DEPOSIÇÃO E CORROSÃO POR CAMADA ATÔMICA:

MODOS DE PROCESSO E APLICAÇÕES

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Sumário

1. História e evolução da tecnologia

2. Processo de “Deposição por Camada Atômica”
   2.1 Modo térmico (Thermal atomic layer deposition - ALD)
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3. Processo de corrosão em nanoescala: “Atomic Layer Etching – ALEt”

4. Algumas aplicações de filmes ALD

5. Resultados do grupo de plasmas do ITA em ALD

6. Considerações finais

Breve história do processo ALD

Atomic Layer Epitaxy (ALE)

1974 →

Dr. Tuomo S. Suntola
Espoo, Finland

https://www.kolster.fi/en/blog/ald-technology-an-invention-in-the-pocket-of-every-finn

Molecular Layering (ML)

? - 1965 →

Prof. Valentin B. Aleskovsky
Prof. Stanislav I. Koltsov
St. Petersburg, USSR

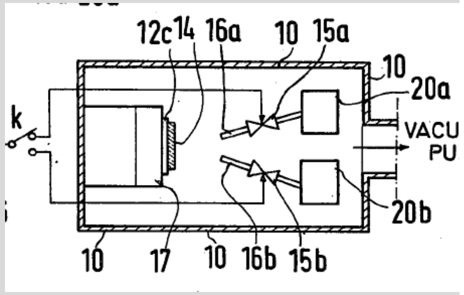
A. A. Malygin et al. Chem. Vap. Deposition 2015, 21, 216–240

1. História e evolução da tecnologia ALD

Breve história do processo ALD

1970

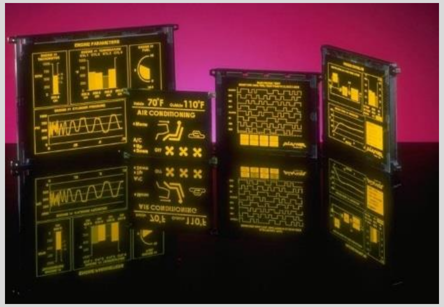
1974 ALD was invented by Dr. Suntola and co-workers



US 4058430

1980

1985 Thin film electroluminescence (TFEL) displays were the first ALD enabled products

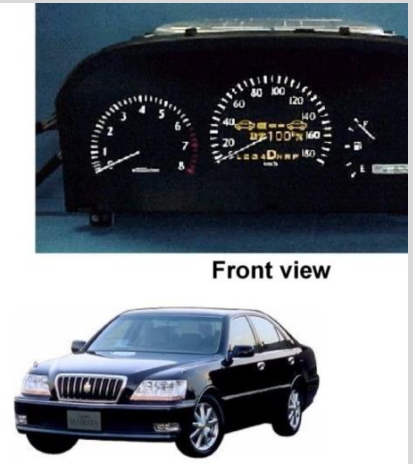


1990

Early 90's more R&D groups arrived to the scene notably from Korea, USA, and Finland

In the 90's IC industry recognizes ALD for new DRAM and gate oxide/metal systems

Late 90's DENSO starts manufacturing transparent TFEL displays for automotive markets using ALD



2000

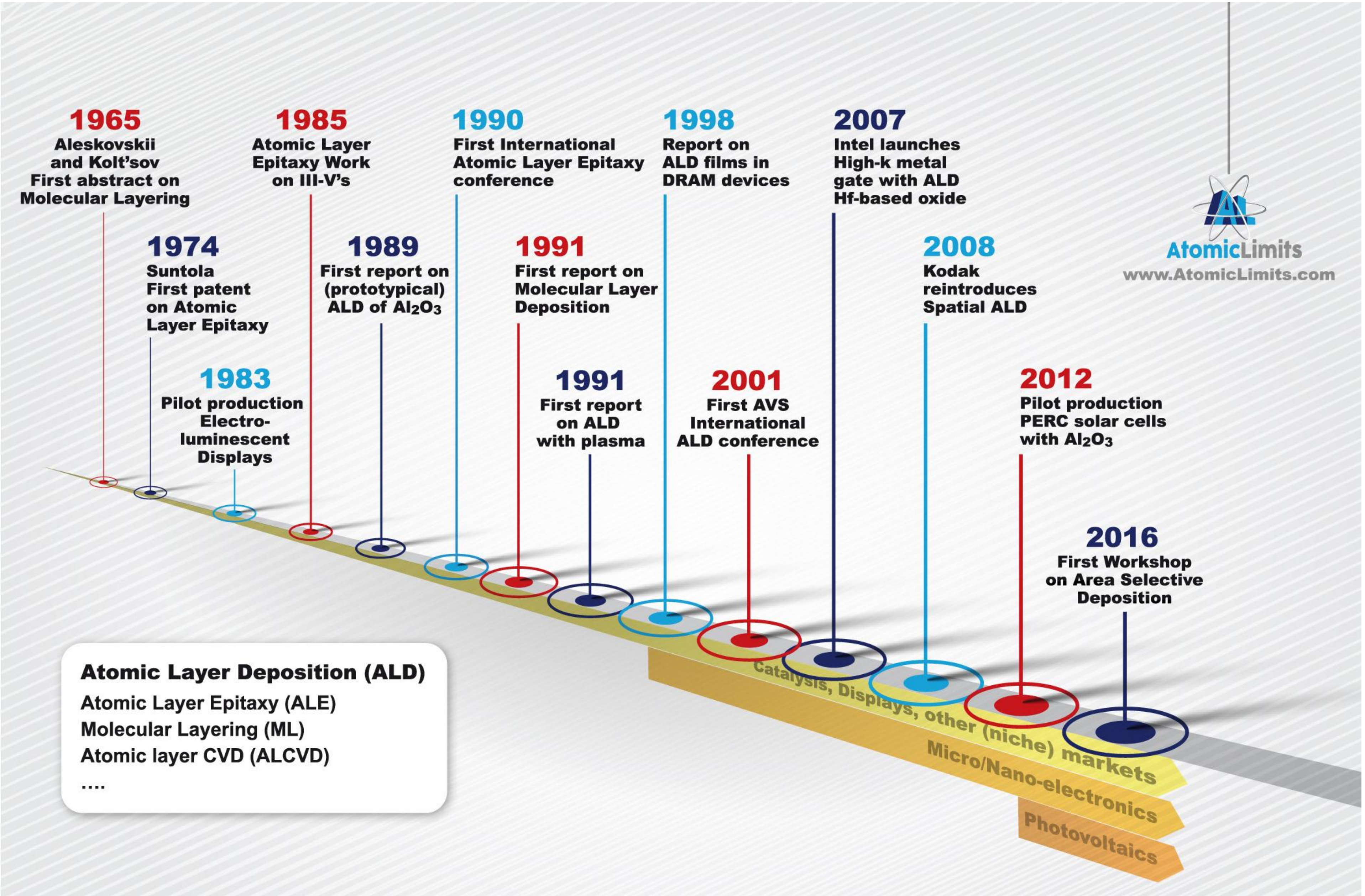
Early 2000's major IC deposition tool vendors offer ALD tools. ALD is part of R&D at every major IC house.

Early 2000's ALD is applied to hard disc manufacturing

2007 First microprocessor products with ALD

Tecnologia de 22 nm (2012)

1. História e evolução da tecnologia ALD



1. História e evolução da tecnologia ALD

Breve história do processo ALD

2018 2021 ?

MILLENNIUM TECHNOLOGY PRIZE

Tuomo Suntola
Enabling smart technology

https://millenniumprize.org/winners/enabling-smart-technology/

1. História e evolução da tecnologia ALD

Artigos sobre história do processo / tecnologia ALD

2013

JVSTA
JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY A

History of atomic layer deposition and its relationship with the American Vacuum Society

Gregory N. Parsons, Jeffrey W. Elam, Steven M. George, Suvi Haukka, Hyeongtag Jeon et al.

Citation: J. Vac. Sci. Technol. A **31**, 050818 (2013); doi: 10.1116/1.4816548
View online: http://dx.doi.org/10.1116/1.4816548
View Table of Contents: http://avspublications.org/resource/1/JVTAD6/v31/i5
Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

2014

Chemical Vapor Deposition

DOI: 10.1002/cvde.201402012

Essay

A Short History of Atomic Layer Deposition: Tuomo Suntola's Atomic Layer Epitaxy**

By *Riikka L. Puurunen**

2015

Chemical Vapor Deposition

DOI: 10.1002/cvde.201502013

Essay

From V. B. Aleskovskii's "Framework" Hypothesis to the Method of Molecular Layering/Atomic Layer Deposition**

By *Anatolii A. Malygin**, *Victor E. Drozd*, *Anatolii A. Malkov*, and *Vladimir M. Smirnov*

1. História e evolução da tecnologia ALD

Artigos sobre história do processo / tecnologia ALD

2017

67 autores!!

Review Article: Recommended reading list of early publications on atomic layer deposition—Outcome of the "Virtual Project on the History of ALD"

Cite as: J. Vac. Sci. Technol. A **35**, 010801 (2017); https://doi.org/10.1116/1.4971389
Submitted: 30 September 2016 . Accepted: 15 November 2016 . Published Online: 16 December 2016

Esko Ahvenniemi, Andrew R. Akbashev, Saima Ali, Mikhael Bechelany, Maria Berdova, Stefan Boyadjiev, David C. Cameron, Rong Chen, Mikhail Chubarov, Veronique Cremers, Anjana Devi, Viktor Drozd, Liliya Elnikova, Gloria Gottardi, Kestutis Grigoras, Dennis M. Hausmann, Cheol Seong Hwang, Shih-Hui Jen, Tanja Kallio, Jaana Kanervo, Ivan Khmelnitskiy, Do Han Kim, Lev Klibanov, Yury Koshtyal, A. Outi I. Krause, Jakob Kuhs, Irina Kärkkänen, Marja-Leena Kääriäinen, Tommi Kääriäinen, Luca Lamagna, Adam A. Łapicki, Markku Leskelä, Harri Lipsanen, Jussi Lyytinen, Anatoly Malkov, Anatoly Malygin, Abdelkader Mennad, Christian Militzer, Jyrki Molarius, Małgorzata Norek, Çağla Özgit-Akgün, Mikhail Panov, Henrik Pedersen, Fabien Piallat, Georgi Popov, Riikka L. Puurunen, Geert Rampelberg, Robin H. A. Ras, Erwan Rauwel, Fred Roozeboom, Timo Sajavaara, Hossein Salami, Hele Savin, Nathanaelle Schneider, Thomas E. Seidel, Jonas Sundqvist, Dmitry B. Suyatin, Tobias Törndahl, J. Ruud van Ommen, Claudia Wiemer, Oili M. E. Ylivaara, and Oksana Yurkevich

COLLECTIONS

1. História e desenvolvimento da tecnologia ALD

Projeto VPHA

Aalto University
Finland

https://www.vph-ald.com/

Vídeo recomendado: https://youtu.be/6zCvaMv58hY

1. História e evolução da tecnologia ALD

Número de publicações sobre ALD ao longo das décadas

PLOS | ONE

2018

RESEARCH ARTICLE

Characterizing the field of Atomic Layer Deposition: Authors, topics, and collaborations

Elsa Alvaro[1]*, Angel Yanguas-Gil[2]

1 Northwestern University Libraries, Northwestern University, Evanston, Illinois, United States of America,
2 Energy Systems Division, Argonne National Laboratory, Lemont, Illinois, United States of America

* elsa.alvaro@northwestern.edu

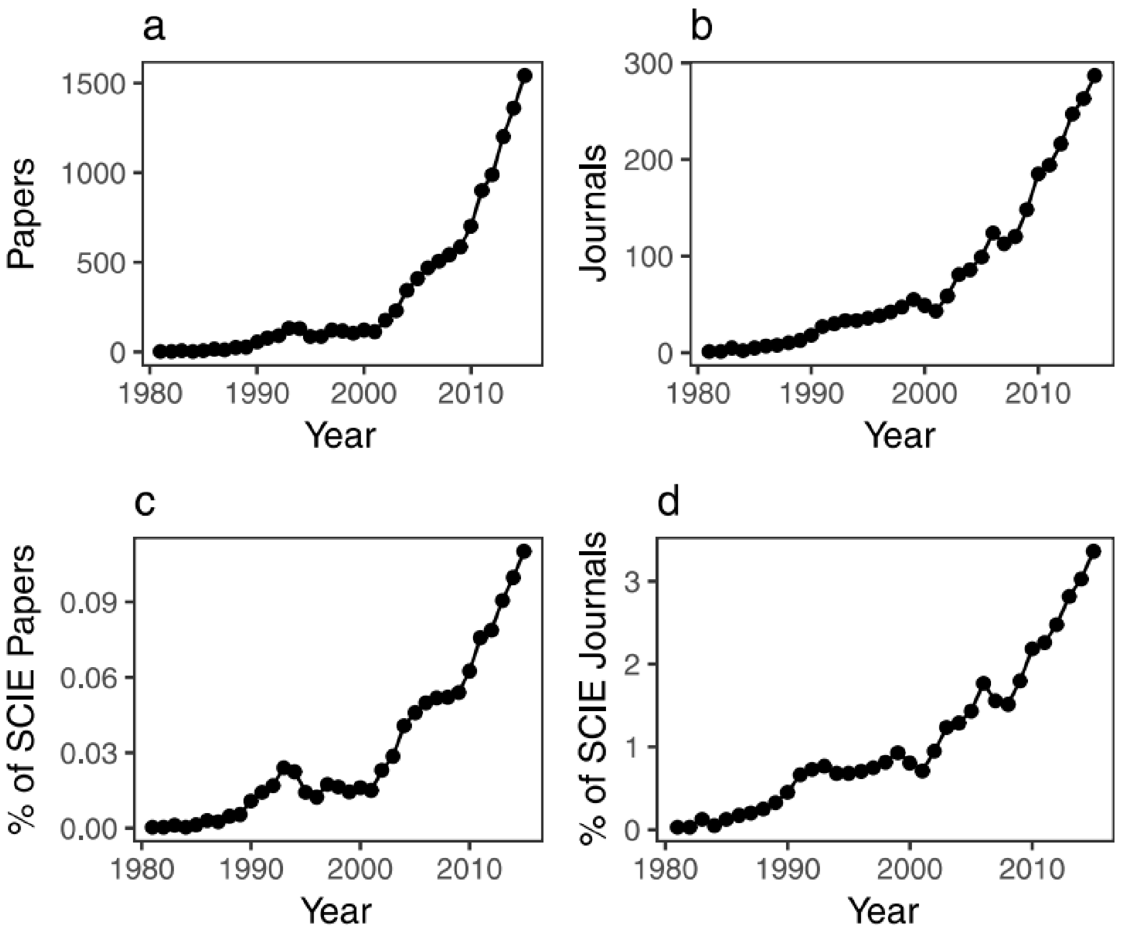


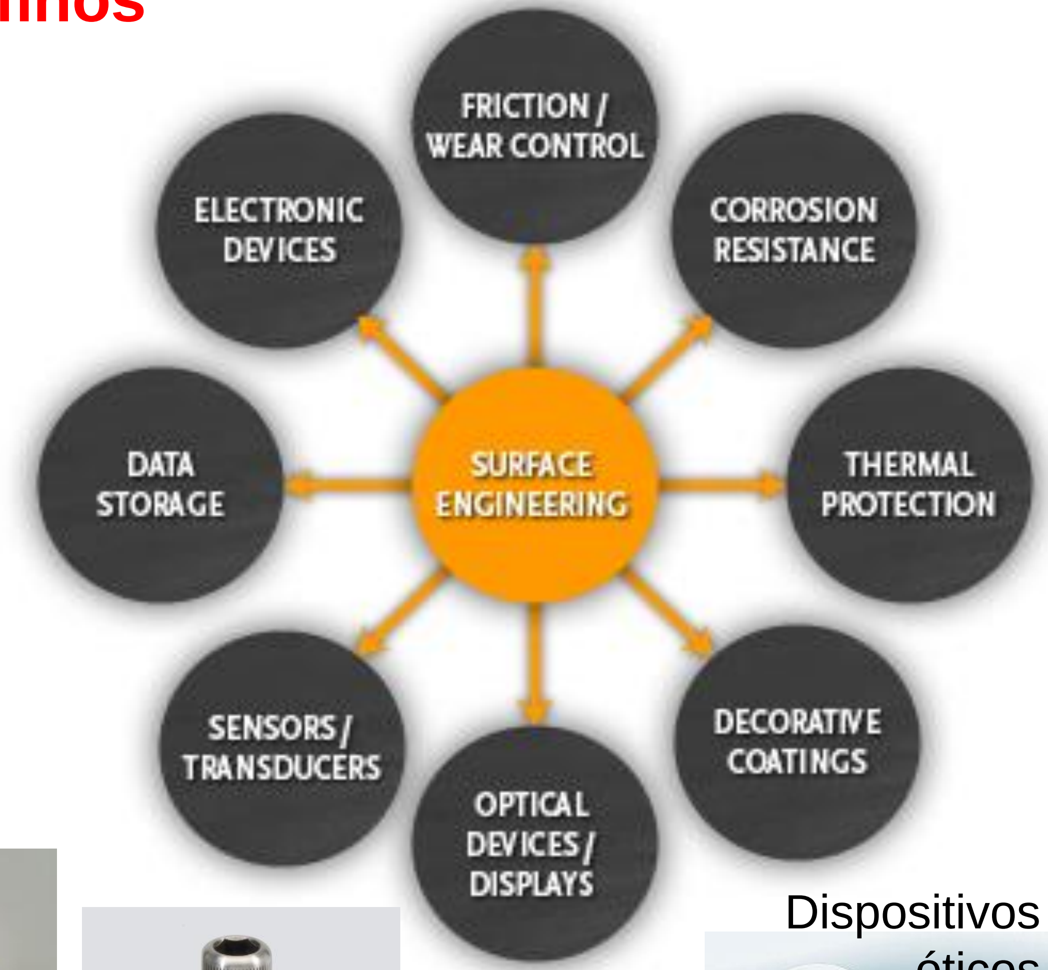
Fig 1. Number of papers (a) and journals (b) that publish ALD research, and percentage among SCIE papers (c) and journals (d).

https://doi.org/10.1371/journal.pone.0189137.g001

2. Processo de deposição por camada atômica

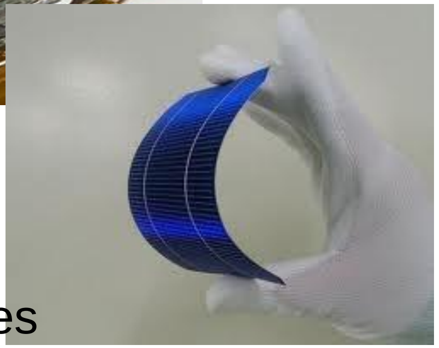
Recobrimentos ou Filmes finos

<u>*Definição*</u>: é uma fina camada de material cuja espessura é da fração de nanometros (nm, uma camda atômica) a vários micrometros (μm).



<u>*Aplicações*</u>:

Displays flexíveis (OLED)



Células solares

Controle de desgaste

Dispositivos óticos

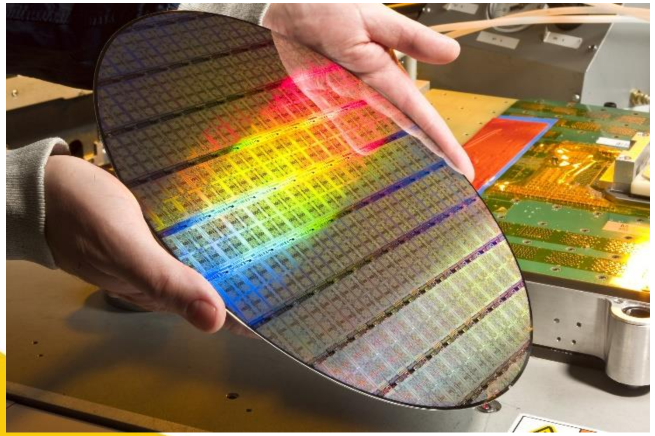
2. Processo de deposição por camada atômica

Recobrimentos ou Filmes finos

Requerimentos para processos de nanofabricação

→ Uniformidade

Filmes uniformes têm espessura e composição iguais (e outras propriedades) em cada posição ao longo de um substrato plano, por exemplo, ao longo de um wafer de 300 mm.



→ Conformidade

Filmes conformes têm a mesma espessura (e propriedades) também dentro de estruturas 3D.

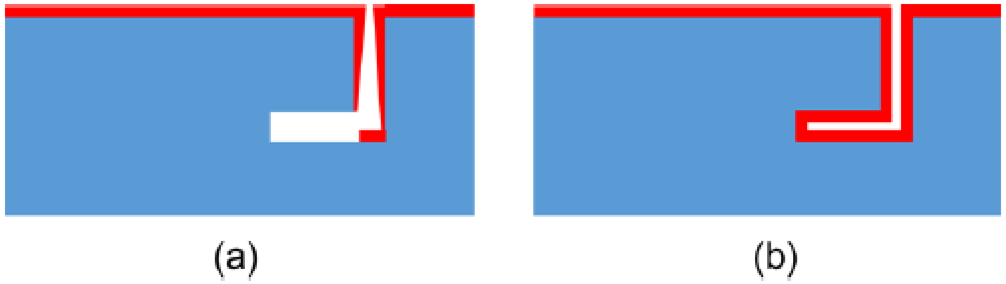


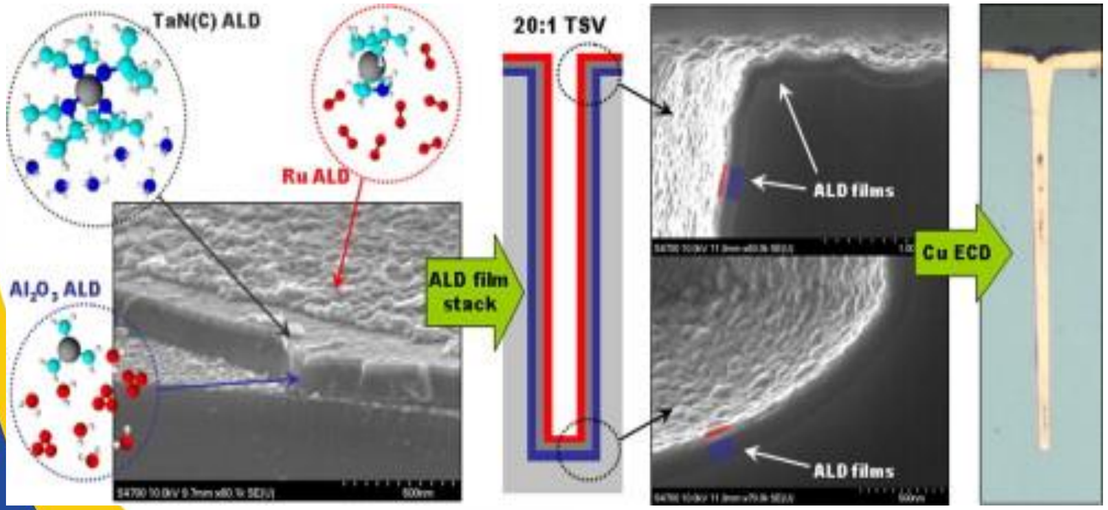
FIG. 2. Schematic representation of a deposition on a 3D structured surface by a line-of-sight technique (a) and by a conformal technique such as ALD (b).

V. Cremers, R.L. Puurunen, J. Dendooven, Appl. Phys. Rev. 6, 021302 (2019).

2. Processo de deposição por camada atômica

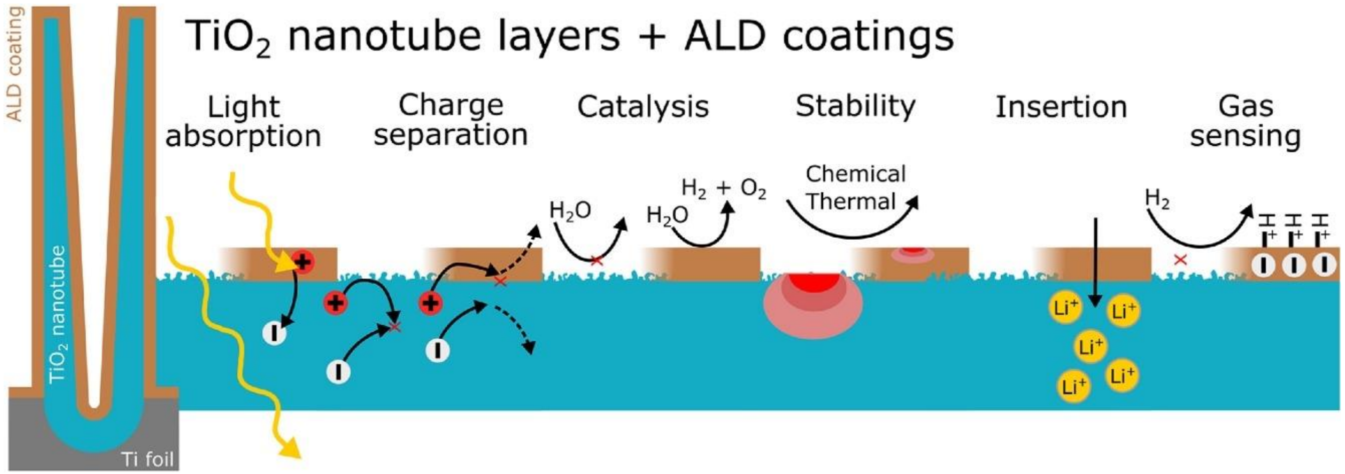
Recobrimentos ou Filmes finos

High-aspect-ratio (HAR) structures + ALD



Atomic layer deposition for high aspect ratio through silicon vias, 2013

https://www.sciencedirect.com/science/article/abs/pii/S0167931713000592

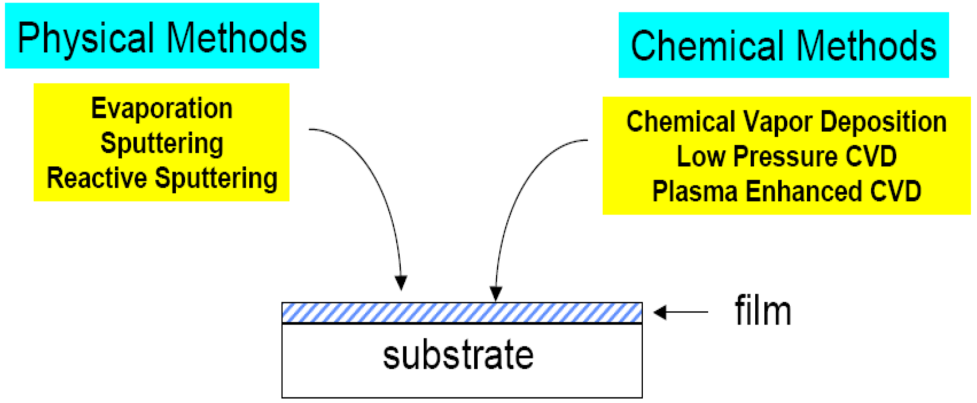


One-dimensional anodic TiO_2 nanotubes coated by atomic layer deposition: Towards advanced applications, 2019

https://www.sciencedirect.com/science/article/pii/S2352940718305341#fig0065

2. Processo de deposição por camada atômica

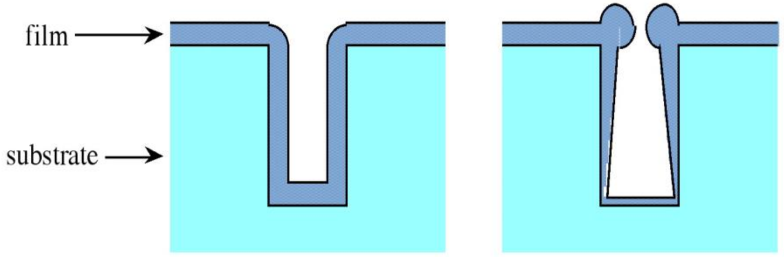
→ **Deposition techniques for thin films technology**



Applications:

Metalization (e.g. Al, TiN, W, silicide)
Poly-Si
dielectric layers; surface passivation.

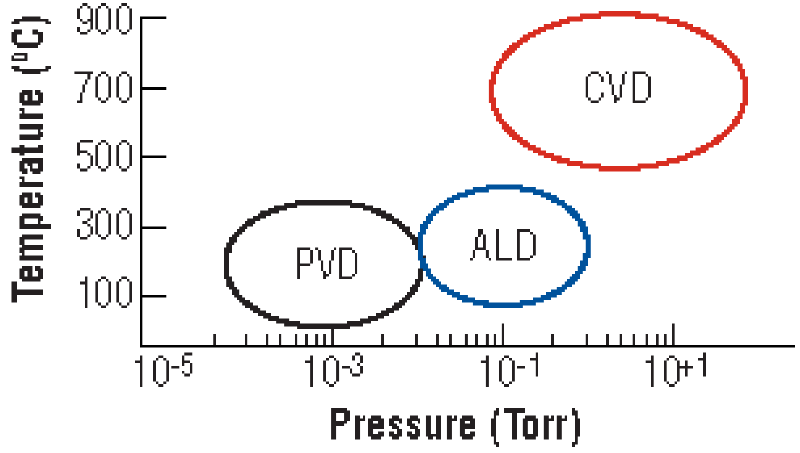
Step coverage

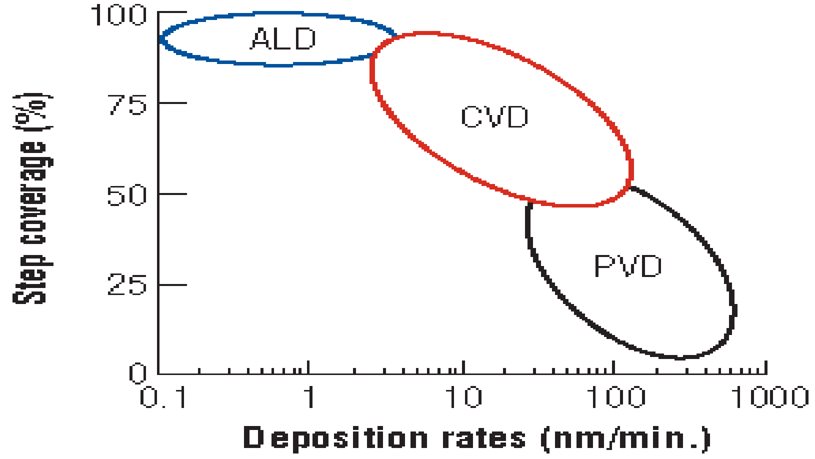


(a) Uniform coverage

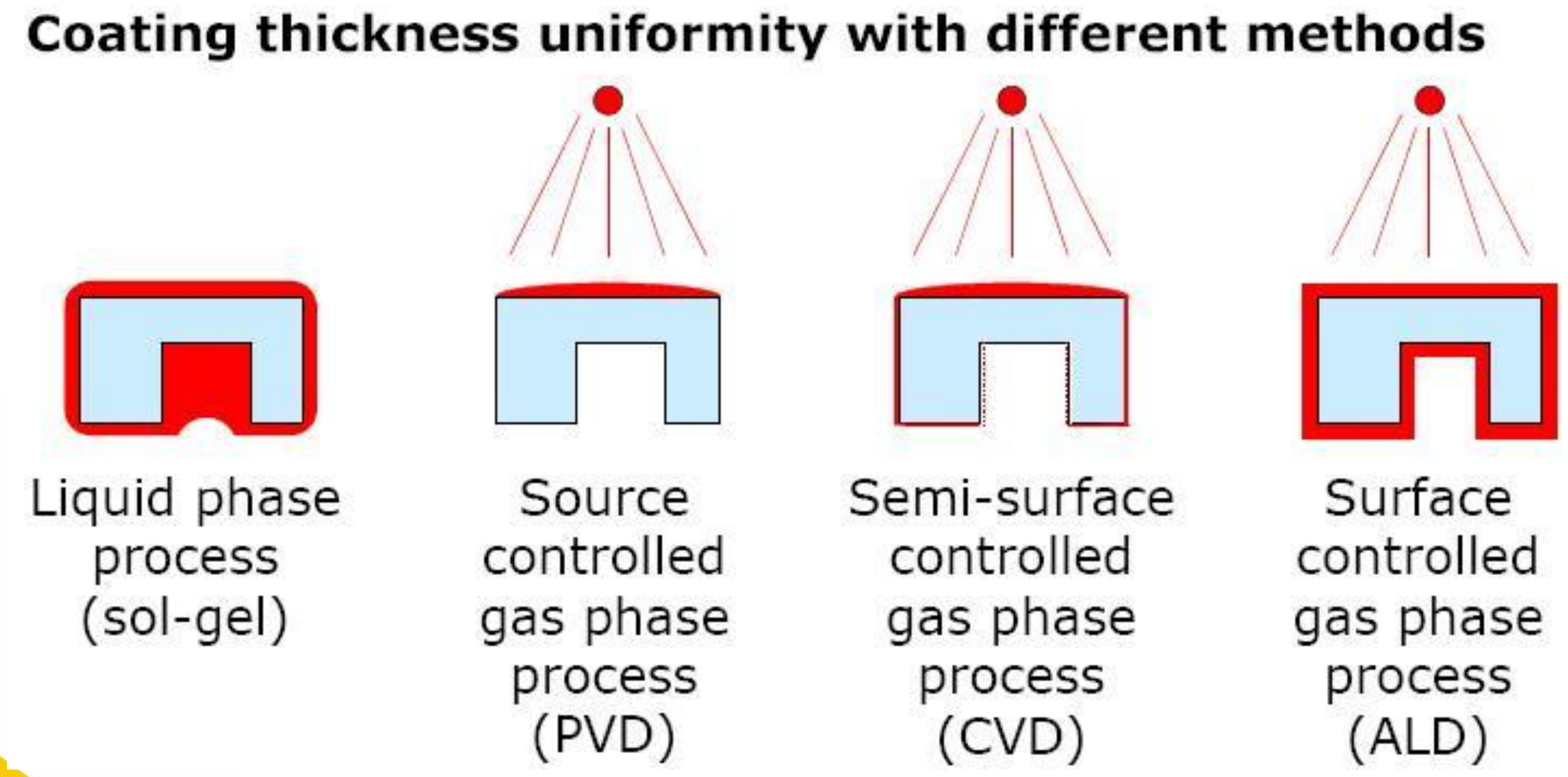
(b) Non-uniform coverage

ALD – Atomic layer deposition
CVD – Chemical vapor deposition
PVD – Physical vapor deposition





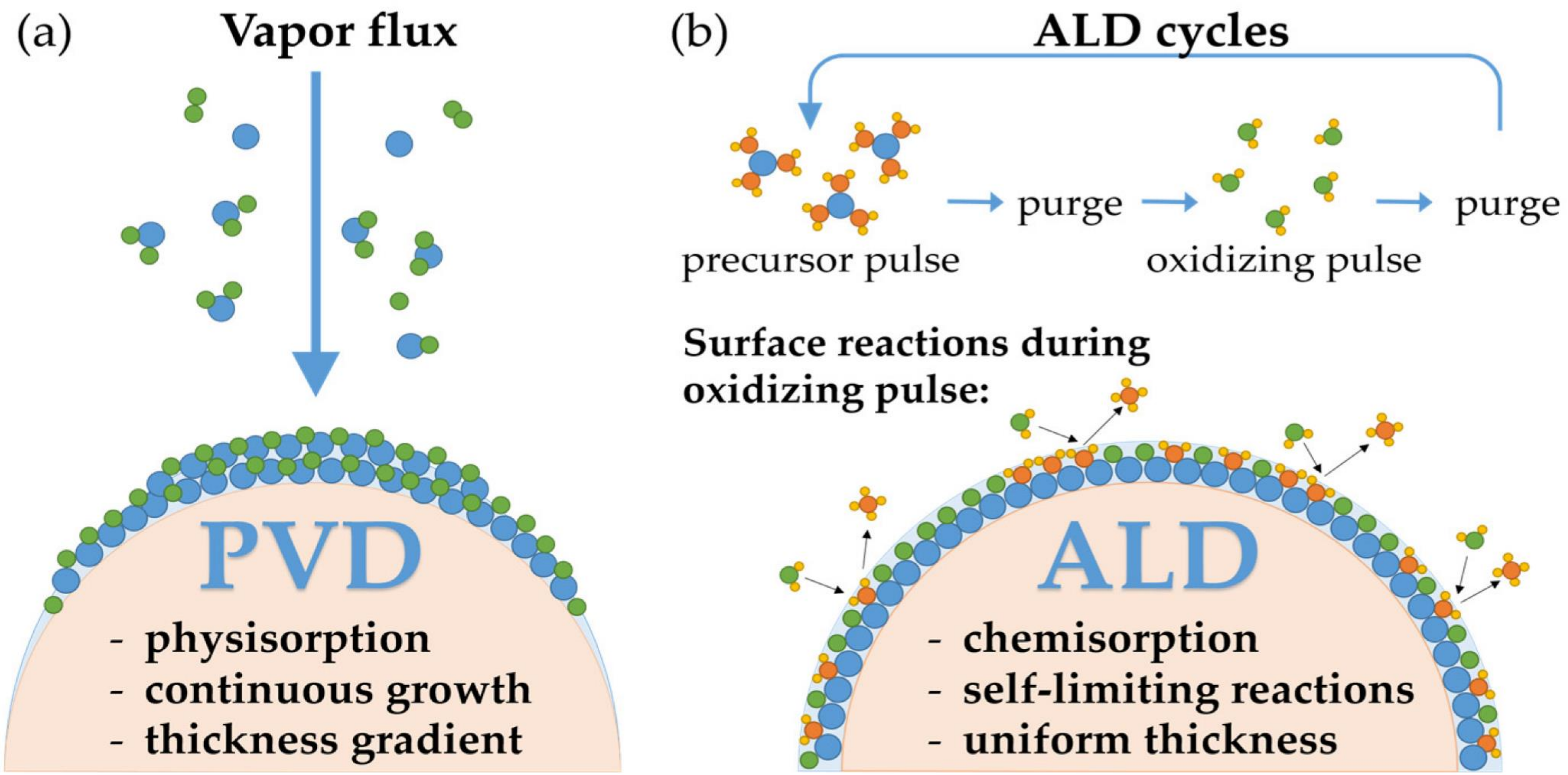
2. Processo de deposição por camada atômica



https://www.nextbigfuture.com/2010/04/equipment-for-roll-to-roll-atomic-layer.html

2. Processo de deposição por camada atômica

Comparativo entre processos de deposição na fase gasosa



analogic-like process

digital-like process

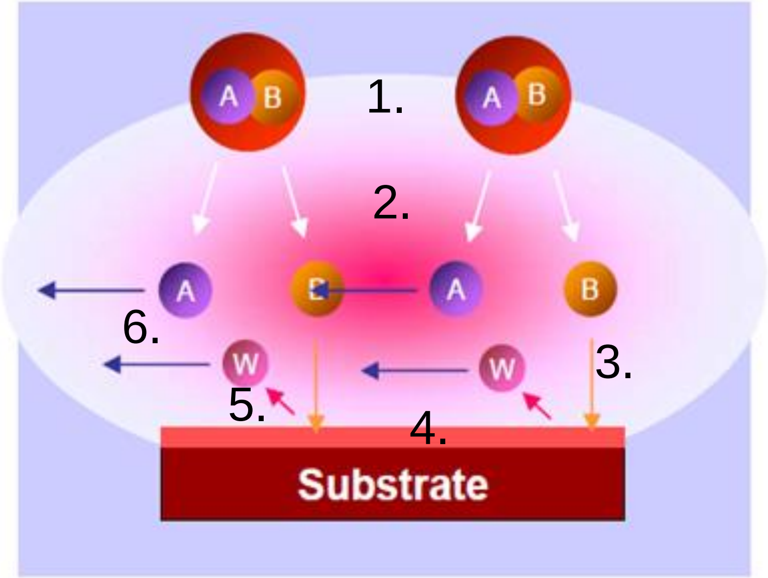
K. Pfeiffer, U. Schulz, A. Tünnermann, A. Szeghalmi, **Antireflection Coatings for Strongly Curved Glass Lenses by Atomic Layer Deposition,** *Coatings* **2017**, *7*(8), 118.

2. Processo de deposição por camada atômica

Técnica CVD - Sequência do processo

Deposição de filmes através de <u>reações químicas na fase vapor</u> e <u>processos de adsorção/dessorção na superfície do substrato</u>.

1. Introdução "continua" de gases reativos na câmara de processos;



2. Decomposição dos gases por:
→ Aquecimento, e/ou;
→ Plasma.

3. Adsorção das espécies fragmentadas do gás
Pela superfície do substrato;

4. Reações ocorrem na superfície do substrato.
O filme começa a ser formado.

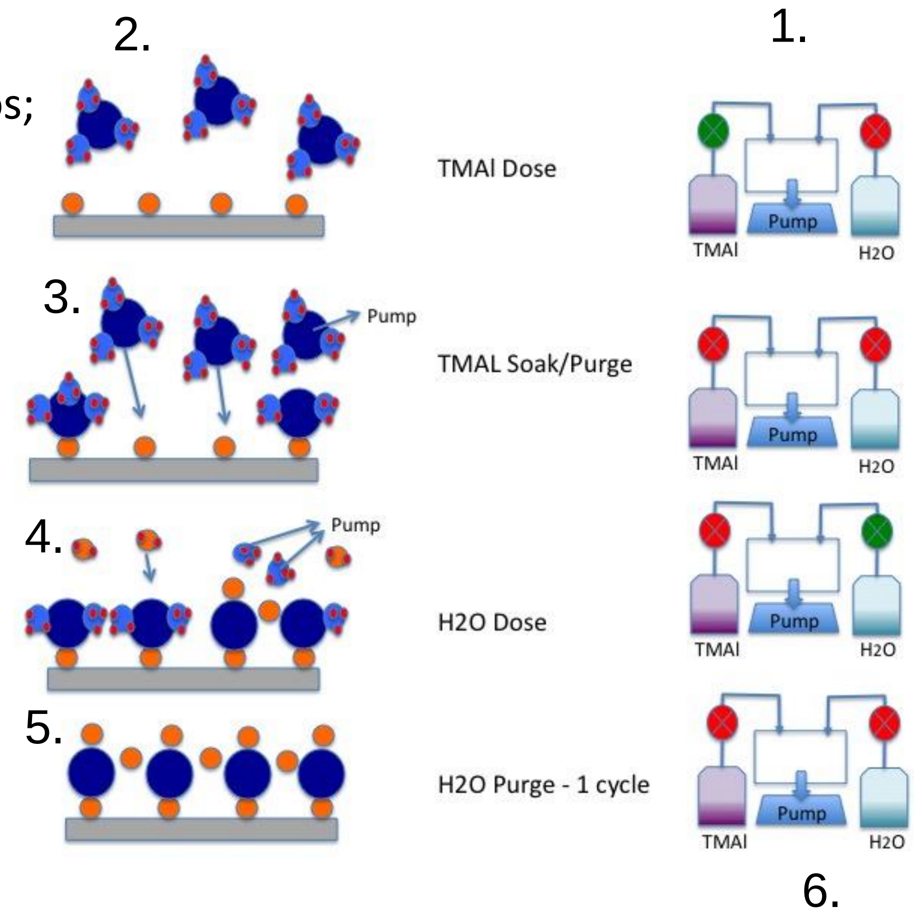
5. Transporte dos sub-produtos voláteis do substrato (dessorção);

6. Exaustão contínua do gás e dos sub-produtos pelo sistema de vácuo (e/ou gás de purga).

2. Processo de deposição por camada atômica

Técnica ALD - Sequência do processo

ALD pode ser definida como uma técnica de deposição de filmes finos que é baseada no uso sequencial de reações auto-limitadas entre as fases gas-sólido.



1. Introdução "pulsada" de gases reativos na câmara de processos;

2. Pulso 1: Precursor metálico reage de uma forma auto-limitada com terminações tipo -OH na superfície do substrato;

3. Pulso 2: Purga com gás inerte (N_2) para limpeza de Sub-produtos na superfície;

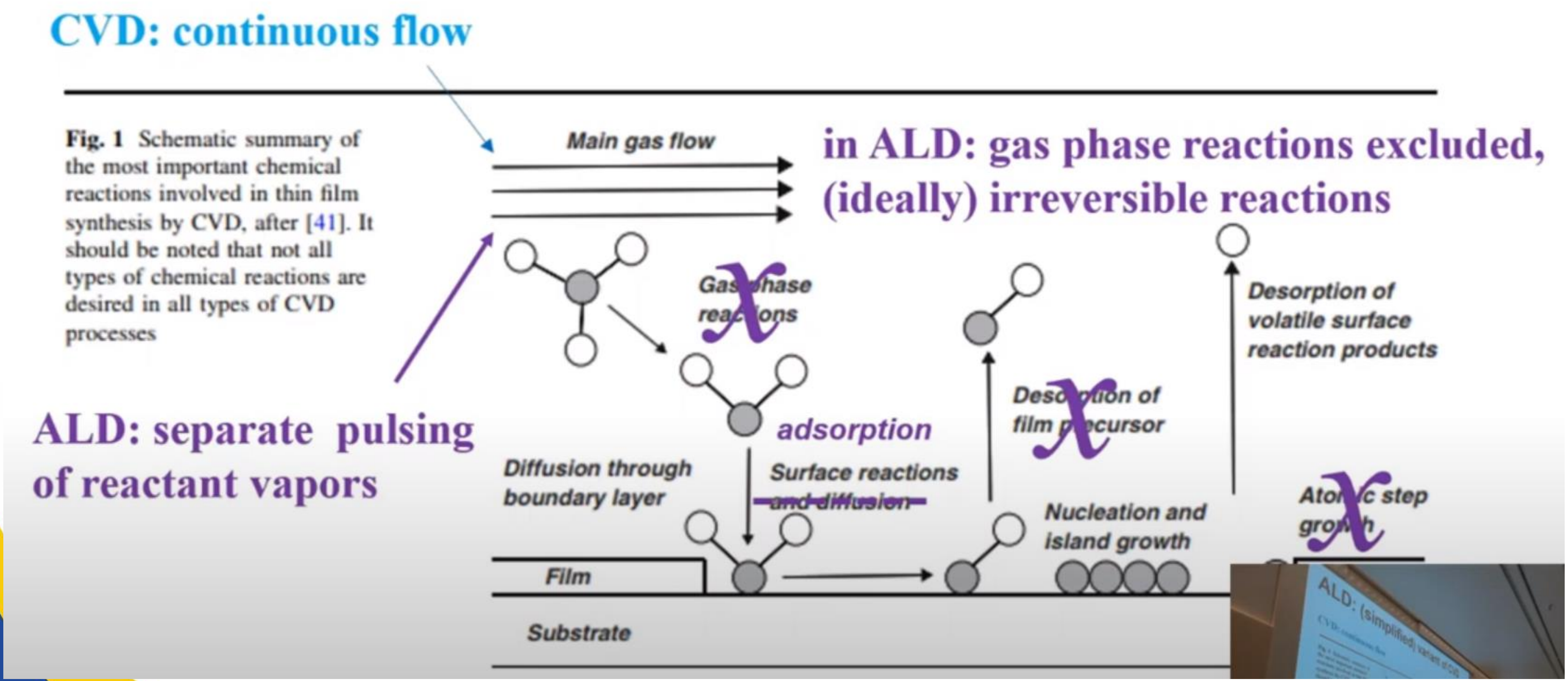
4. Pulso 3: Precursor ligante reage de forma auto-limitada com as espécies adsorvidas do precursor metálico;
   → Modo térmico, ou;
   → Modo plasma

5. Pulso 4: Purga com gás inerte (N_2) para limpeza de Sub-produtos na superfície;

Repete "N" vezes

6. Exaustão contínua do gás e dos sub-produtos pelo sistema de vácuo (e/ou gás de purga).

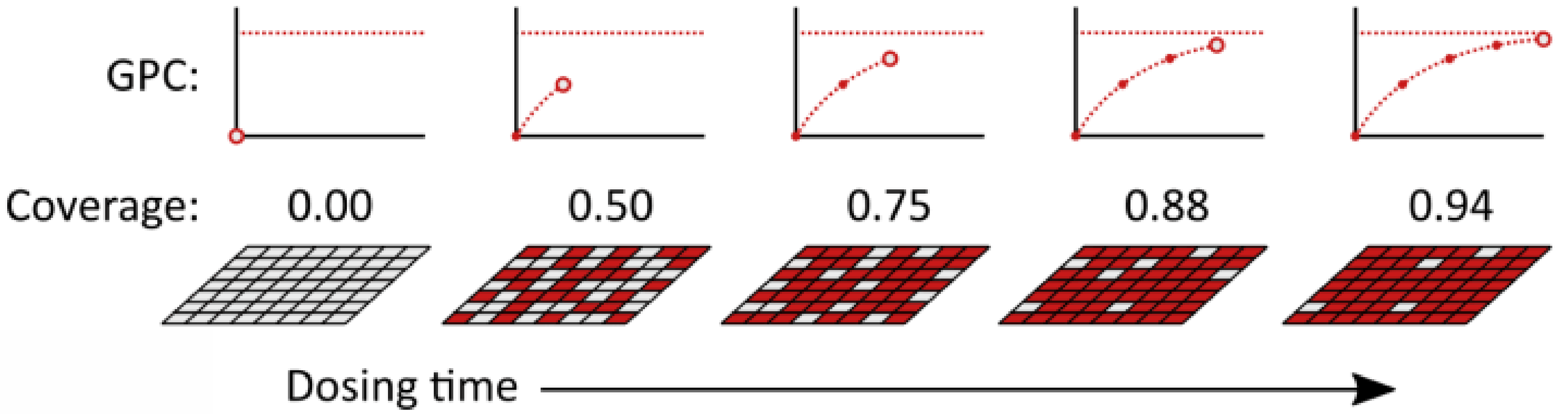
2. Processo de deposição por camada atômica

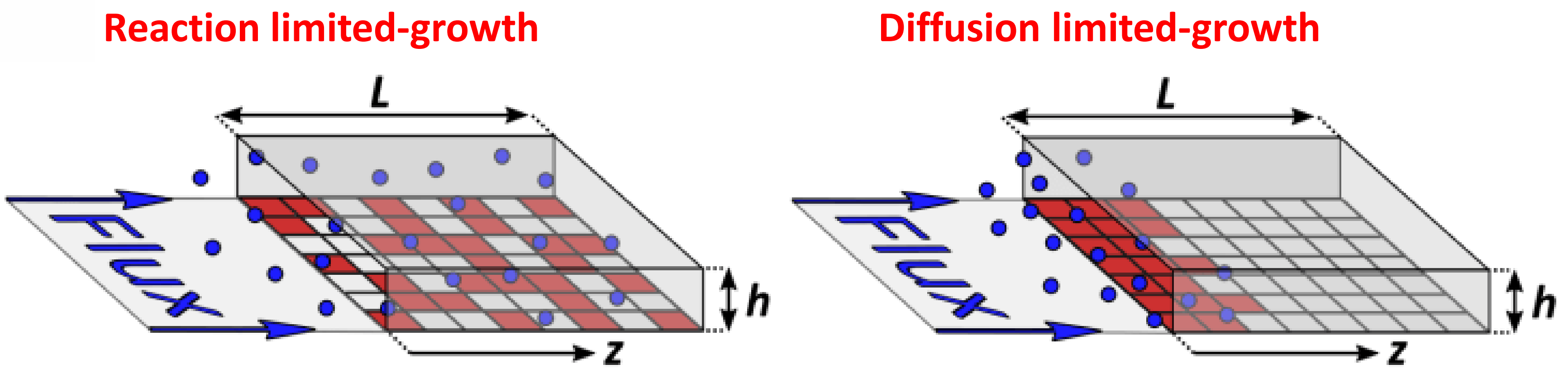


https://youtu.be/6zCvaMv58hY

2. Processo de deposição por camada atômica

Reação superficial auto-limitada





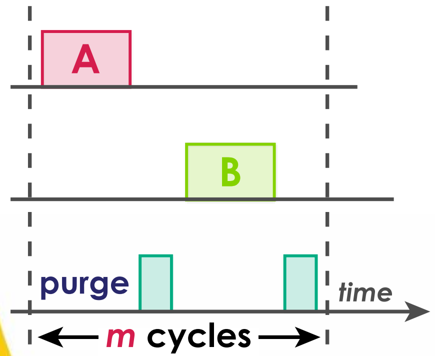
https://www.atomiclimits.com/2020/02/08/basic-insights-into-ald-conformality-a-closer-look-at-ald-and-thin-film-conformality/

2. Processo de deposição por camada atômica

Tipos de Ciclos

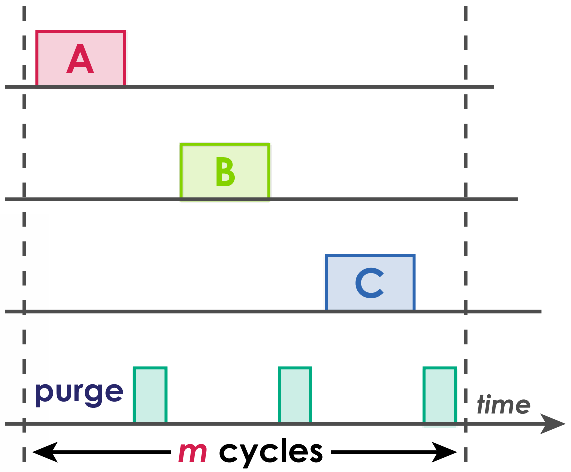
Regular

$(AB)_m$



Multistep

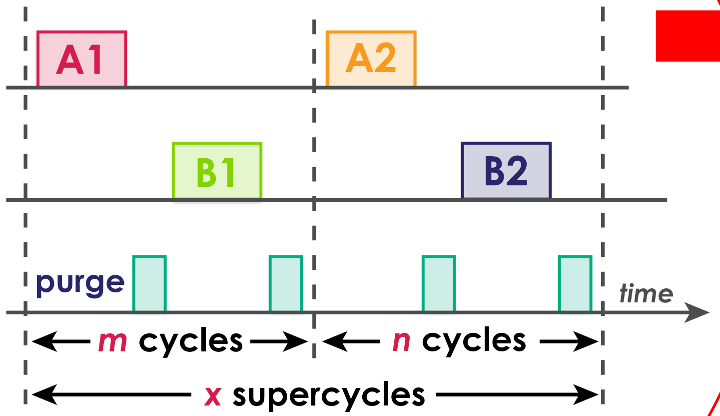
$(ABC)_m$



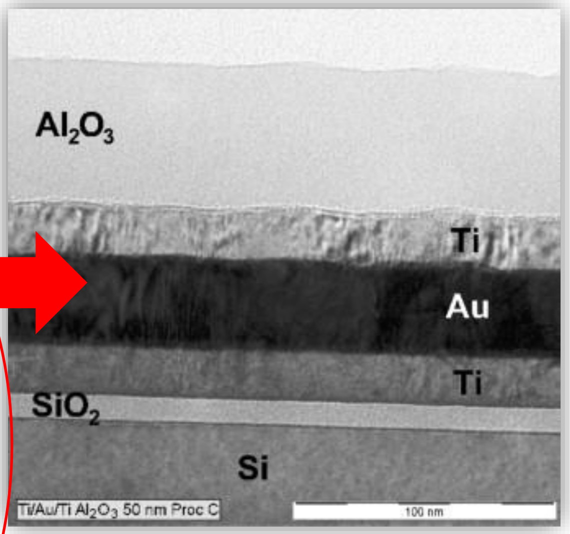
Filmes dopados

Supercycle

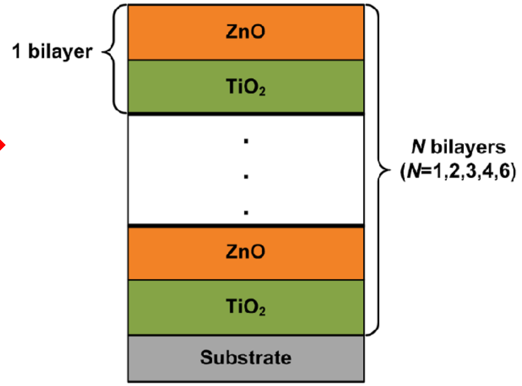
$((A1B1)_m(A2B2)_n)_x$



Multilayer films



Nanolaminates

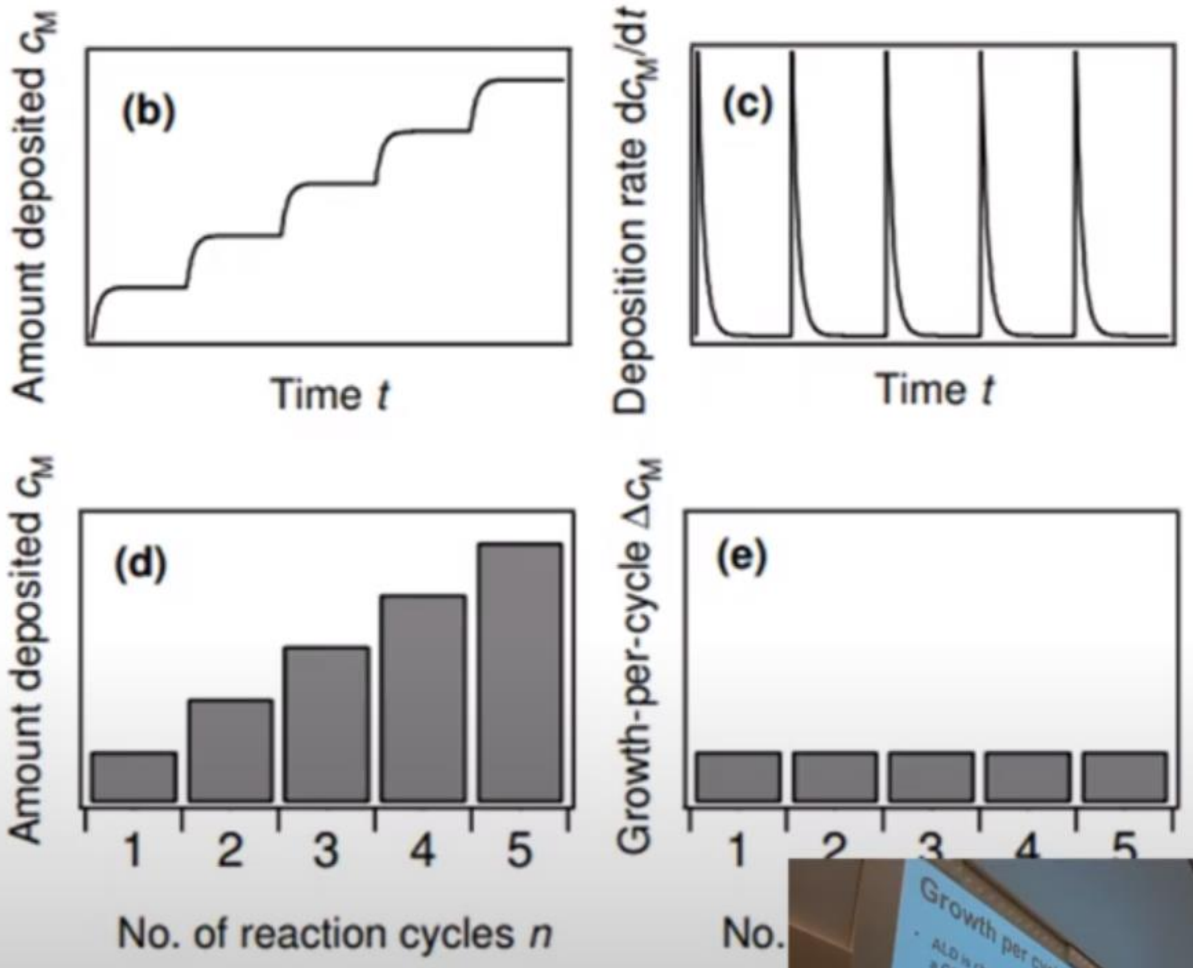


Harm Knoops, Atomic Layer Deposition in Handbook of Crystal Growth, DOI: 10.1016/B978-0-444-63304-0.00027-5

2. Processo de deposição por camada atômica

Growth per cycle

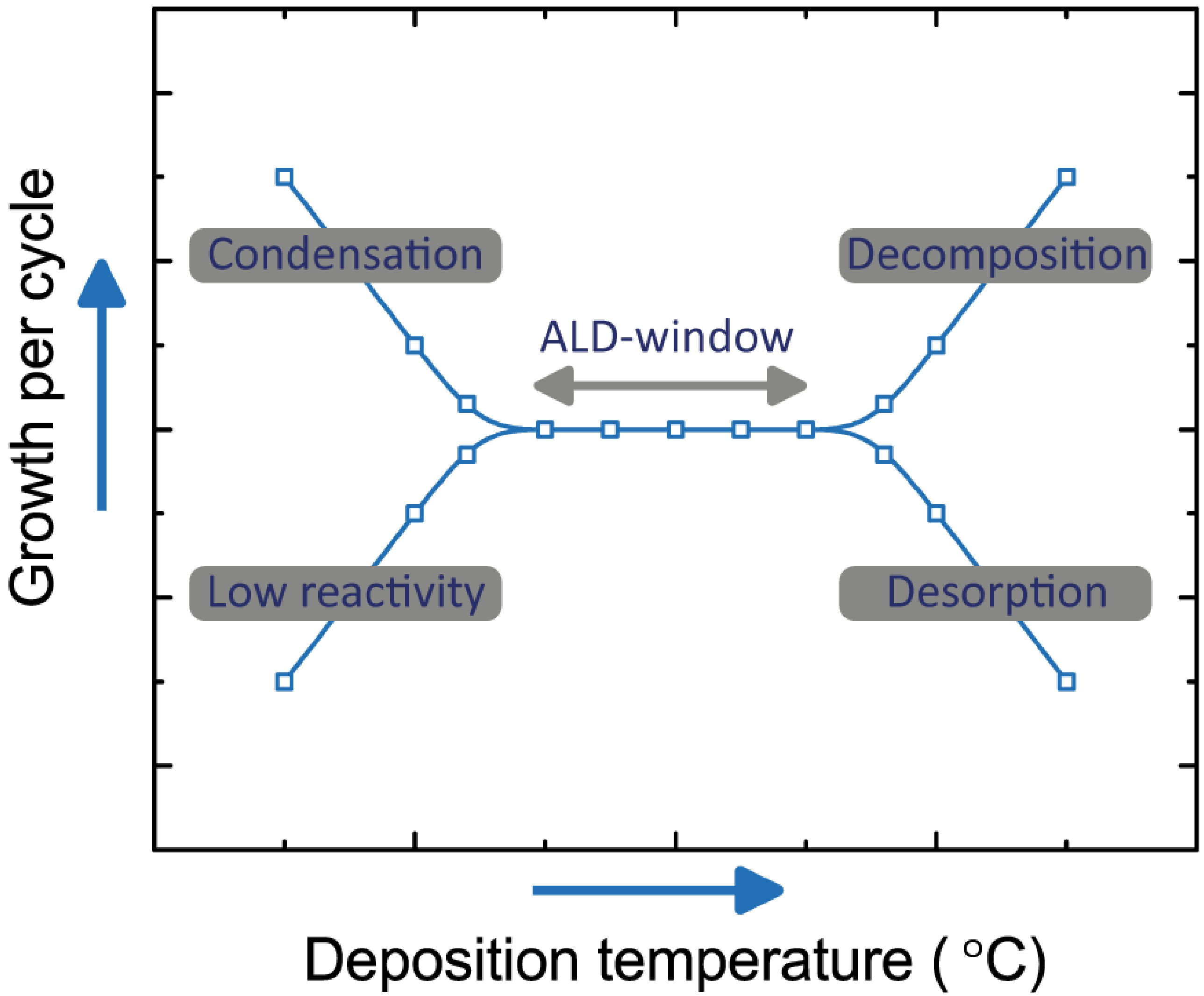
- ALD is characterized by a GPC, which depends typically on:
    - reactants
    - temperature
    - substrate
- In ALD, there is no ”growth rate” in the sense as e.g. in CVD



https://youtu.be/6zCvaMv58hY

2. Processo de deposição por camada atômica

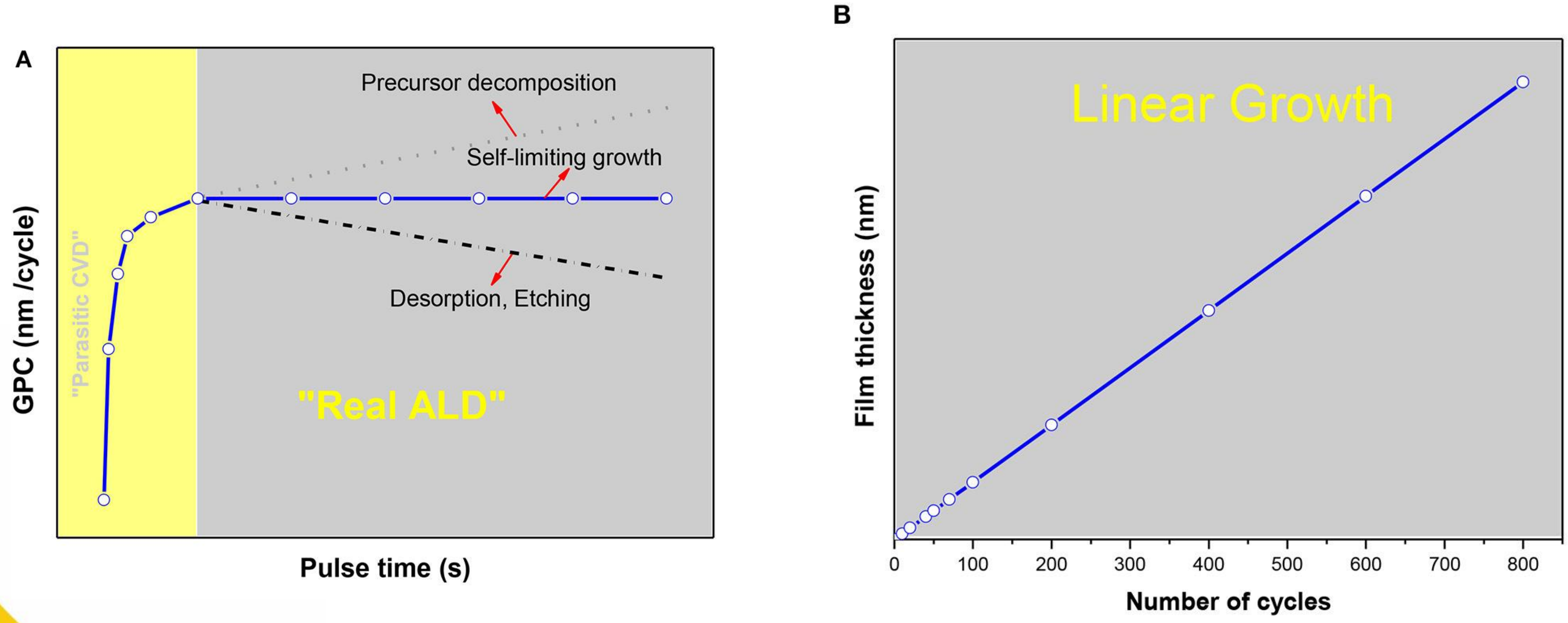
Janela do processo ALD – Dependência da temperatura



Martijn Vos, Atomic Layer Deposition Process Development – 10 steps to successfully develop, optimize and characterize ALD recipes, AtomicLimits (2019)

2. Processo de deposição por camada atômica

Janela do processo ALD – Dependência do tempo de pulso do precursor

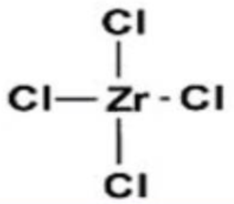
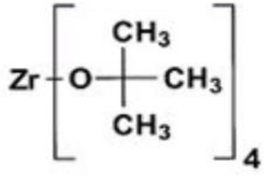
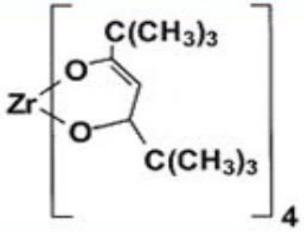
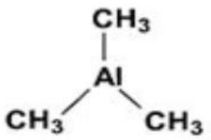


Chiappim W, Fraga MA, Maciel HS and Pessoa RS (2020) An Experimental and Theoretical Study of the Impact of the Precursor Pulse Time on the Growth Per Cycle and Crystallinity Quality of TiO2 Thin Films Grown by ALD and PEALD Technique. Front. Mech. Eng. 6:551085.
doi: 10.3389/fmech.2020.551085

2. Processo de deposição por camada atômica

2. Processo de deposição por camada atômica

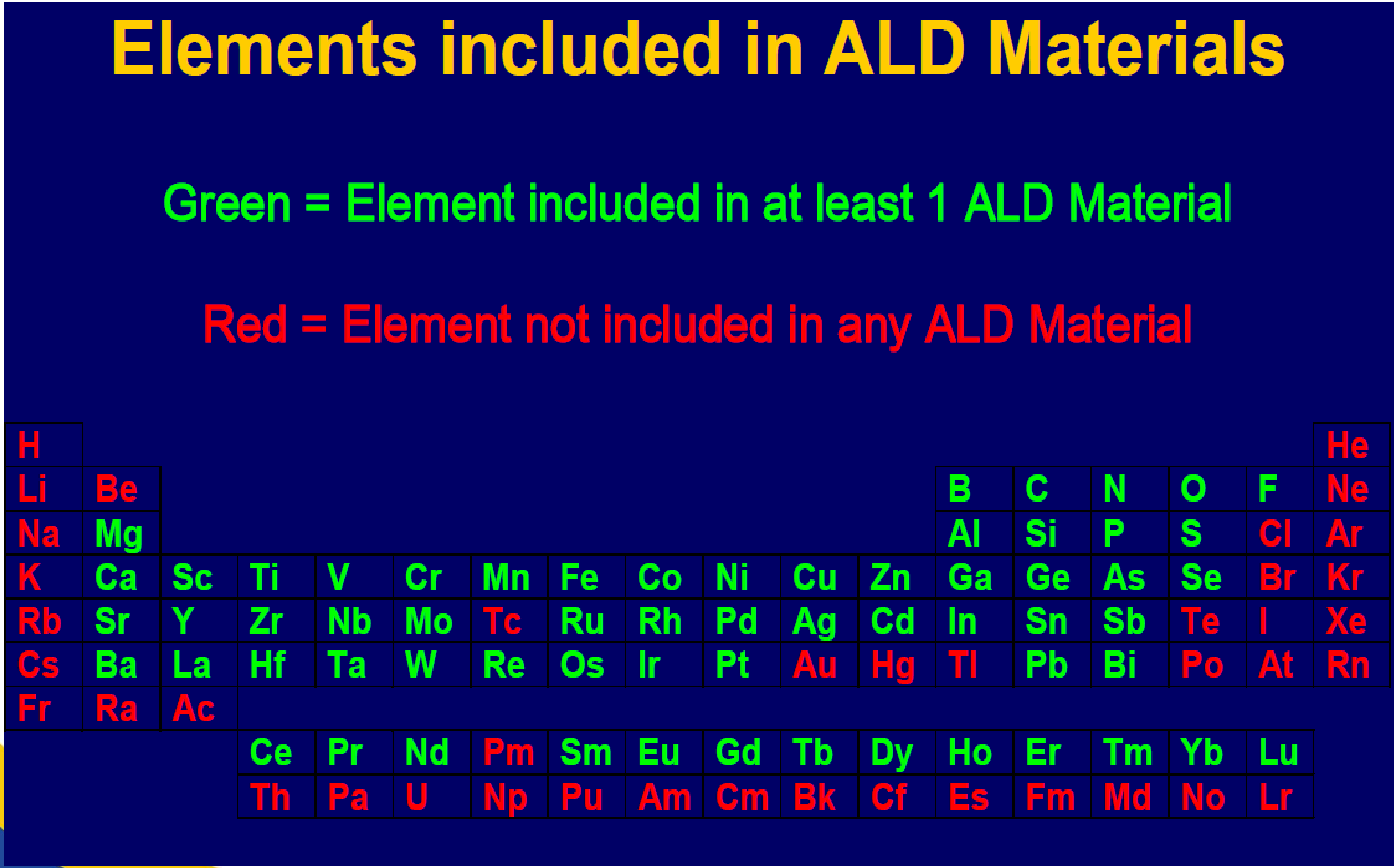
Precursor Chemistry

Inorganic	Metallo organic	Organo metallic
Metal Halides	***ß-diketone complexes and Alkoxides***	
	 	 
Adv: – Thermal stability – Reactivity Disadv: – By products – Vapour pressure	Adv: – Vapour pressure Disadv: – Thermal stability – Reactivity – Molecule size	Adv: – Thermal stability – Reactivity – By products – Vapour pressure Disadv: – Cost and availability

H_2O or O_3 are commonly used as one of the reactant for Oxide materials

Fraunhofer IST

2. Processo de deposição por camada atômica



2. Processo de deposição por camada atômica

Pure Elements Made by ALD

Green = ALD processes known for 16 Pure Elements

Red = no process known for ALD of the Element

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

2. Processo de deposição por camada atômica

Pure Elements Made by ALD

Green = ALD processes known for 16 Pure Elements

Red = no process known for ALD of the Element

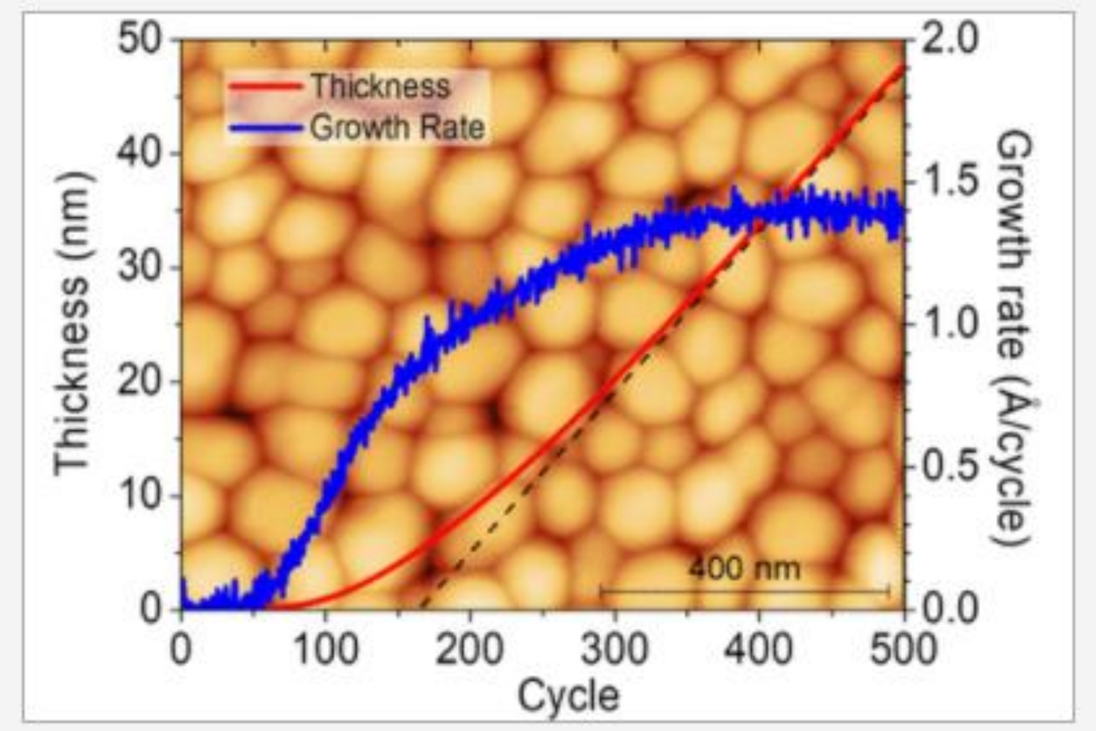
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

2. Processo de deposição por camada atômica

Thermal Atomic Layer Deposition of Gold: Mechanistic Insights, Nucleation, and Epitaxy

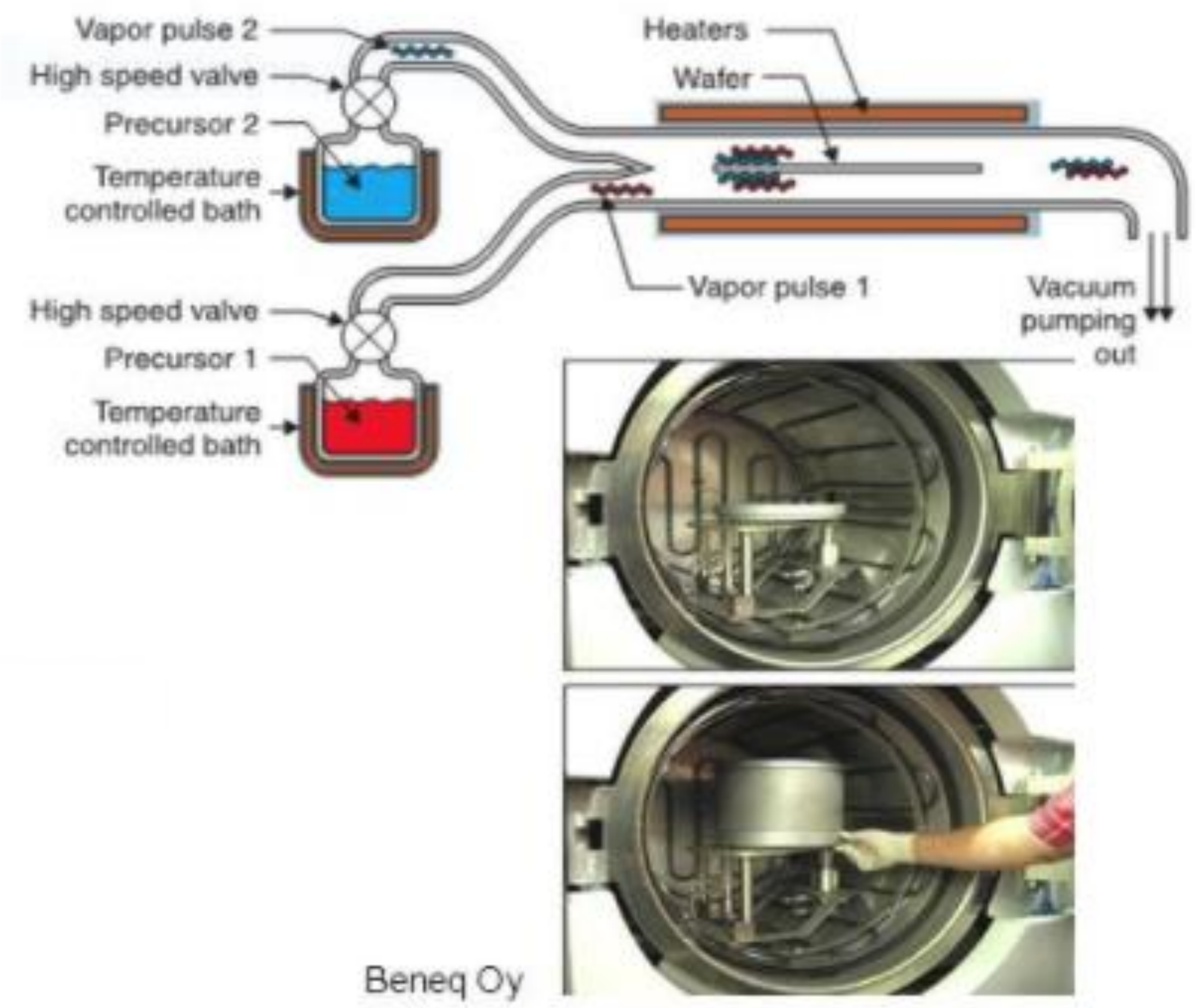
Pengfei Liu, Yuchen Zhang, Cong Liu, Jonathan D. Emery, Anusheela Das, Michael J. Bedzyk, Adam S. Hock*, and Alex B. F. Martinson*

Cite this: *ACS Appl. Mater. Interfaces* 2021, 13, 7, 9091−9100
Publication Date: February 9, 2021
https://doi.org/10.1021/acsami.0c17943



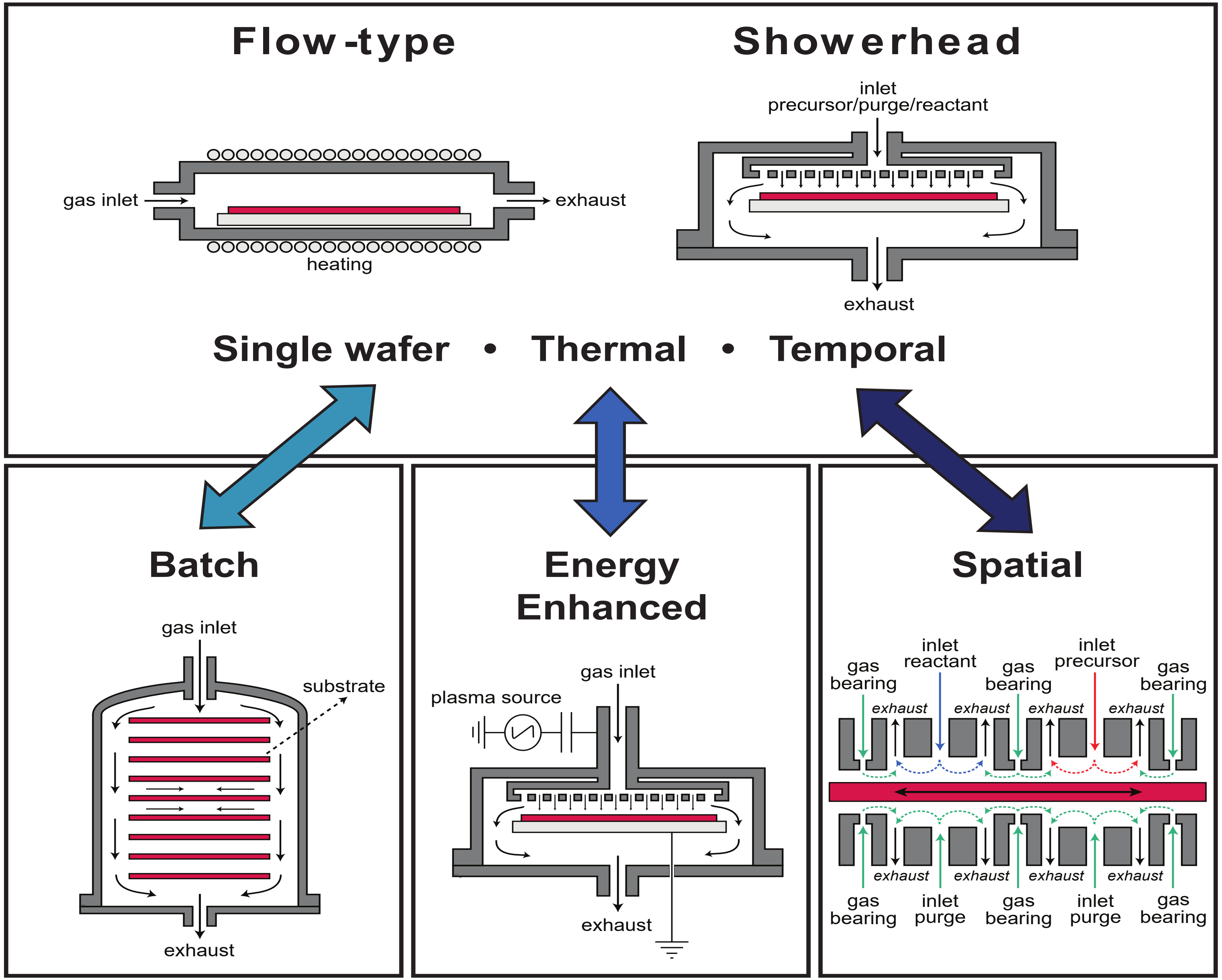
ALD térmico, Equipamento:

- Energia térmica é a principal fonte;
- Não há radicais, somente reações de superfície.
- Reações de adsorção auto-limitadas;
- Uso de precursores reativos (baixa temperatura de processo).



2. Processo de deposição por camada atômica

ALD térmico,
Tipos de reatores:



2. Processo de deposição por camada atômica

Reator ALD - Exemplos

F-850 reactor,
Microchemistry in 1998

Pulsar,
ASM

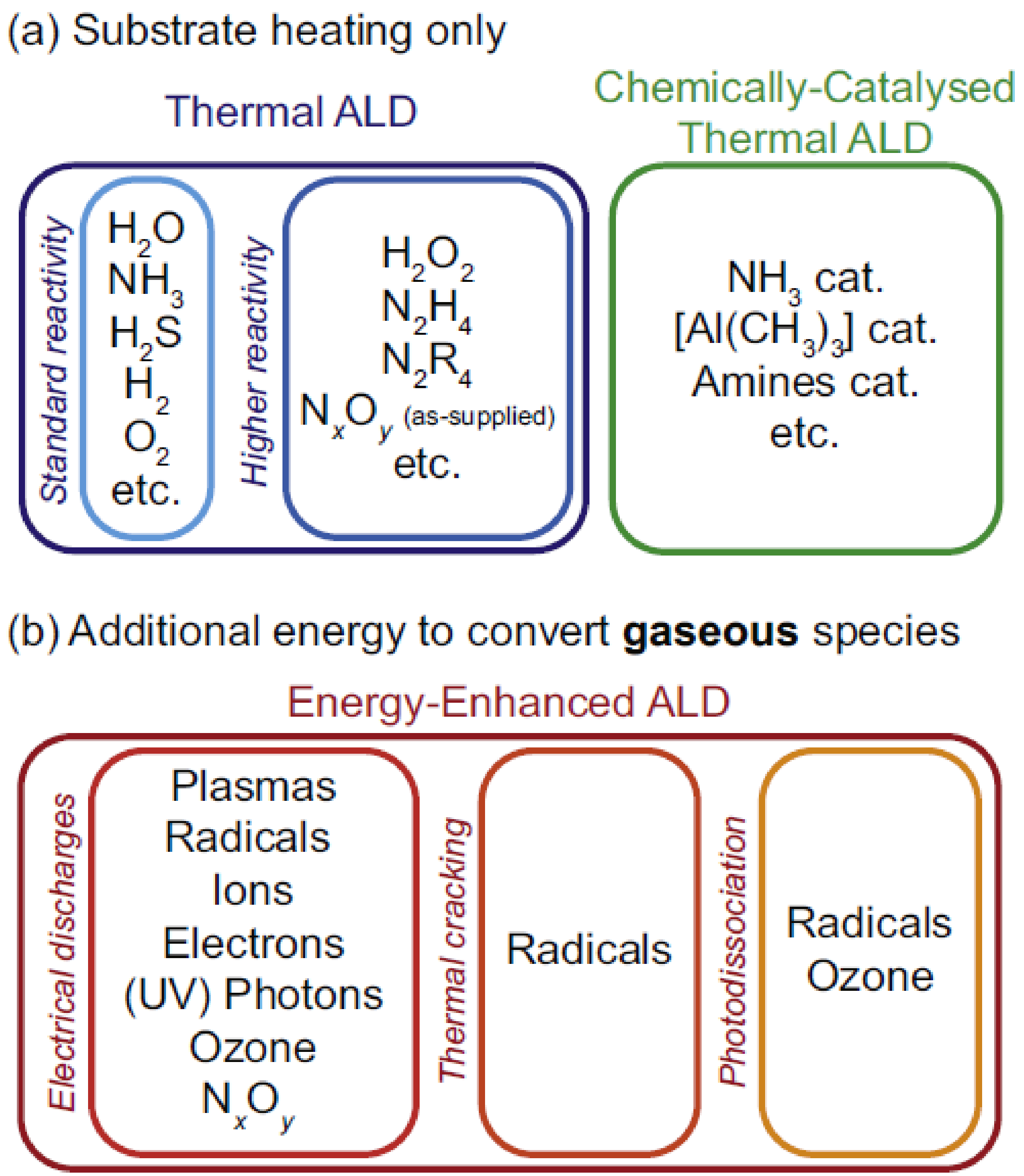
SUNALE™ ALD Reactors,
Picosun Oy

2. Processo de deposição por camada atômica

Reator ALD - Exemplos

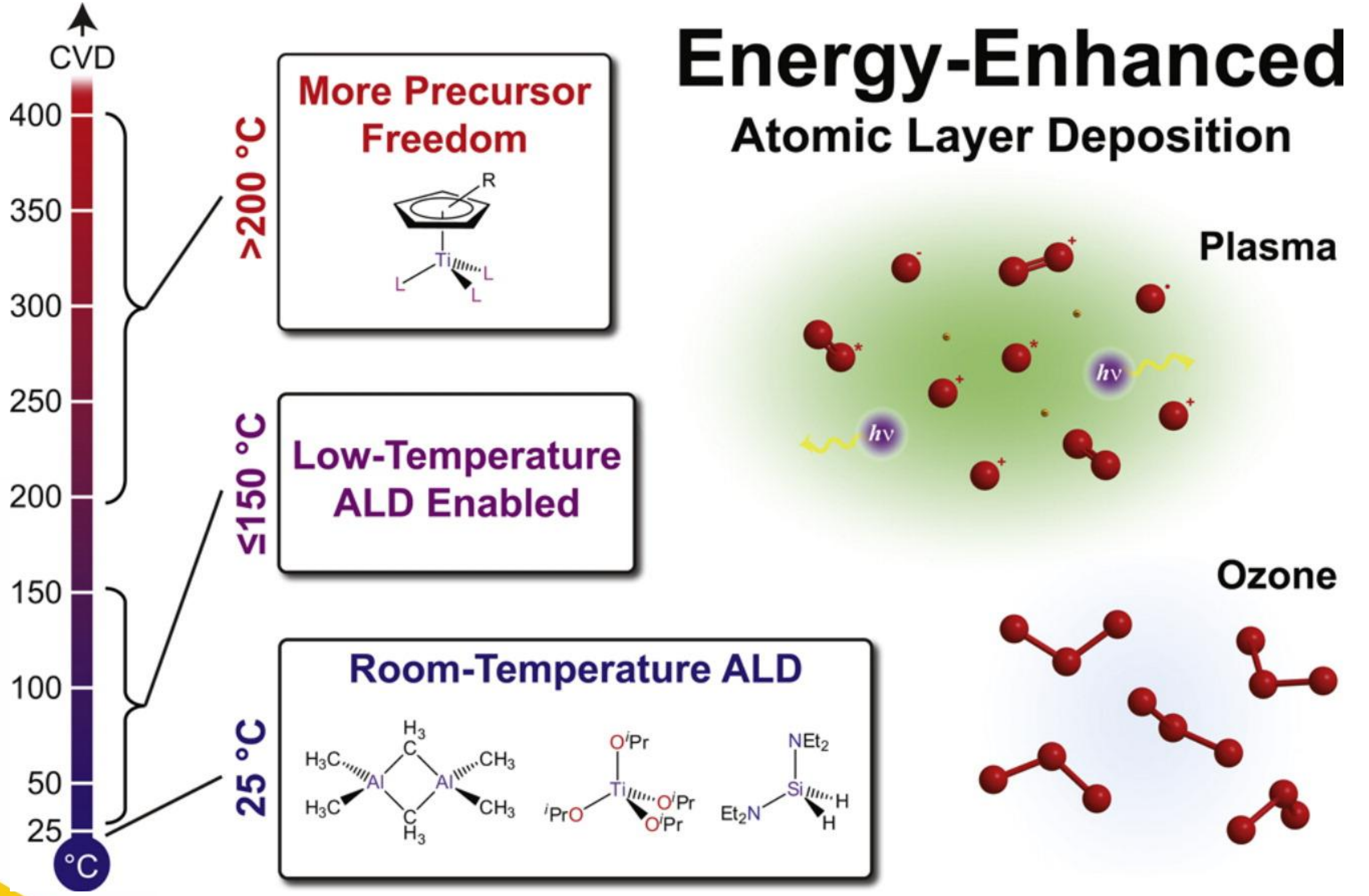
Mais de 50% das empresas fabricantes de reatores ALD estão na Finlândia.

2. Processo de deposição por camada atômica



https://doi.org/10.1016/j.ccr.2013.06.015

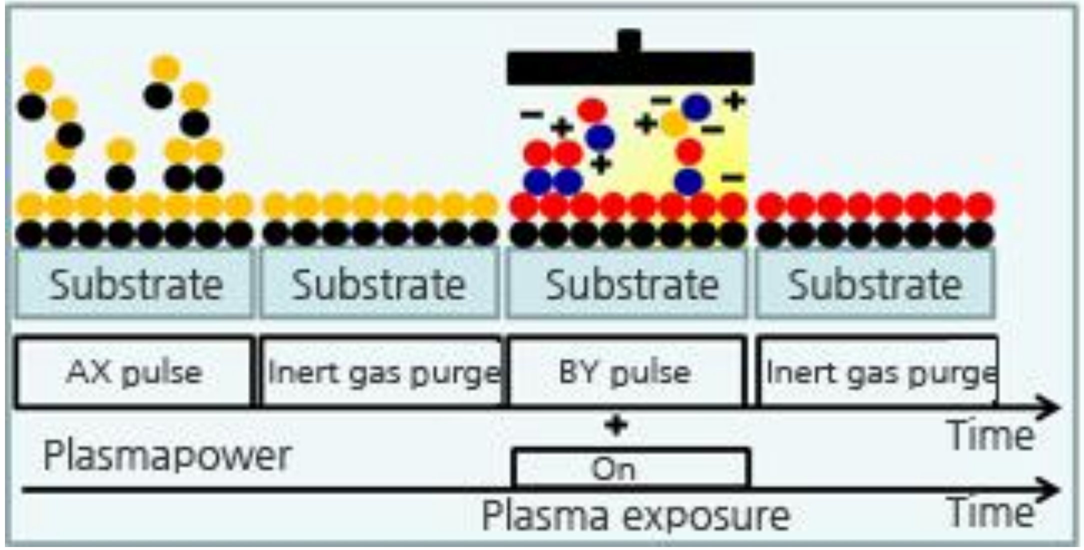
2. Processo de deposição por camada atômica

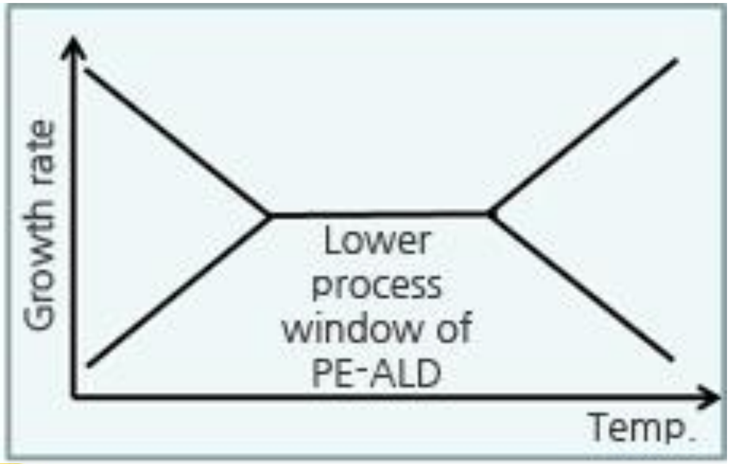


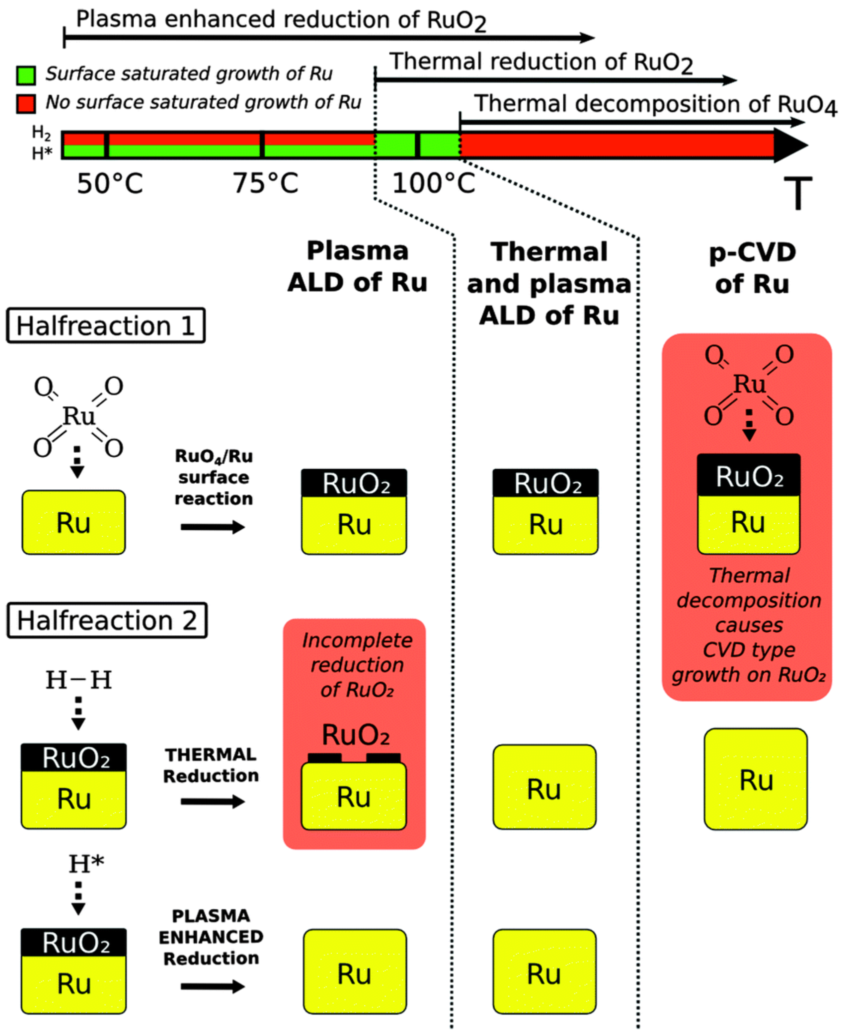
https://doi.org/10.1016/j.ccr.2013.06.015

2. Processo de deposição por camada atômica

→ Plasma enhanced atomic layer deposition (PEALD)



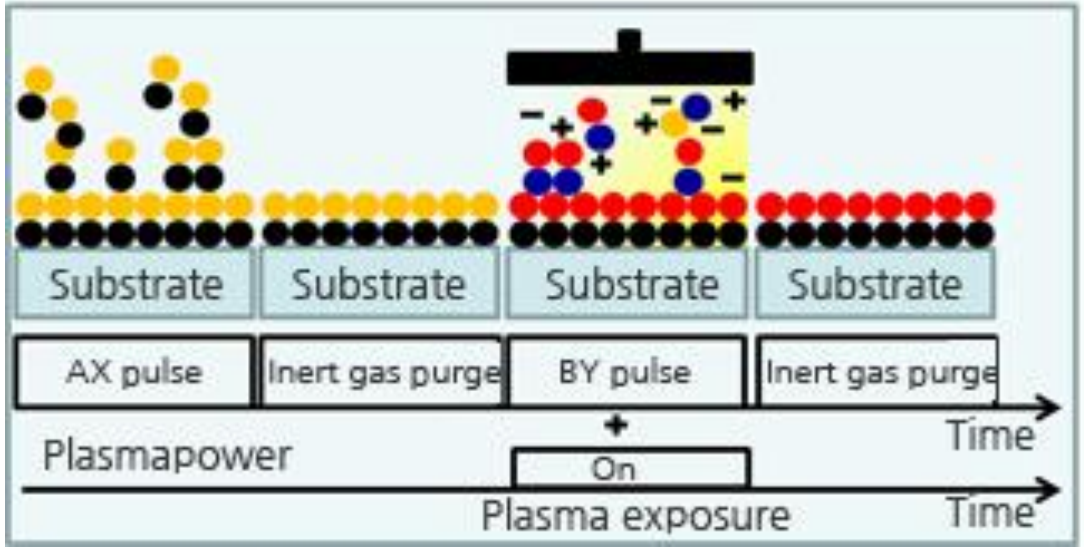




M. M. Minjauw, J. Dendooven, B. Capon, M. Schaekers, C. Detavernier, Near room temperature plasma enhanced atomic layer deposition of ruthenium using the RuO4-precursor and H2-plasma, . Mater. Chem. C, 2015,3, 4848-4851

2. Processo de deposição por camada atômica

→ Plasma enhanced atomic layer deposition (PEALD)



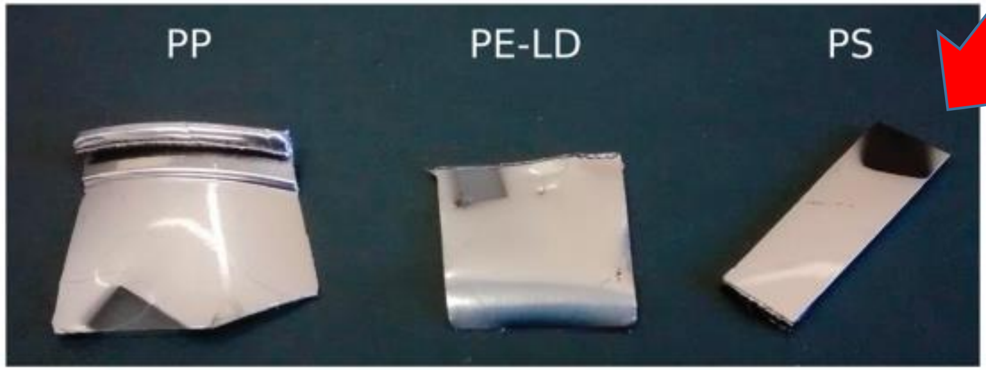
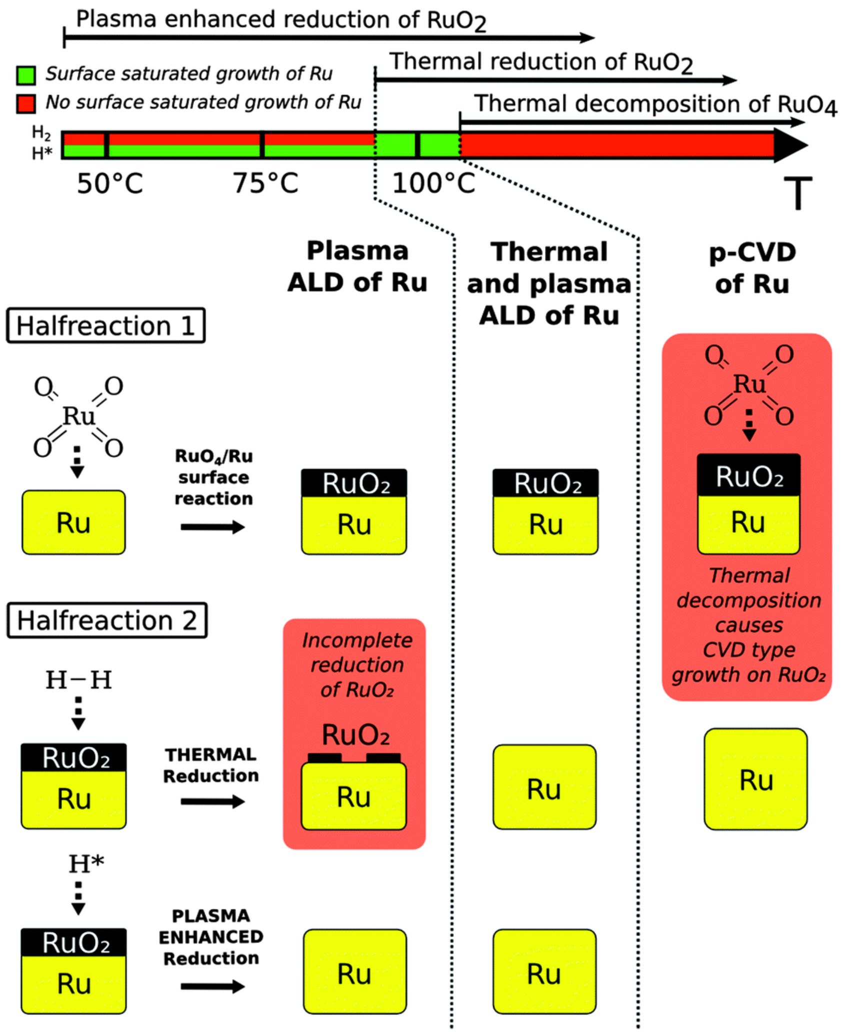


Fig. 4 Picture of the Ru films grown on different types of polymers.

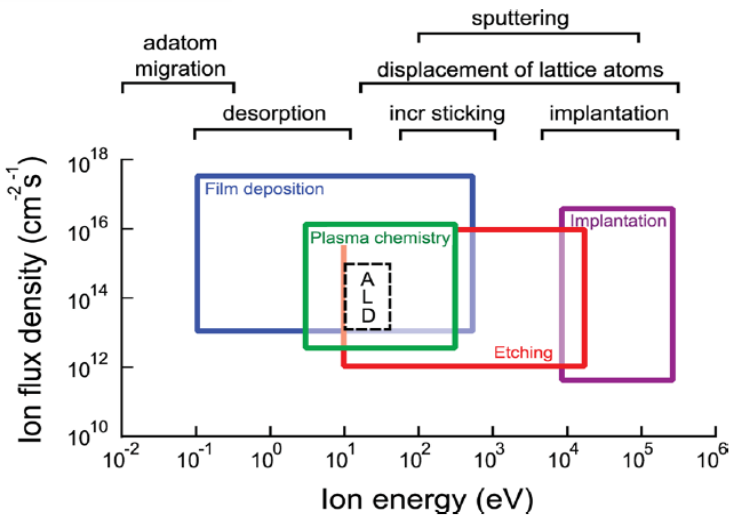


M. M. Minjauw, J. Dendooven, B. Capon, M. Schaekers, C. Detavernier, Near room temperature plasma enhanced atomic layer deposition of ruthenium using the RuO4-precursor and H2-plasma, . Mater. Chem. C, 2015,3, 4848-4851

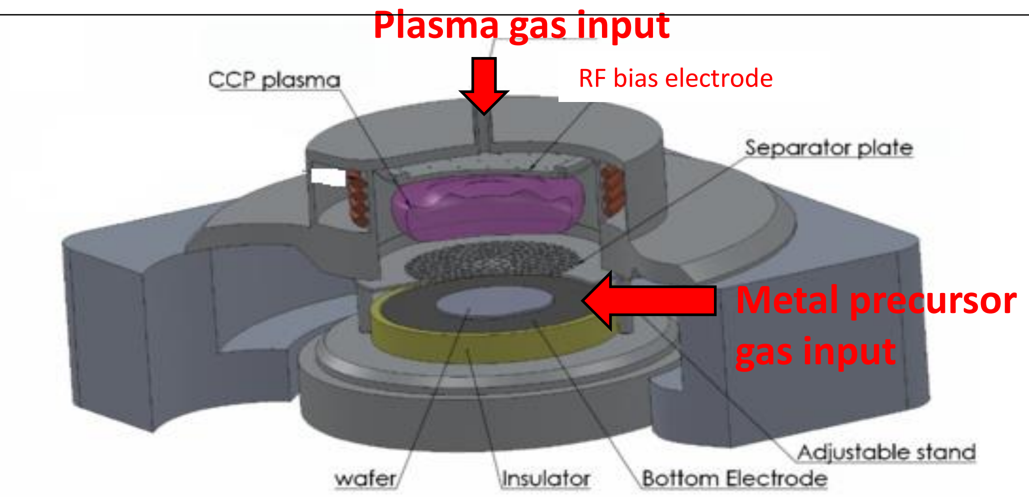
2. Processo de deposição por camada atômica

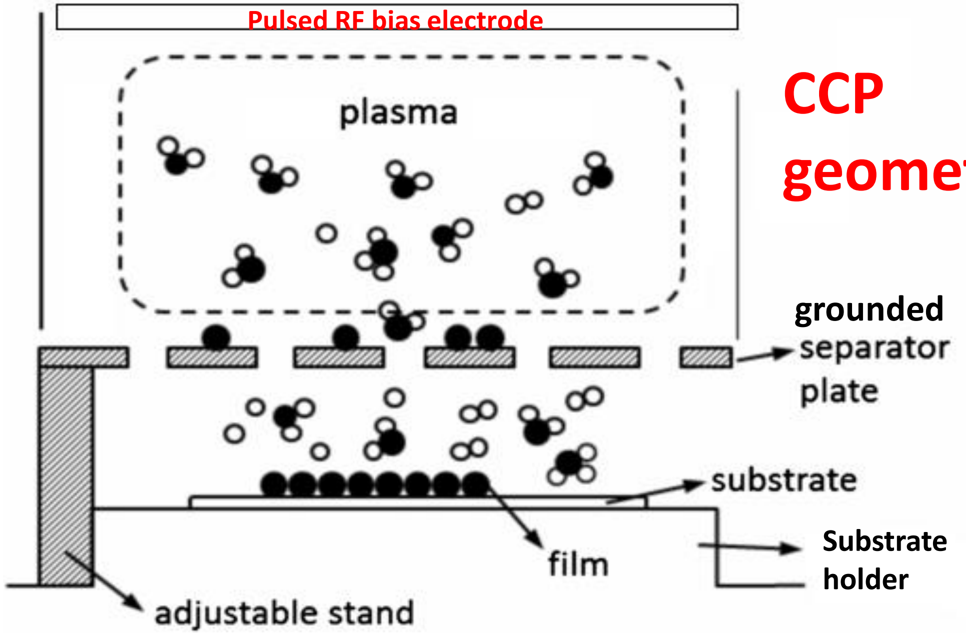
→ Key differences between plasma-assisted ALD and thermal ALD

- Reactive species → high reactivity at substrate surface;
- Low process temperature due ion assisted bombardment;
- Electron impact reactions, etc.



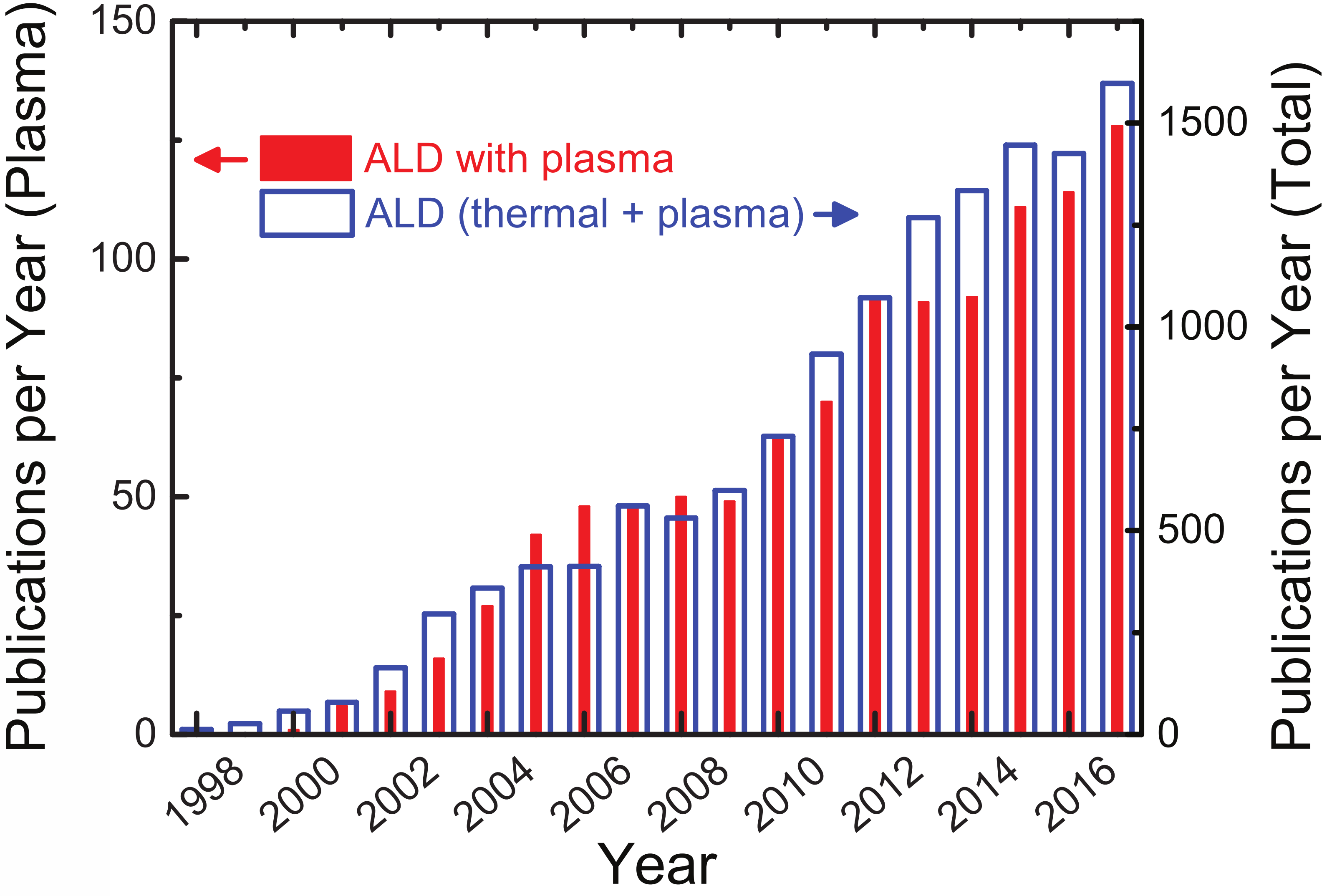
H. B. Profijt et al., J. Vac. Sci. Technol. A 29(5), (2011).





CCP geometry

2. Processo de deposição por camada atômica



Harm Knoops, Status and prospects of plasma-assisted atomic layer deposition, JVSTA, 37, 030902 (2019), DOI: 10.1116/1.5088582. CC BY

2. Processo de deposição por camada atômica

Beneq

Process Characteristics

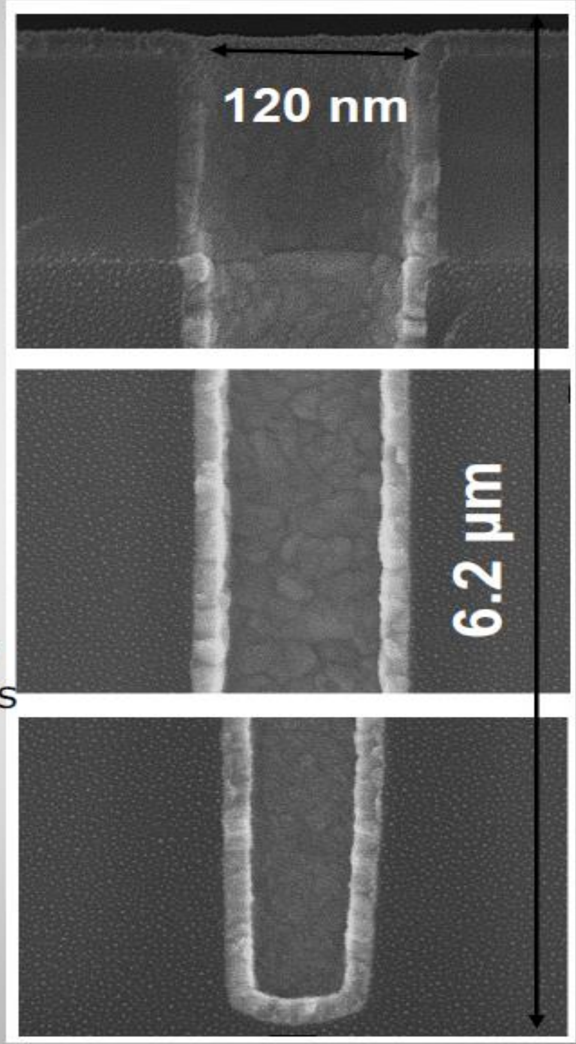
ALD Process is based on

Chemisorption
- Suitable temperature for chemical bonding, no thermal decomposition
- Covalent bonding ⇨ excellent adhesion

Saturation
- Sufficient dosing of precursor material
- Self-terminating reactions ⇨ extremely precise dosing not required

Surface controlled reactions
- Film thickness is independent of substrate geometry ⇨ uniform film onto deep trenches and 3D structures

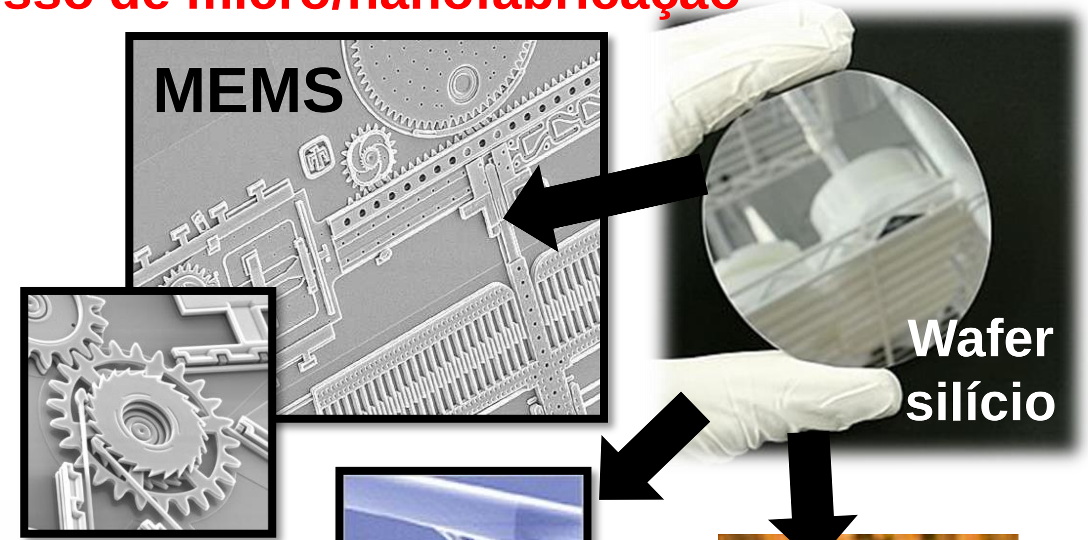
Sequential
- Digital growth
- Sufficient purging needed between pulses
- Good flow dynamics required to ensure rapid gas changes

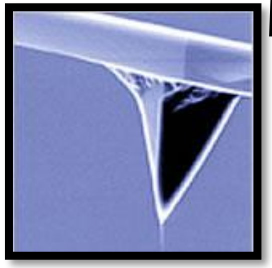


3. Corrosão em Nanoescala: Atomic Layer Etching

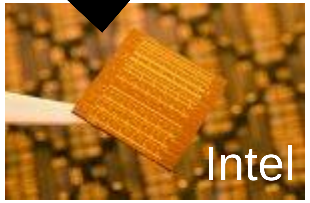
Corrosão de materiais

Processo de micro/nanofabricação



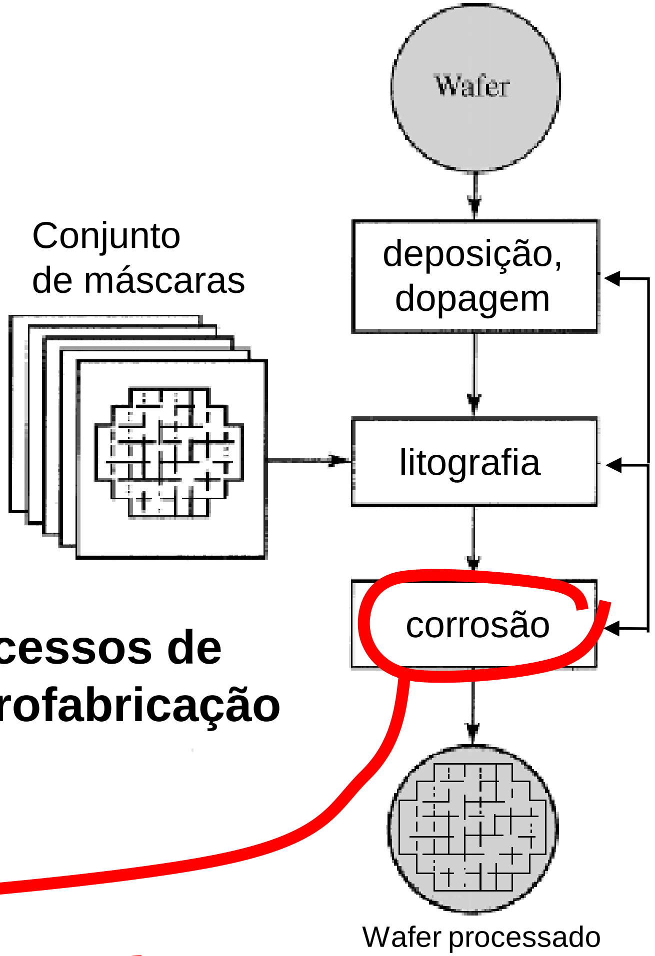


Ponteira AFM

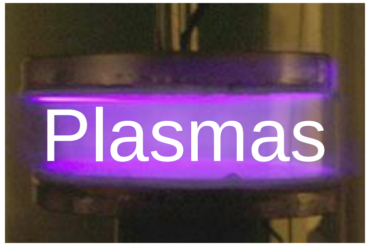


Chips, DRAM

Processos de microfabricação



- úmida;
- seca.



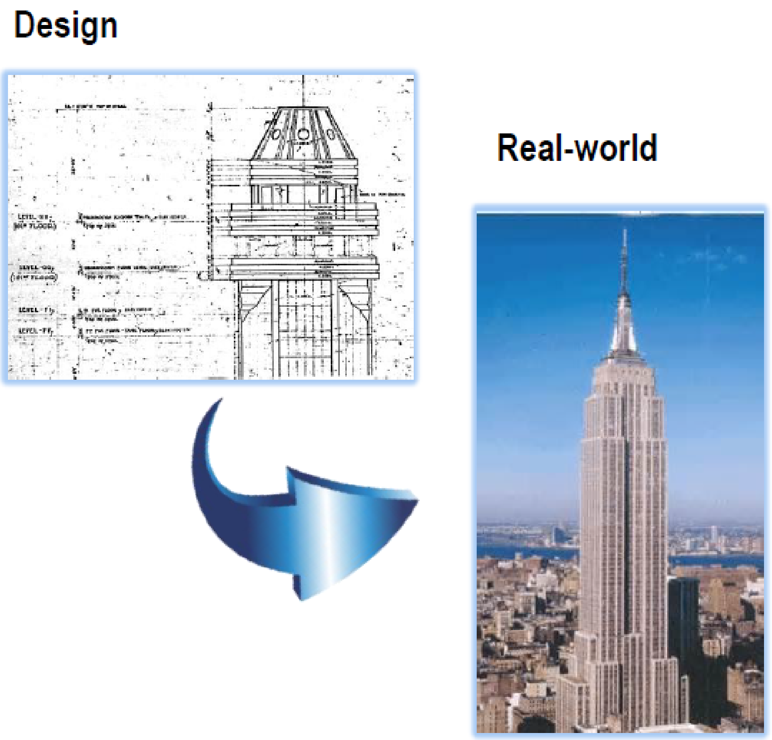
Caract. requeridas

- elevada anisotropia;
- alta taxa de corrosão;
- razão-de-aspécto.

3. Corrosão em Nanoescala: Atomic Layer Etching

The Need for Atomic Scale Fidelity

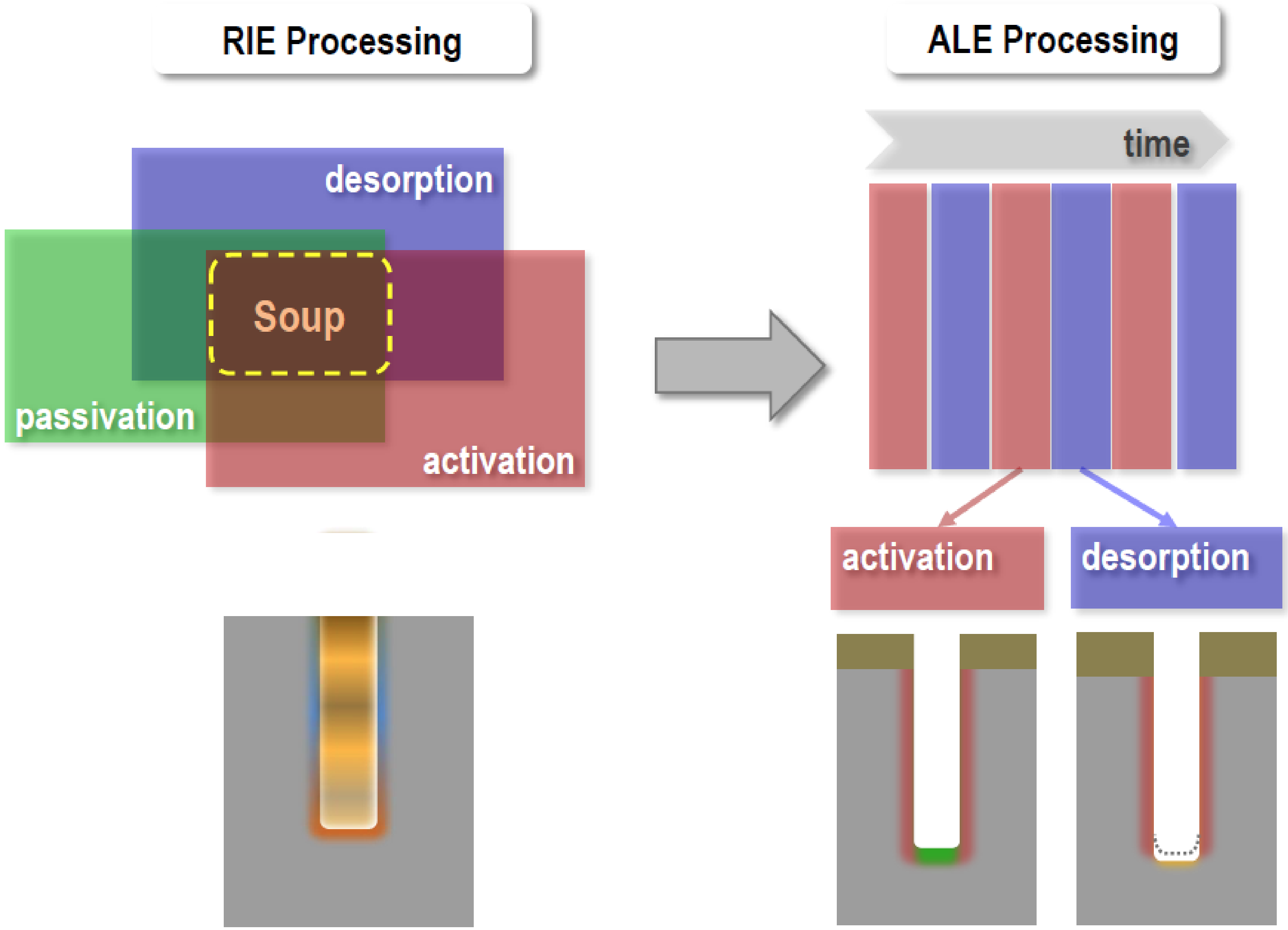
- Goal of IC manufacturing is to produce structures with highest possible degree of matching to the intent of the design engineers
- *def.* fi•del•i•ty: the degree to which something matches or copies something else" (Merriam-Webster)
- Fidelity goes beyond statistical criteria such as accuracy and precision and has customer end goal in mind
- Selectivity is fidelity in the vertical direction, CD is fidelity in horizontal direction



New approach is needed to achieve atomic scale fidelity in etch.

Lam Research Corporation,
SEMATECH ALEt Workshop, 2014

3. Corrosão em Nanoescala: Atomic Layer Etching



Single unit steps (simple chemistry) repeated in cycles...

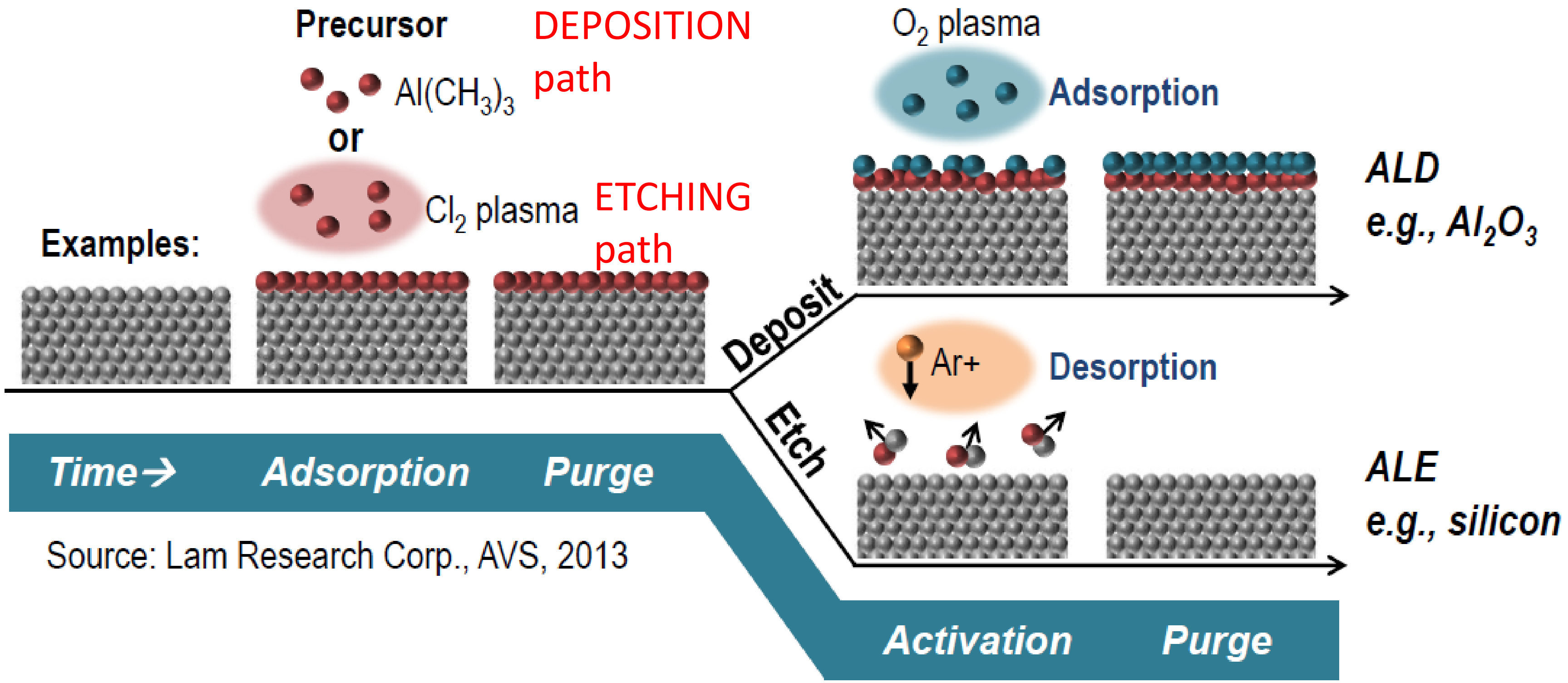
...to achieve atomic scale fidelity

Layer by layer etch with atomic scale fidelity

Lam Research Corporation, SEMATECH ALEt Workshop, 2014

3. Corrosão em Nanoescala: Atomic Layer Etching

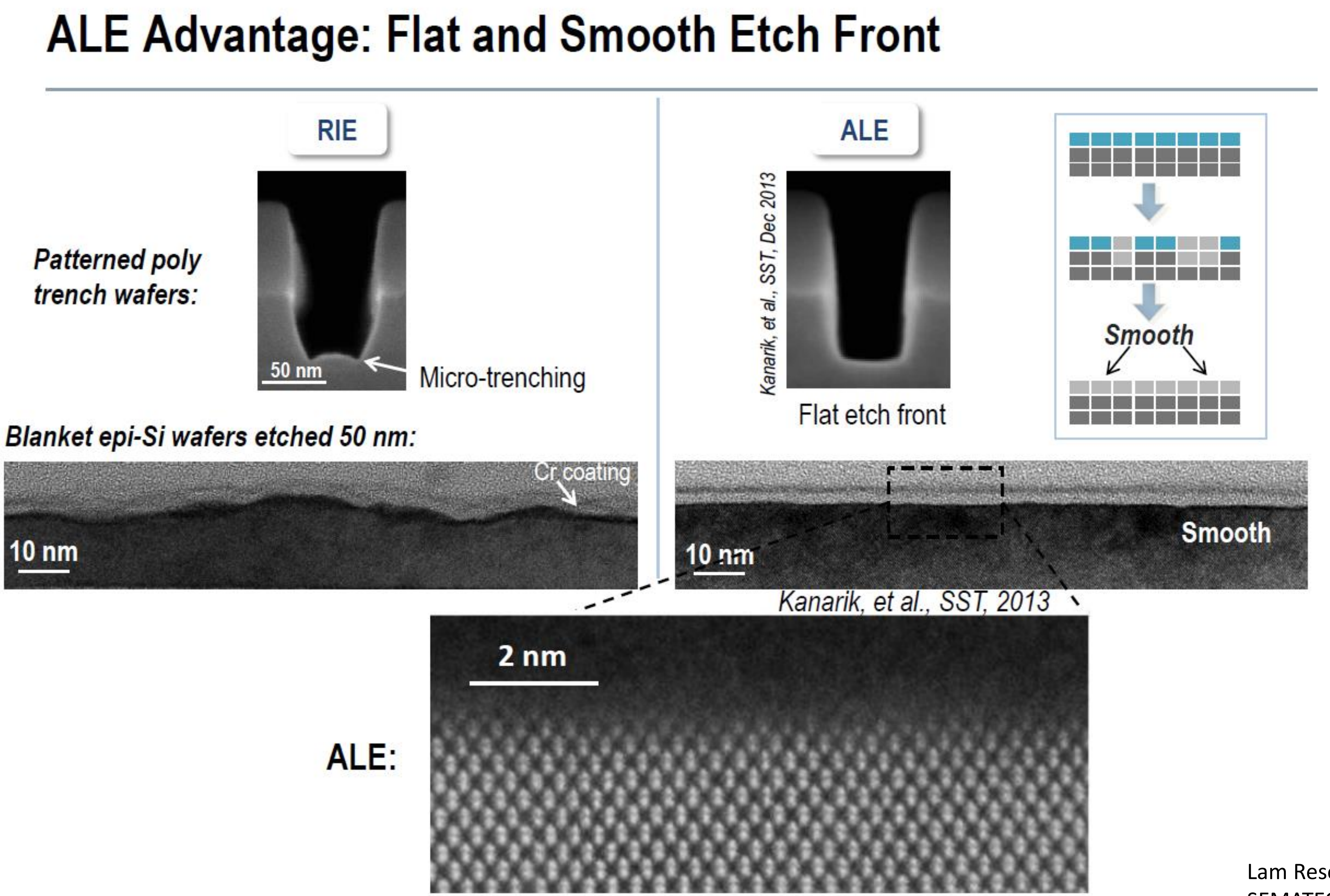
ALE Analogy to ALD



Source: Lam Research Corp., AVS, 2013

Lam Research Corporation,
SEMATECH ALEt Workshop, 2014

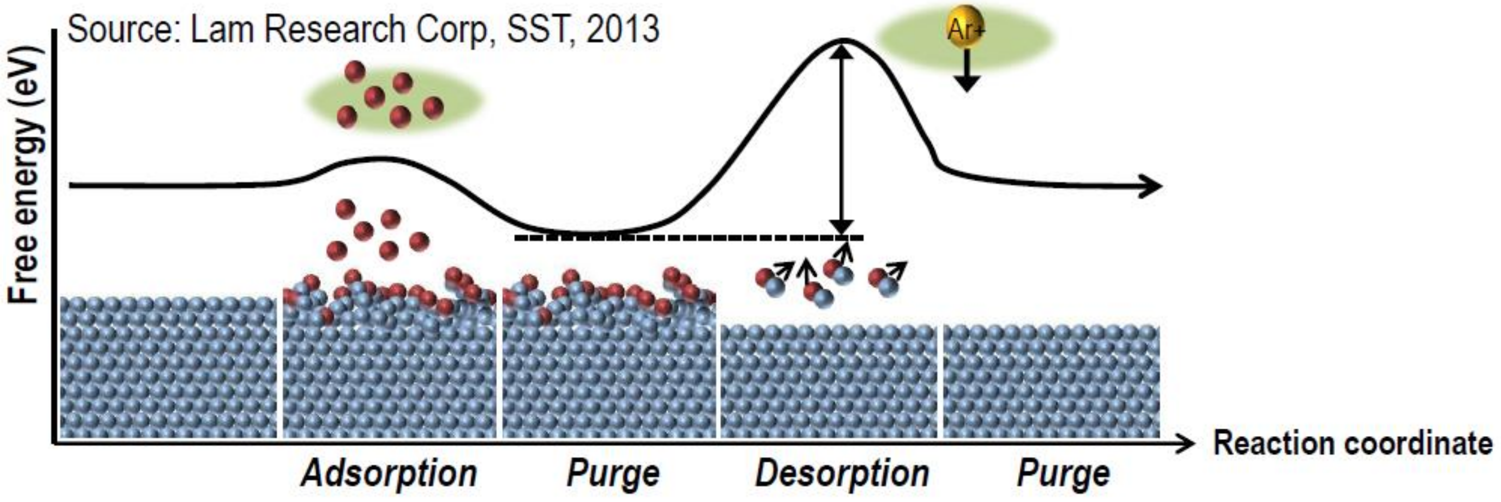
3. Corrosão em Nanoescala: Atomic Layer Etching



Lam Research Corporation, SEMATECH ALEt Workshop, 2014

3. Corrosão em Nanoescala: Atomic Layer Etching

Overcoming Throughput Challenge of ALE



Key factors that limit cycle time:

1. Gas switching is a function of reactor design
2. Adsorption and desorption can be plasma-enhanced

1. KEREN J. KANARIK et. al., Moving atomic layer etch from lab to fab, Solid State Technology 2014
2. Lam Research Corporation, SEMATECH ALEt Workshop, 2014

3. Corrosão em Nanoescala: Atomic Layer Etching

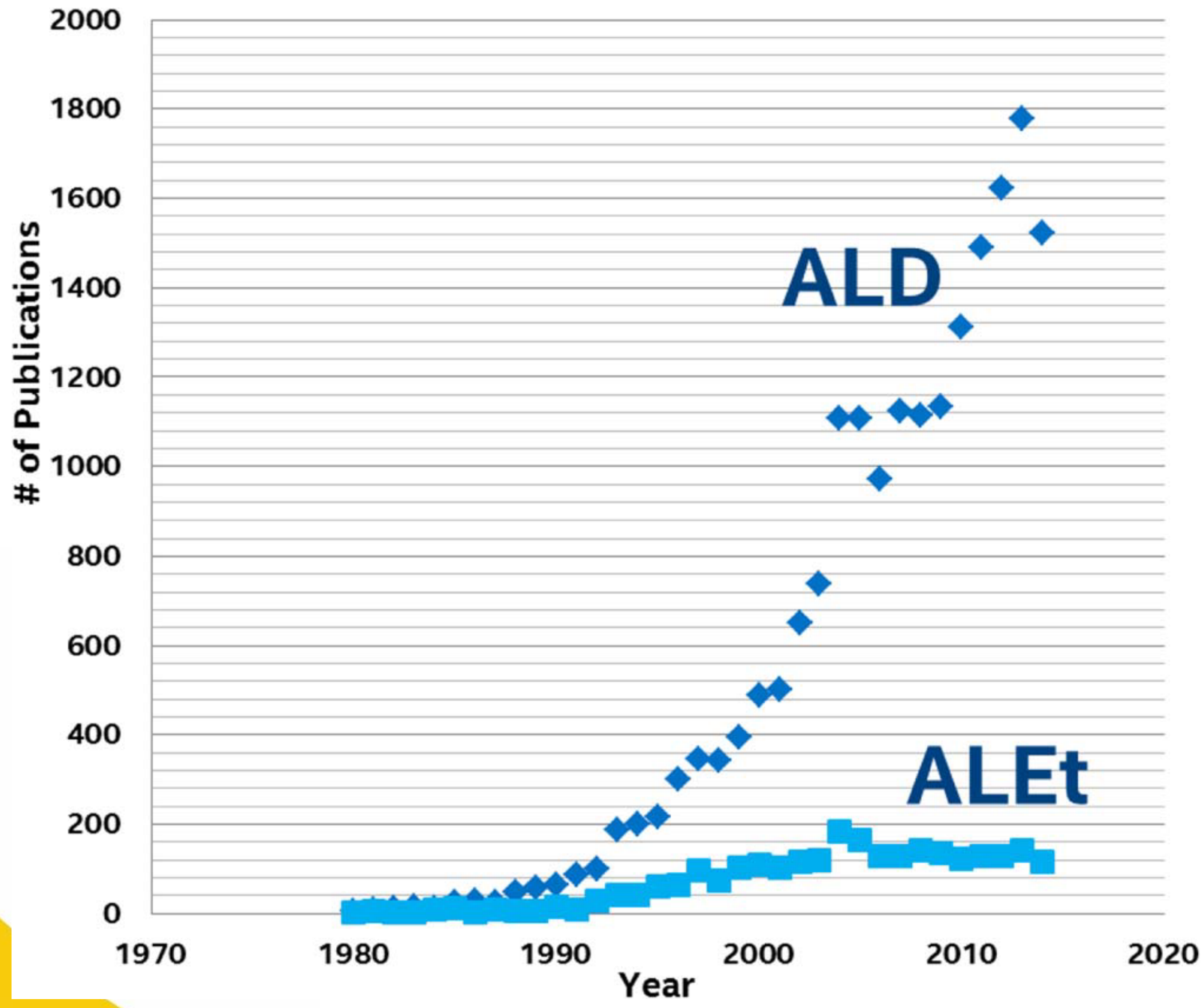
Atomic Layer Etching Equipment

Details:

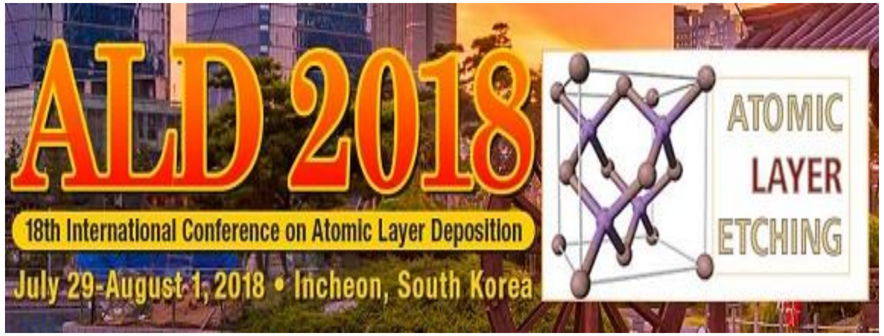
- Ultra low damage | Ultra high selectivity | Ultra accurate depth control.
- Etch rates 2 to 7Å/cycle.
- Demonstrated results in a-Si, Si, SiO_2, MoS_2 layer etching
- Fast recipe control down to 10ms.
- ALD-style gas dose delivery using "ALD valves" with 10ms open-close response.
- Ultra low power operation.
- Ability to etch in ALE or normal etch mode.

https://www.indiamart.com/oxford-instruments/nanotechnology-tools.html

3. Corrosão em Nanoescala: Atomic Layer Etching

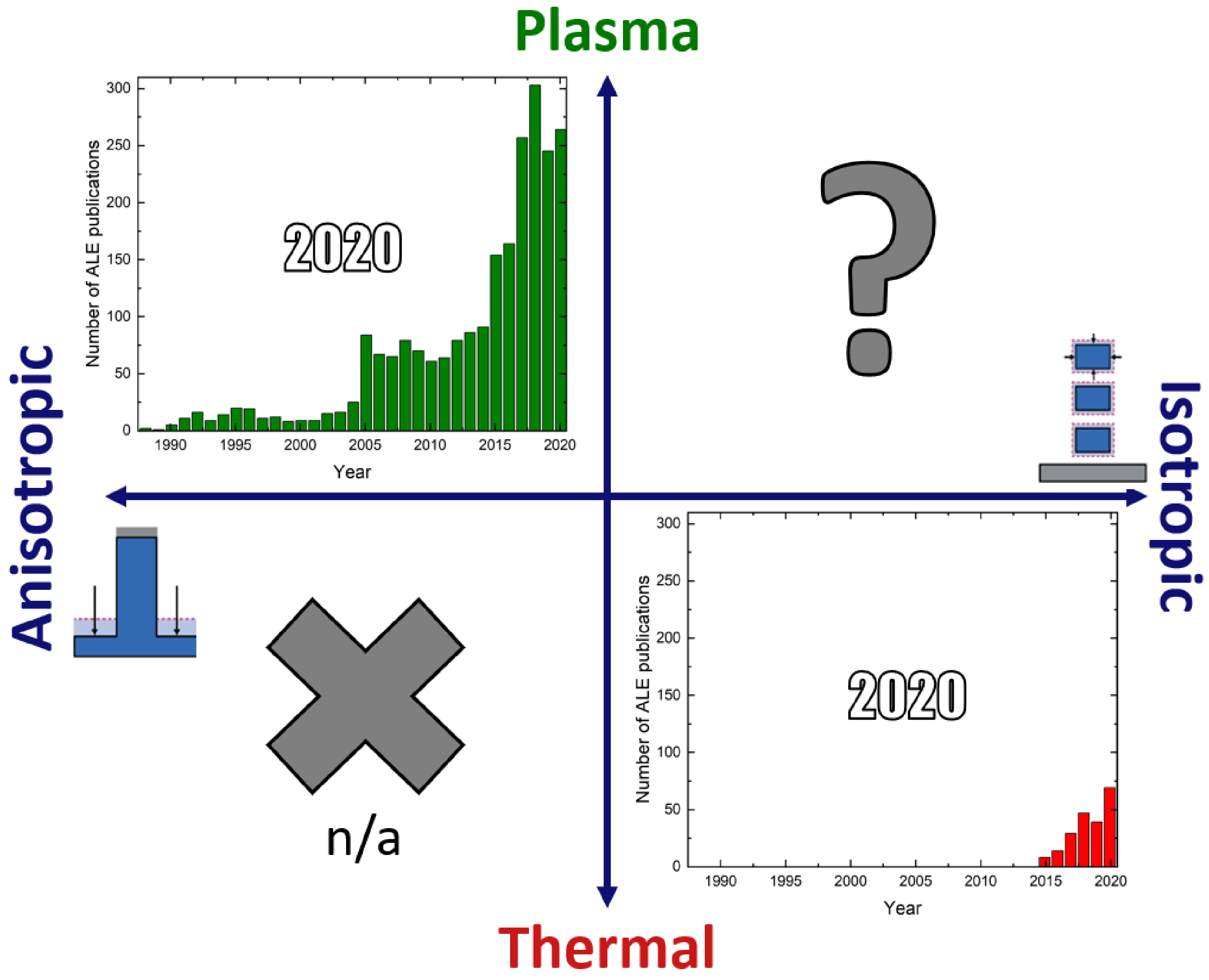


Graphs showing comparison of number of publications in ALD versus ALEt. Plot constructed from a SCOPUS database search for the terms "Atomic Layer Etching" and "Atomic Layer Deposition", retrieved on December 3rd 2014.



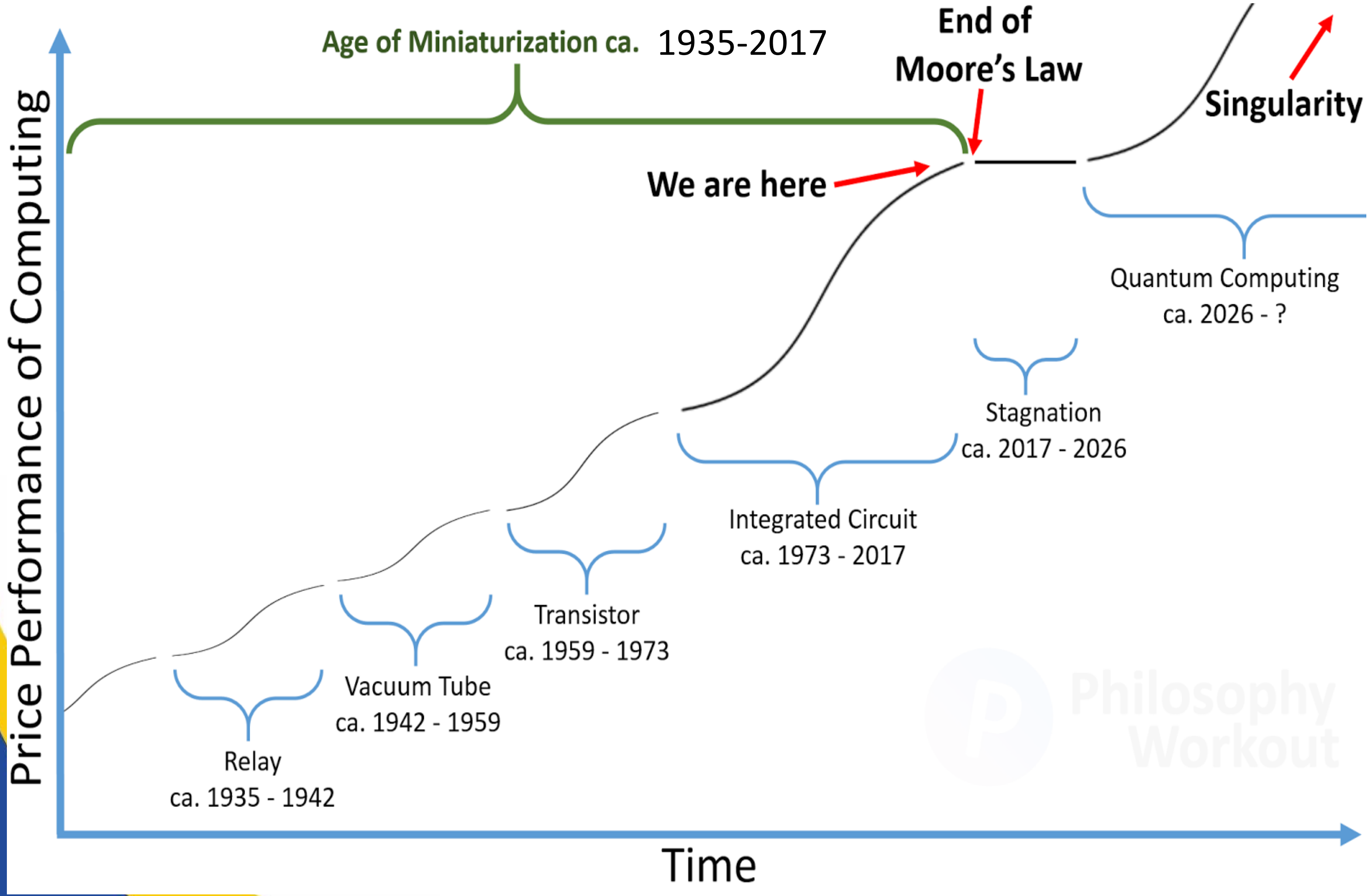
3. Corrosão em Nanoescala: Atomic Layer Etching

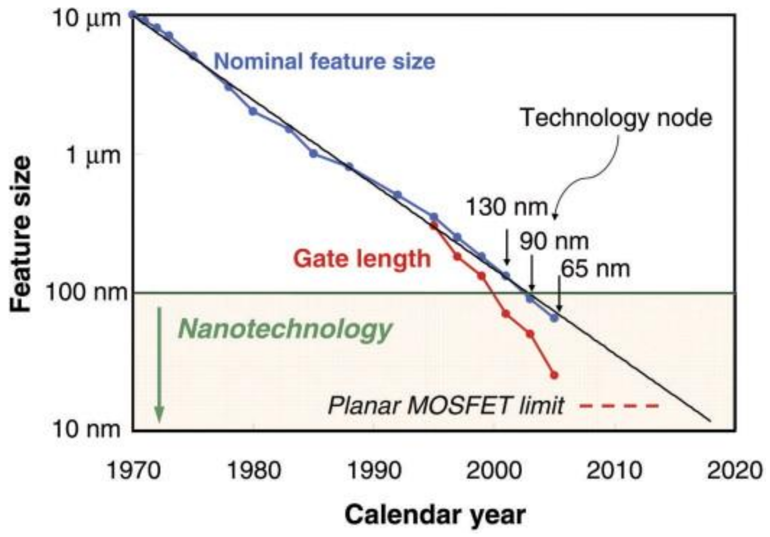
Timeline of ALE Publications



Nicholas Chittock, AVS ALD/ALE conference, ALE Student Award Presentation 2020.

4. Aplicações de ALD



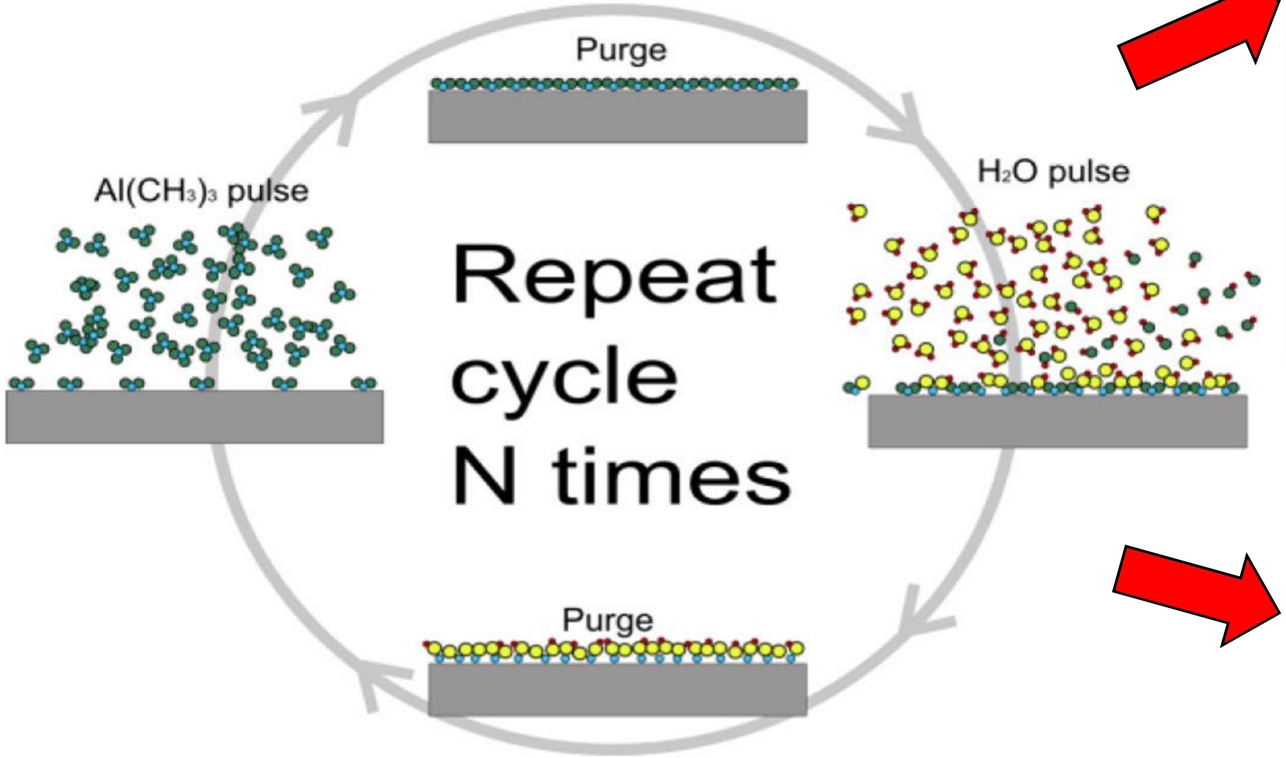


S. E. Thompson, S. Parthasarathy, Moore's law: the future of Si microelectronics, Materials Today, Volume 9, Issue 6, June 2006, Pages 20-25

O uso de materiais inovadores tais como o silício na forma de "wafer" e dielétricos "high-k" sintetizados por ALD tem permitido manter as predições da Lei de Moore.

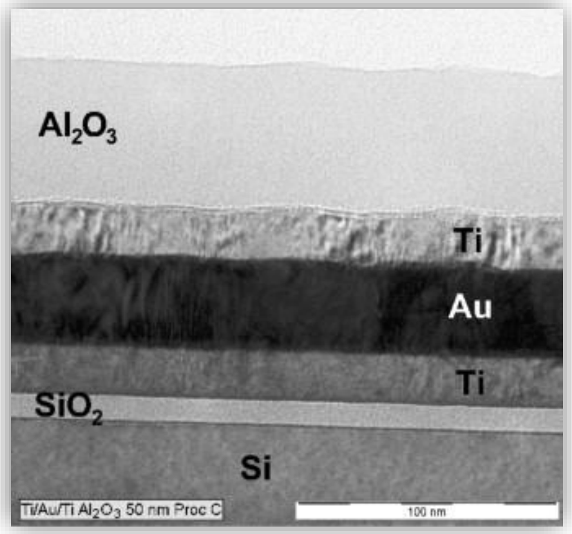
4. Aplicações de ALD

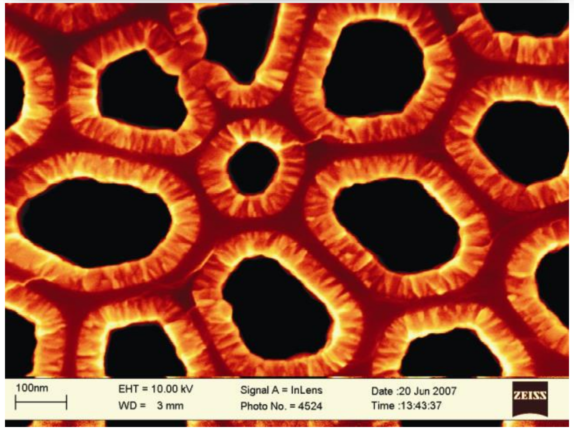
ALD Mechanisms



Ref: BEBEQ Oy

Multilayer film

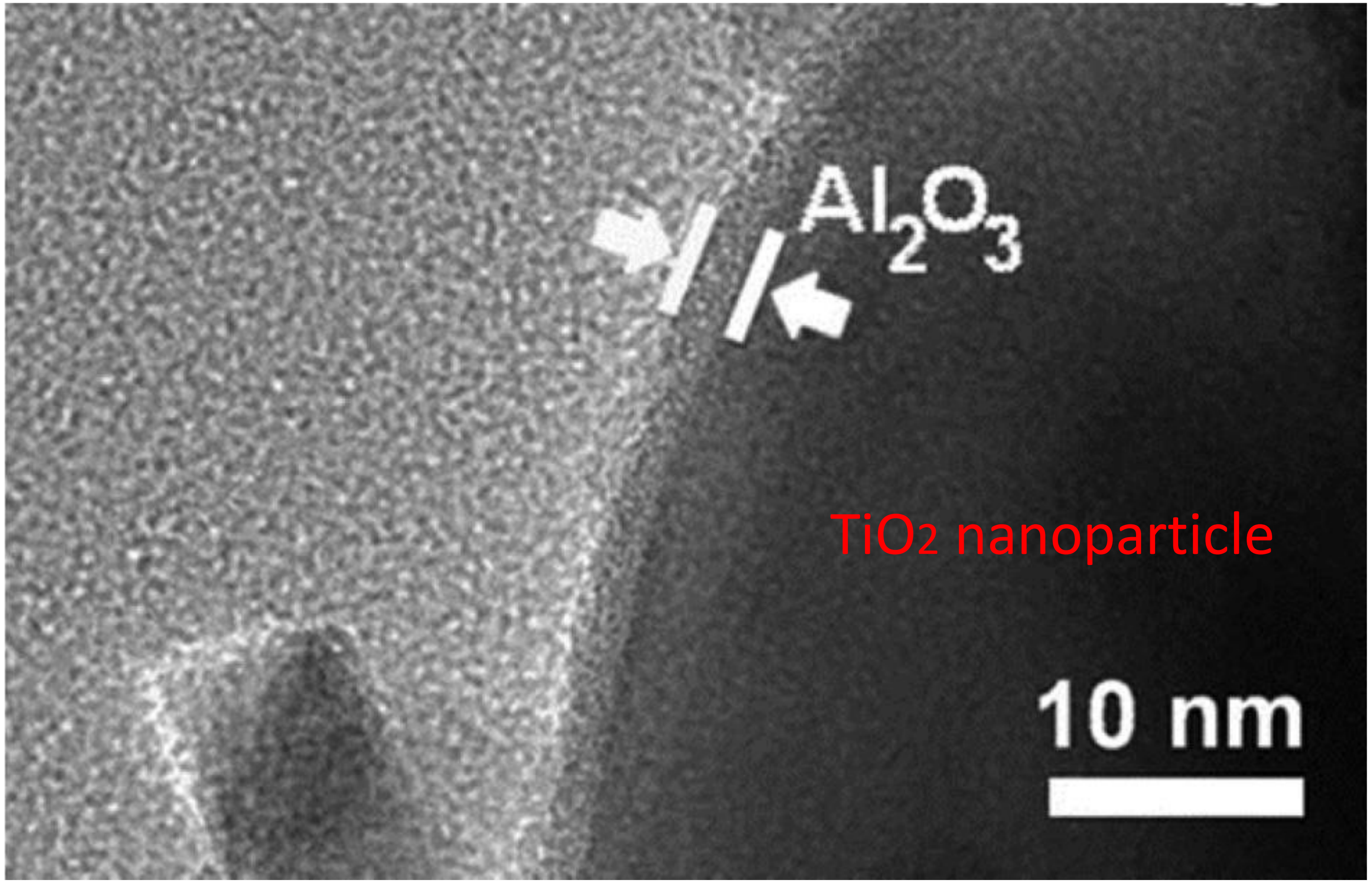




ALD ZnO Coating on porous material

4. Aplicações de ALD

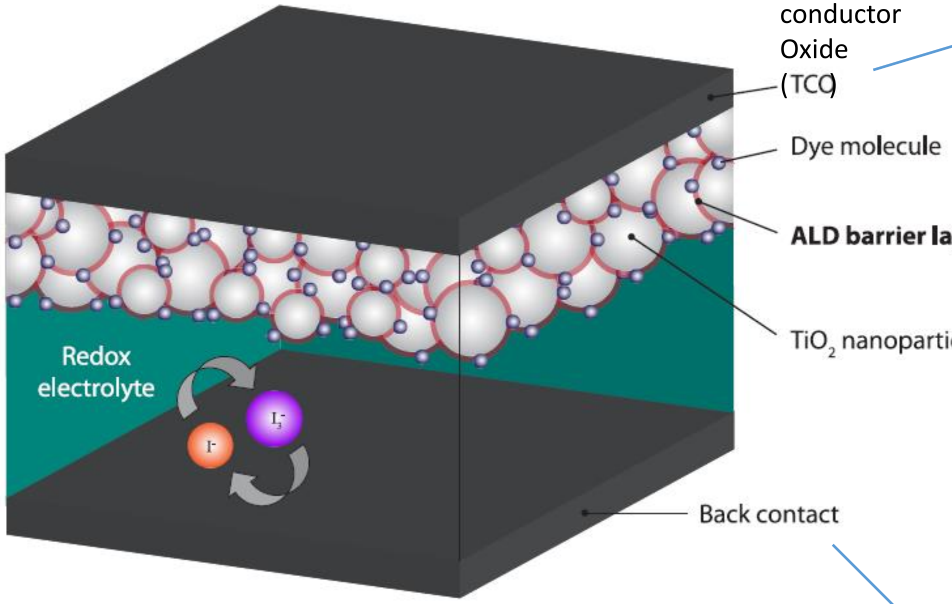
→ **APLICAÇÃO: PEALD para recobrir nanopartículas**



A. F. Palmstrom et al., Nanoscale. 7 (2015) 12266-12283

4. Aplicações de ALD

→ APLICAÇÃO: PEALD para construção de células solares fotoeletroquimicas



Fluorine tin oxide films

Nanoparticle or Doped-TiO_2 film

Al_2O_3 ultra-thin films

Nanostructured ALD thin films

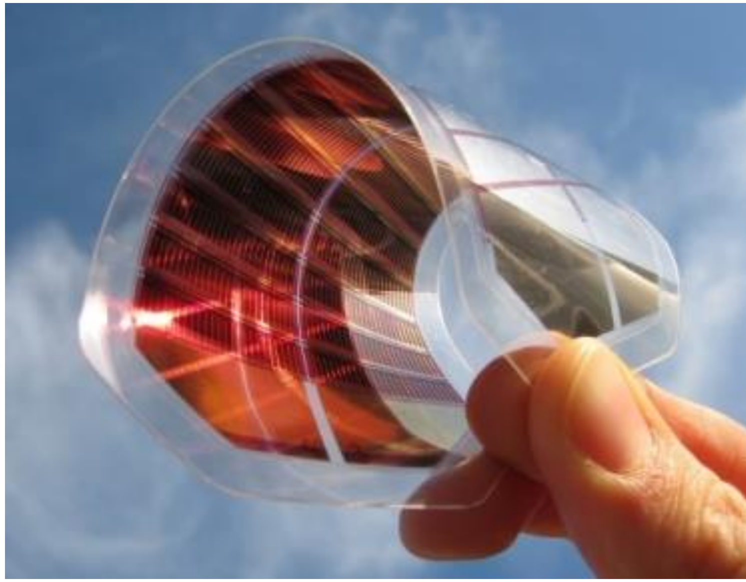
- TiO_2
- ZnO
- Cu_2O (water splliting)

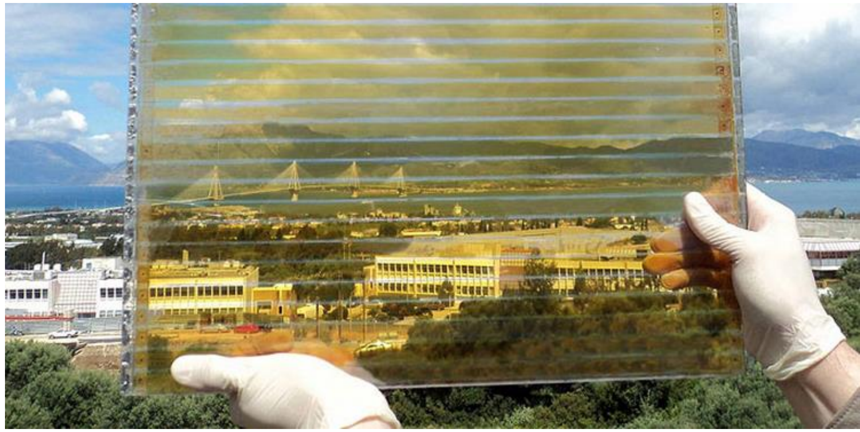
Platinum thin films
Nano carbon thin films

Dye-sensitized solar cell (DSSC)

Main requirements:

- Surface area;
- Film crystallinity;
- Controlled/Narrow band-gap.

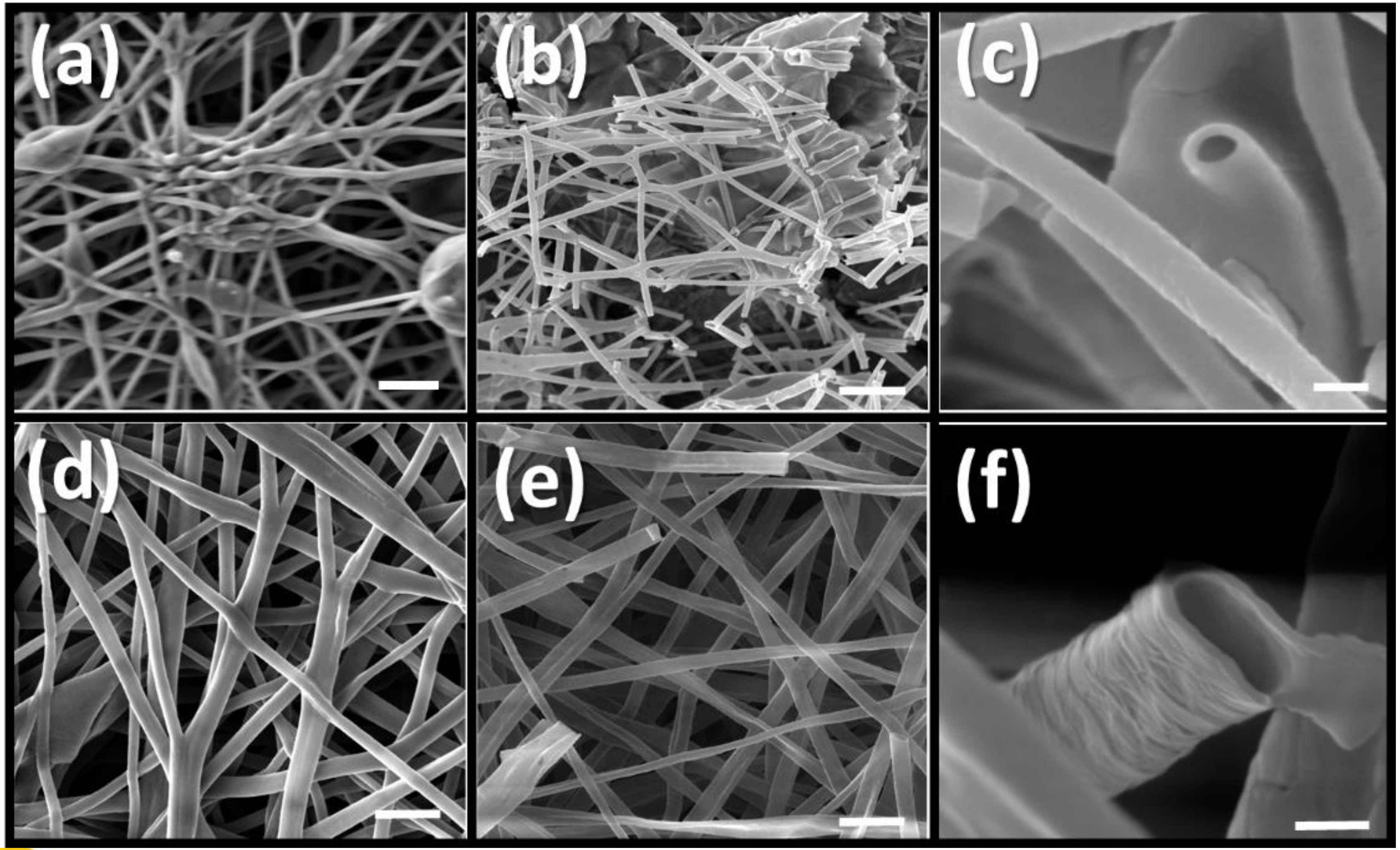




J. A. van Delft et al., Semicond. Sci. Technol. 27 (2012) 074002 (13pp)

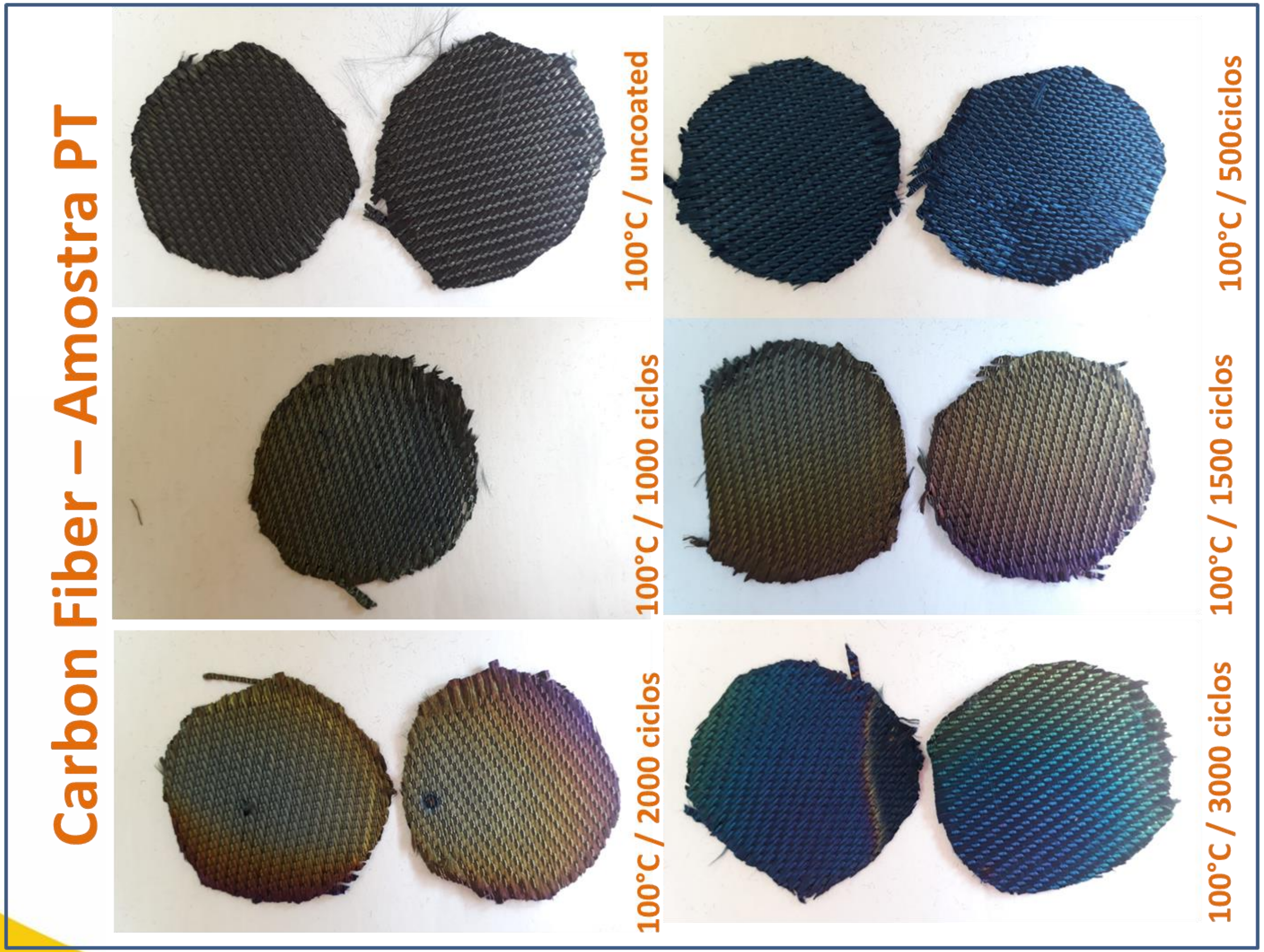
4. Aplicações de ALD

→ APPLICATION: ALD coating of nanofibers (PBAT / ALD TiO_2)



4. Aplicações de ALD

→ APPLICATION: ALD coating of carbon fibers



4. Aplicações de ALD

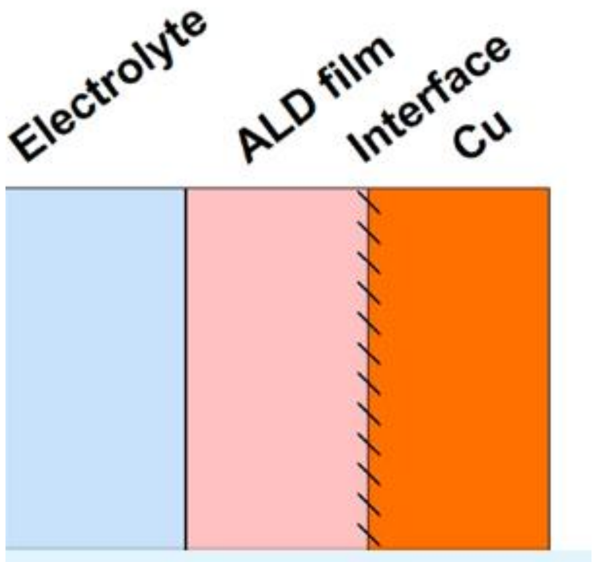
ACS APPLIED MATERIALS & INTERFACES
Research Article
www.acsami.org

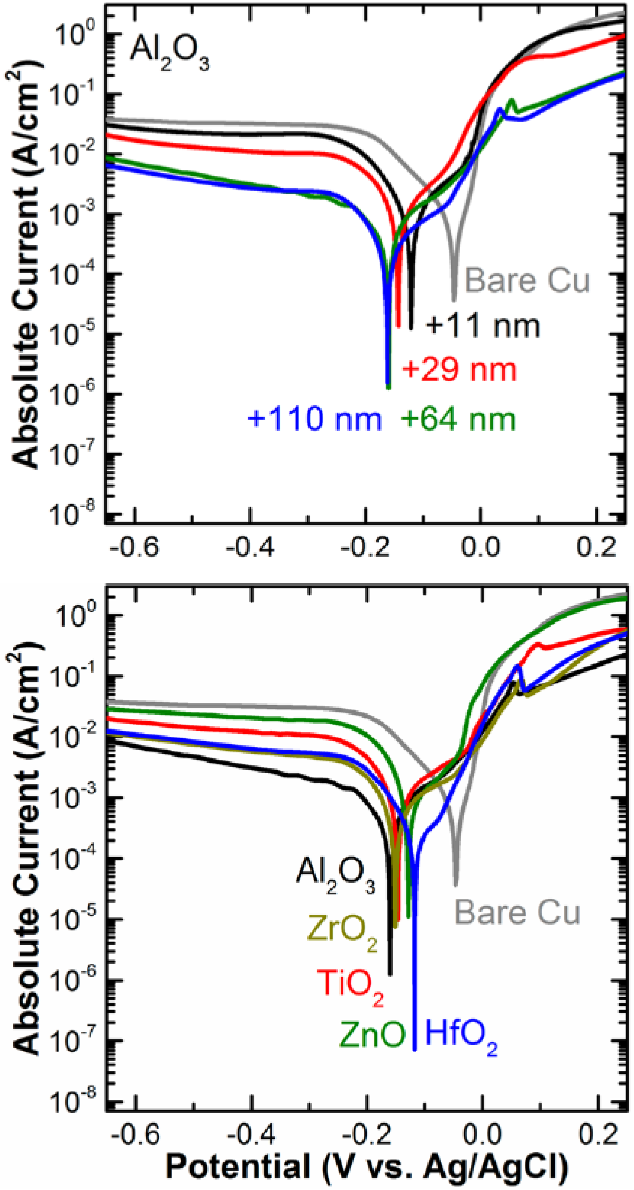
Corrosion Protection of Copper Using Al_2O_3, TiO_2, ZnO, HfO_2, and ZrO_2 Atomic Layer Deposition

James S. Daubert, Grant T. Hill, Hannah N. Gotsch, Antoine P. Gremaud, Jennifer S. Ovental, Philip S. Williams, Christopher J. Oldham, and Gregory N. Parsons*

Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina 27695, United States

DOI: 10.1021/acsami.6b13571
ACS Appl. Mater. Interfaces 2017, 9, 4192−4201





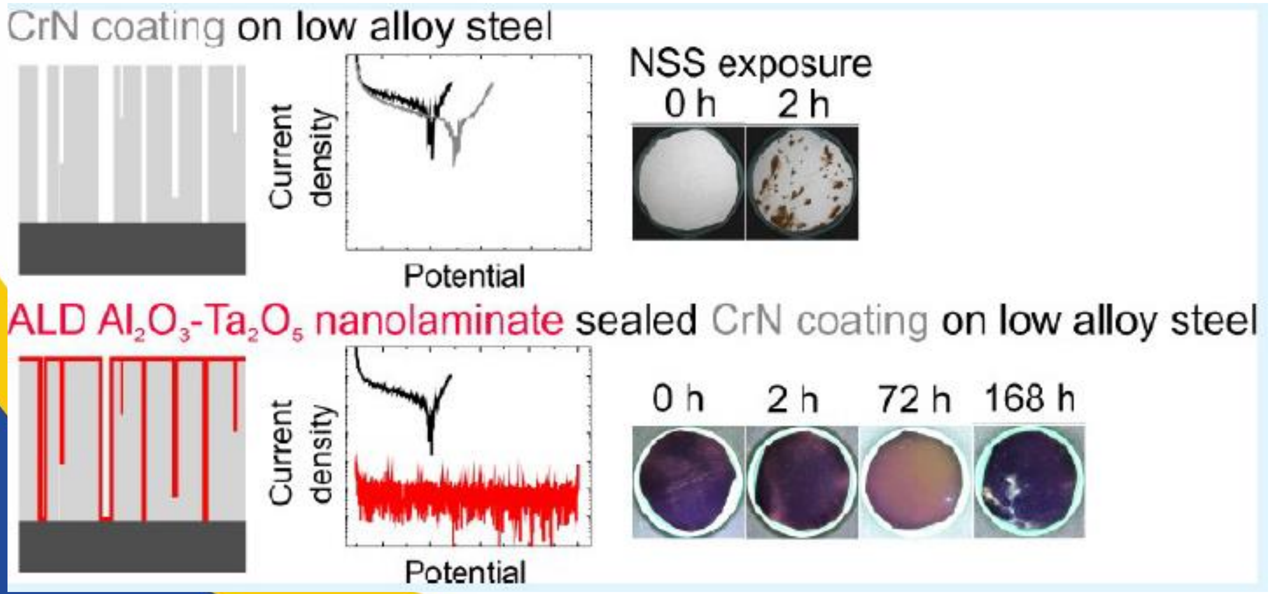
4. Aplicações de ALD

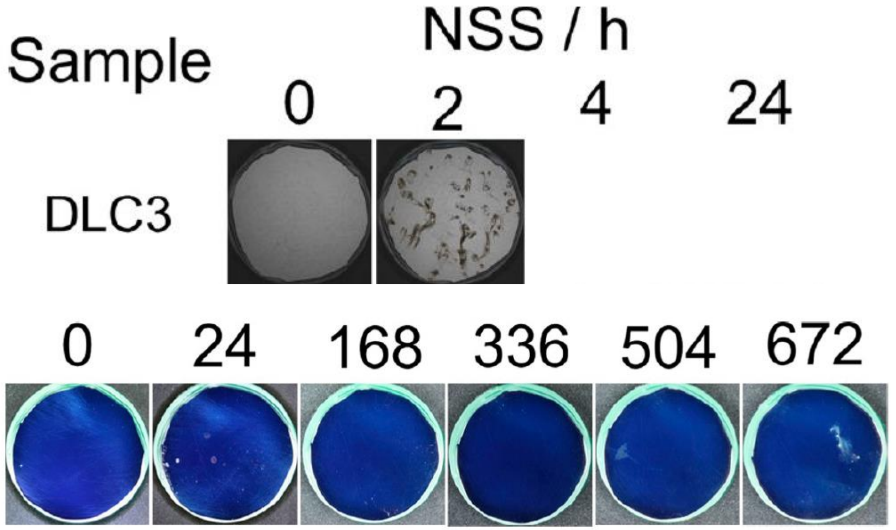
ACS APPLIED MATERIALS & INTERFACES
Research Article
www.acsami.org

Sealing of Hard CrN and DLC Coatings with Atomic Layer Deposition

Emma Härkönen,*[,†] Ivan Kolev,[‡] Belén Díaz,[§] Jolanta Światowska,[§] Vincent Maurice,[§] Antoine Seyeux,[§] Philippe Marcus,[§] Martin Fenker,[||] Lajos Toth,[⊥] György Radnoczi,[⊥] Marko Vehkamäki,[†] and Mikko Ritala[†]

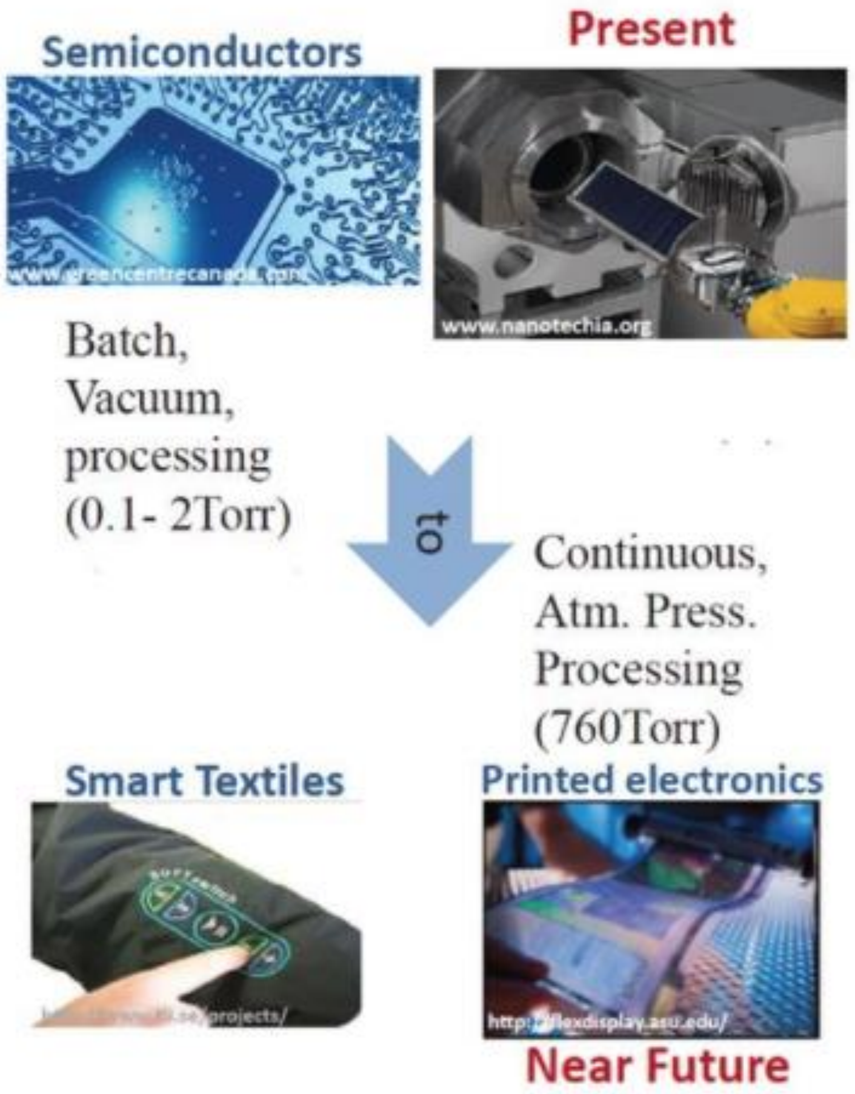
[†]Laboratory of Inorganic Chemistry, University of Helsinki, P.O. Box 55, FIN-00014 Helsinki, Finland
[‡]Hauzer Techno Coating BV, 5928 LL Venlo, the Netherlands
[§]Laboratoire de Physico-Chimie des Surfaces, CNRS (UMR 7075), Chimie ParisTech (ENSCP), F-75005 Paris, France
[||]FEM Research Institute, Precious Metals and Metals Chemistry, D-73525 Schwäbisch Gmünd, Germany
[⊥]Research Centre for Natural Sciences HAS (MTA TKK), 1025 Budapest, Hungary





Images of steel coated with ALD graded mixture sealed 2.85 μm DLC (DLC3-graded) after different times (hours) of NSS exposure.

4. Aplicações de ALD



Physical sensors

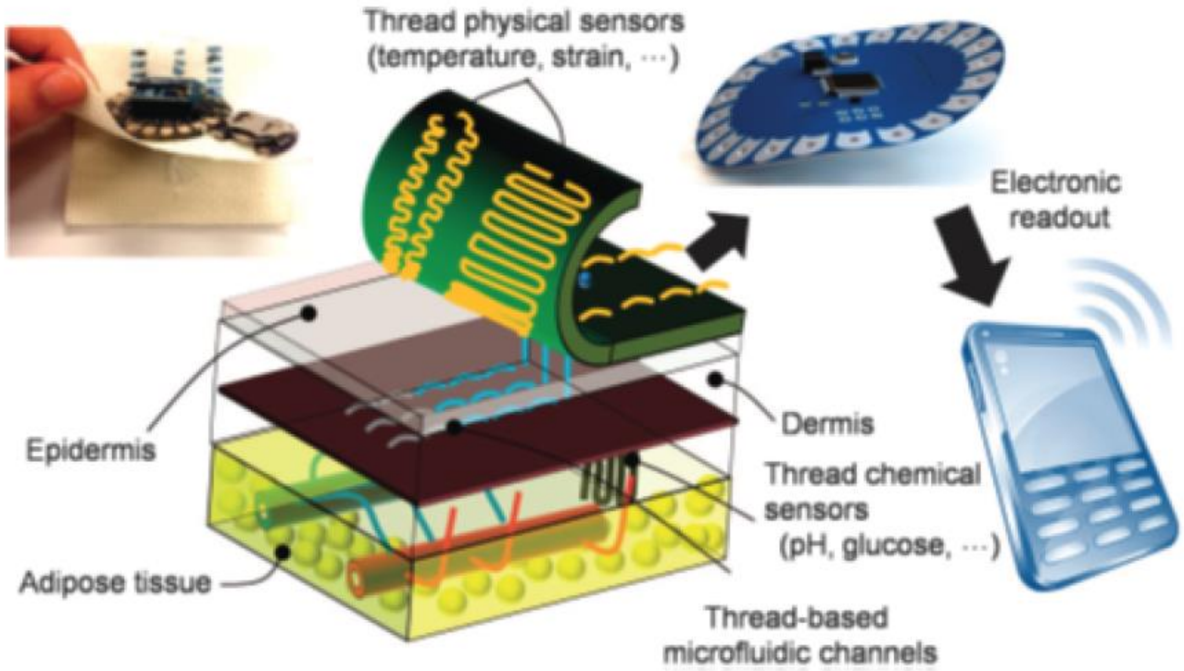
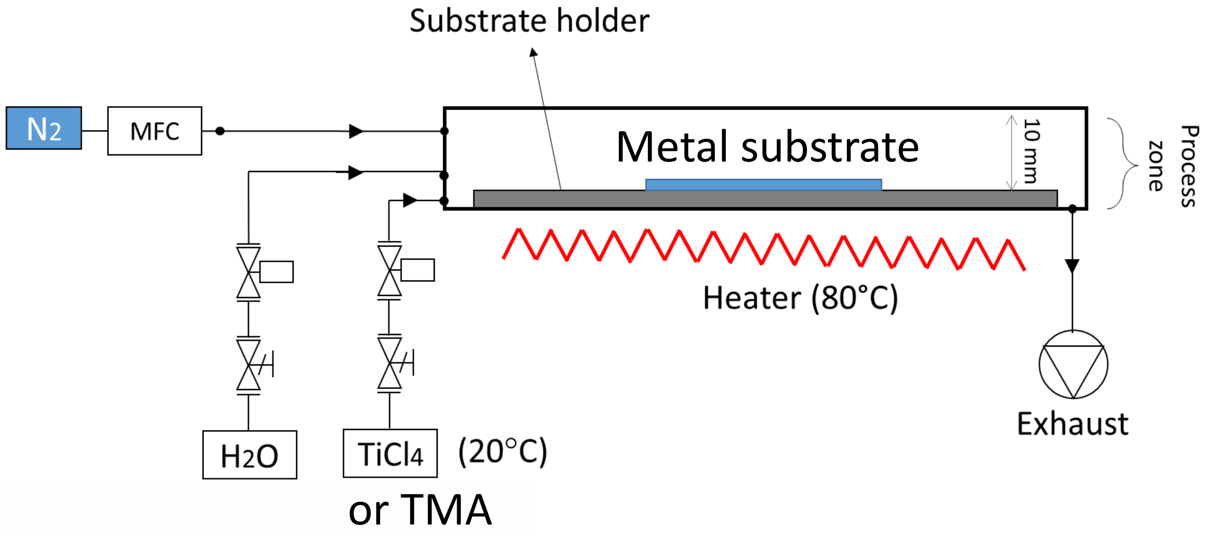


그림 3. 센서 (pH, glucose), 전극으로서 사용되는 전자섬유

5. Alguns resultados recentes do grupo

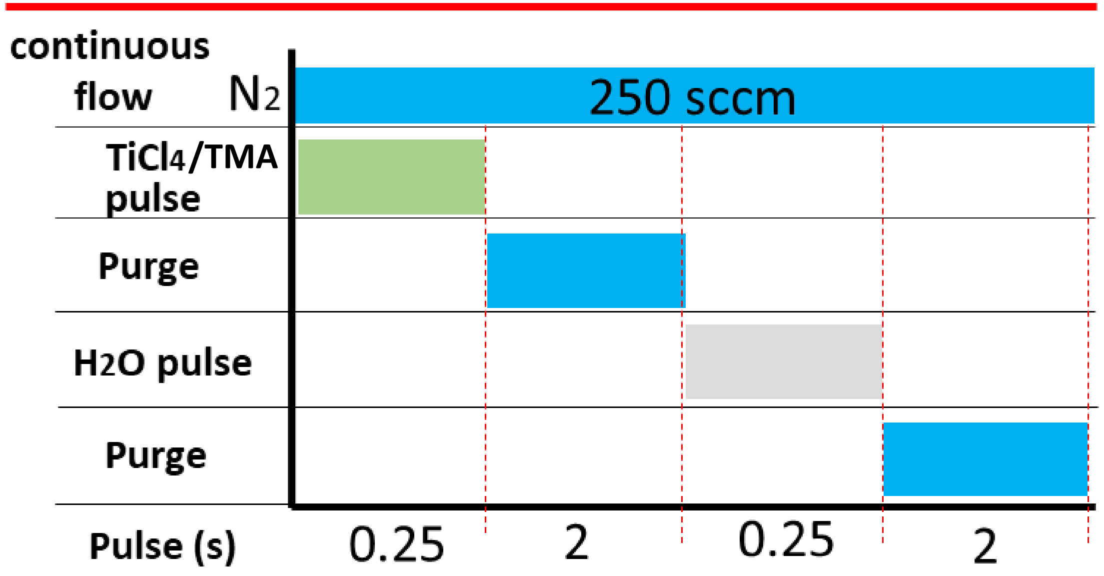
Thermal ALD reactor and TiO2 or Al_2O_3 deposition parameters

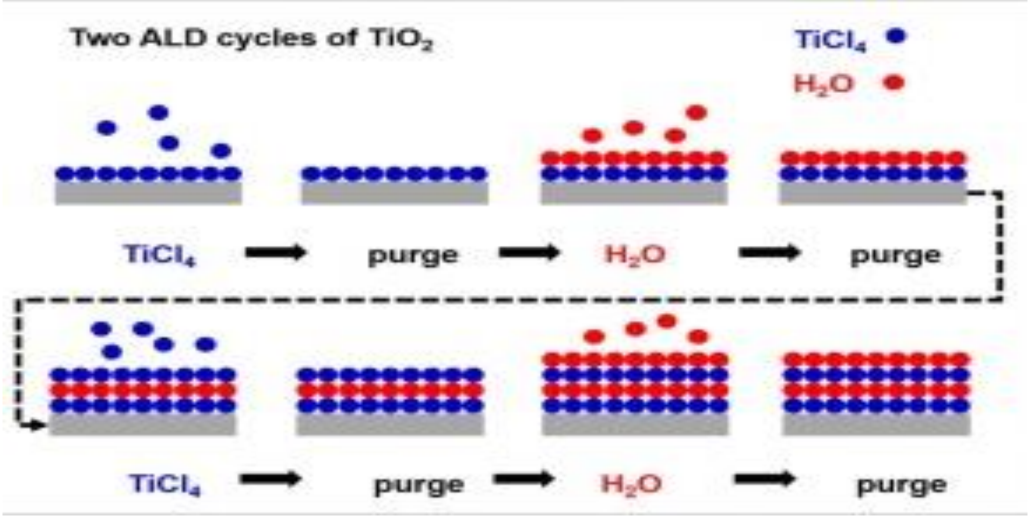


Schematic diagram of the Beneq TFS 200 reactor

Process pressure: 1 mbar
Process temperature: 80°C
Total cycle number: 500-2000

Thermal ALD cycle

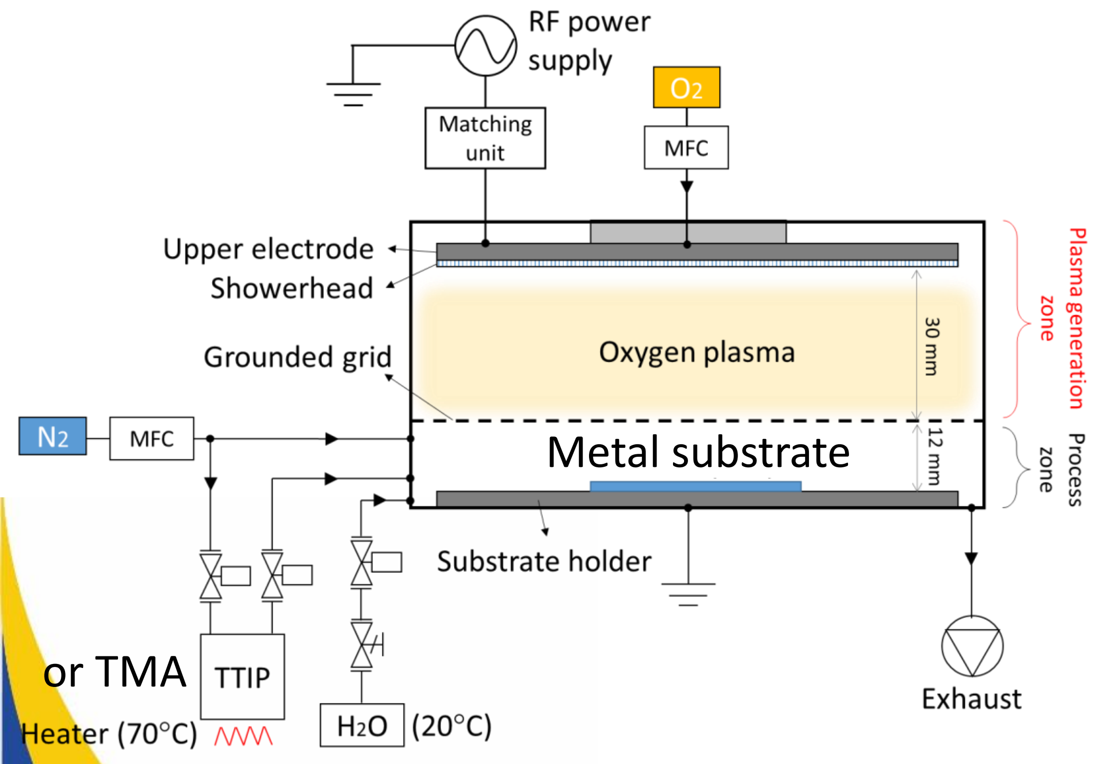




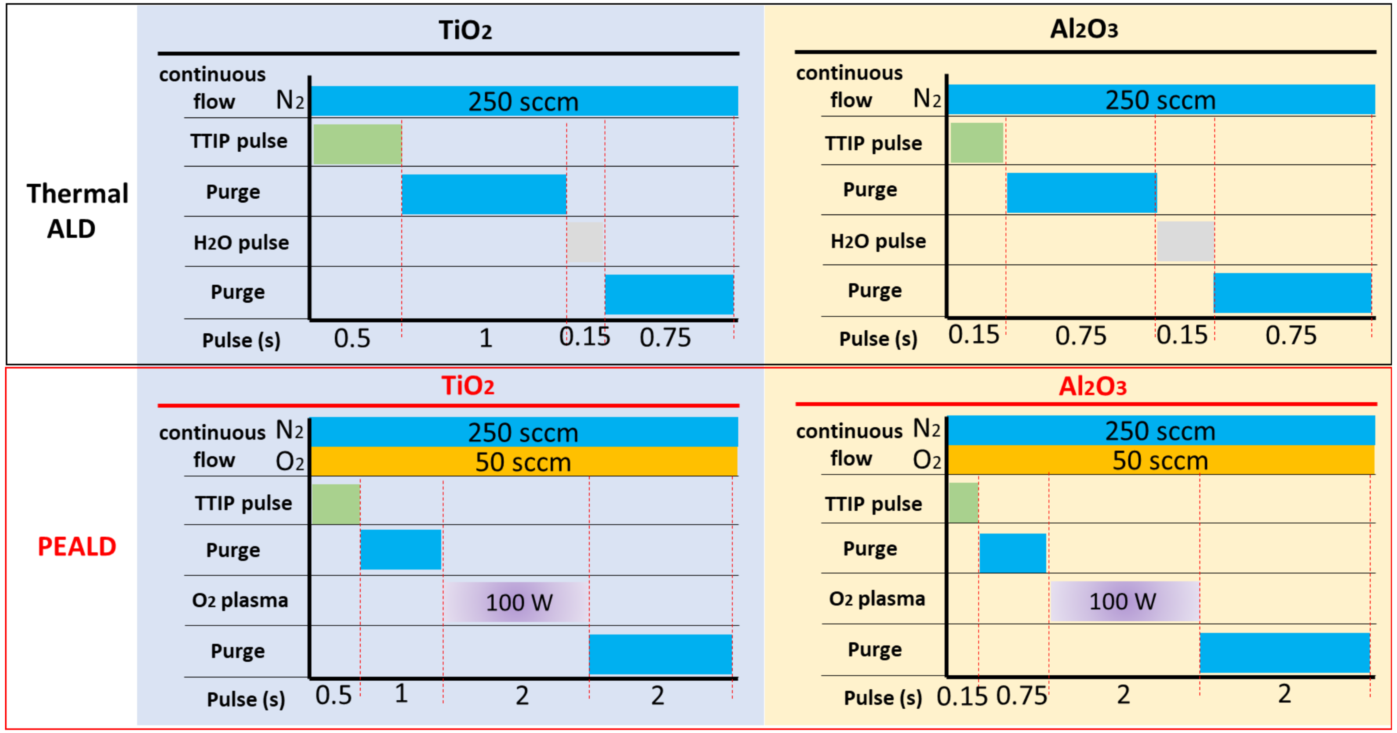
W. Chiappim, G. E. Testoni, A. C. O. C. Doria, R. S. Pessoa, et al. ***Nanotechnology***, 27 (2016), 305701.

5. Alguns resultados recentes do grupo

PEALD reactor and TiO_2/Al_2O_3 nanolaminate deposition parameters



Schematic diagram of the
Beneq TFS 200 PEALD reactor
(Remote capacitively coupled plasma)

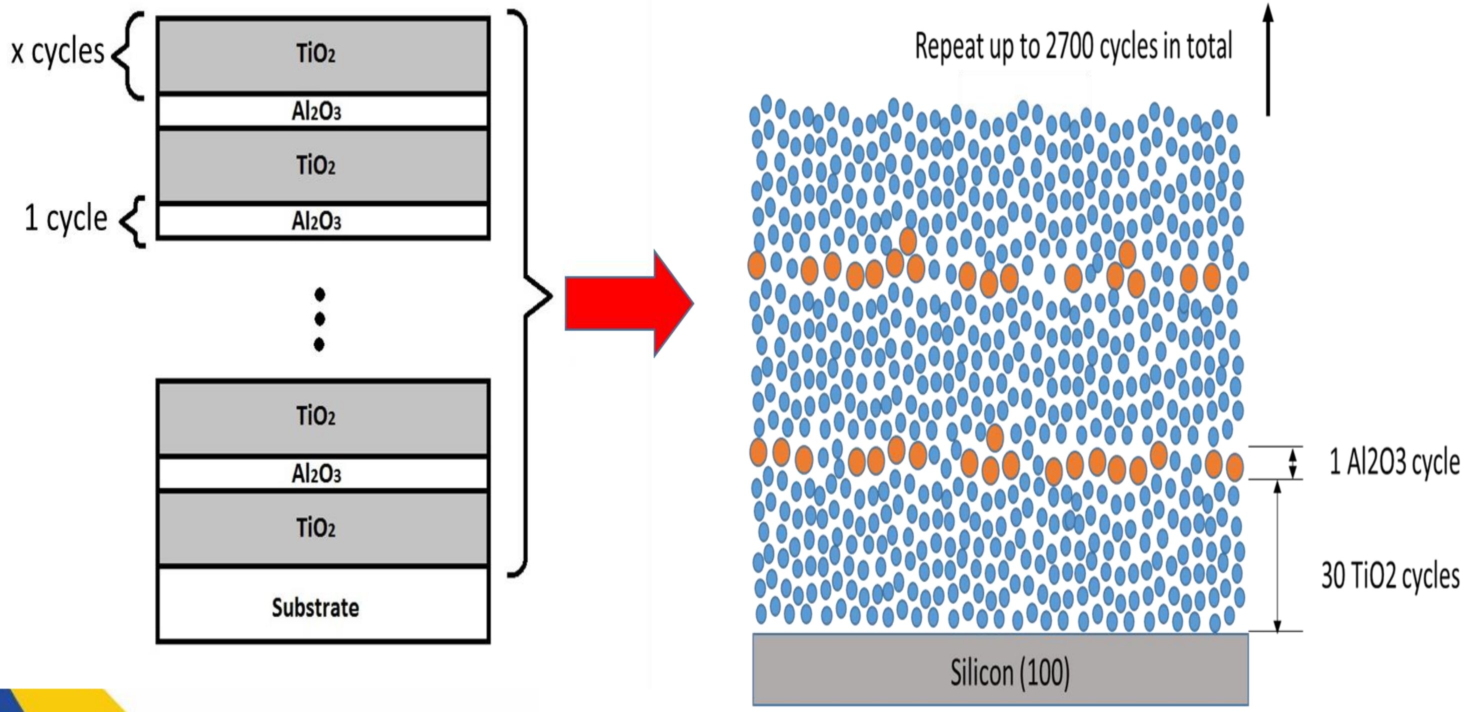


Process pressure: 1 mbar
Process temperature: 250°C
Total cycle number: 2700
Number of Al_2O_3 partial-monolayers: 10 - 90

W. Chiappim, G. E. Testoni, A. C. O. C. Doria, R. S. Pessoa, et al.
Nanotechnology, 27 (2016), 305701.

5. Alguns resultados recentes do grupo

Nanolaminate design:
TiO_2 film / Al_2O_3 partial-monolayer



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Applied Physics
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IOP Publishing — Journal of Physics D: Applied Physics
J. Phys. D: Appl. Phys. 49 (2016) 375301 (14pp) — doi:10.1088/0022-3727/49/37/375301

Influence of the Al_2O_3 partial-monolayer number on the crystallization mechanism of TiO_2 in ALD TiO_2/Al_2O_3 nanolaminates and its impact on the material properties

G E Testoni[1,2], W Chiappim[1,2], R S Pessoa[1,2], M A Fraga[3], W Miyakawa[4], K K Sakane[1], N K A M Galvão[2], L Vieira[1,2] and H S Maciel[1,2]

[1] Nanotechnology and Plasmas Processes Laboratory, Universidade do Vale do Paraíba (Univap), São José dos Campos, SP, 12244-000, Brazil
[2] Plasma and Processes Laboratory, Instituto Tecnológico de Aeronáutica (ITA-DCTA), São José dos Campos, SP, 12228-900, Brazil
[3] Associate Laboratory of Sensors and Materials, Instituto Nacional de Pesquisas Espaciais (INPE), São José dos Campos, SP, 12227-010, Brazil
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CrossMark

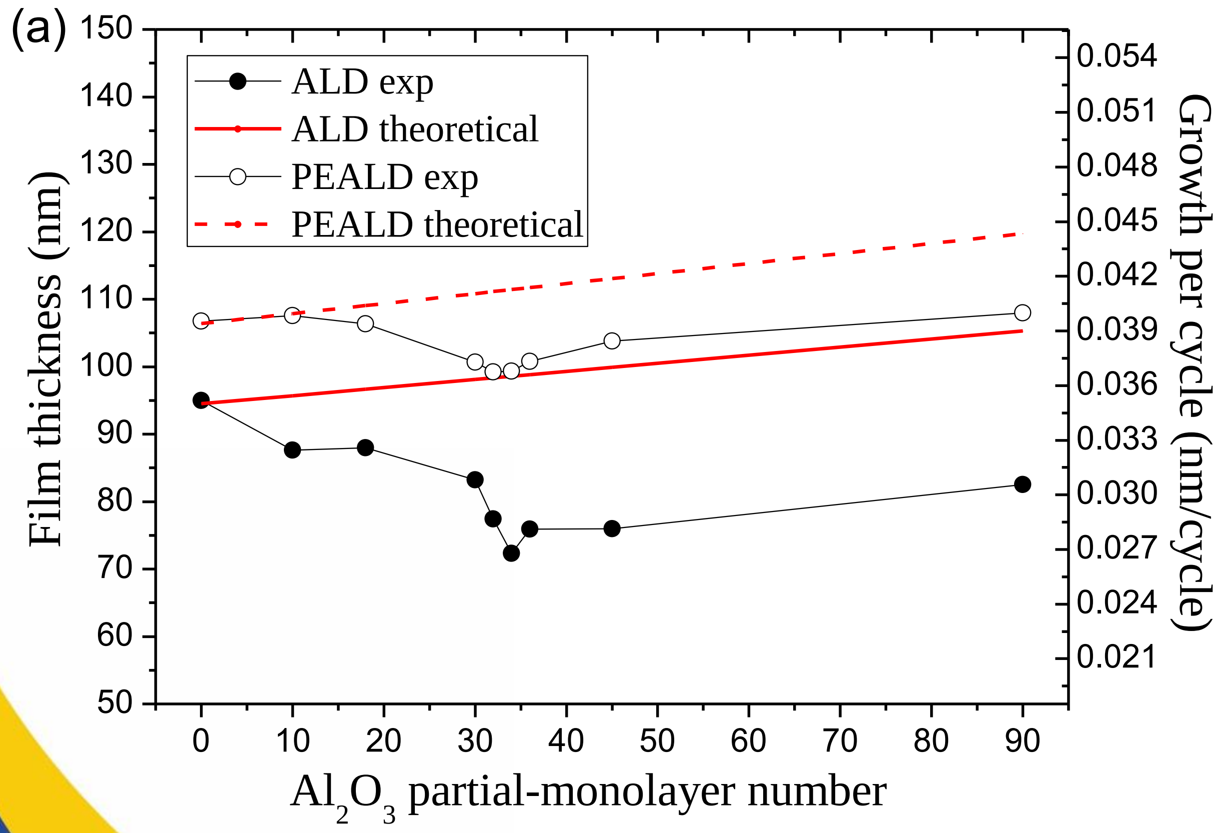
Abstract

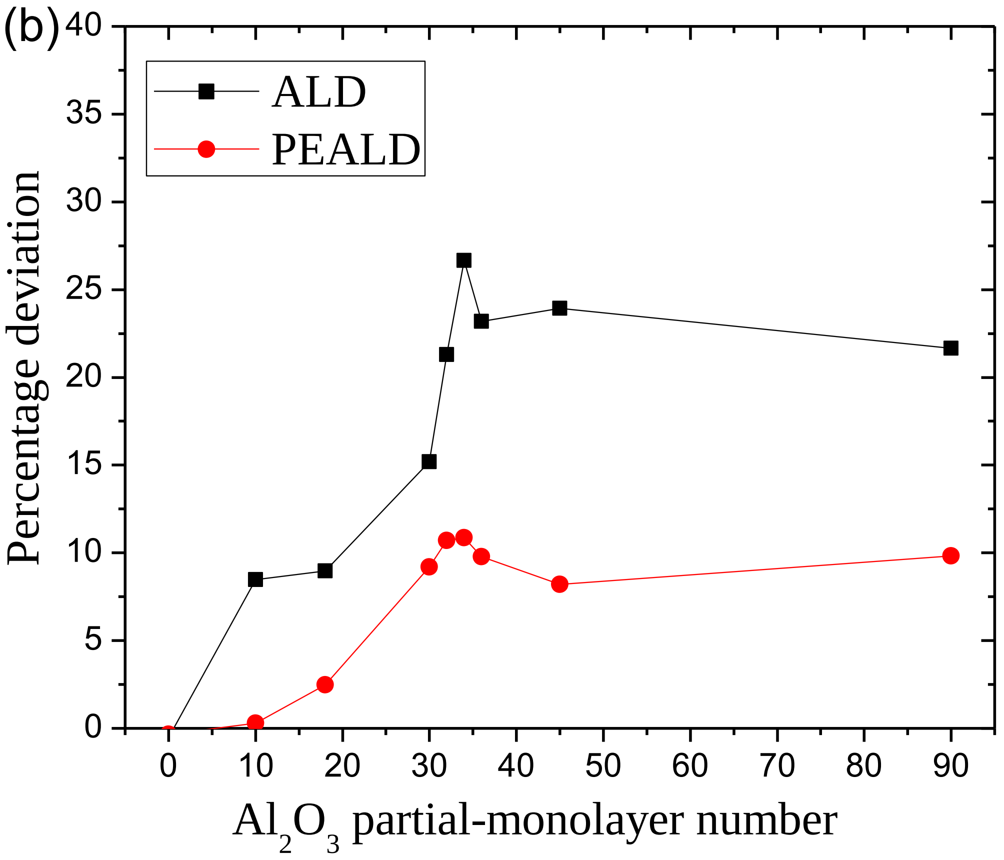
TiO_2/Al_2O_3 nanolaminates are being investigated to obtain unique materials with chemical, physical, optical, electrical and mechanical properties for a broad range of applications that include electronic and energy storage devices. Here, we discuss the properties of TiO_2/Al_2O_3 nanolaminate structures constructed on silicon (100) and glass substrates using atomic layer deposition (ALD) by alternatively depositing a TiO_2 sublayer and Al_2O_3 partial-monolayer using TTIP–H_2O and TMA–H_2O precursors, respectively. The Al_2O_3 is formed by a single TMA–H_2O cycle, so it is a partial-monolayer because of steric hindrance of the precursors, while the TiO_2 sublayer is formed by several TTIP–H_2O cycles. Overall, each nanolaminate incorporates a certain number of Al_2O_3 partial-monolayers with this number varying from 10–90 in the TiO_2/Al_2O_3 nanolaminate grown during 2700 total reaction cycles of TiO_2 at a temperature of 250 °C. The fundamental properties of the TiO_2/Al_2O_3 nanolaminates, namely film thickness, chemical composition, microstructure and morphology were examined in order to better understand the influence of the number of Al_2O_3 partial-monolayers on the crystallization mechanism of TiO_2. In addition, some optical, electrical and mechanical properties were determined and correlated with fundamental characteristics. The results show clearly the effect of Al_2O_3 partial-monolayers as an internal barrier, which promotes structural inhomogeneity in the film and influences the fundamental properties of the nanolaminate. These properties are correlated with gas phase analysis that evidenced the poisoning effect of trimethylaluminum (TMA) pulse during the TiO_2 layer growth, perturbing the growth per cycle and consequently the overall film thickness. It was shown that the changes in the fundamental properties of TiO_2/Al_2O_3 nanolaminates had little influence on optical properties such as band gap and transmittance. However, in contrast, electrical properties as resistivity and mechanical properties as hardness and elastic modulus were shown to be very dependent. From these analyses, several applications could be suggested for different kinds of nanolaminates obtained in this work.

G. E. Testoni, W. Chiappim, R. S. Pessoa, et al. *Journal of Physics D: Applied Physics* 49, (2016) 375301.

5. Alguns resultados recentes do grupo

Growth per cycle

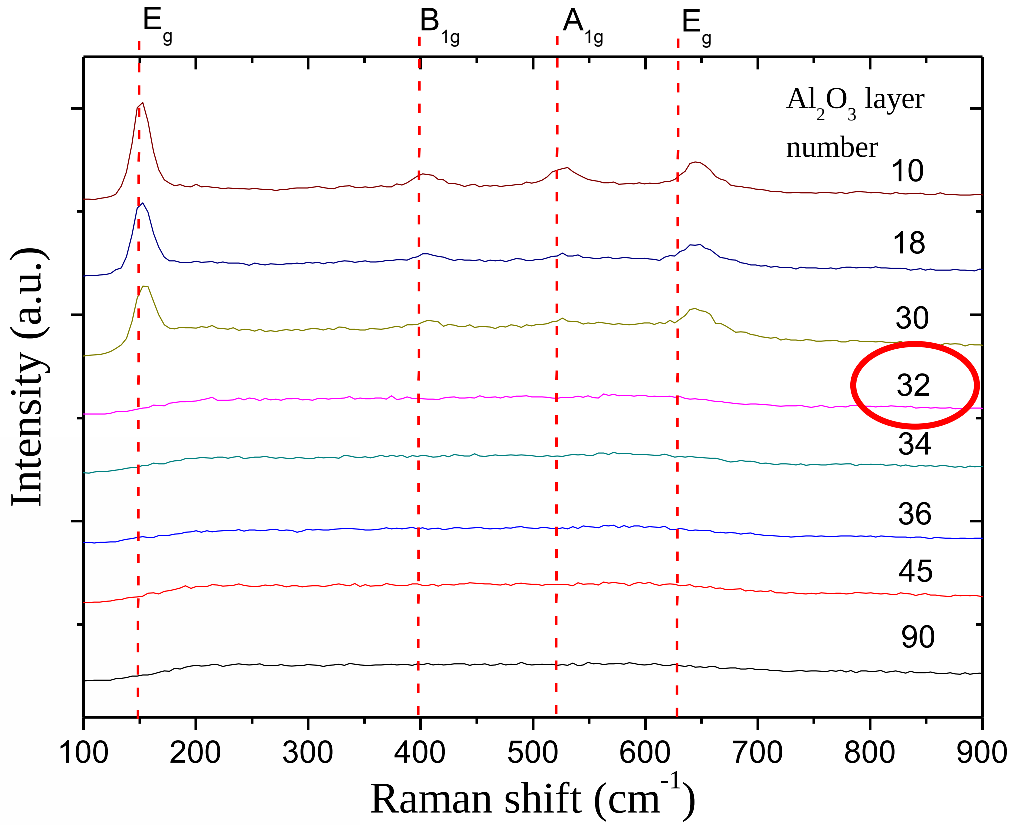




$$GPC_{nanolaminate} = \frac{(GPC_{TiO_2} \times n_{cycle,TiO_2} + GPC_{Al_2O_3} \times n_{cycle,Al_2O_3})}{n_{cycle,total}}$$

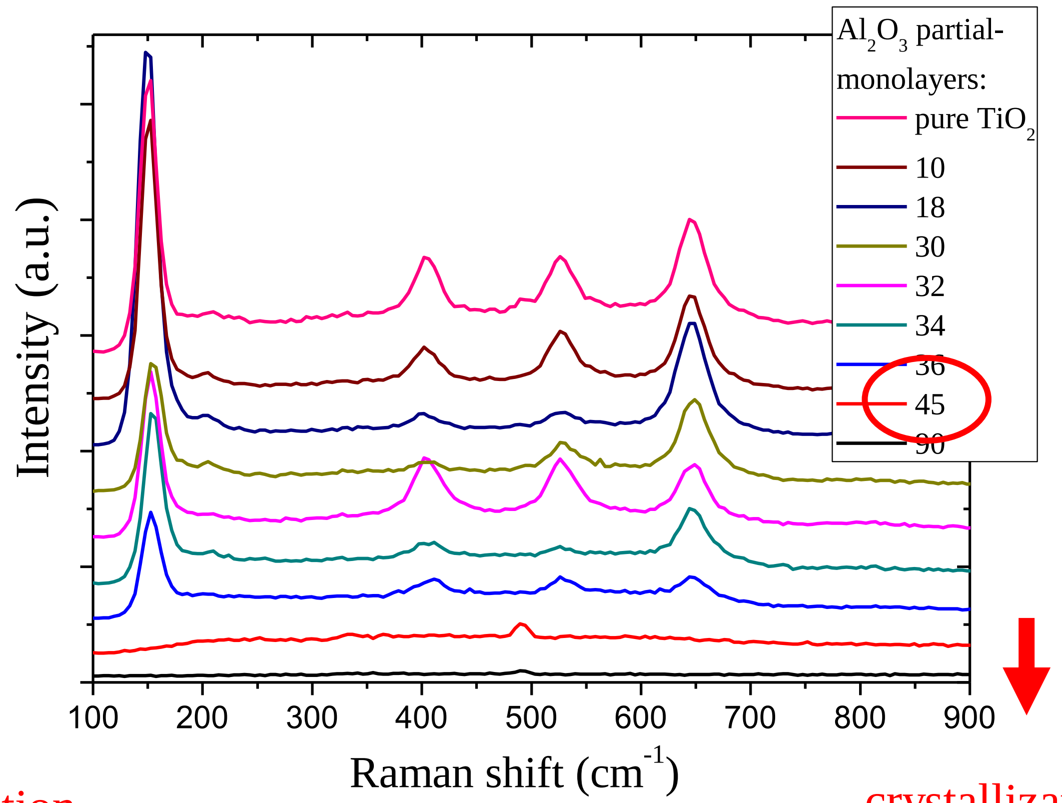
5. Alguns resultados recentes do grupo

Nanolaminate structure



crystallization stop

Thermal ALD



crystallization stop

PEALD

↳ MORE ENERGETIC PROCESS

5. Alguns resultados recentes do grupo

Morphology

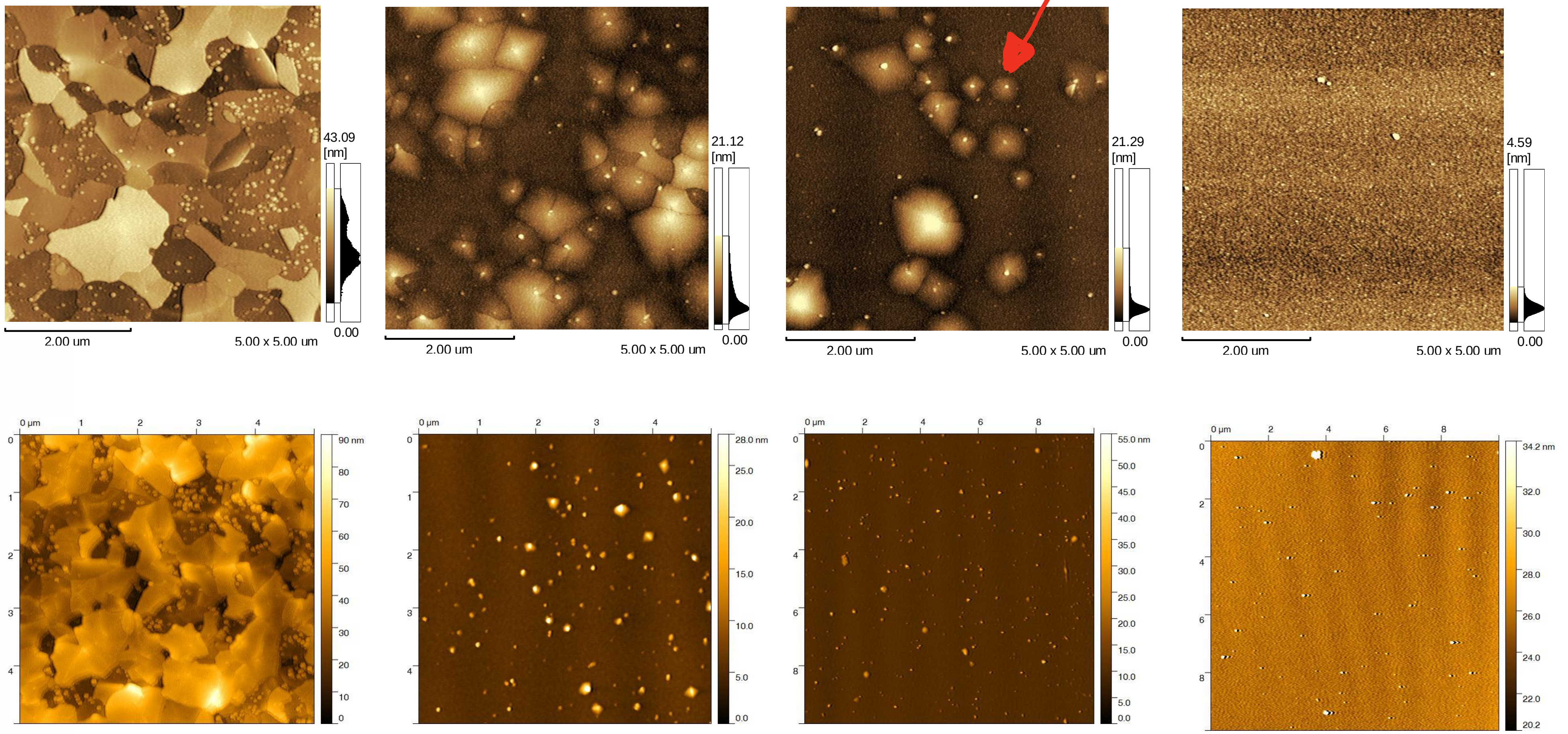
Al_2O_3 partial-monolayer number

10 | 32 | 36 | 45

TiO_2 CRYSTAL

PEALD

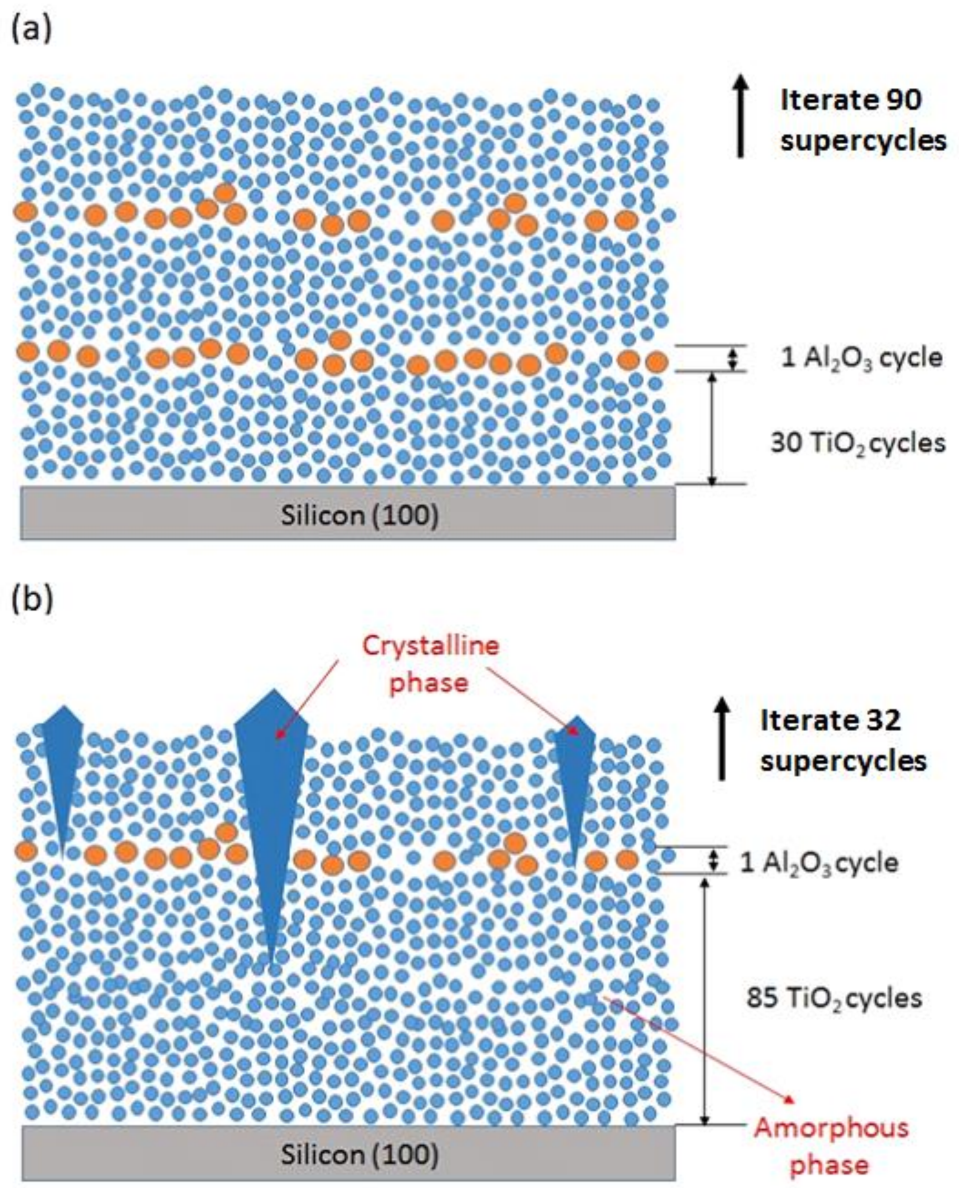
Thermal ALD



5. Alguns resultados recentes do grupo

Morphology

Proposed mechanism of TiO_2 crystallinity stop



5. Alguns resultados recentes do grupo

ELSEVIER

Surface and Coatings Technology

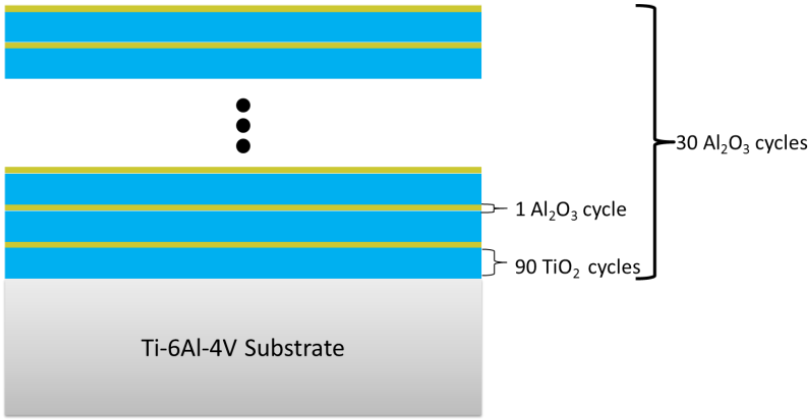
Volume 349, 15 September 2018, Pages 1077-1082

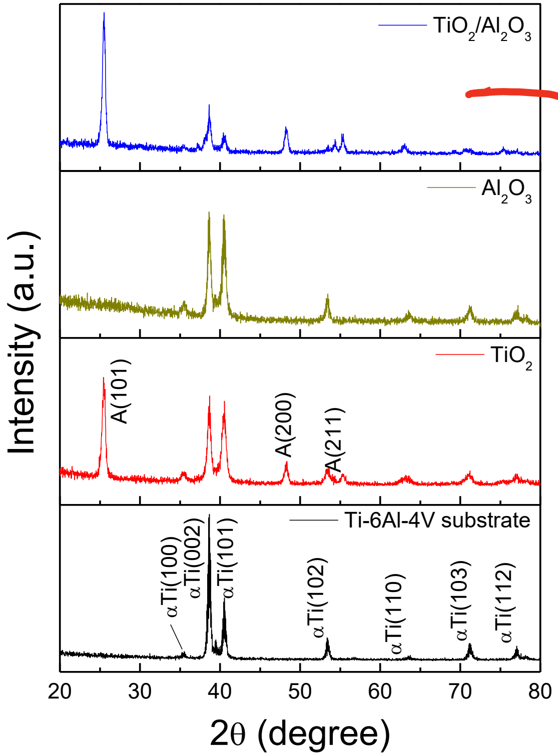
Tribocorrosion behavior of TiO_2/Al_2O_3 nanolaminate, Al_2O_3, and TiO_2 thin films produced by atomic layer deposition

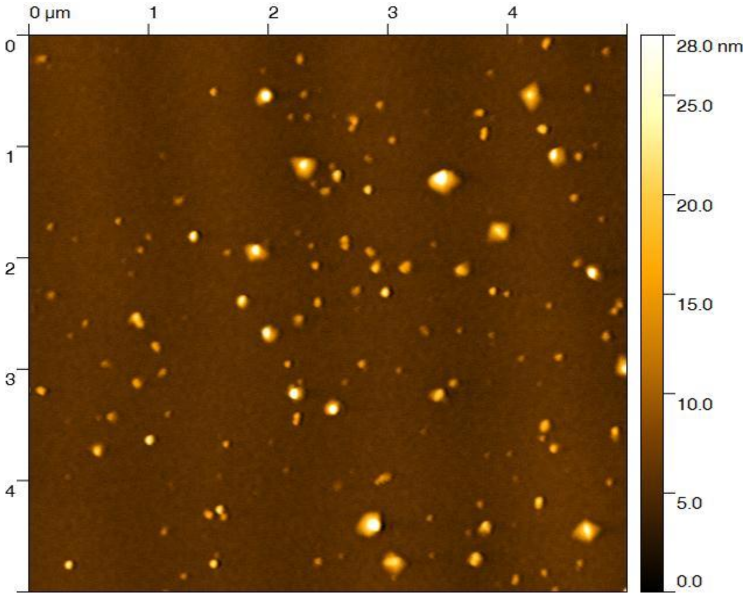
Polyana Alves Radi [a, b], Giorgio Ernesto Testoni [c], Rodrigo Sávio Pessoa [a, b], Homero Santiago Maciel [a, b], Luís Augusto Rocha [d, e, f], Lucia Vieira [a, b]

⊞ Show more

https://doi.org/10.1016/j.surfcoat.2018.06.036







5. Alguns resultados recentes do grupo

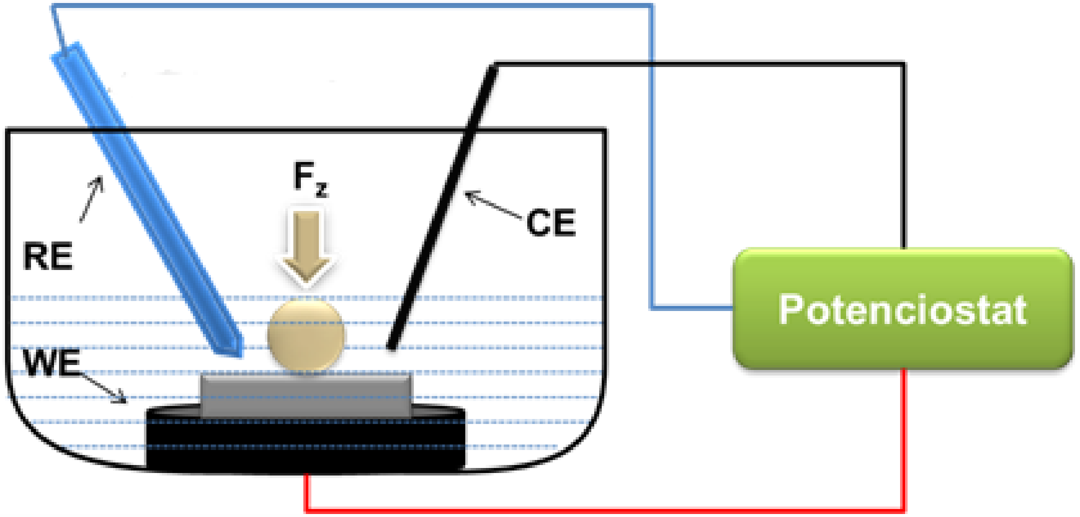
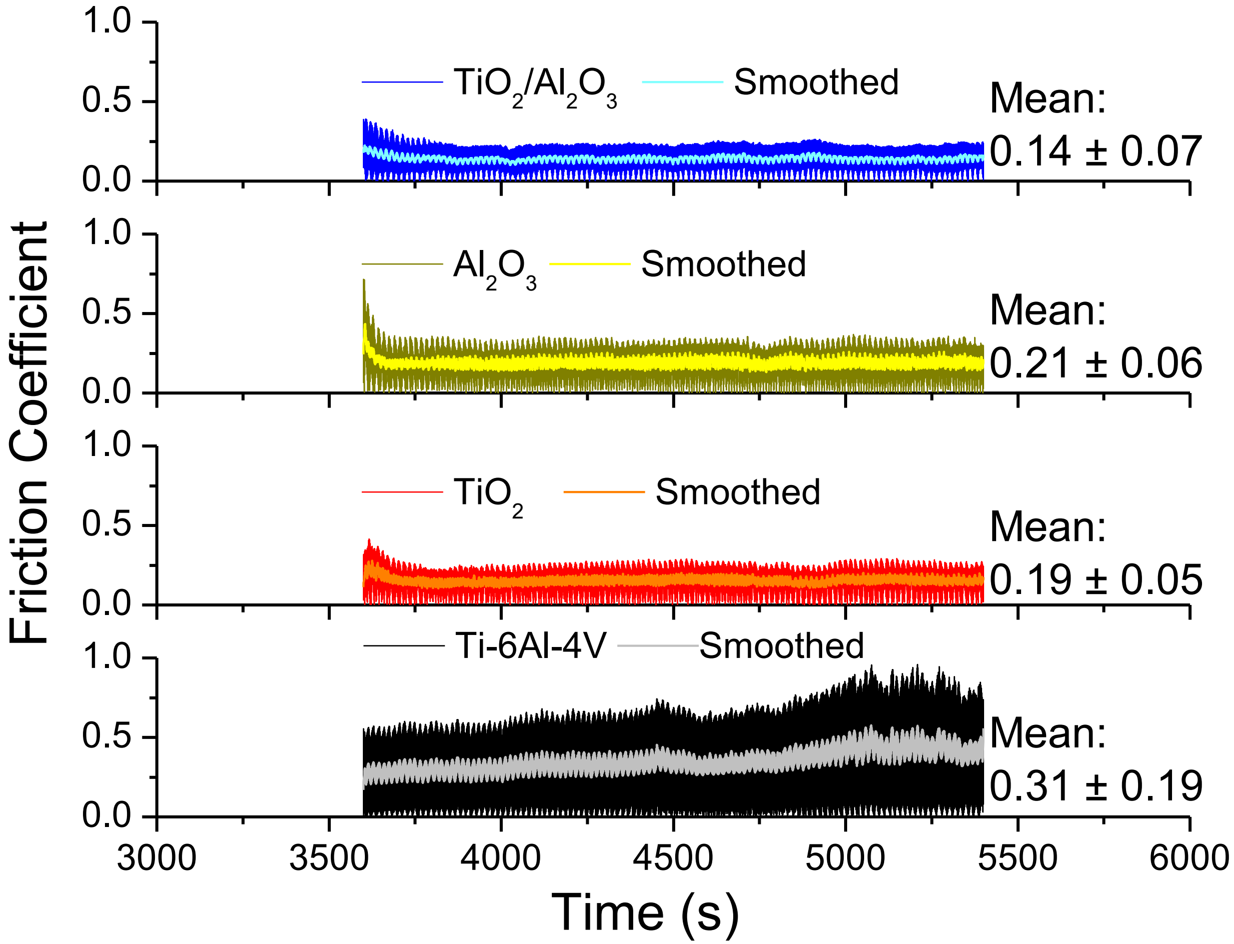


Figure - Schematic drawing of tribocorrosion cell showing the reference electrode (RE) Ag/AgCl, the platinum counter electrode (CE) and the working electrode (WE) on Ringer's solution based on ASTM G119-93 .



→ Results indicate that the TiO_2/Al_2O_3 nanolaminate film is a promising top coating with low friction coefficient.

5. Alguns resultados recentes do grupo

Thermal Atomic layer deposition of TiO2 thin films (100 ºC)

Aluminum (Al) substrate

Precursor molecules

$TiCl_4$ (0.25 s) + H_2O (0.25 s)
N_2 purge = 2 s
Reaction cycle number = 1000 → 100 nm

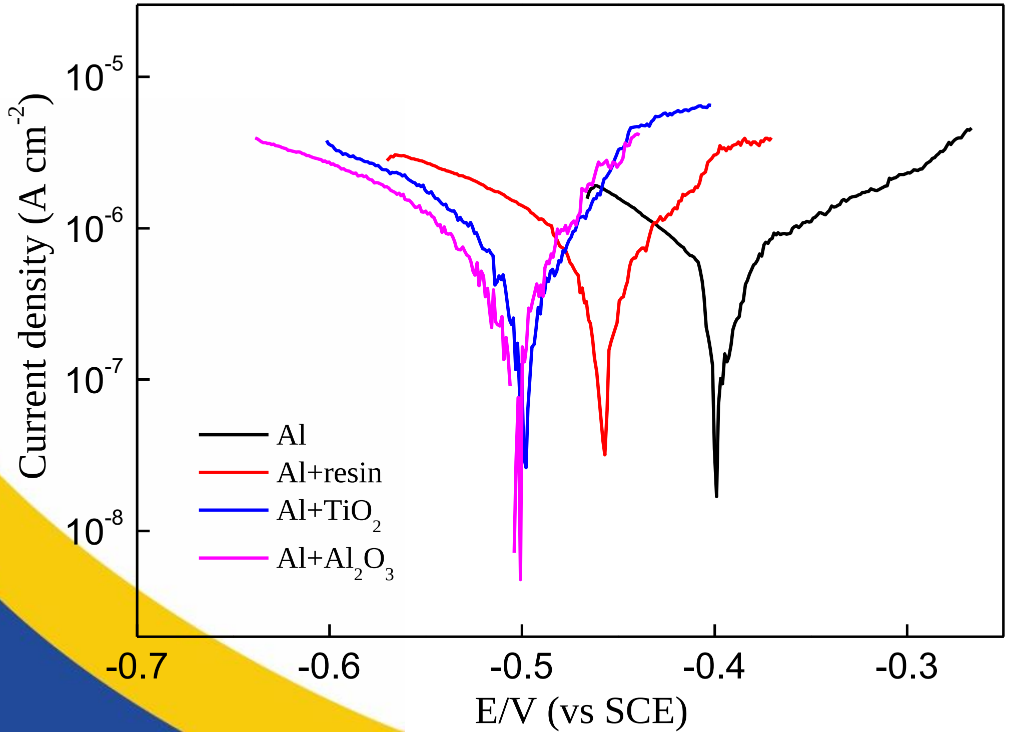
Material characterization

- ✓ Grazing incidence XRD
- ✓ Scanning Electron Microscopy (SEM)
- ✓ Profilometry
- ✓ Fourier-transform infrared spectroscopy (FT-IR) with ATR

standard three-electrode electrochemical cell

Electrochemical analyzes

- ✓ Polarization curve
- ✓ Nyquist plot
- ✓ Bode magnitude plot
- ✓ Bode phase plot

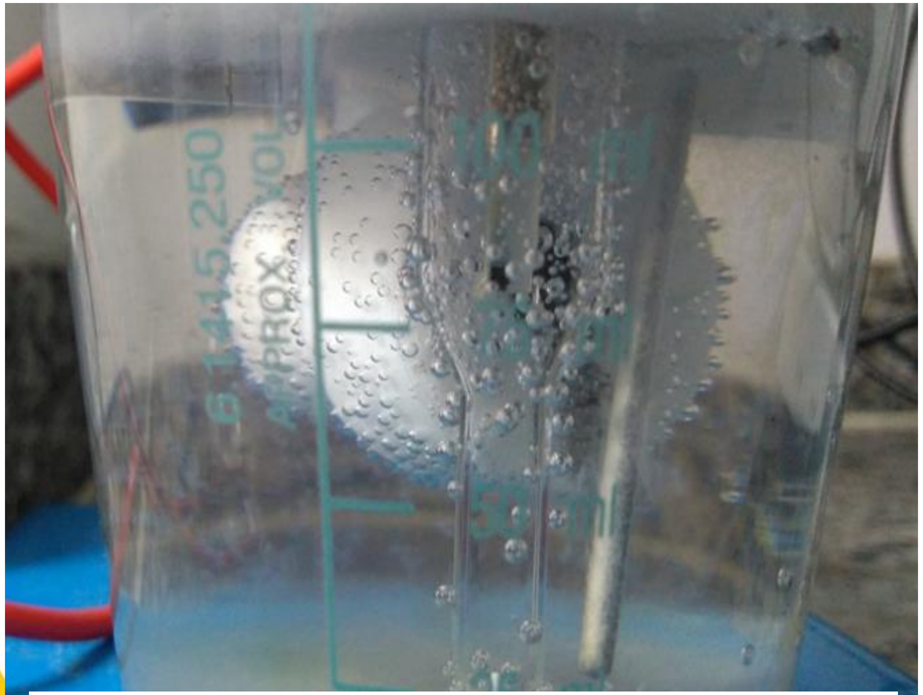


Samples	V_{corr} (V vs Ag/AgCl)	j_{corr} (10^{-6} A.cm^2)	R_p (10^4 Ω/cm^2)	EP (%)	P_{eff} (%)
Al	-0.40	9.06	2.77	100.0	-
Al+resin	-0.46	7.56	2.20	96.0	7.1
Al+TiO_2	-0.50	1.24	2.19	11.4	86.3
Al+Al_2O_3	-0.55	1.79	2.27	20.4	80.0

Dias, V.; Maciel, H.; Fraga, M.; Lobo, A.O.; Pessoa, R.; Marciano, F.R. Atomic Layer Deposited TiO_2 and Al_2O_3Thin Films as Coatings for Aluminum Food Packaging Application. *Materials* **2019**, *12*, 682.

5. Alguns resultados recentes do grupo

Aluminum corrosion in 0.5 M NaCl eletrolyte



Materials Research Express

PAPER • OPEN ACCESS

Atomic layer deposition of TiO_2 and Al_2O_3 thin films for the electrochemical study of corrosion protection in aluminum alloy cans used in beverage

V M Dias[1,2], W Chiappim[3], M A Fraga[4], H S Maciel[1,5], F R Marciano[6] and R S Pessoa[7,1,5]

Published 22 July 2020 • © 2020 The Author(s). Published by IOP Publishing Ltd

Materials Research Express, Volume 7, Number 7

Citation V M Dias *et al* 2020 *Mater. Res. Express* 7 076408

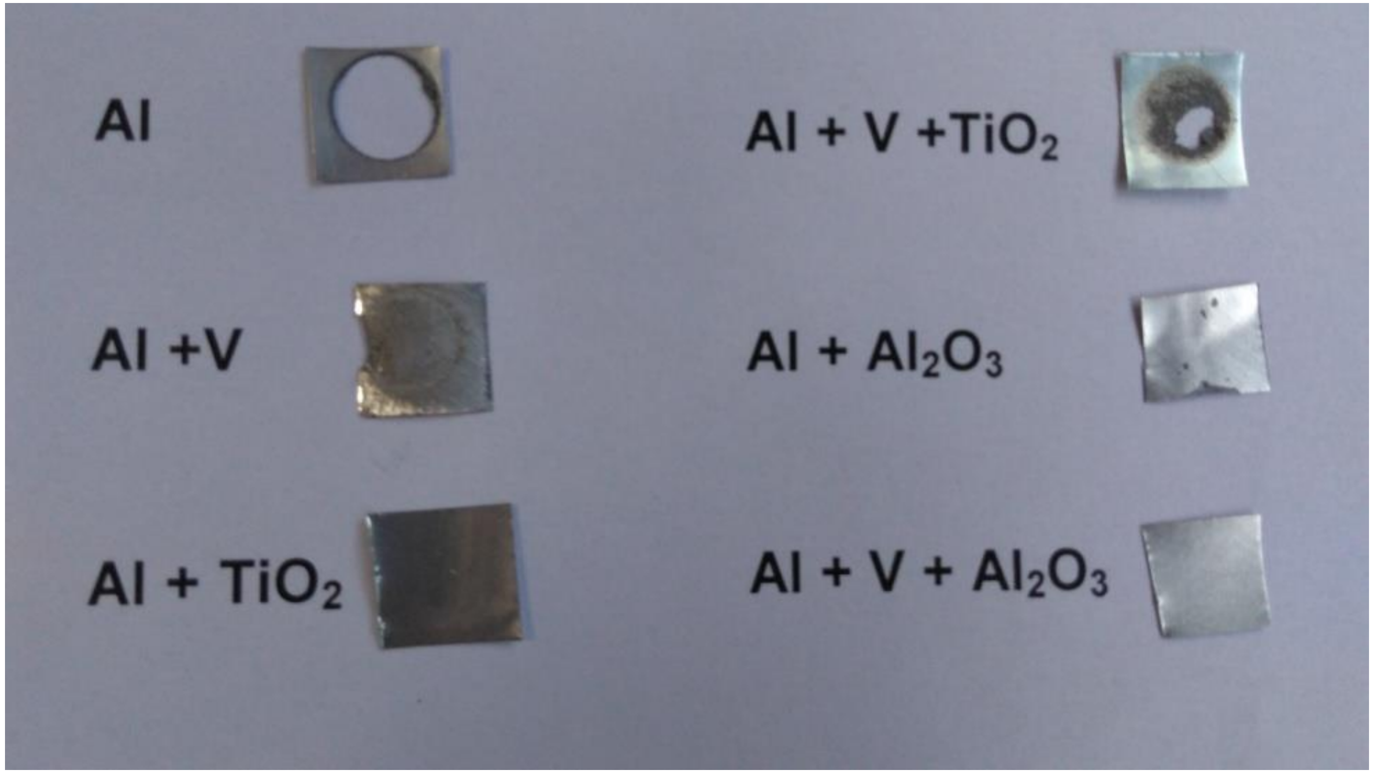


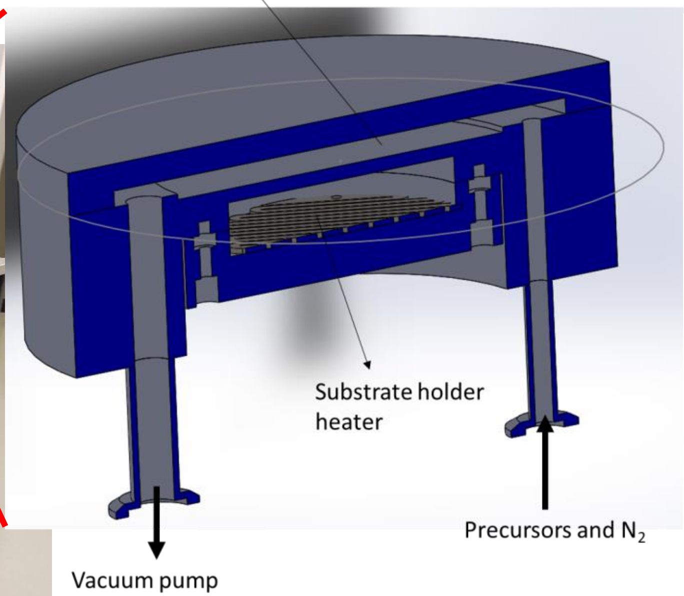
Figure - Image of the samples after the treatment in 0.5 M NaCl electrolyte for 6 h.

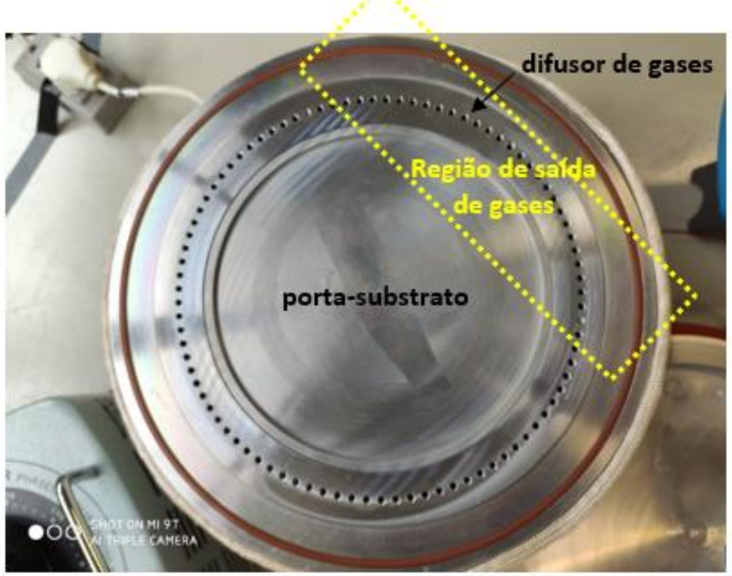
Where: V = resin (verniz)

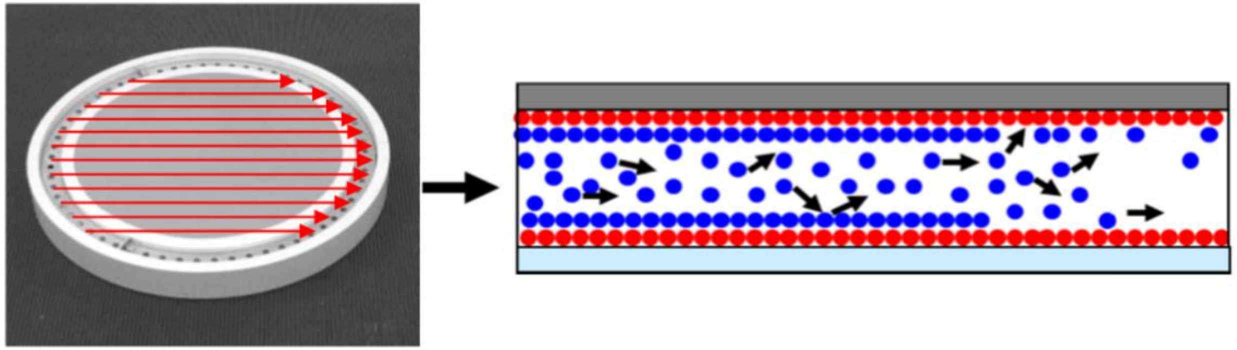
5. Alguns resultados recentes do grupo

Desenvolvimento de reator ALD térmico tipo fluxo cruzado

Homemade cross-flow ALD reactor



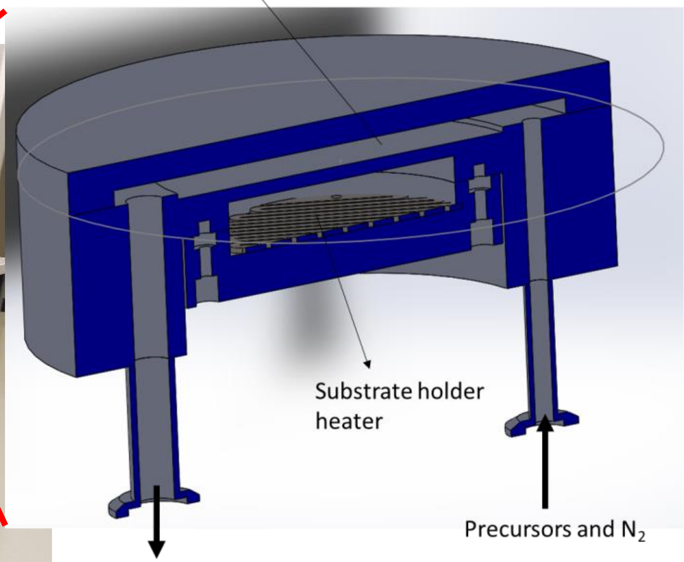




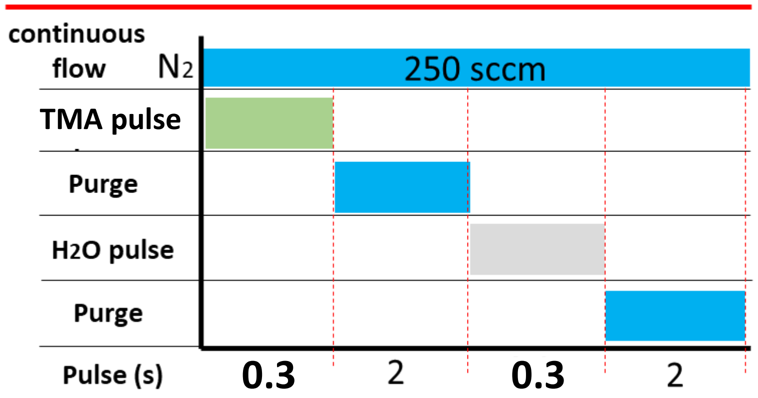
5. Alguns resultados recentes do grupo

Desenvolvimento de reator ALD térmico tipo fluxo cruzado

Homemade cross-flow ALD reactor



Process pressure: 0.8 mbar
Process temperature: 80°-200°C
Total cycle number: 1-1000



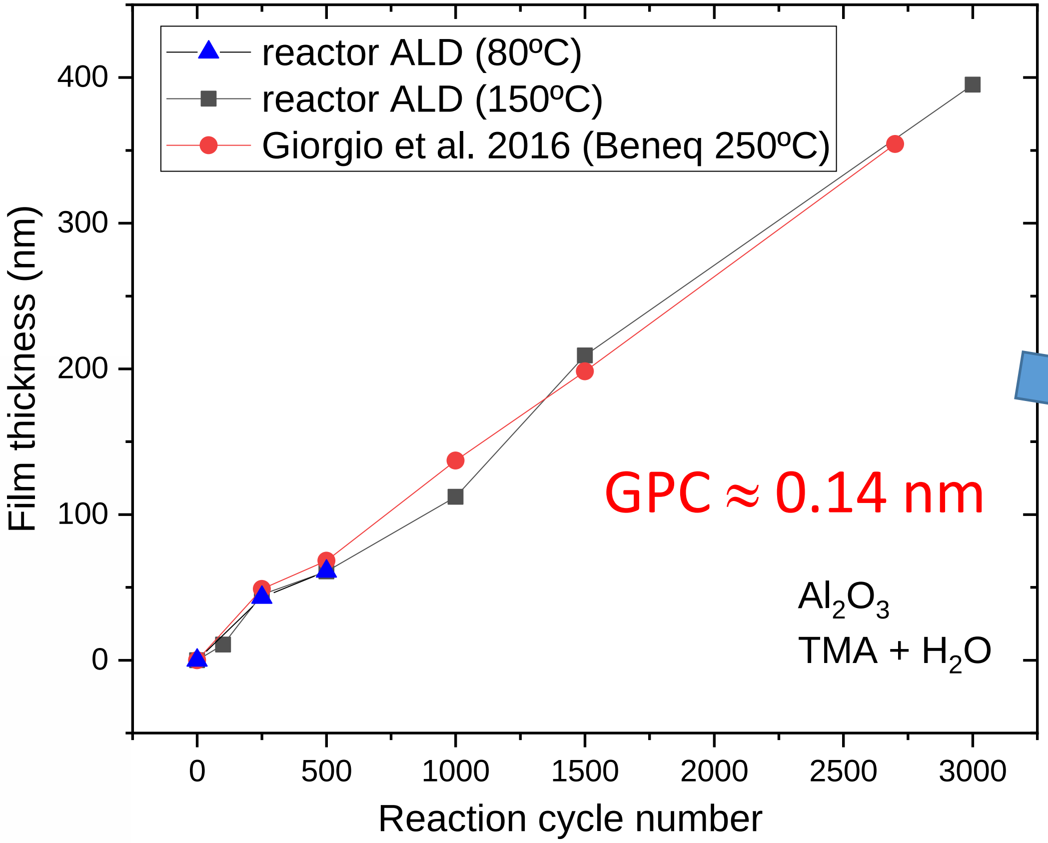
Silicon wafer – 150°C / 1000 cycles

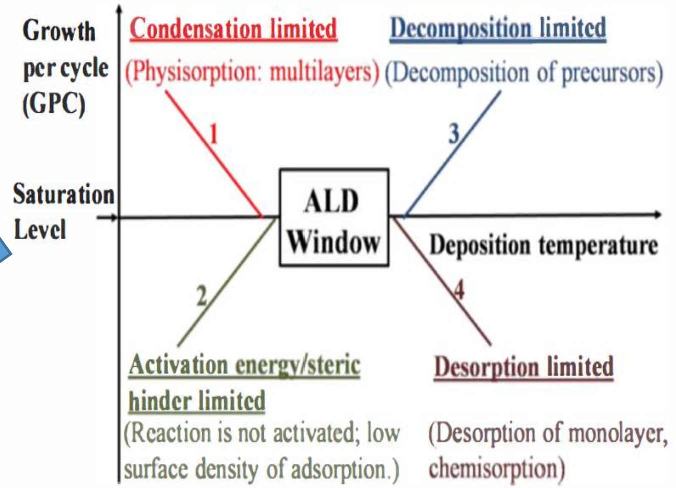
Resultados não publicados

5. Alguns resultados recentes do grupo

Desenvolvimento de reator ALD térmico tipo fluxo cruzado

Film thickness versus reaction cycle number





[6] G. Yuan et al., A Brief Overview of Atomic Layer Deposition and Etching in the Semiconductor Processing, *17th International Conference on Electronic Packaging Technology*, **2016**.

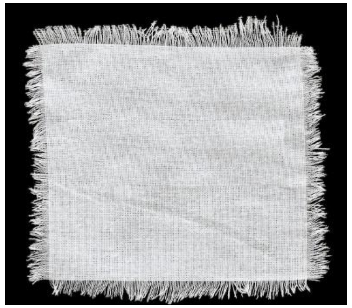
[5] G. E. Testoni et al., Influence of the Al_2O_3 partial-monolayer number on the crystallization mechanism of TiO_2 in ALD TiO_2/Al_2O_3 nanolaminates and its impact on the material properties, *Journal of Physics D: Applied Physics*, **2016**, 49, 375301.

Resultados não publicados

5. Alguns resultados recentes do grupo

Recobrimento de máscaras de TNT com filmes de ALD Al_2O_3

Atomic layer deposition of fabrics

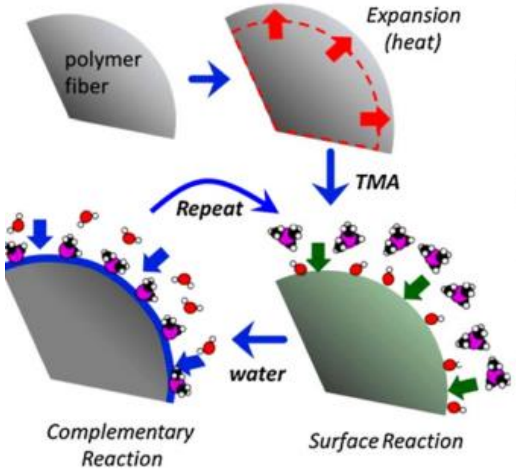


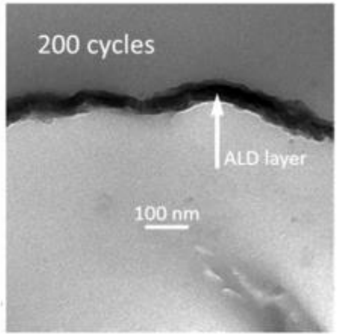
Textile material

ALD process

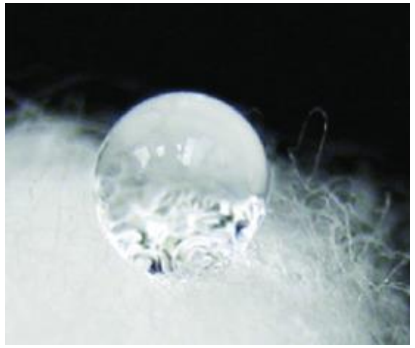
Material is grown at a controlled atomic level and conform

Textile covered with nanomaterial





Surface functionalization

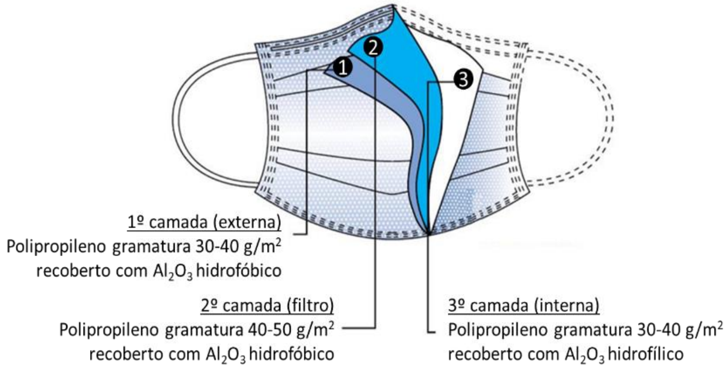


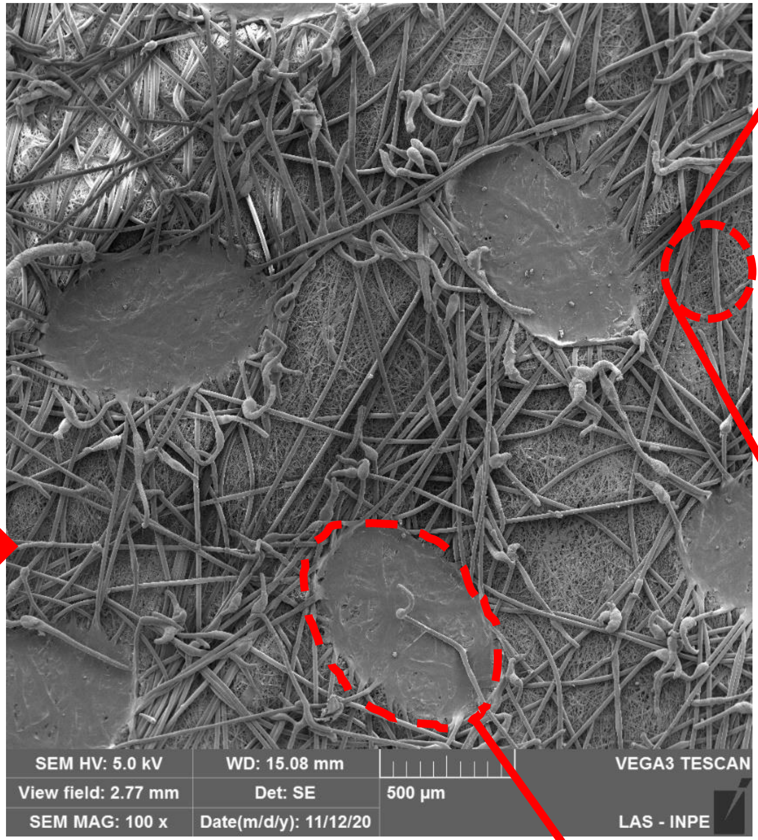
[3] A. H. Brozena et al., Atomic layer deposition on polymer fibers and fabrics for multifunctional and electronic textiles, J. Vac. Sci. Technol. A **2016**, 34, 010801.

5. Alguns resultados recentes do grupo

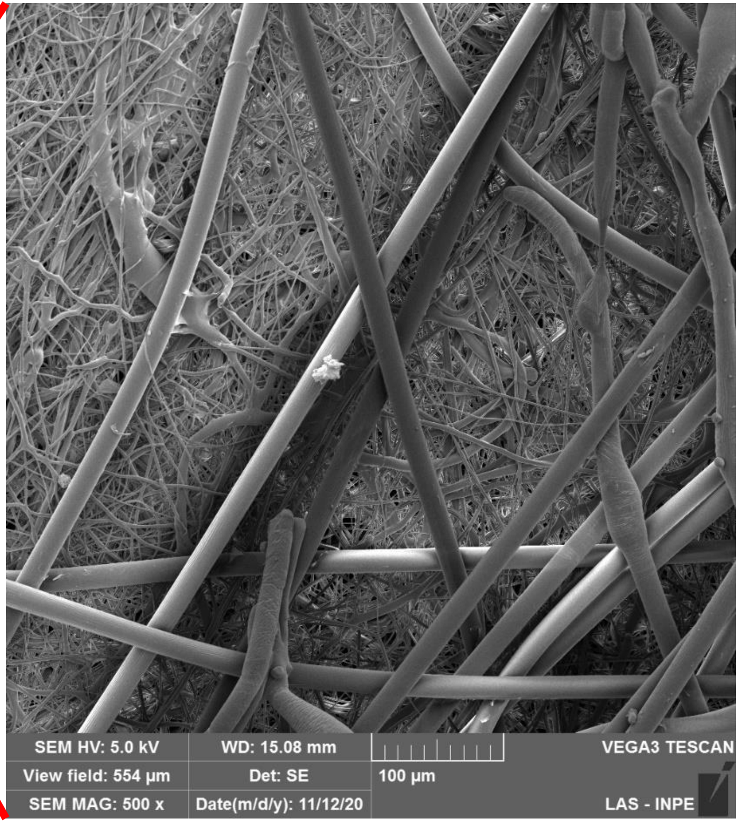
Recobrimento de máscaras de TNT com filmes de ALD Al_2O_3

TNT substrate morphology





Melted fibers



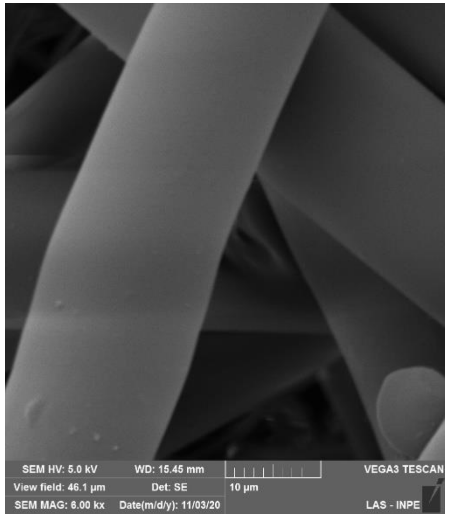
Spun fibers

Resultados não publicados

5. Alguns resultados recentes do grupo

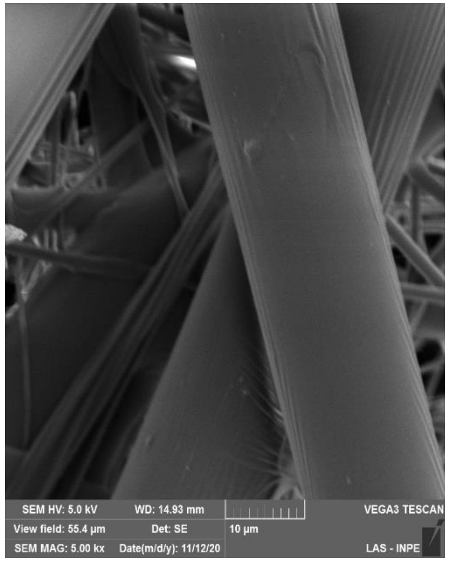
Recobrimento de máscaras de TNT com filmes de ALD Al_2O_3

Al_2O_3-coated TNT morphology

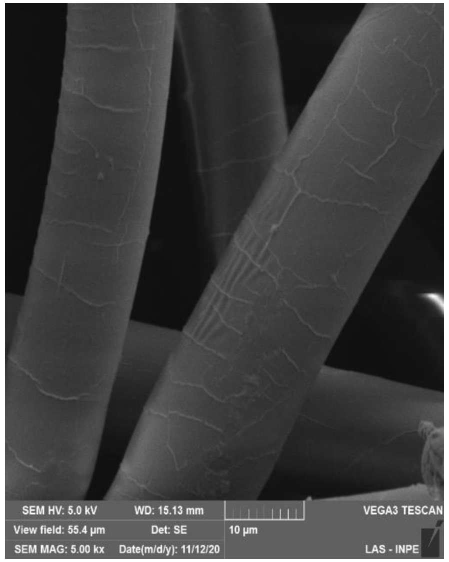


TNT control

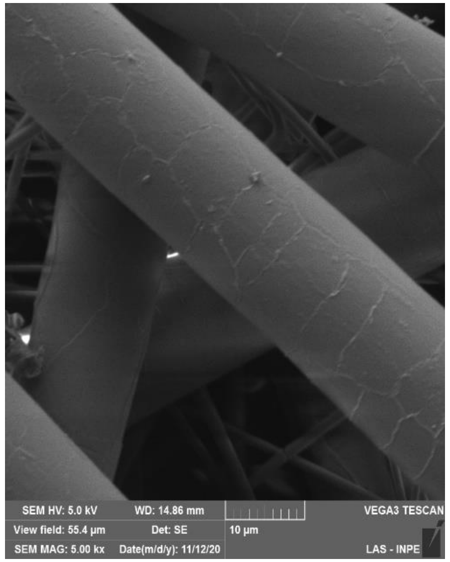
50 cycles



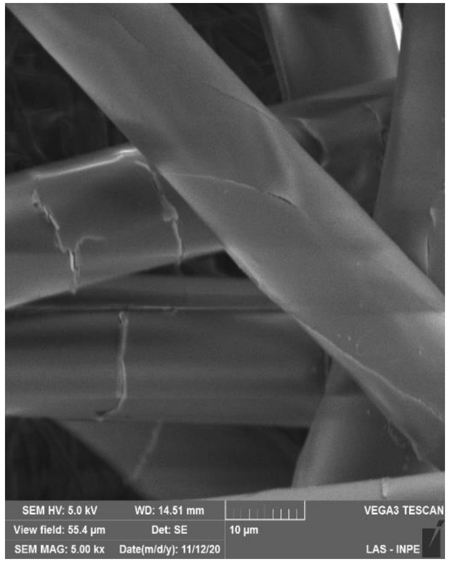
250 cycles



500 cycles



1000 cycles

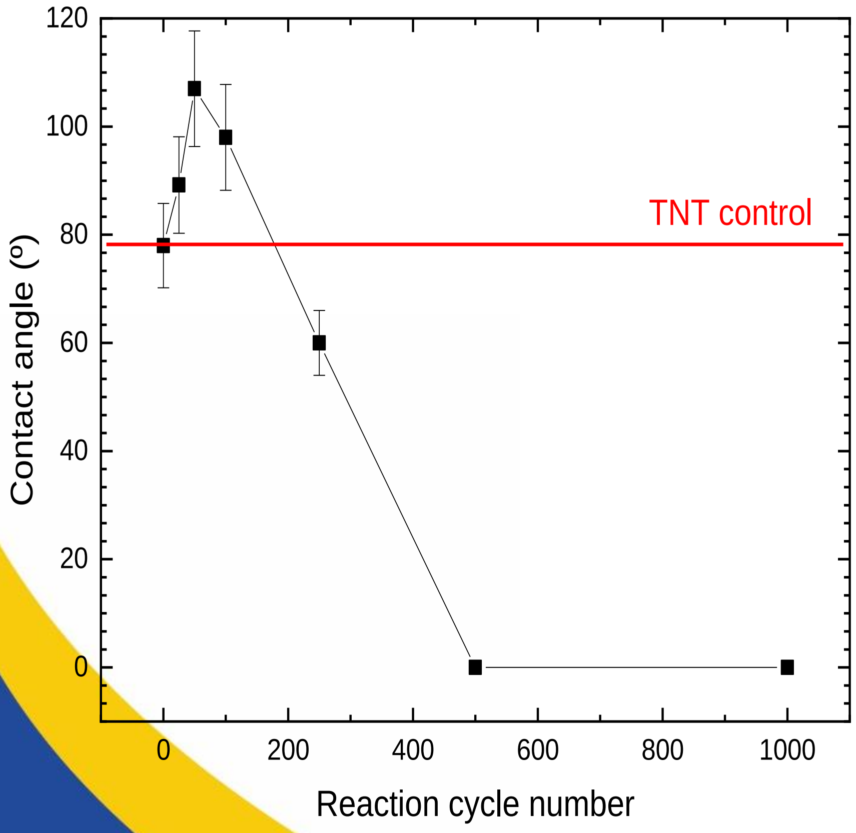


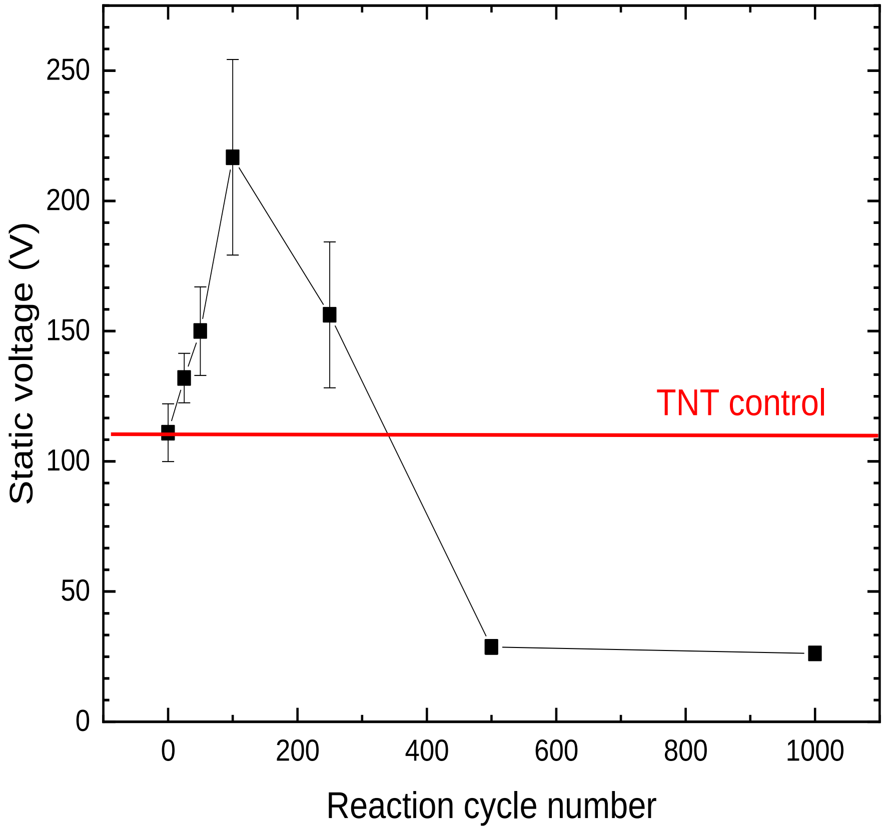
Resultados não publicados

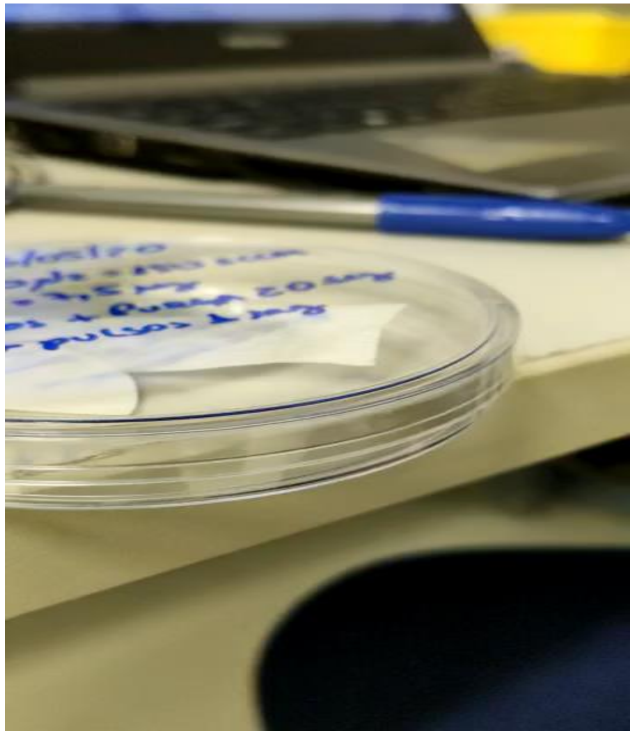
5. Alguns resultados recentes do grupo

Recobrimento de máscaras de TNT com filmes de ALD Al_2O_3

Contact angle & Electrostatic analysis





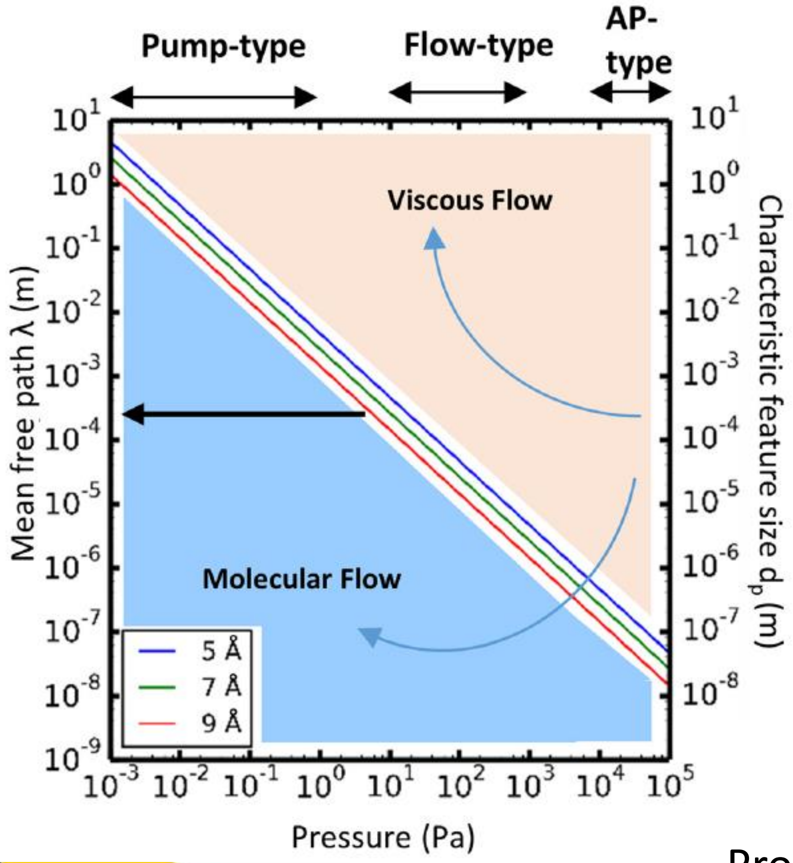


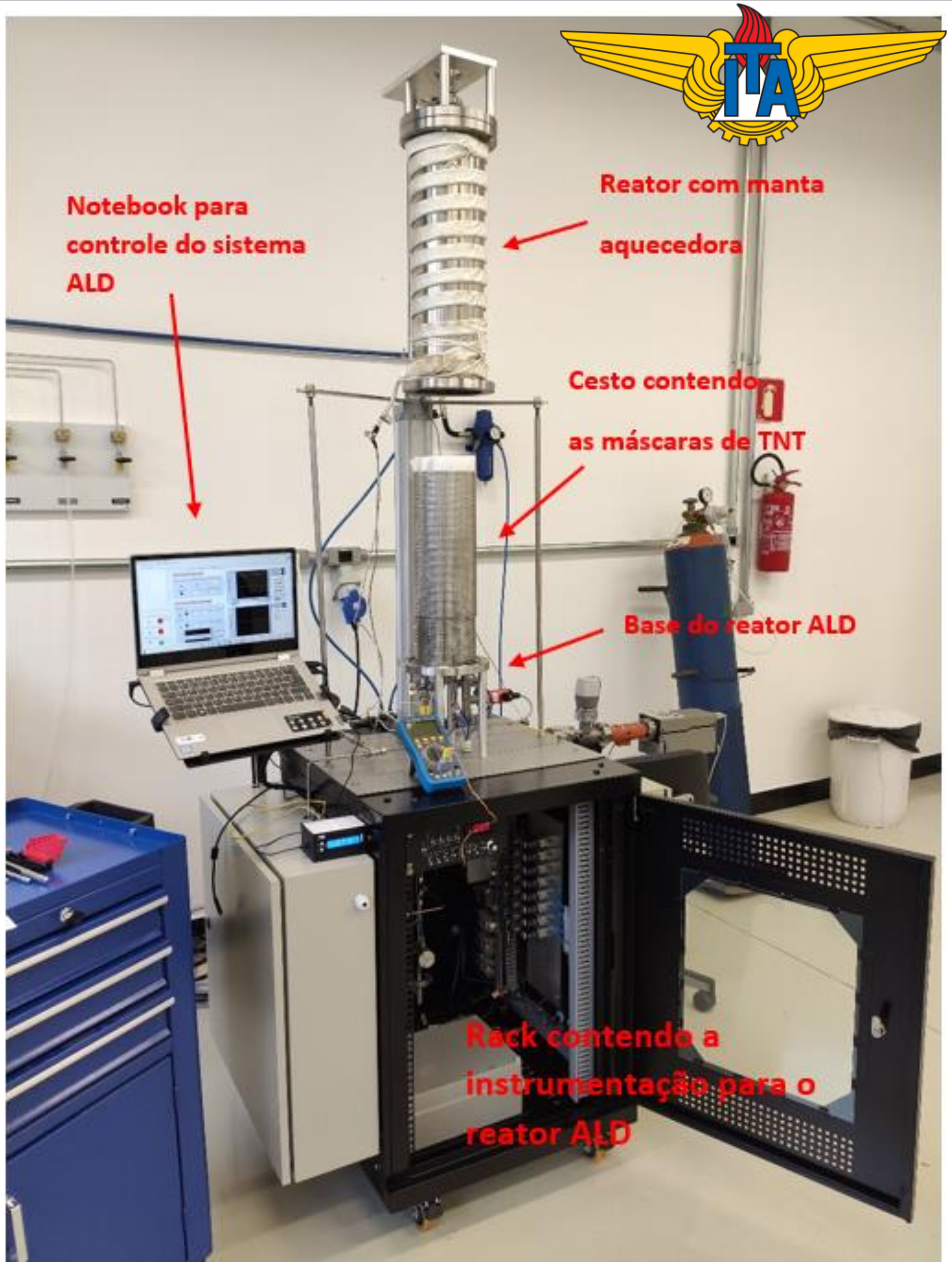
Resultados não publicados

5. Alguns resultados recentes do grupo

Desenvolvimento de reator ALD térmico tipo fluxo viscoso

V. Cremers, R.L. Puurunen, J. Dendooven, Appl. Phys. Rev. 6, 021302 (2019).

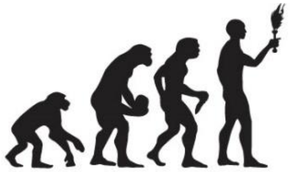


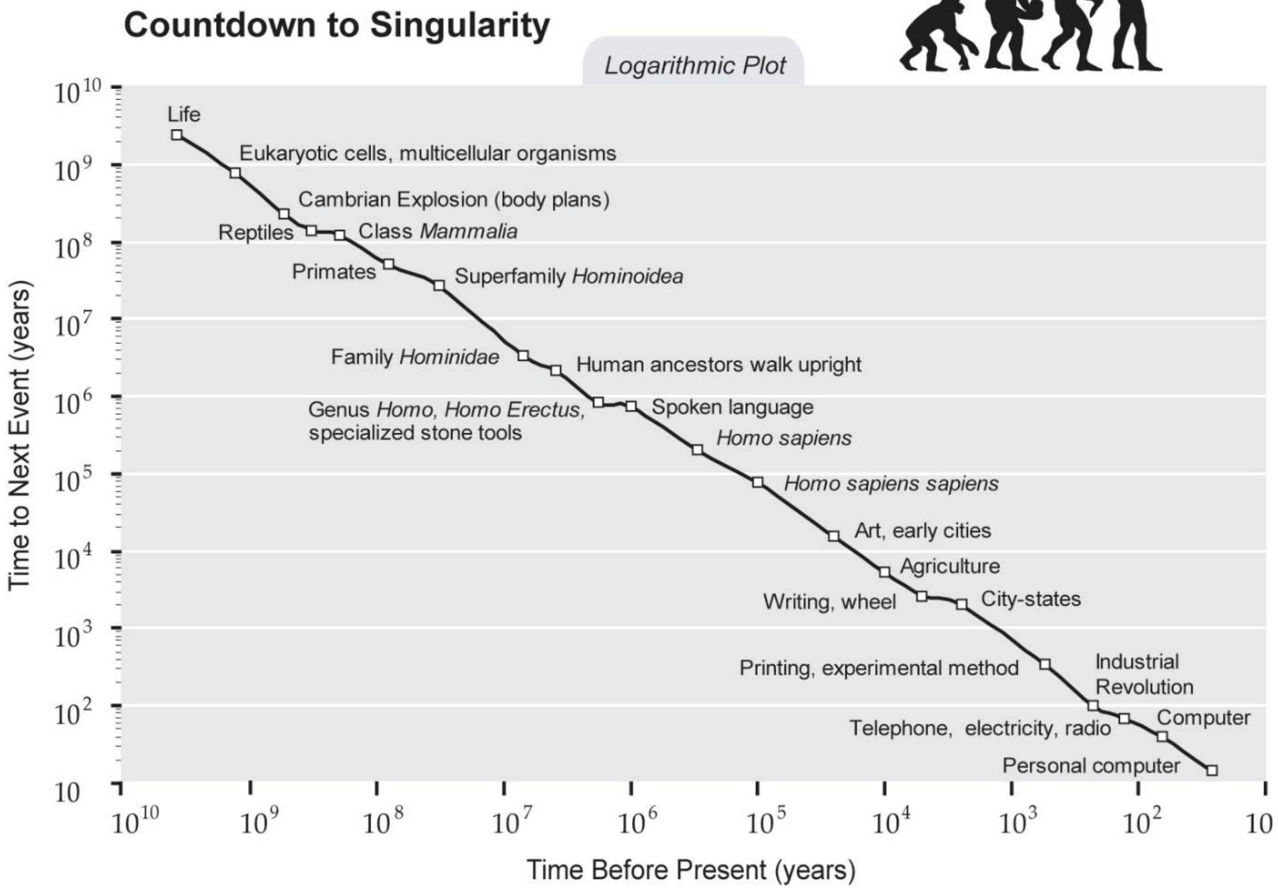


Projeto DEMP-COVID-ITA
Ministério Público do Trabalho

6. Considerações finais

http://www.atomiclimits.com/2017/07/03/the-dawn-of-atomic-scale-processing-the-growing-importance-of-atomic-layer-deposition-and-etching/





Obrigado!

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