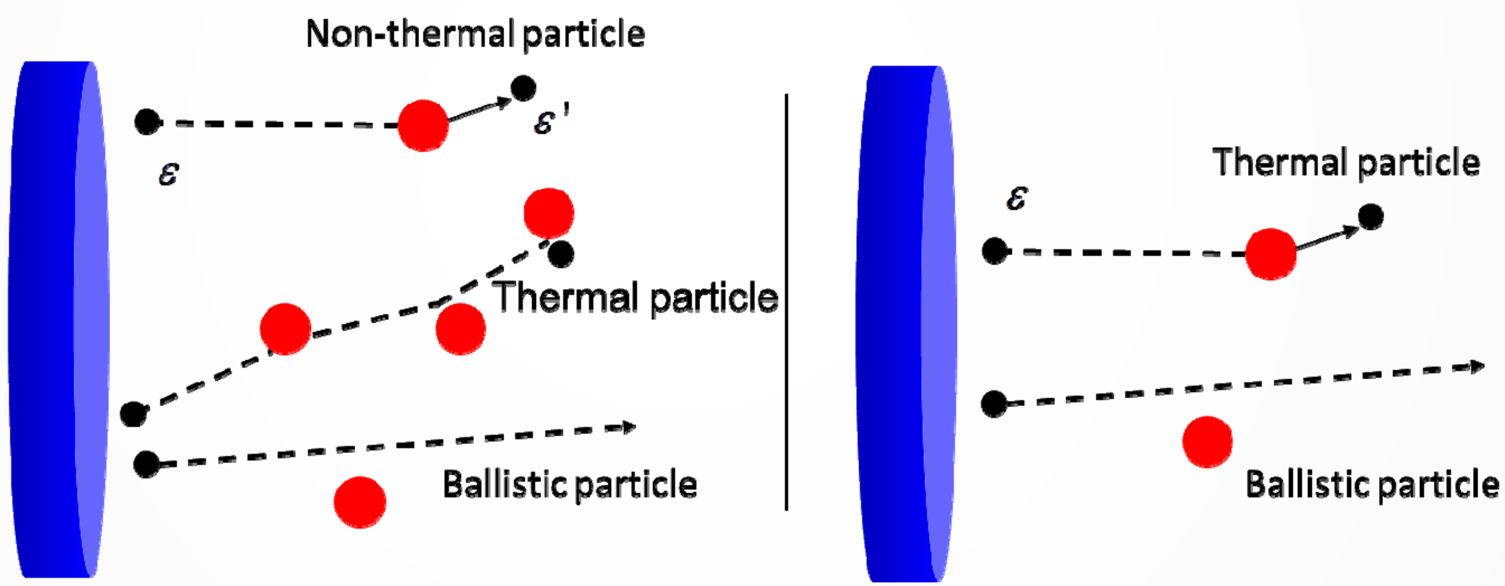
Isotropic Deposition
Growth Mode



What happens on the light side? Thermalization of sputtered particles

The relevance of the **surface shadowing mechanism** makes collisional processes in the **plasma phase** relevant

Realistic Description | Simplified Description | **Single Thermalizing Collision**



$$\lambda = \frac{1}{n\sigma}$$

$$\lambda_T = \frac{1}{n\sigma_T}$$

$$\frac{\lambda_T}{\lambda} = \frac{\sigma}{\sigma_T} \approx \nu$$

Thermalization cross-section

Keller-Simmons Formula

$$r = \Phi_0 \frac{p_0 L_0}{pL}\left[1 - \exp\left(-\frac{pL}{p_0 L_0}\right)\right]$$

Generalized Keller-Simmons Formula

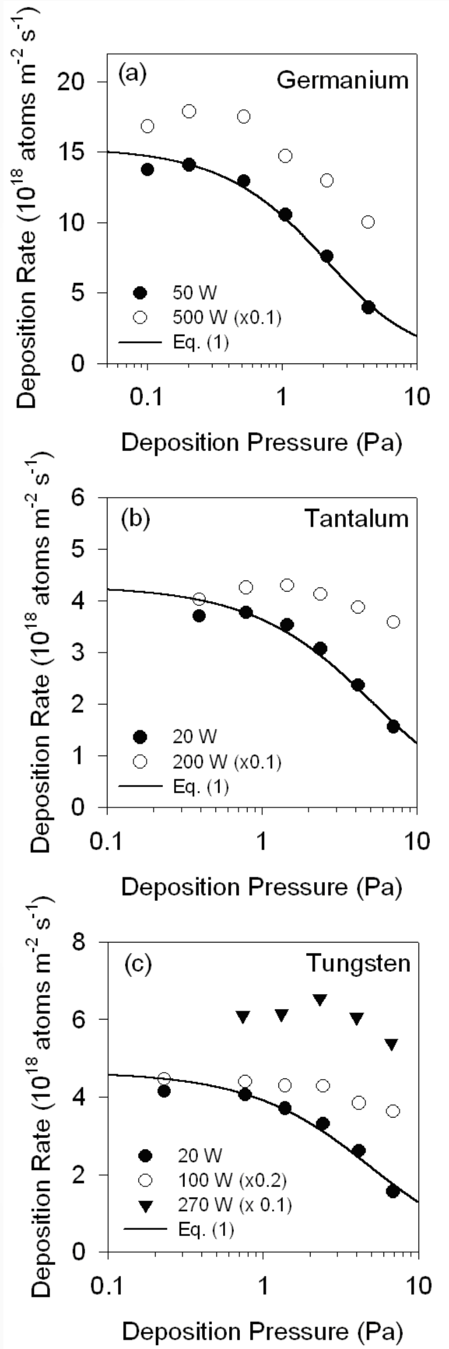
$$r = \Phi_0 \left(\frac{1}{\delta + \chi}\right)\left[1 + \chi - (1+\chi)^{-\delta/\chi}\right]$$

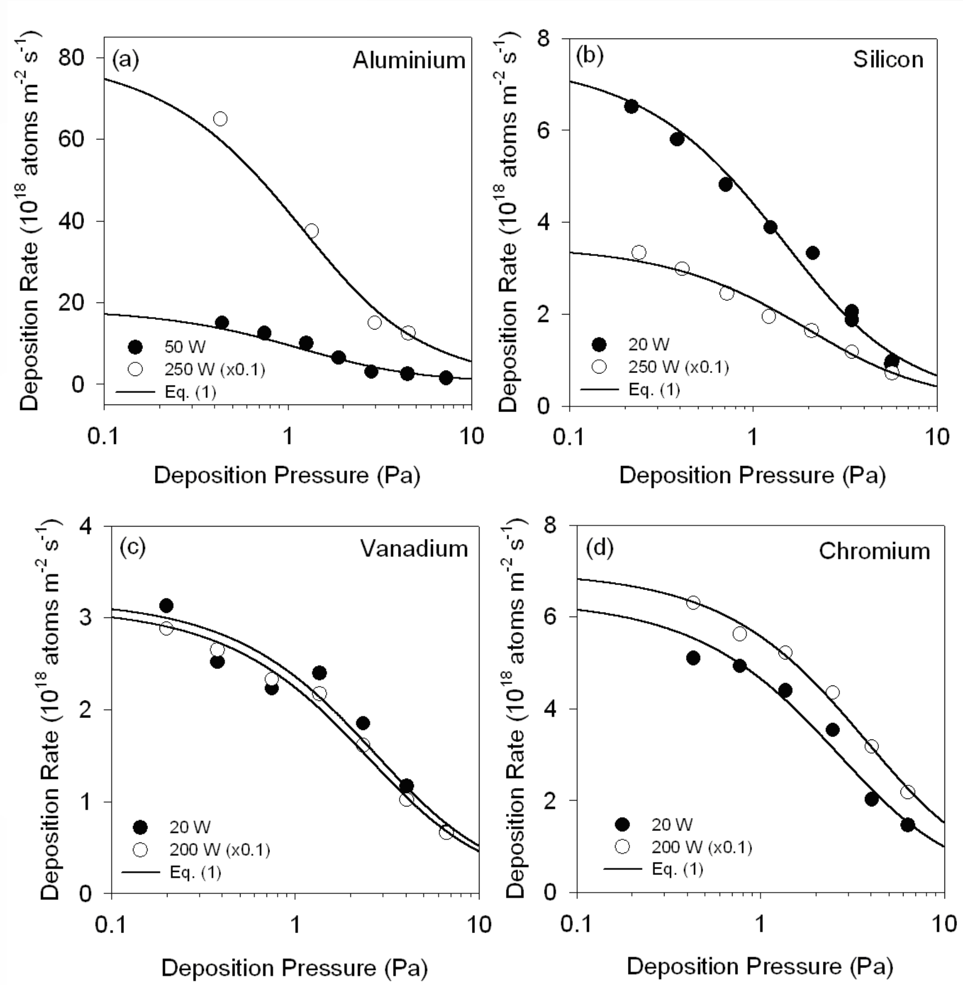
$$\delta = \frac{L}{\lambda_T(L)}, \quad \chi = \frac{T_c}{T_s} - 1$$

$$\lim_{T_c \to T_s} r = \Phi_0 \frac{\lambda_T(L)}{L}\left[1 - \exp\left(-\frac{L}{\lambda_T(L)}\right)\right]$$

KS Formula with $p_0 L_0 = \frac{k_B T_s}{\sigma_T}$

Experimental Data on Deposition Rate

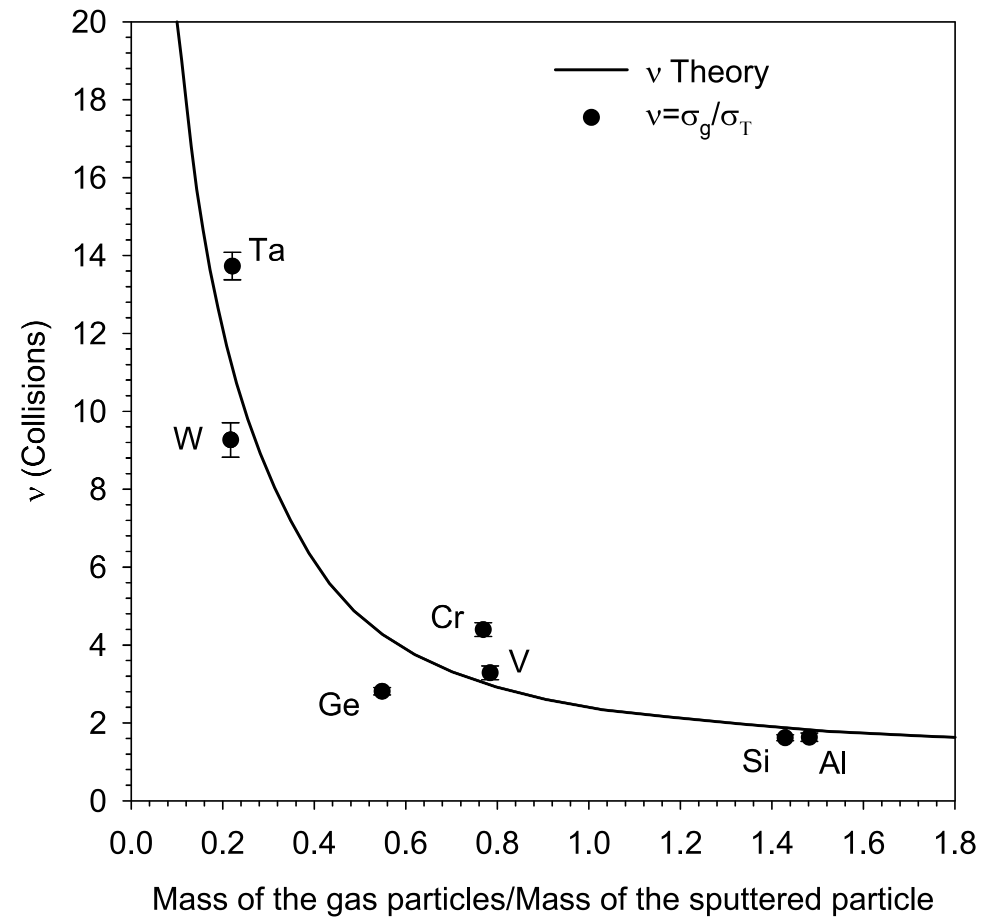




T.P. Drüsedau, Surf. & Coat. Technol. **174-175**, 470 (2003)
T.P. Drüsedau, J. Vac. Sci. Technol. A **20**(2), 459 (2002)
T.P. Drüsedau, M. Lohmann, and B. Garke, J. Vac. Sci. Technol. A **16**(4), 2728 (1998).

Results of the fit

	P_w (W)	α_0 (atoms m^{-2} s^{-1})	α_1 (m^3 J^{-1})	α_2	T_s (K)	σ (m^2)	T_c (K)	$(p_0L_0)_{Eq. (3)}$ (Pa cm)	$(p_0L_0)_{KS}$ (Pa cm)
Al	50	$1.8\times10^{19}\pm2\times10^{18}$	1.5±0.1	1.0±0.1	370*	$9.6\times10^{-20}\pm6\times10^{-21}$	370±40	5.2±0.7	4.6*
	250	$8\times10^{19}\pm4\times10^{18}$	1.5±0.1	1.00±0.03	370±50		370±60	5.2±0.9	4.6*
Si	50	$7.5\times10^{18}\pm3\times10^{17}$	1.29±0.06	1.15±0.07	373*	$8.3\times10^{-20}\pm4\times10^{-21}$	430±30	6.8±0.6	7.5*
	250	$3.48\times10^{19}\pm6\times10^{17}$	1.03±0.03	1.27±0.05	460±40		590±70	9±1	8.4*
V	20	$3.2\times10^{18}\pm10^{17}$	0.75±0.04	1.3±0.1	473*	$6.1\times10^{-20}\pm3\times10^{-21}$	610±50	12±1	14.3±3*
	200	$3.11\times10^{19}\pm5\times10^{17}$	0.78±0.01	1.17±0.04	450±30		530±50	11±1	12.6±1*
Cr	20	$6.4\times10^{18}\pm2\times10^{17}$	0.75±0.03	1.21±0.07	373*	$4.8\times10^{-20}\pm2\times10^{-21}$	450±30	12±1	13.5±1.8*
	200	$6.98\times10^{19}\pm7\times10^{17}$	0.54±0.01	1.24±0.03	520±30		640±50	17±2	18.7±1.2*
Ge	50	$1.53\times10^{19}\pm2\times10^{17}$	0.89±0.03	1.14±0.04	470*	$7.2\times10^{-20}\pm2\times10^{-21}$	540±20	9.7±0.6	9.4*
Ta	20	$4.29\times10^{18}\pm7\times10^{16}$	0.39±0.01	1.22±0.06	373*	$2.5\times10^{-20}\pm6\times10^{-21}$	460±20	23±1	24.9±2.9*
W	20	$4.7\times10^{18}\pm10^{17}$	0.42±0.02	1.24±0.09	470*	$3.4\times10^{-20}\pm2\times10^{-21}$	580±40	22±2	24*



$$\lambda_T = \frac{1}{n\sigma_T}, \frac{\lambda_T}{\lambda} = \frac{\sigma}{\sigma_T} \approx \nu$$

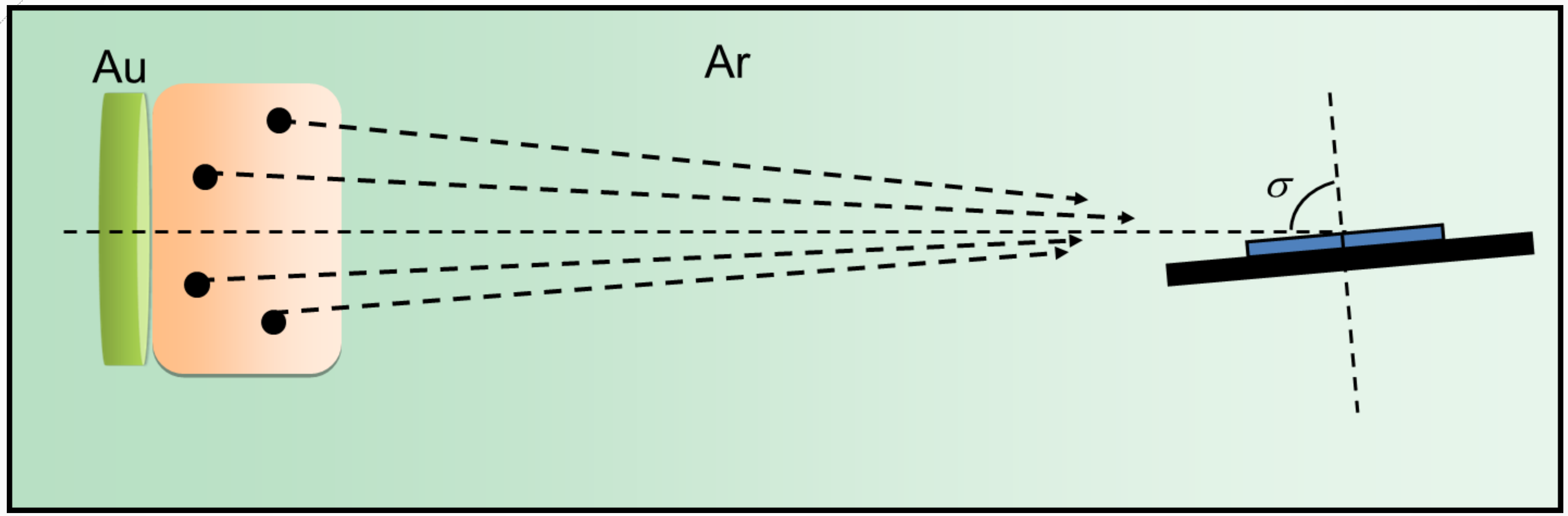
$$\Xi = \frac{L}{\lambda_T}$$

Thermalization Degree of Sputtered Particles

$\Xi << 1$ Sputter Flux highly directed
Highly Energetic

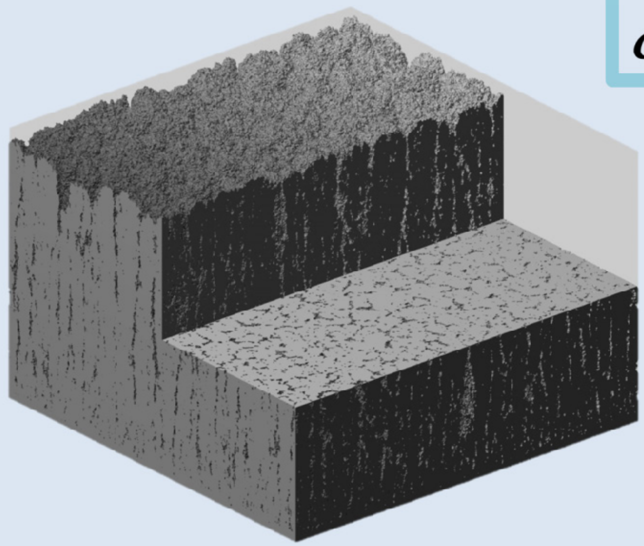
$\Xi >> 1$ Sputter Flux thermalized
Isotropic momentum distribution
Low Energy

Magnetron Sputtering Deposition at Oblique Angles



We analyzed the influence of the tilt angle and the influence of gas pressure

Film was kept far from the (DC) plasma during growth

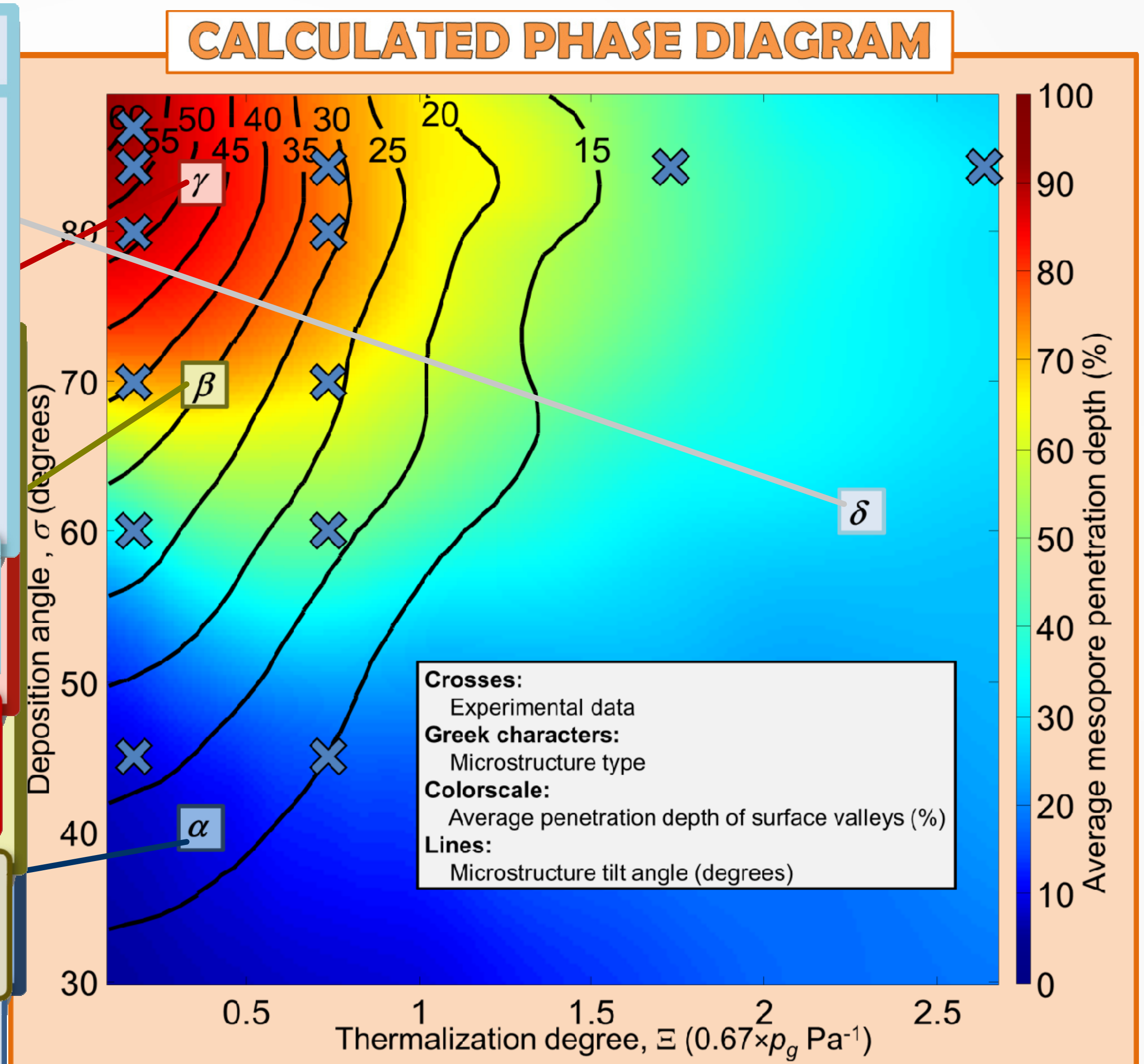


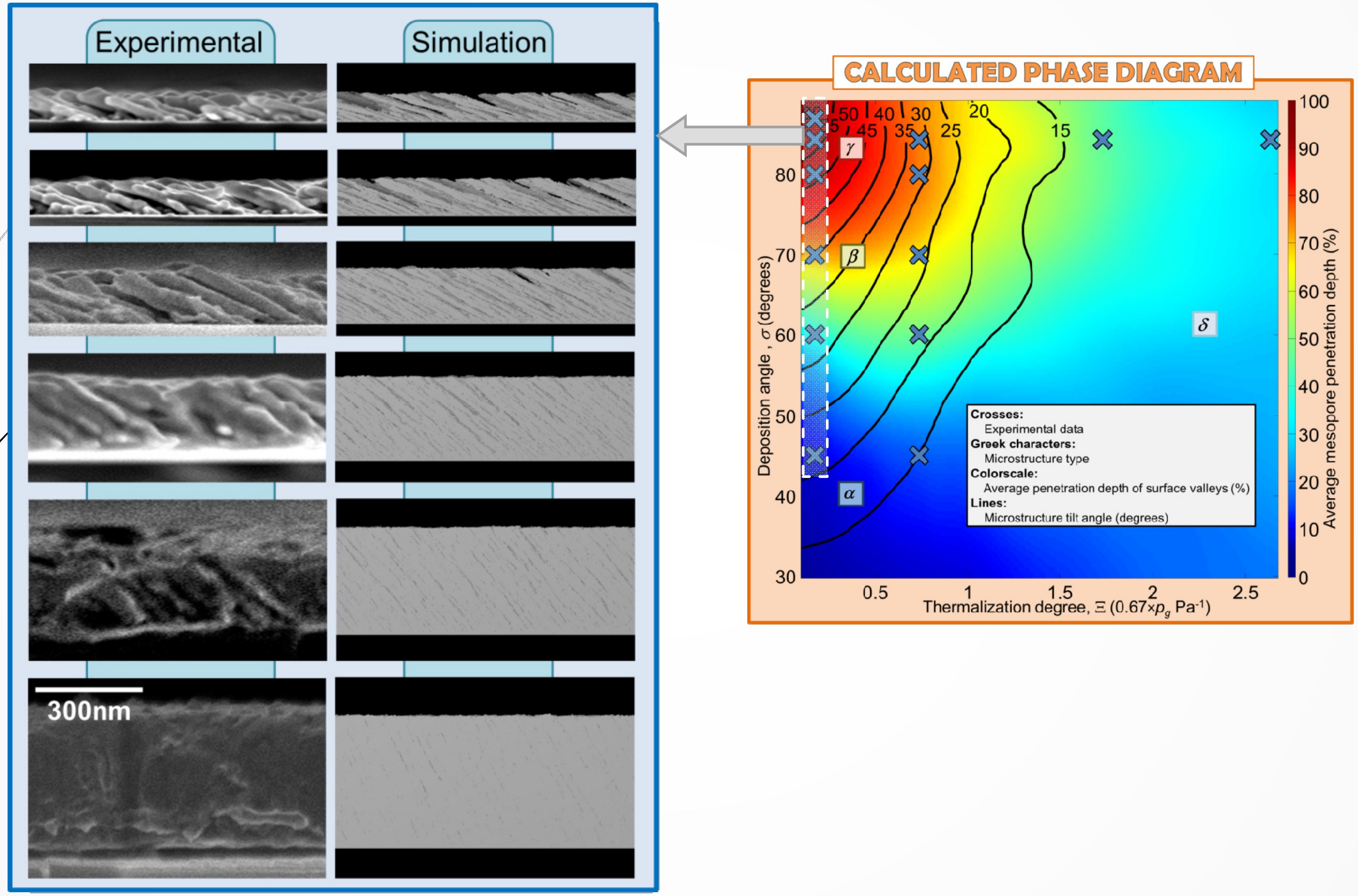
Features	Found at
- Porous - Coalescent vertical columns - High density of occluded pores	- Any σ - High Ξ (>>1)

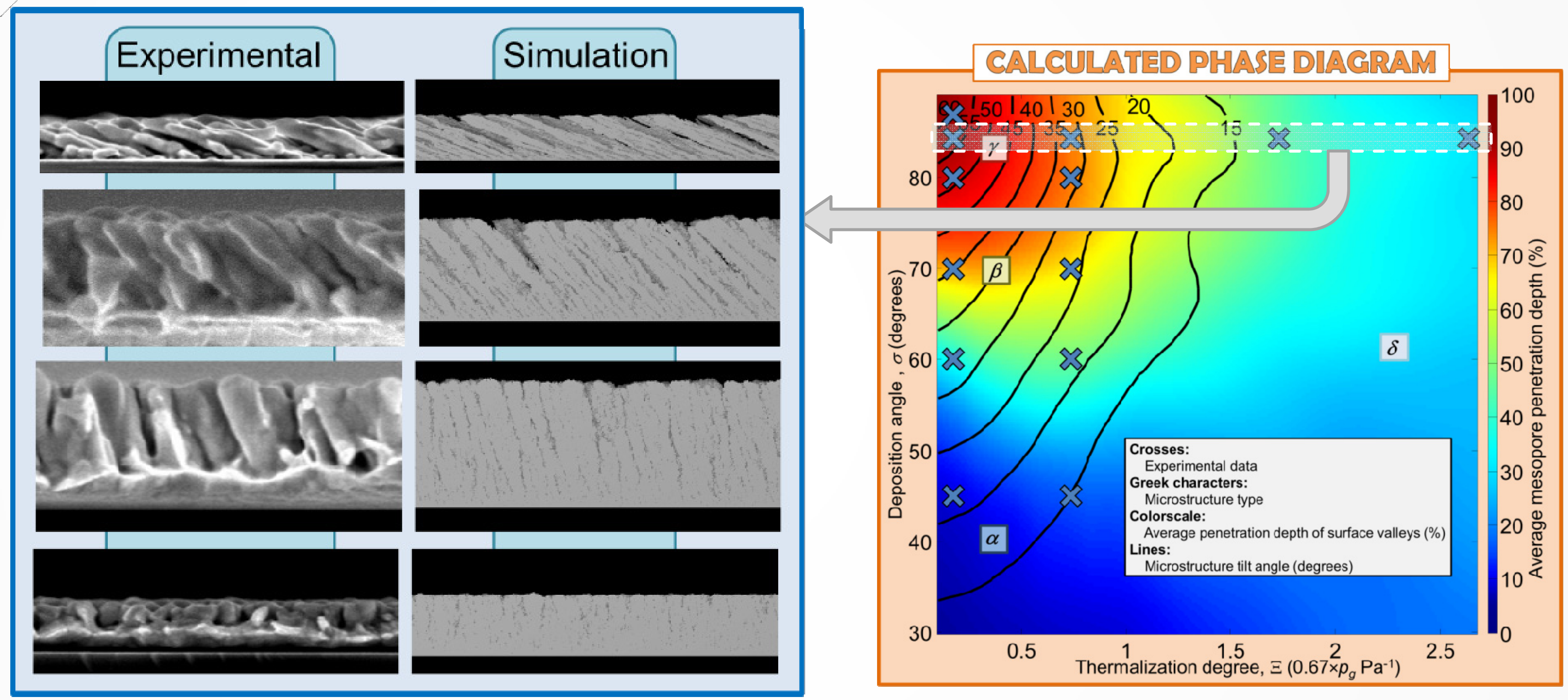
Features	Found at
- Porous - Tilted, isolated columns	- High σ (>80°) - Low Ξ (<1)

Features	Found at
- Rather compact - Tilted mesopores that percolate from surface to the substrate	- Intermediate σ (60° -80°) - Low Ξ (<1)

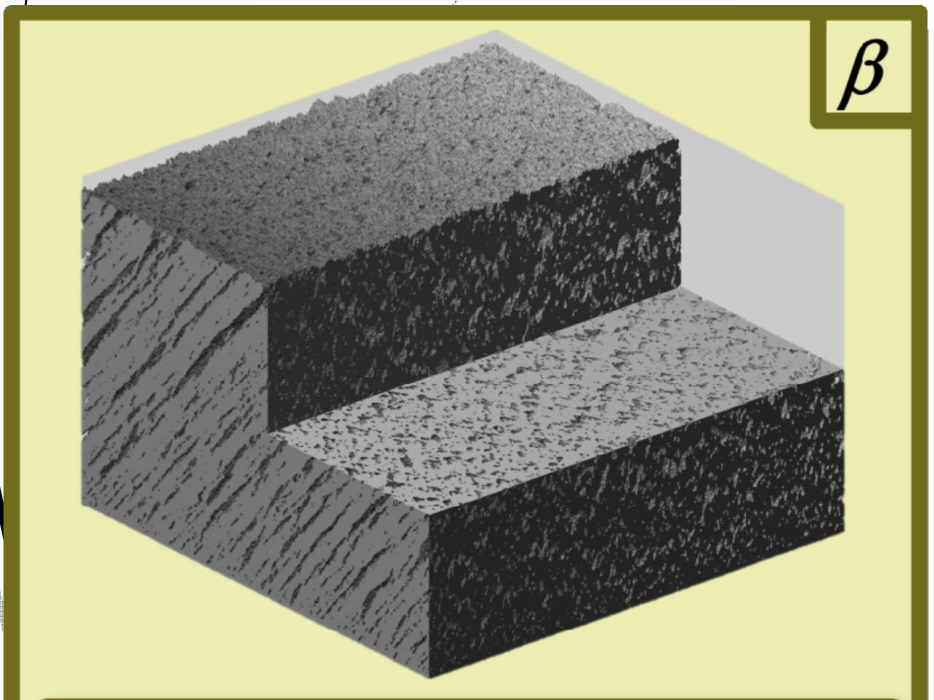
- Compact - No geometrical pattern - Very small density of pores	- Low σ (<60°) - Low Ξ (<1)



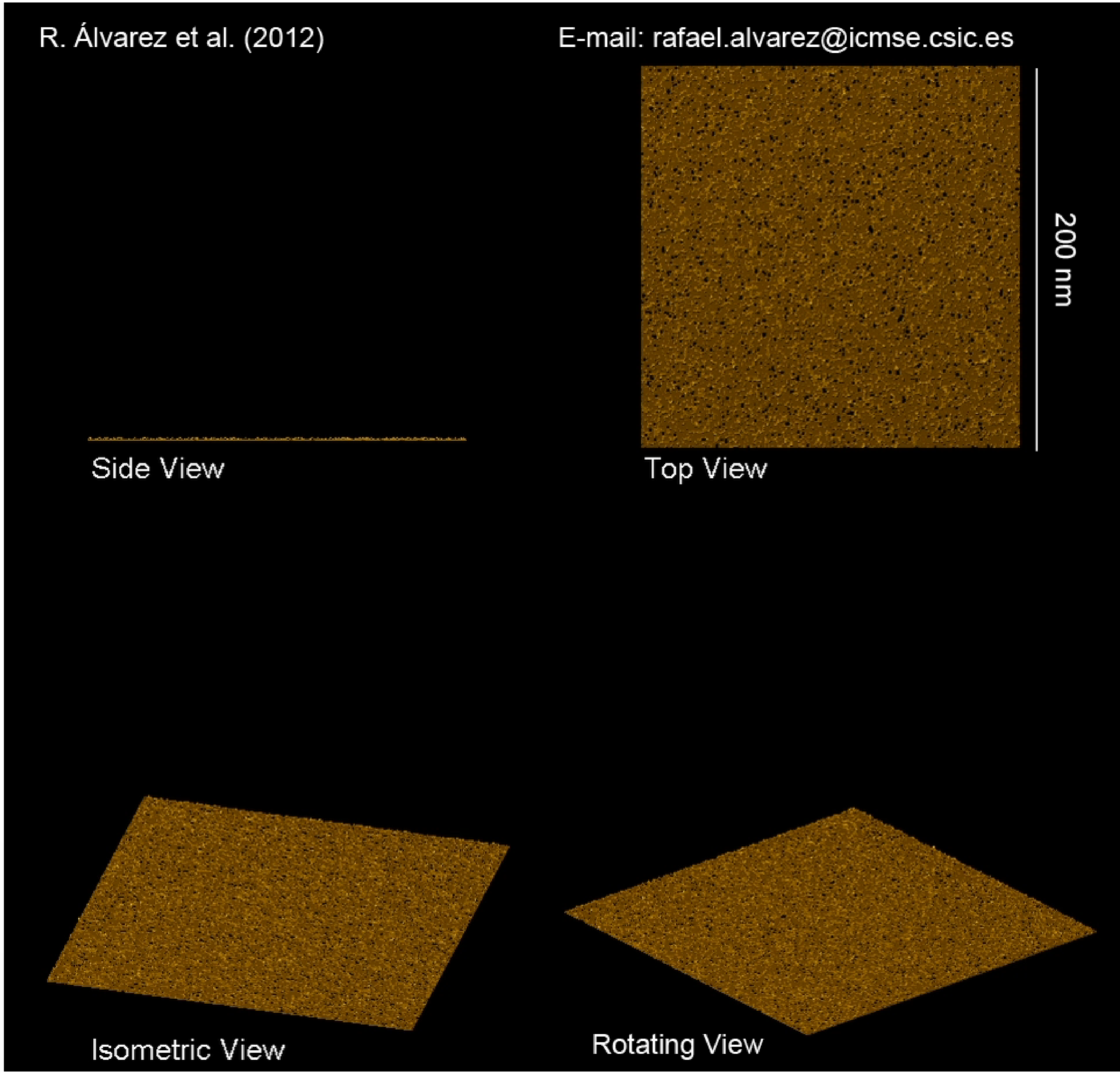

Experimental
Simulation
300nm
CALCULATED PHASE DIAGRAM
Deposition angle , σ (degrees)
Thermalization degree, Ξ (0.67×p_g Pa^{-1})
Average mesopore penetration depth (%)
γ
β
α
δ
Crosses:
Experimental data
Greek characters:
Microstructure type
Colorscale:
Average penetration depth of surface valleys (%)
Lines:
Microstructure tilt angle (degrees)


Experimental
Simulation
CALCULATED PHASE DIAGRAM
Crosses:
Experimental data
Greek characters:
Microstructure type
Colorscale:
Average penetration depth of surface valleys (%)
Lines:
Microstructure tilt angle (degrees)
Deposition angle, α (degrees)
Thermalization degree, Ξ (0.67×p_g Pa^-1)
Average mesopore penetration depth (%)
α
β
γ
δ

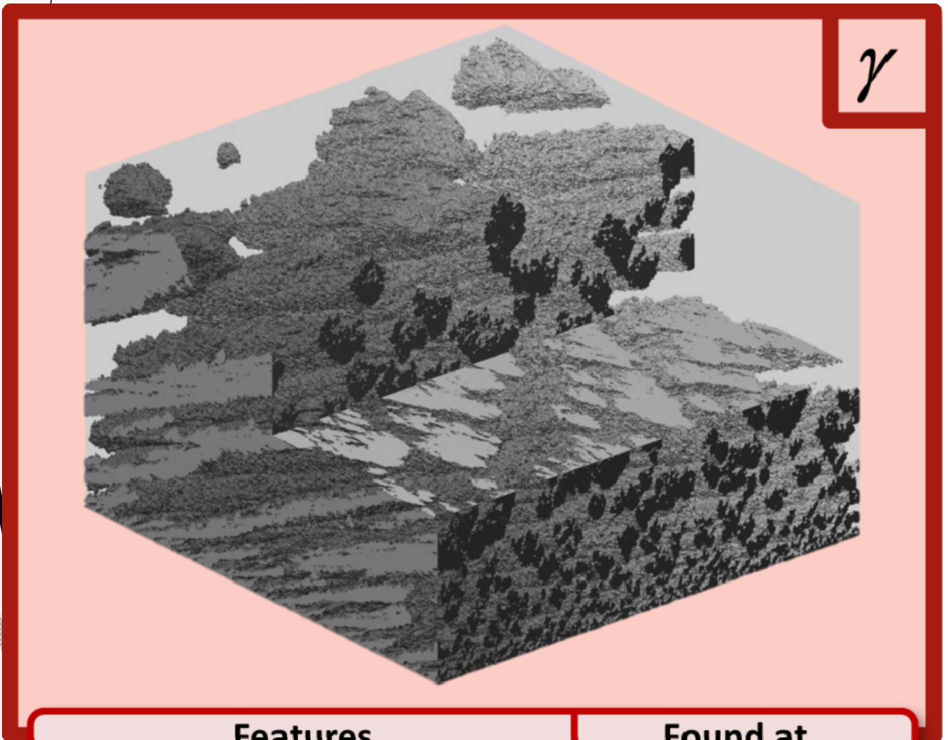
Percolating Mesopores



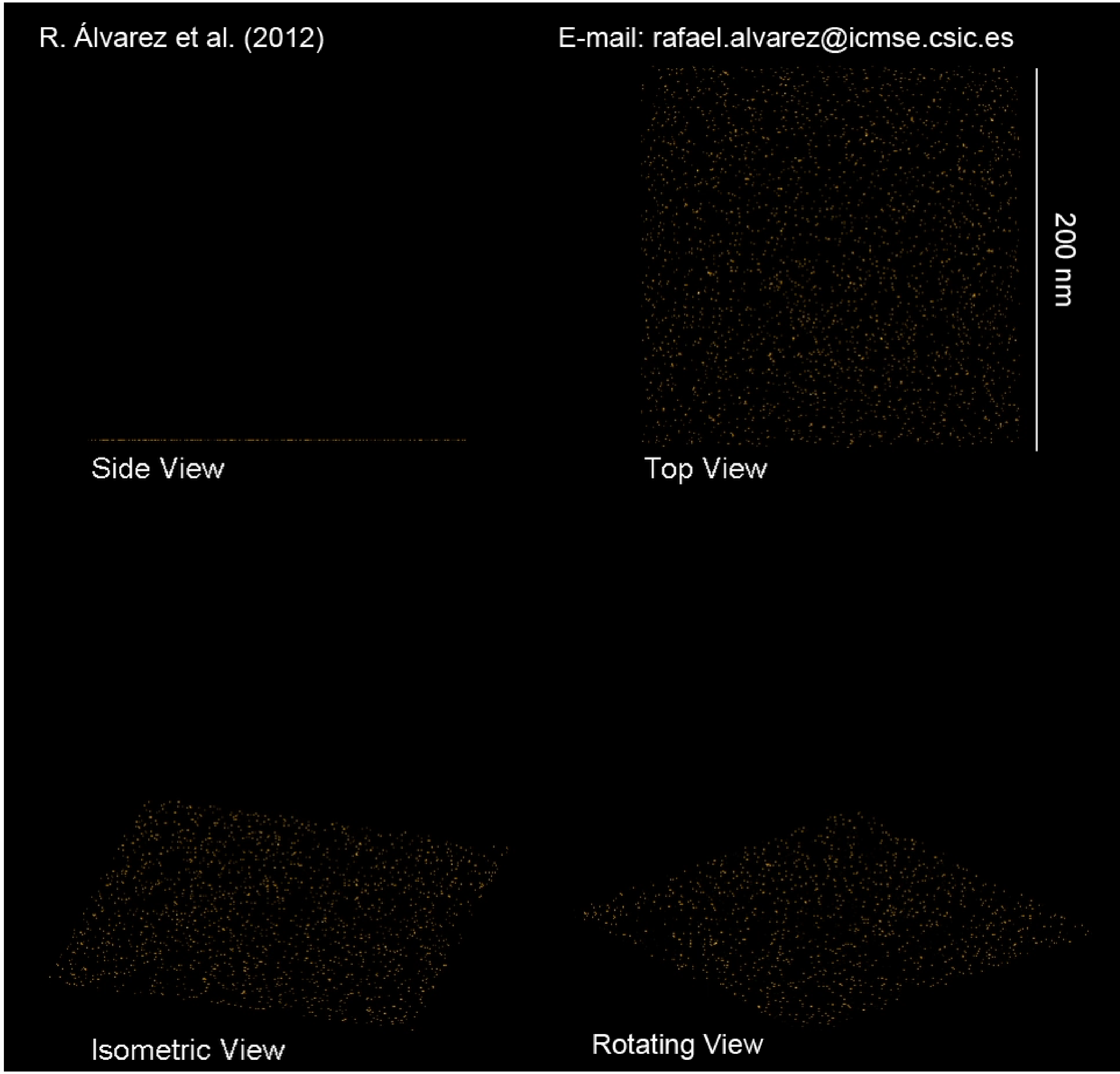
Features	Found at
- Rather compact - Tilted mesopores that percolate from surface to the substrate	- Intermediate σ (60° -80°) - Low Ξ (<1)



Columnar Microstructure



Features	Found at
- Porous	- High σ (>80°)
- Tilted, isolated columns	- Low Ξ (<1)



Is it possible to design nanomaterials by computer?

Approximate information on the nanostructure can be obtained

- Experiments in simple conditions
- Search of key non-dimensional quantities
- Atomistic analysis
- Extrapolation to more technologically-applicable conditions

Computational techniques have been used to predict experimental nanostructures

- Synthesized experimentally
- Under closure (patent)

Important facts to keep in mind

- Using vacuum and plasma-assisted techniques it is possible to grow porous structures.
- Despite the complexity of the phenomenon it is possible to carry out a bottom-up research.
- In simplified conditions it is possible to use computer simulations to design materials
  - Provide experimental conditions to synthesize the desired nanostructures
- Many processes need to be analyzed and fundamental research is necessary (both, from theoretical and experimental points of view)