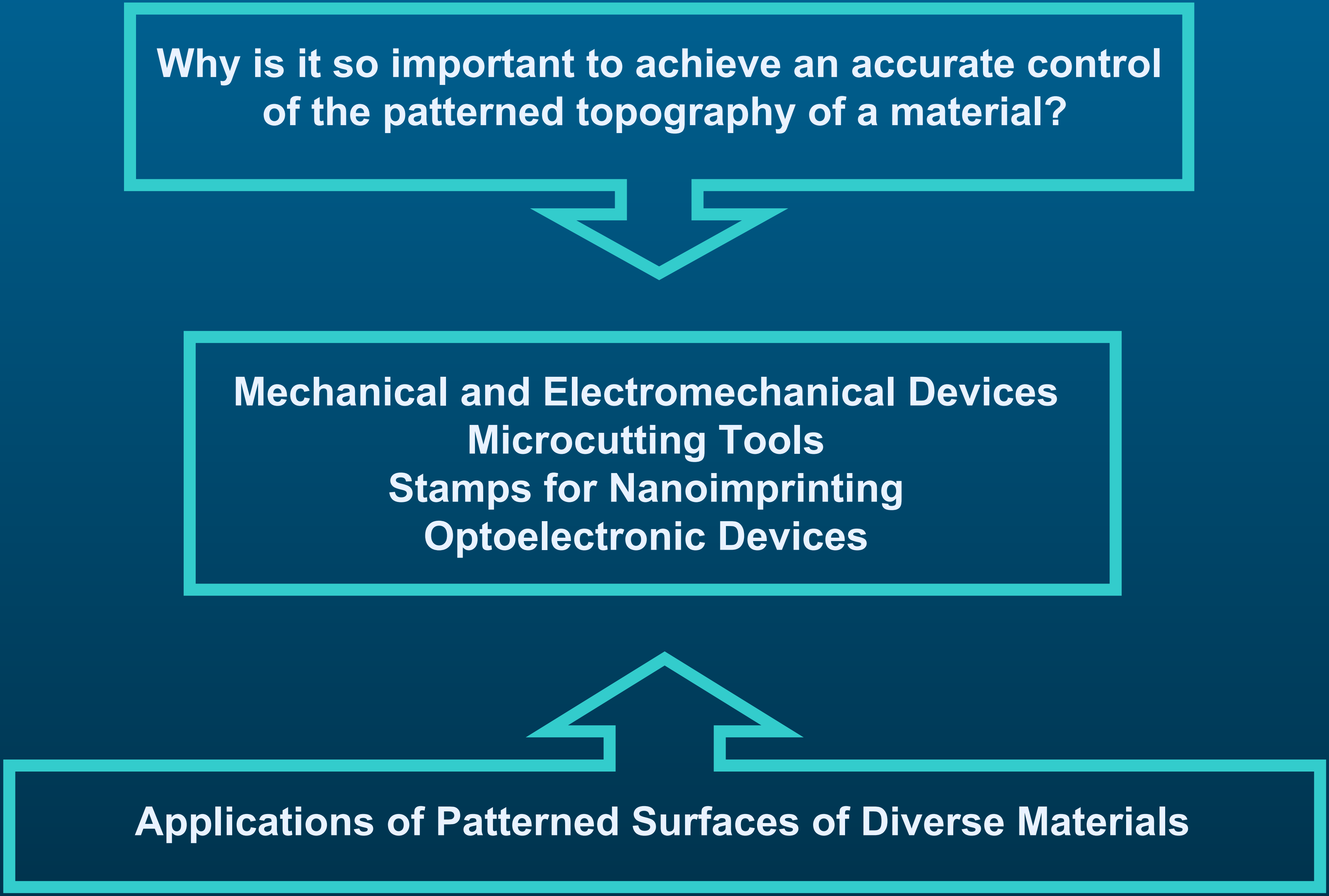
Surface Patterning of MEMS-Related Materials

Omar Azzaroni

Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas
Universidad Nacional de La Plata – CONICET – Argentina

Pan-American Advanced Studies Institute on MicroElectroMechanical Systems
San Carlos de Bariloche, 21-30 June – Patagonia – Argentina



Why is it so important to achieve an accurate control of the patterned topography of a material?

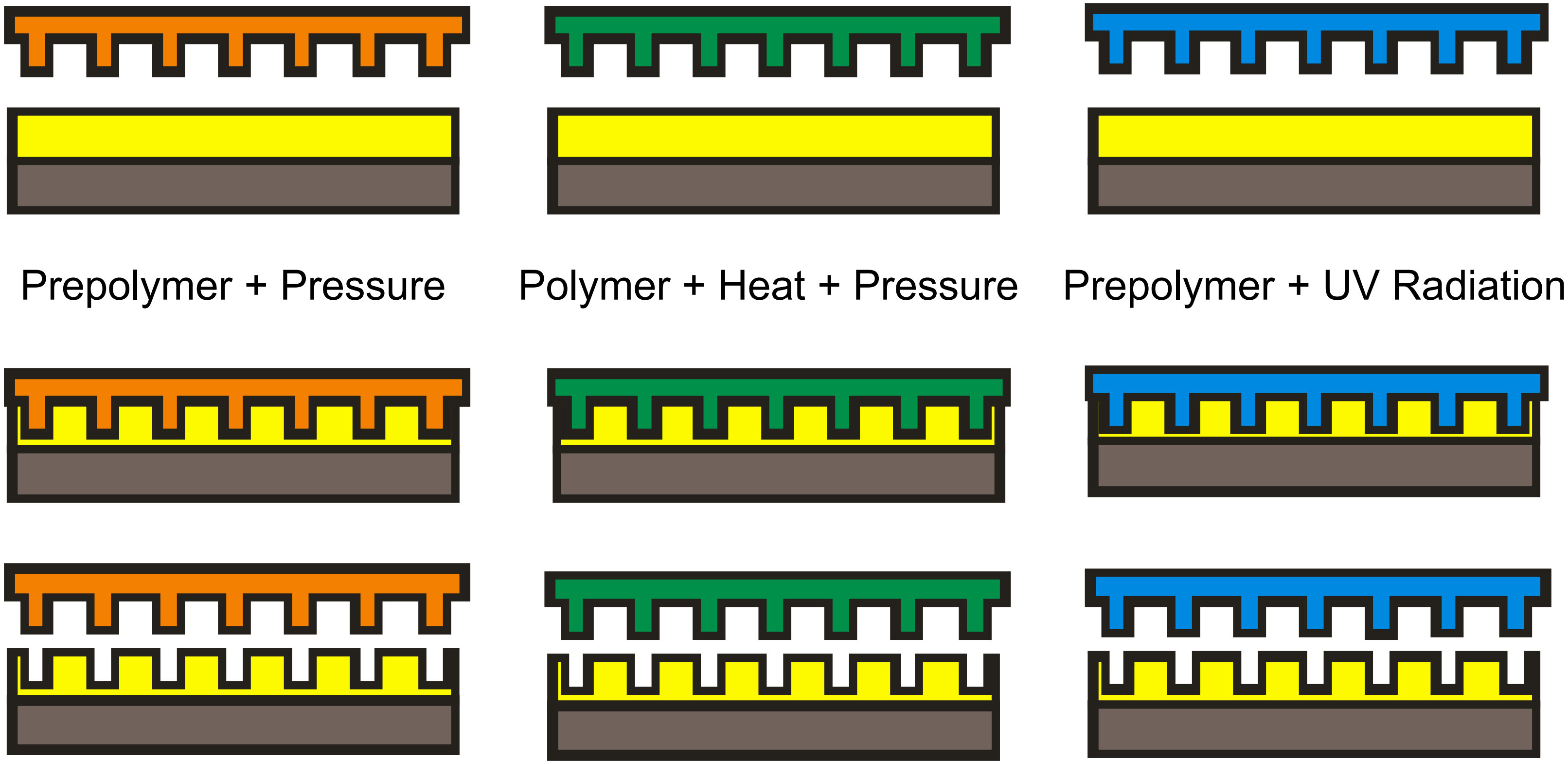
Mechanical and Electromechanical Devices
Microcutting Tools
Stamps for Nanoimprinting
Optoelectronic Devices

Applications of Patterned Surfaces of Diverse Materials

- Lithographic Techniques
  - E-Beams
  - Ion Beams
  - UV Radiation
  - X-Rays
- Micro-Nanofabrication Alternative Methods
  - Soft Lithography
  - Nanoimprinting
  - Scanning Probe Lithography

Some alternative patterning methods:

- Scanning Probe Microscopy
- Metastable Ions
- Femtosecond laser pulses
- Laser-focused deposition
- Laser-assisted direct imprinting
- Soft Lithography



PDMS stamp

Silicon stamp

Quartz stamp

Prepolymer + Pressure

Polymer + Heat + Pressure

Prepolymer + UV Radiation

Soft Lithography

Nanoimprint Lithography

Step and Flash Lithography

Soft Lithographic Techniques

Replica Molding

Microtransfer Molding

Micromolding in Capillaries

Solvent-Assisted Micromolding

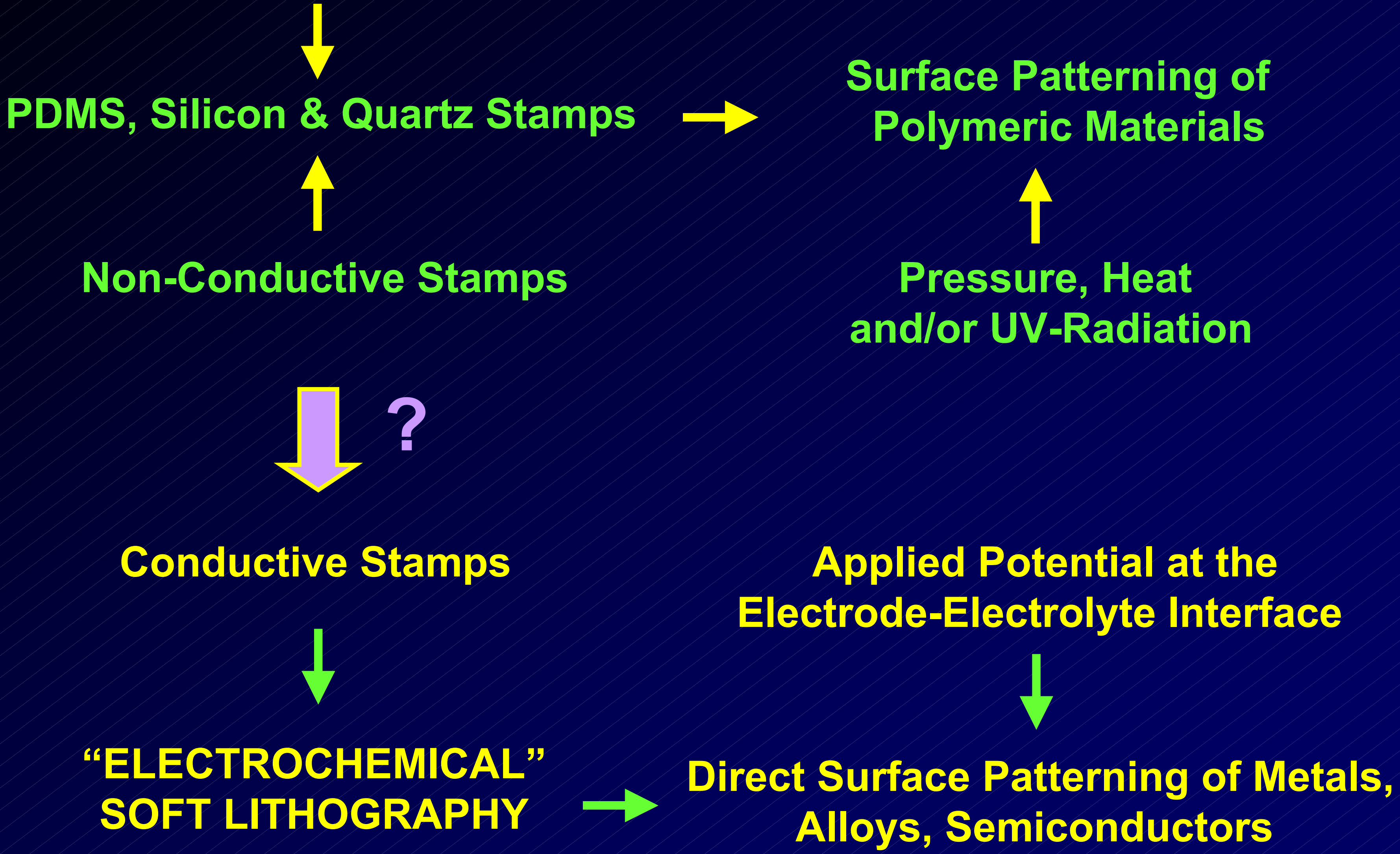
Microcontact Printing

Nanotransfer Printing

Nanoimprint Lithography

Step and Flash Imprint Lithography

SOFT LITHOGRAPHIC TECHNIQUES



PDMS, Silicon & Quartz Stamps

Non-Conductive Stamps

Surface Patterning of Polymeric Materials

Pressure, Heat
and/or UV-Radiation

?

Conductive Stamps

"ELECTROCHEMICAL"
SOFT LITHOGRAPHY

Applied Potential at the
Electrode-Electrolyte Interface

Direct Surface Patterning of Metals,
Alloys, Semiconductors

Molding Strategies…Why?

Simple

High Throughput

Replica-Molding Approach

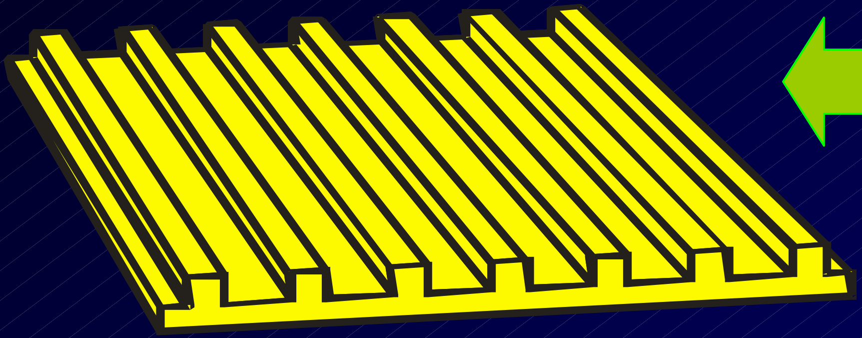
Low Cost

Holograms, Compact Disks, Diffraction Gratings

SURFACE-CHEMISTRY RELATED PROBLEMS

~~DIRECT ELECTROCHEMICAL DEPOSITION ONTO THE METALLIC STAMP~~

STRONG ADHESION TO THE METALLIC STAMP !!!

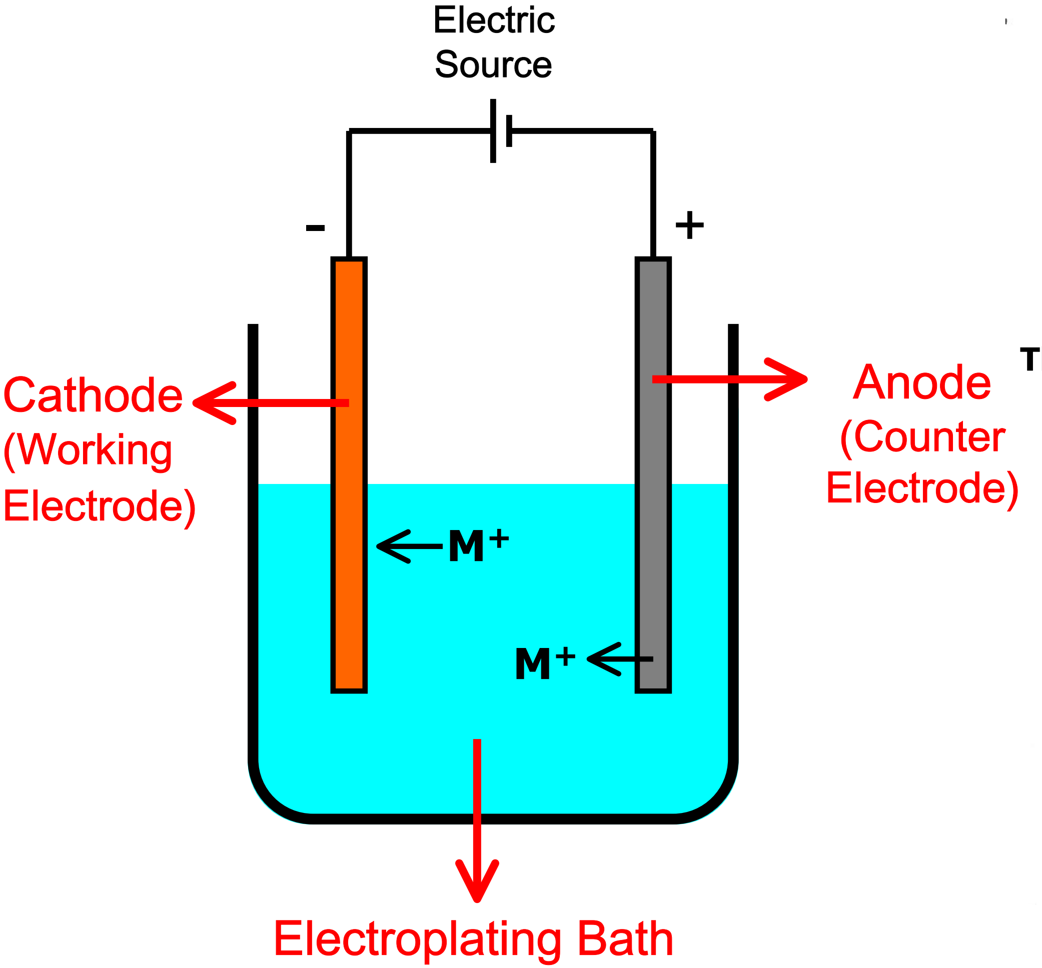


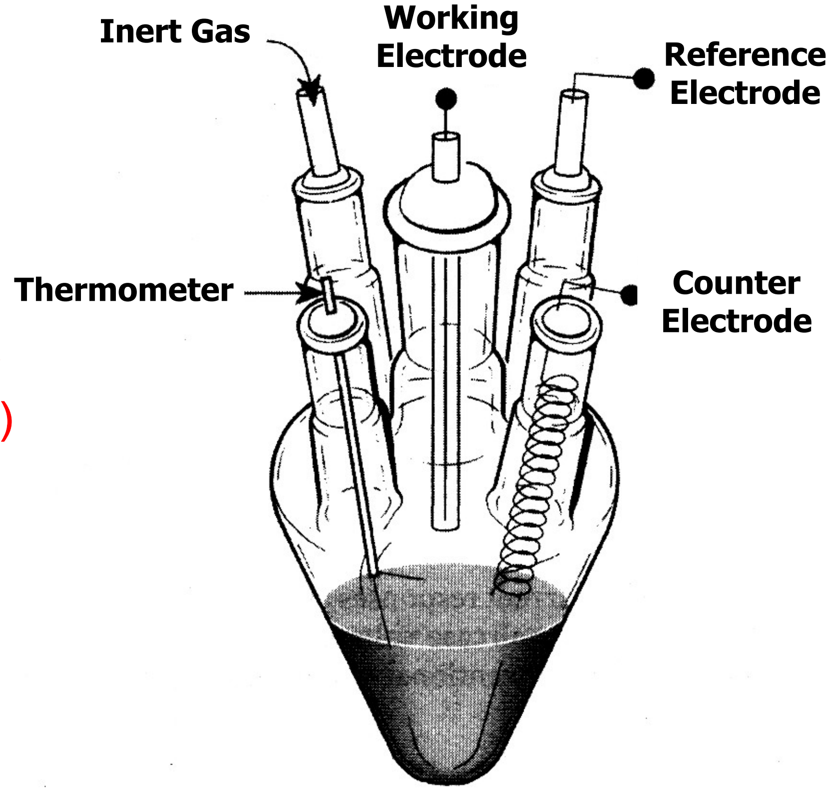
SELF-ASSEMBLED MONOLAYERS ARE USED AS ANTI-ADHESIVE COATINGS

CONDUCTIVE STAMP

ELECTROCHEMICAL DEPOSITION IN PRESENCE OF SELF-ASSEMBLED MONOLAYERS

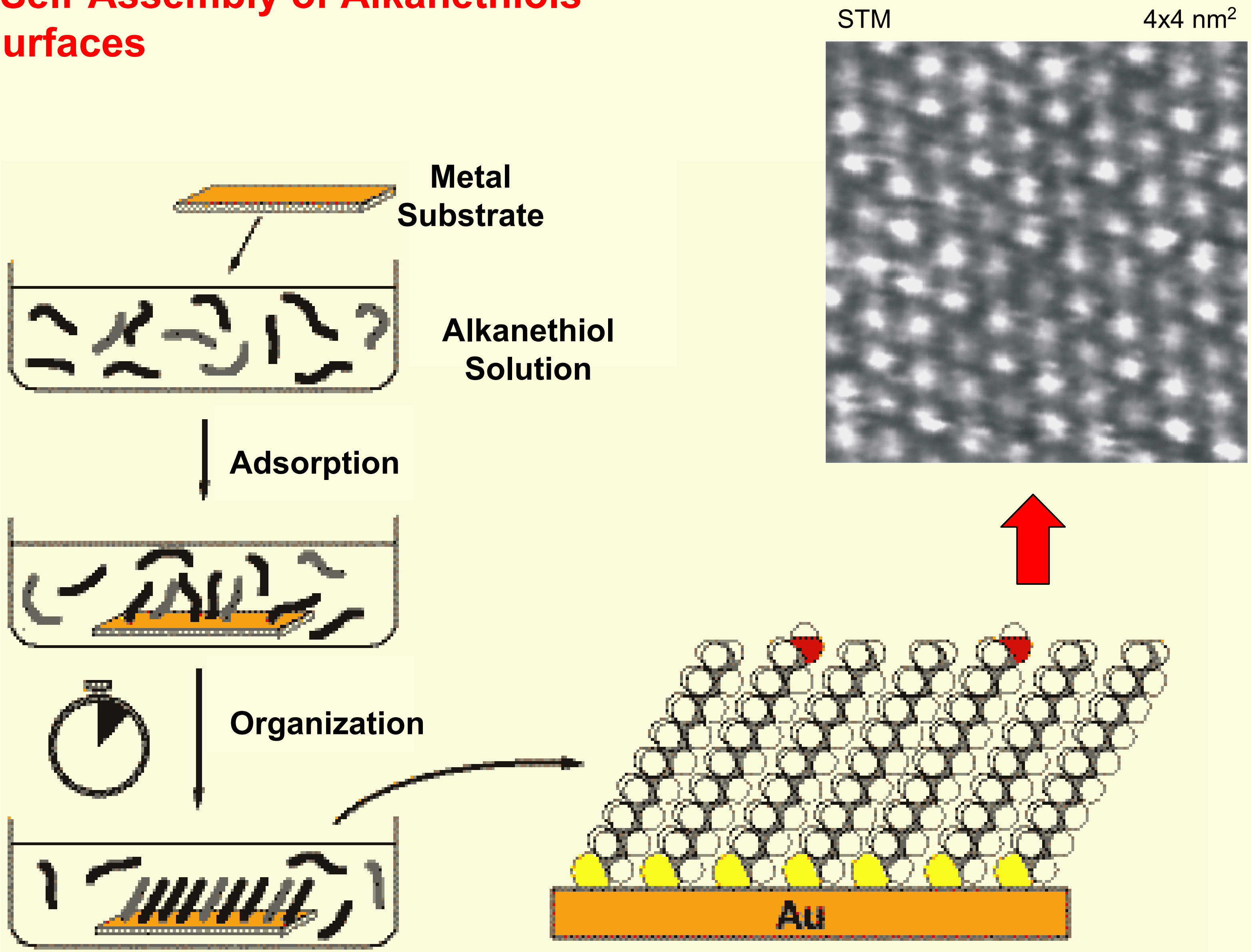
Electrochemical Deposition - Electroplating





Conventional Electrochemical Cell

Molecular Self-Assembly of Alkanethiols on Metal Surfaces



STM

4x4 nm^2

Metal Substrate

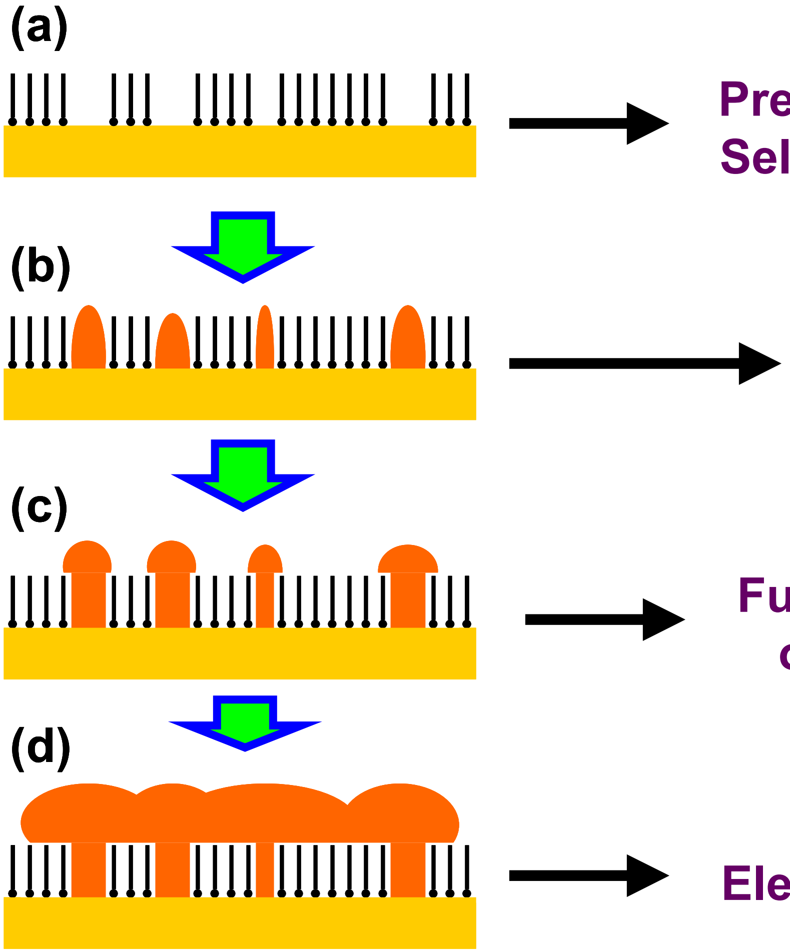
Alkanethiol Solution

Adsorption

Organization

O.Azzaroni, M.E. Vela, H. Martín, A. Hernández-Creus, G. Andreasen and R.C. Salvarezza, Langmuir 17 (2001) 6647

Mechanism of Electrodeposition onto SAMs



Presence of Defects on the Self-Assembled Monolayer

Nucleation on the Defective Sites

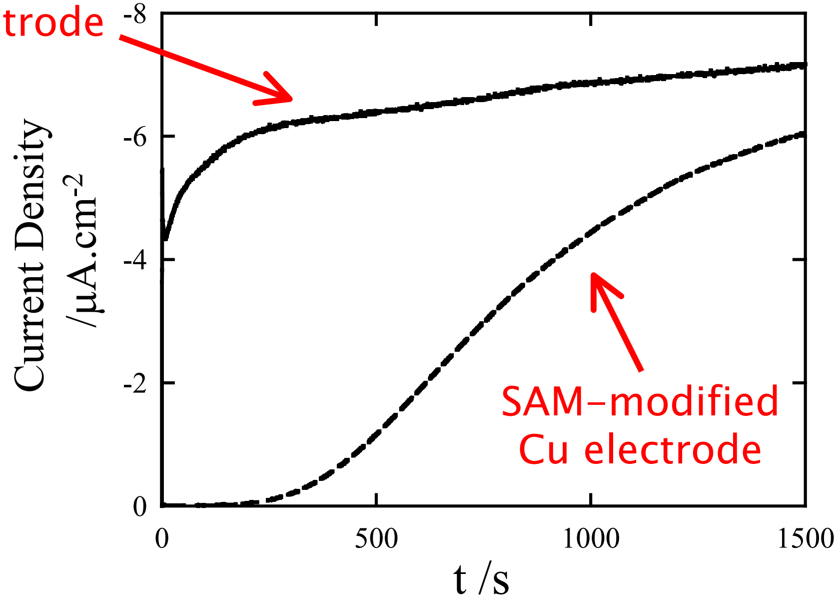
Further Growth of the Electrodeposit on the Self-Assembled Monolayer

Electroformation of a Continuous Film

P.L. Schilardi, O. Azzaroni and R.C. Salvarezza, Langmuir 17 (2001) 2748

Metal Electrodeposition onto Self-Assembled Monolayers

Potential-Controlled Electrodeposition

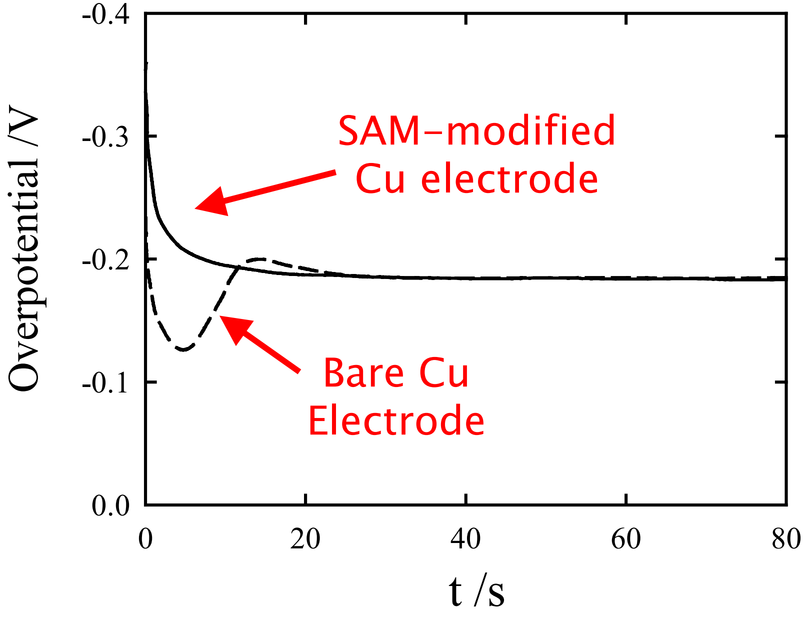


Bare Cu Electrode

SAM−modified Cu electrode

$\eta = -90$mV
Electrolyte: $CuSO_4.5H_2O$ 0,6 M + H_2SO_4 0,5 M

Current-Controlled Electrodeposition



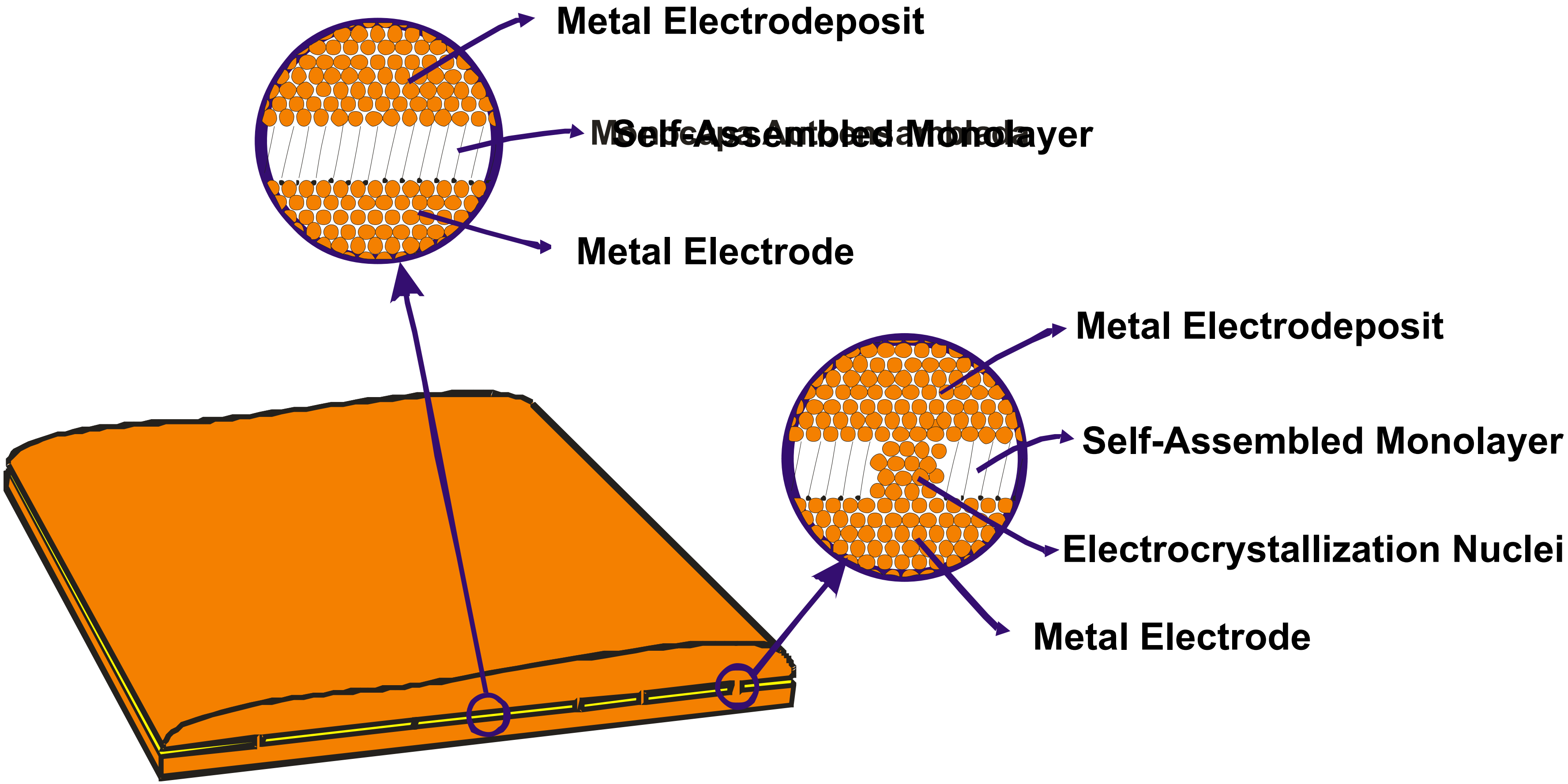
SAM−modified Cu electrode

Bare Cu Electrode

$j = -20$ mA.cm^{-2}
Electrolyte: $CuSO_4.5H_2O$ 0,6 M + H_2SO_4 0,5 M

O. Azzaroni, P.L. Schilardi and R.C. Salvarezza, Electrochim.Acta 48 (2003) 457

Electrodeposit-SAM-Electrode Interface



Metal Electrodeposit

Self-Assembled Monolayer

Metal Electrode

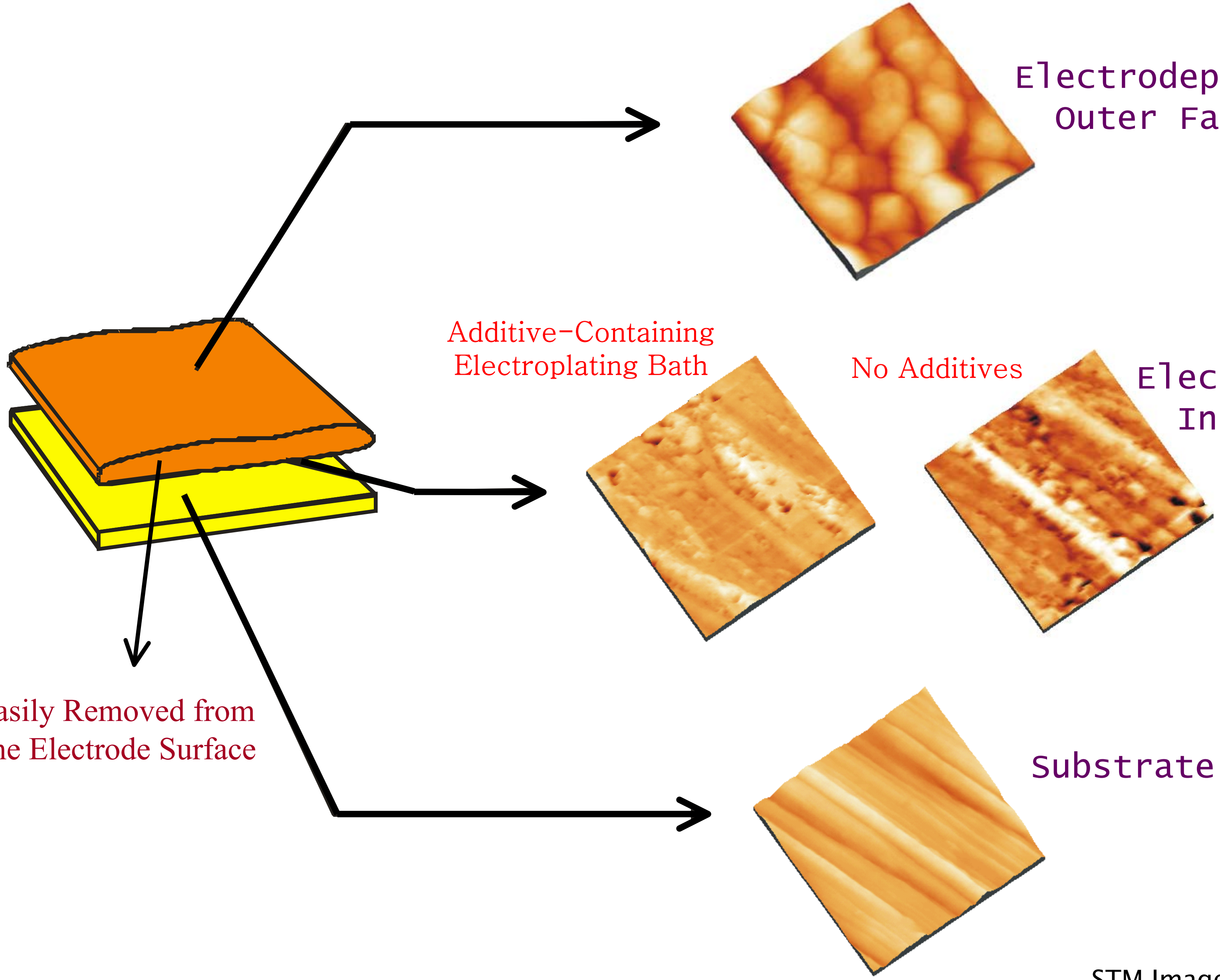
Metal Electrodeposit

Self-Assembled Monolayer

Electrocrystallization Nuclei

Metal Electrode

Adhesive Properties of the Electrodeposits in Presence of SAMs



Electrodeposit
Outer Face

Additive-Containing
Electroplating Bath

No Additives

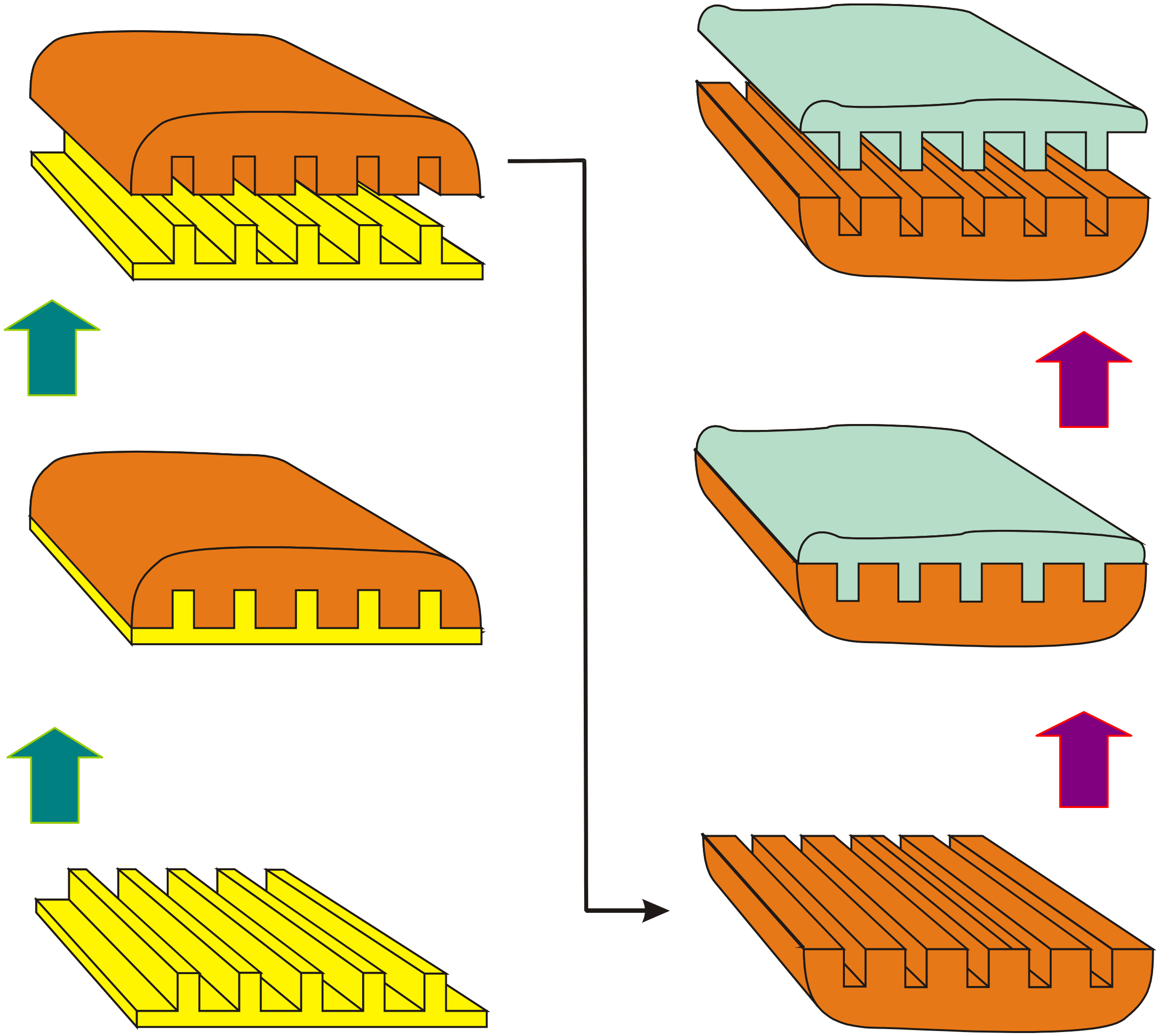
Electrodeposit
Inner Face

Easily Removed from
the Electrode Surface

Substrate

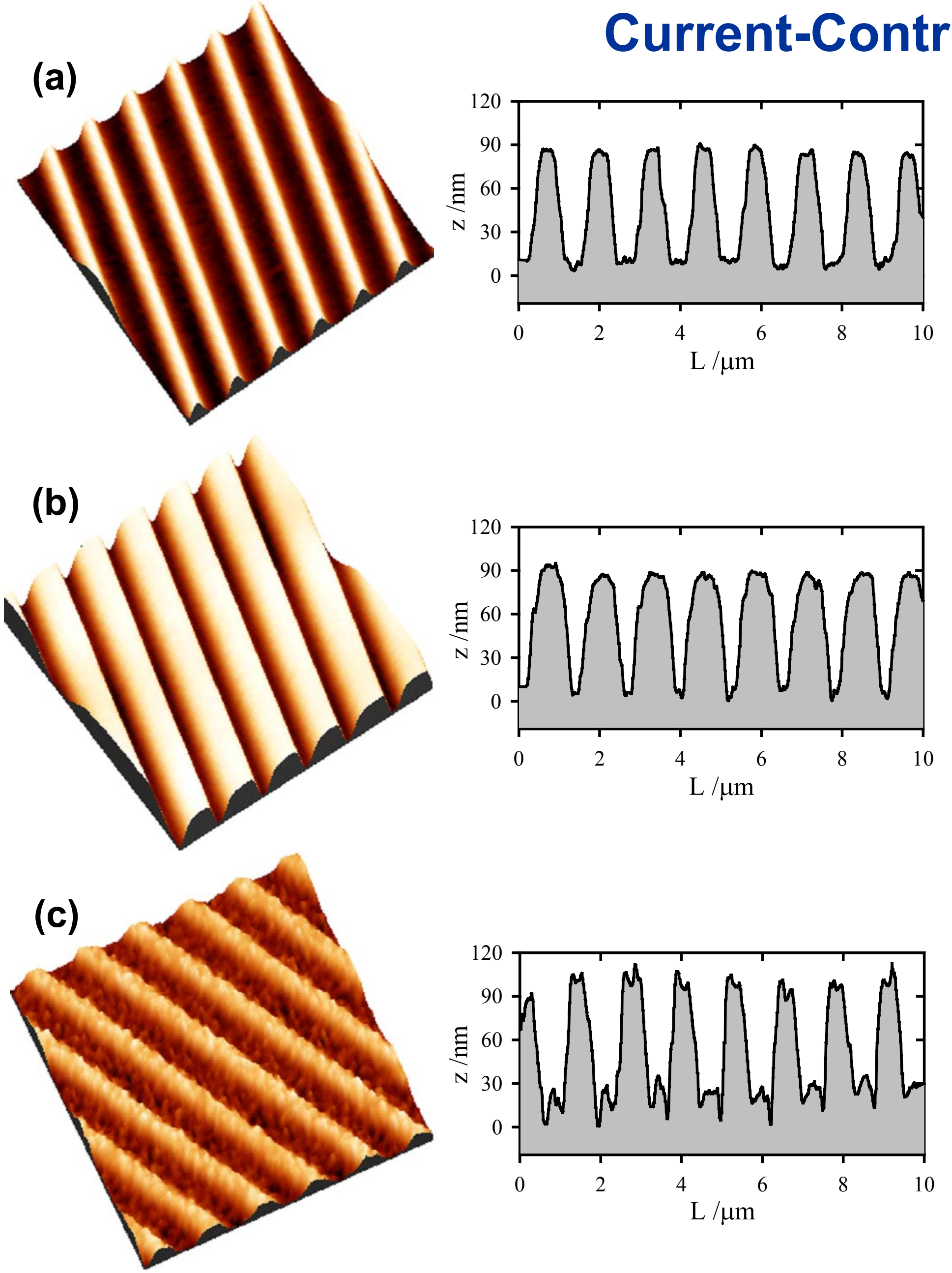
STM Images (10 x 10 μm^2)

Electrochemical Replica-Molding



O. Azzaroni, P.L. Schilardi and R.C. Salvarezza, “Encyclopedia of Nanoscience and Nanotechnology”, edited by H.S. Nalwa (ASP, California, 2004)

Current-Controlled Cu Electrodeposition



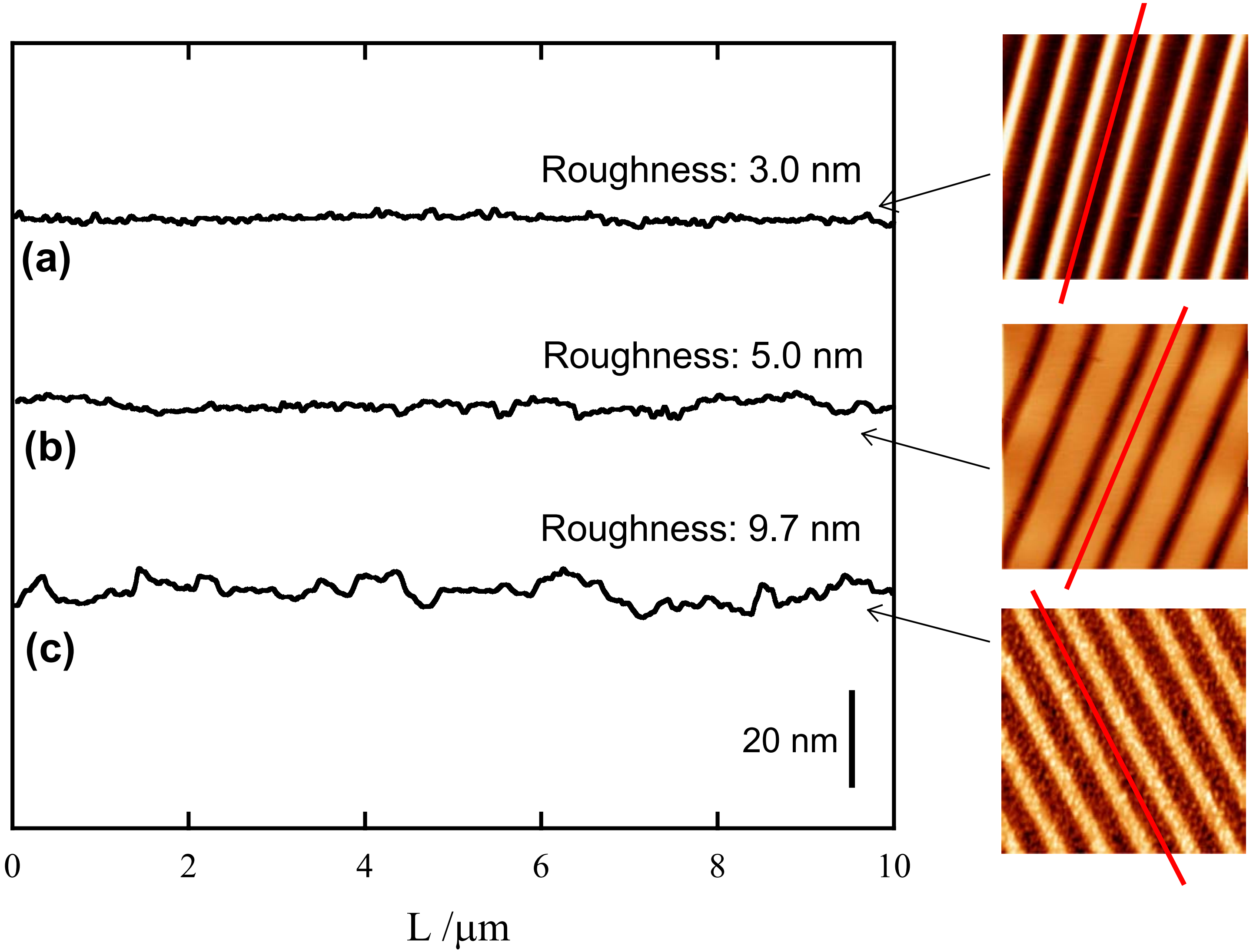
Cu
Stamp

Molded Cu
Surface

Replicated Cu
Surface

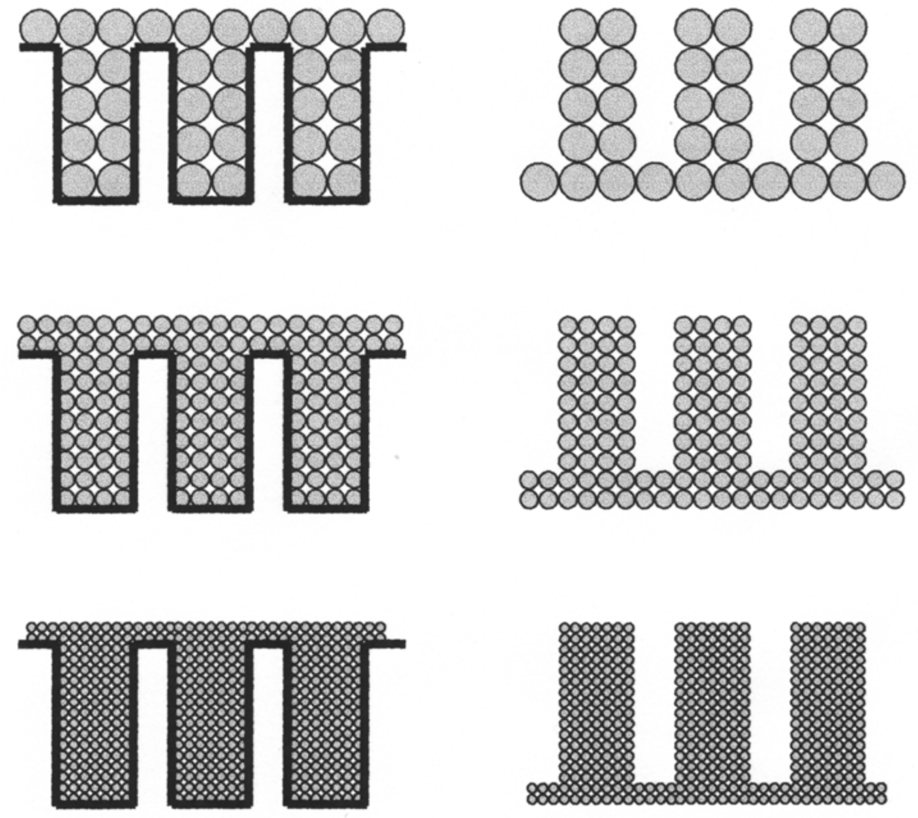
Imágenes STM (10 x 10 μm^2)

Electrochemical Replica-Molding
Roughness Analysis



Electrochemical Replica-Molding at the Microscale

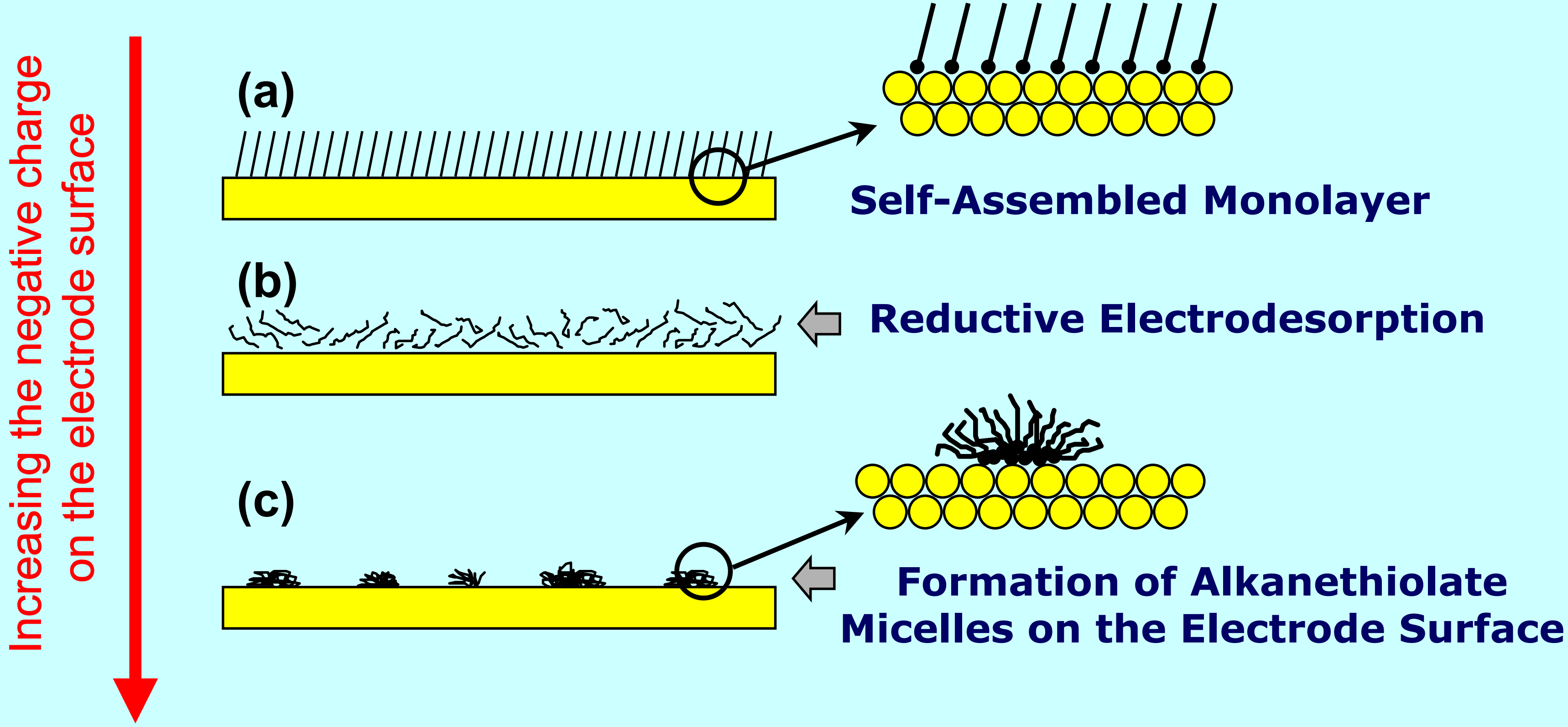
Grain Size Effects



Grain Size and Smoothness Can Be Controlled by Adding Organic Additives to the Electroplating Bath

A. De Virgiliis, O. Azzaroni, R.C. Salvarezza and E.V. Albano, Appl.Phys.Lett. 82 (2003) 1953
P.L. Schilardi, O. Azzaroni and R.C. Salvarezza, Phys.Rev.B 62 (2000) 13098

Electrochemical Stability of the Self-Assembled Monolayer at the Electrode-Electrolyte Interface



Increasing the negative charge on the electrode surface

(a)

Self-Assembled Monolayer

(b)

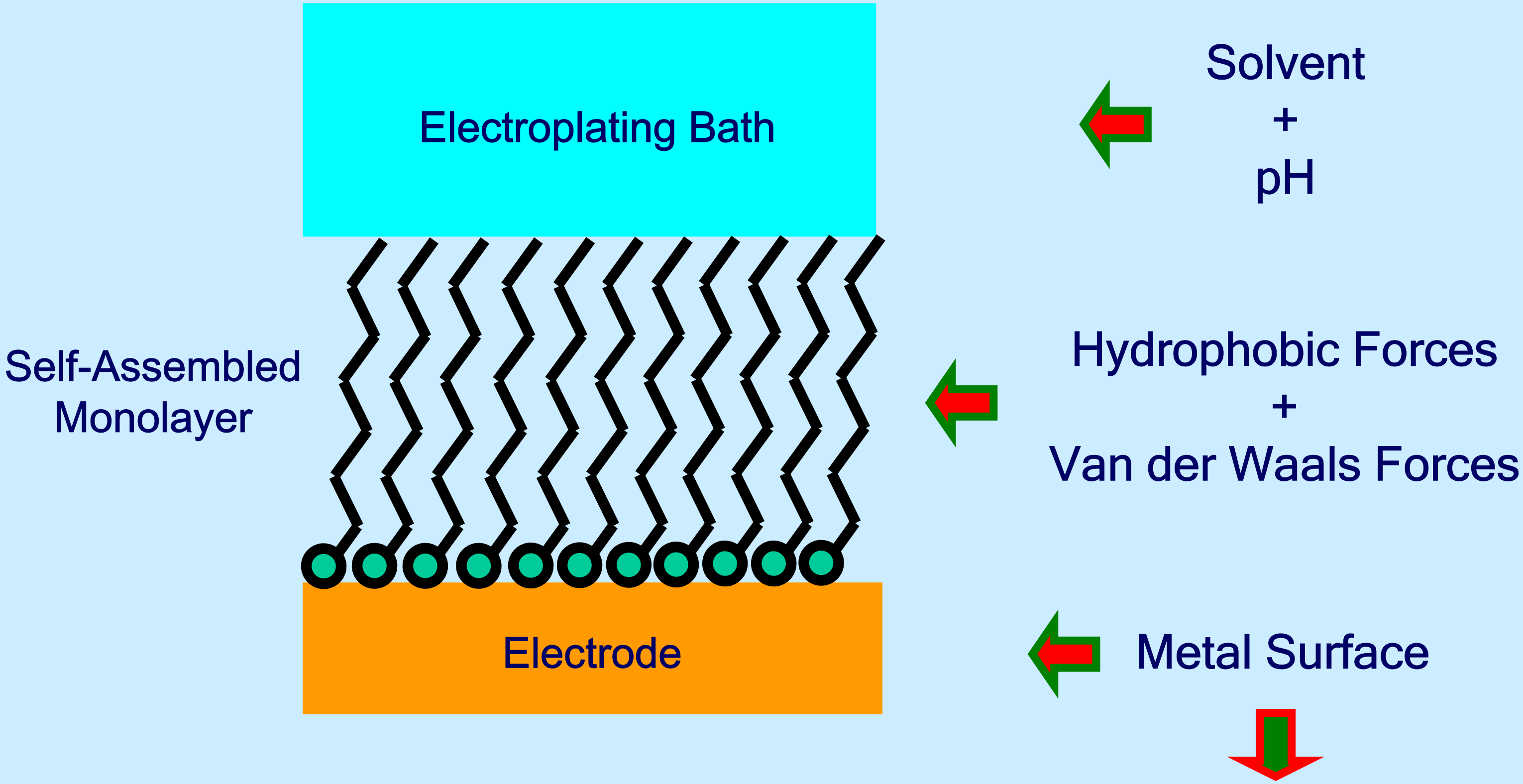
Reductive Electrodesorption

(c)

Formation of Alkanethiolate Micelles on the Electrode Surface

O.Azzaroni, M.E. Vela, G. Andreasen, P. Carro and R.C. Salvarezza, J.Phys.Chem.B 106 (2002) 12267

Main factors ruling the stability of SAMs in electrochemical environments



Solvent
+
pH

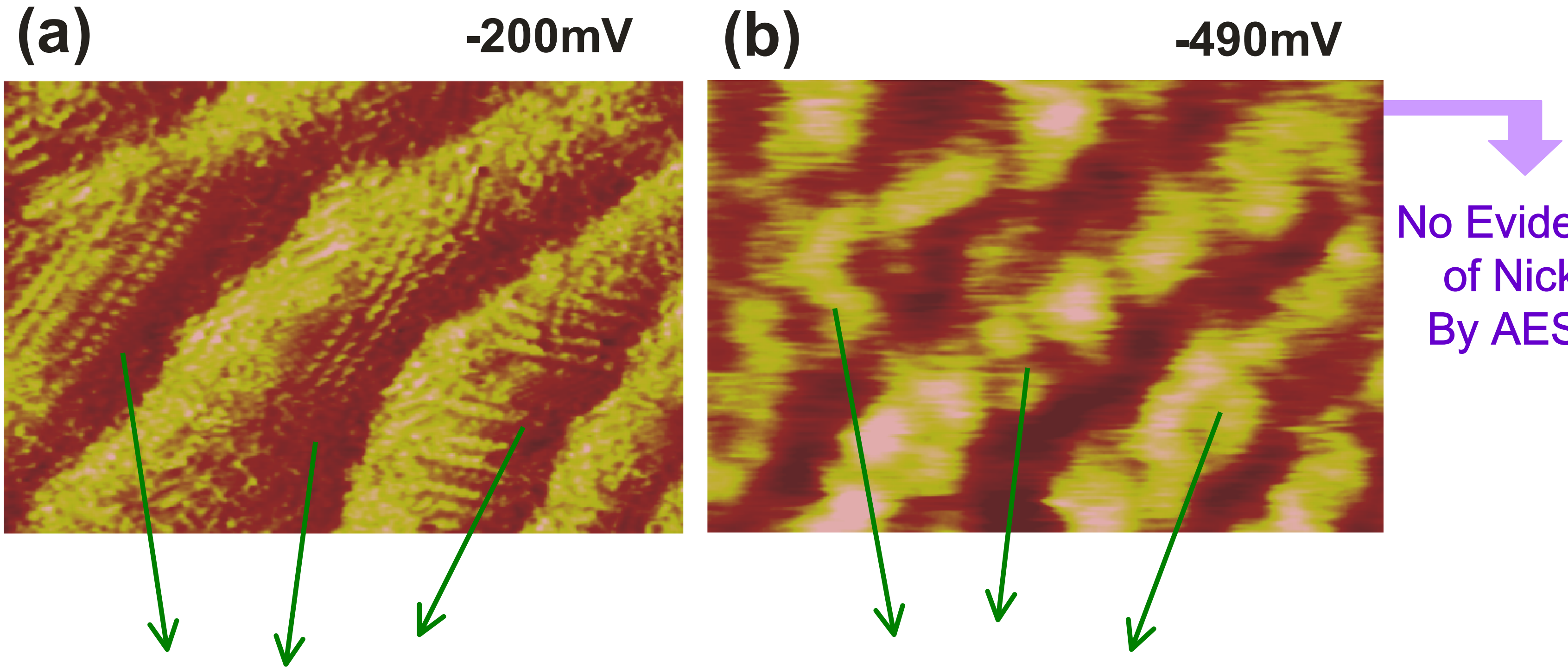
Hydrophobic Forces
+
Van der Waals Forces

Metal Surface

The Electrochemical Stability of SAMs is Extremely Sensitive to the Nature of the Metal Surface !!!

O.Azzaroni, M.E. Vela, M. Fonticelli, B.Blum, G. Benítez, P. Carro and R.C. Salvarezza, J.Phys.Chem.B 107 (2003) 13346

Electrochemical Micromolding → Electrodeposition of Nickel



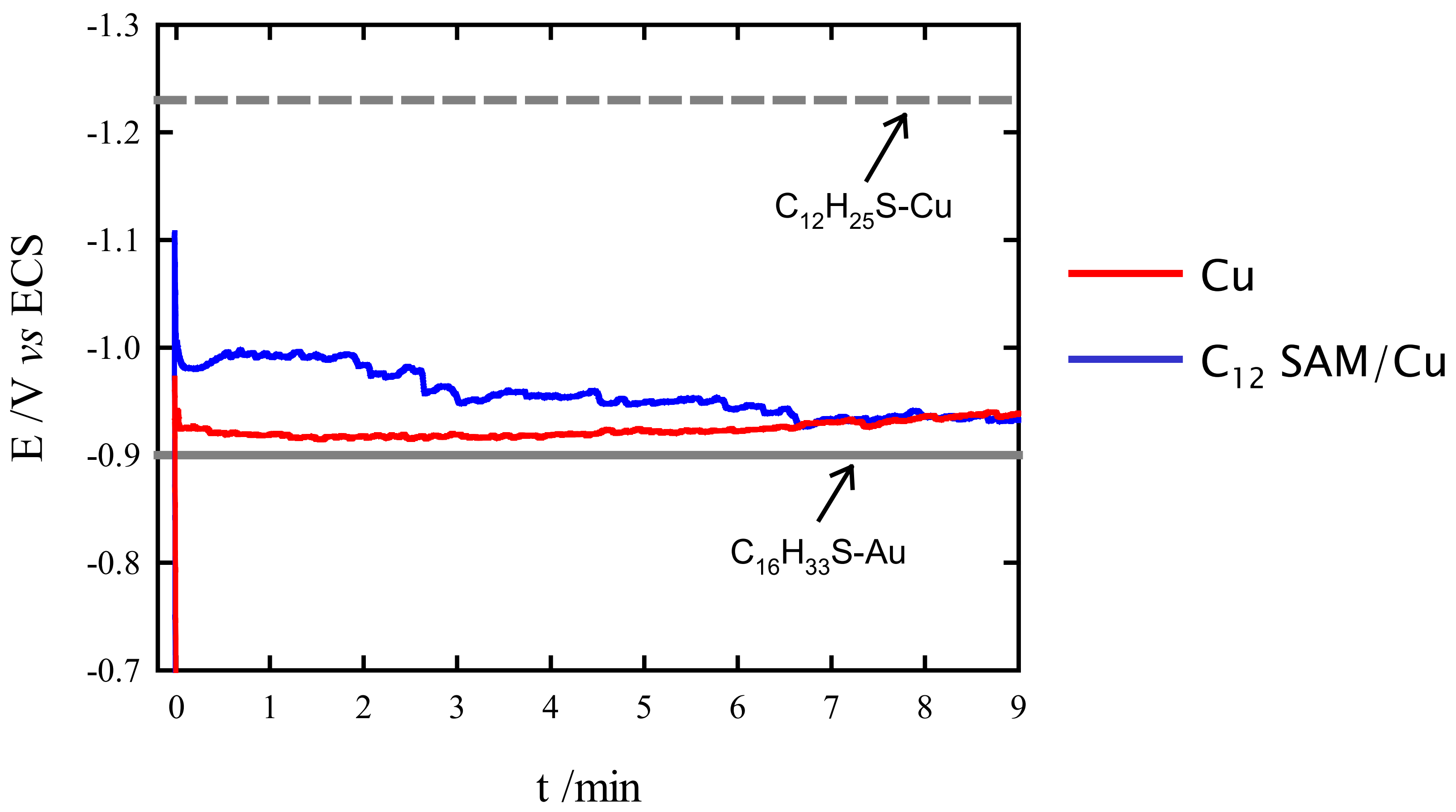
No Evidence
of Nickel
By AES !!!

Alkanethiolate Monolayer
Self-Assembled onto the Au Surface

Formation of Alkanethiolate
Micelles on the Au Surface

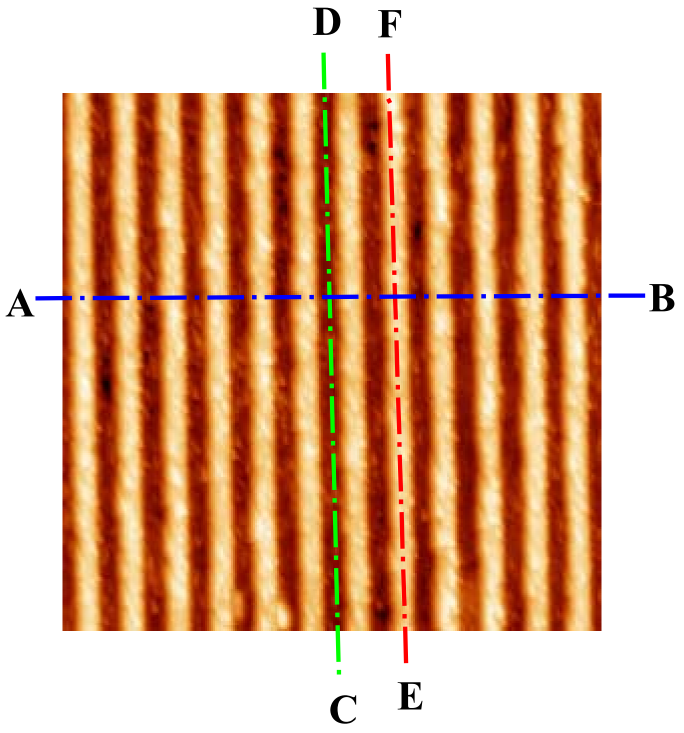
EC-STM images (25 x 40 nm^2). All the potentials are referred to the SCE. Hexanethiolate-modified Au(111).
Electrolyte: $NiSO_4.7H_20$ 1,14M + $NiCl_2.6H_2O$ 0,25M + H_3BO_3 0,61M (pH = 2).

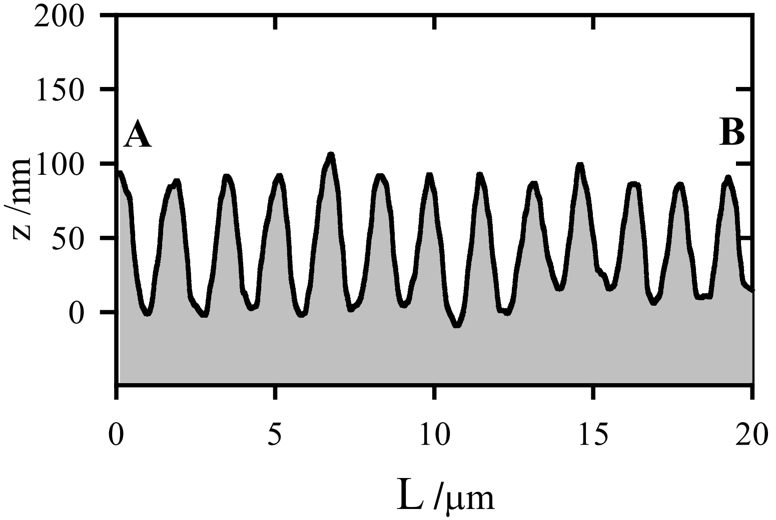
Current-Controlled Nickel Electrodeposition onto SAM-Modified Metal Stamps

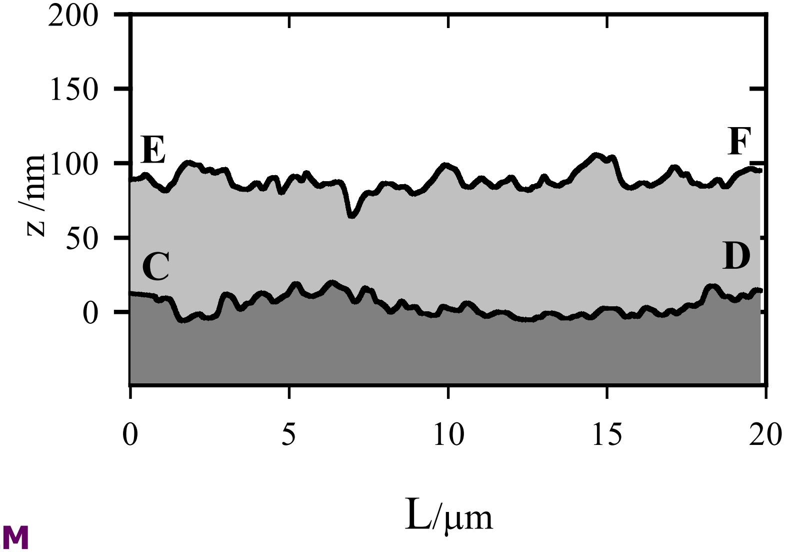


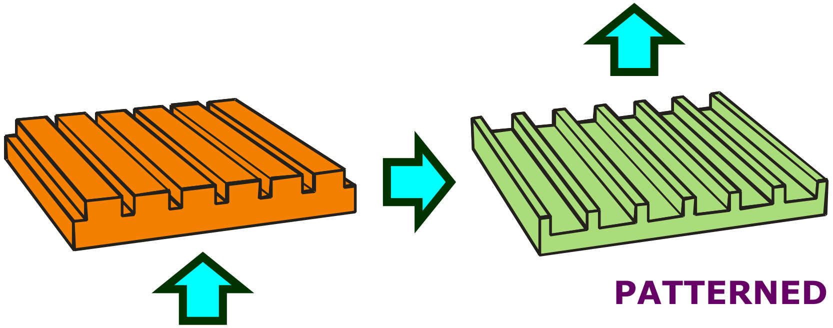
j = −40 mA.cm^{-2}
Electrolyte: $NiSO_4.7H_20$ 1,14M + $NiCl_2.6H_2O$ 0,25M + H_3BO_3 0,61M. T= 326 K

Relief-Transfer on Nickel Films by Direct Electrochemical Micromolding







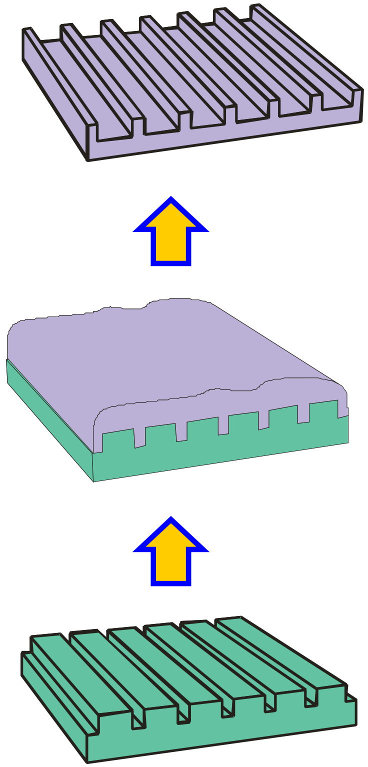


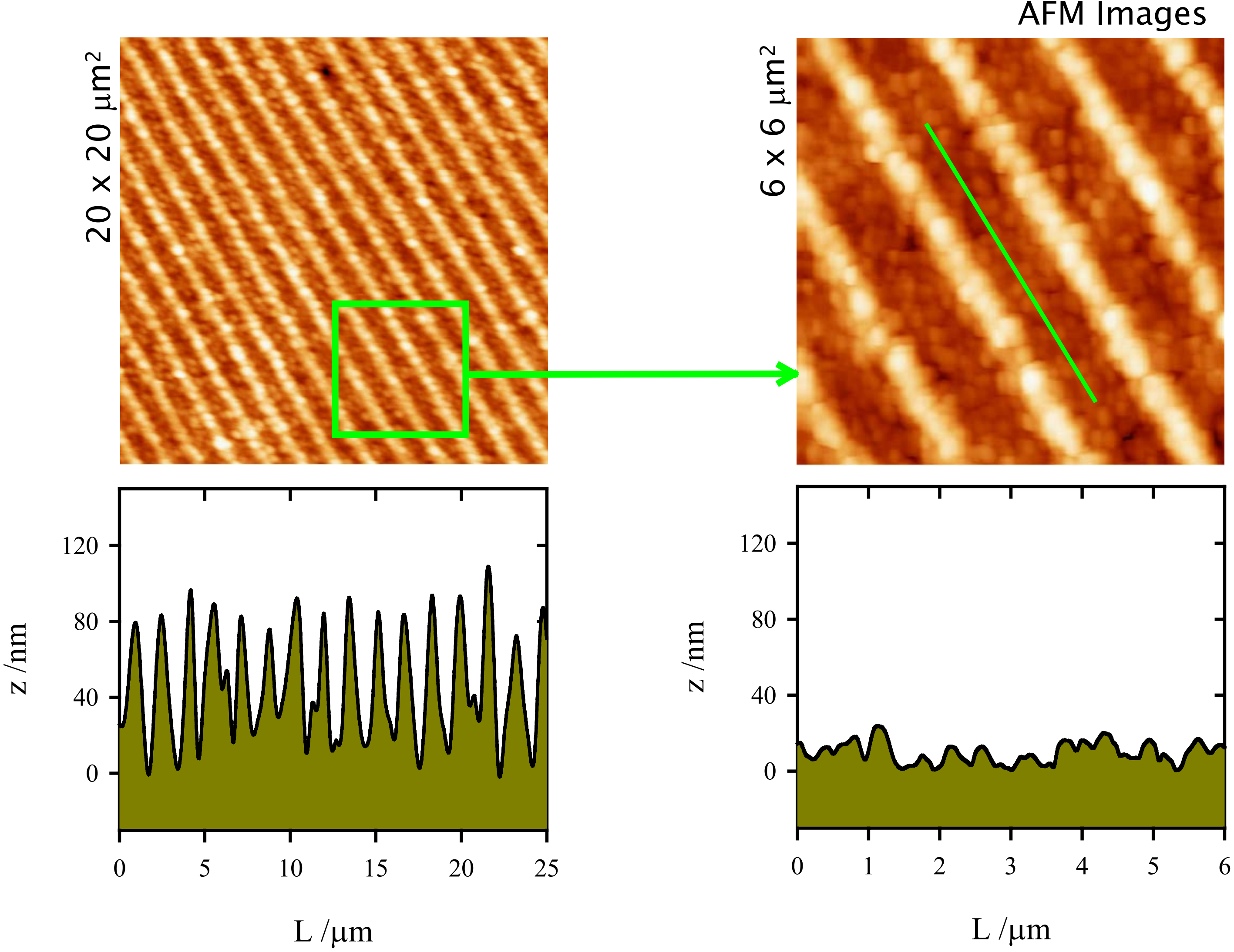
PATTERNED NICKEL FILM

CONDUCTIVE STAMP

AFM Image (20 x 20 µm^2)

Surface Patterned Bulk Ternary Alloy Electrochemical Depositon of $Fe_{11}Co_{38}Ni_{51}$

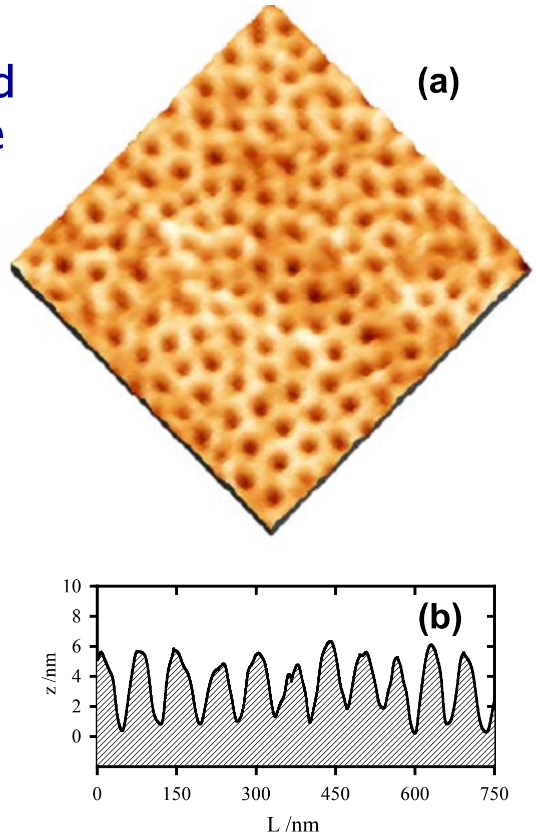


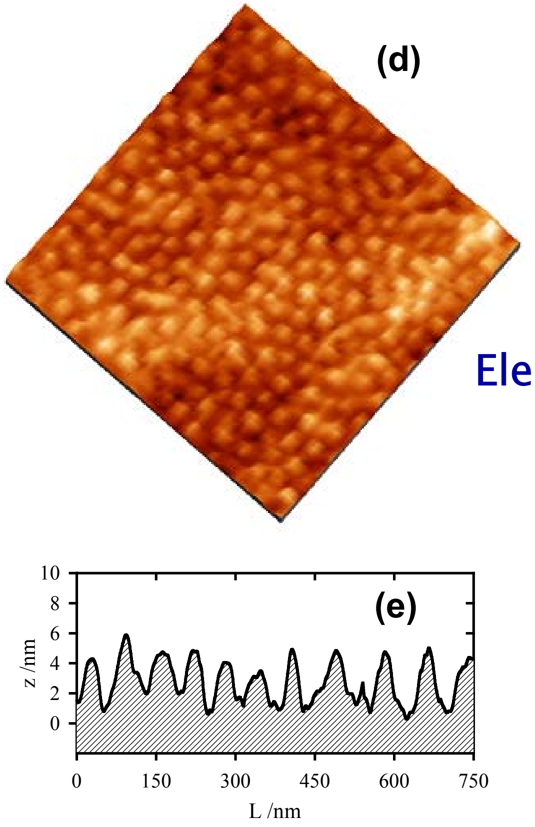


O. Azzaroni, P.L Schilardi and R.C. Salvarezza, Appl.Phys.Lett. 80 (2002) 1061

Downsizing the patterning scale
Electrochemical Nanomolding → Cu Electrodeposition

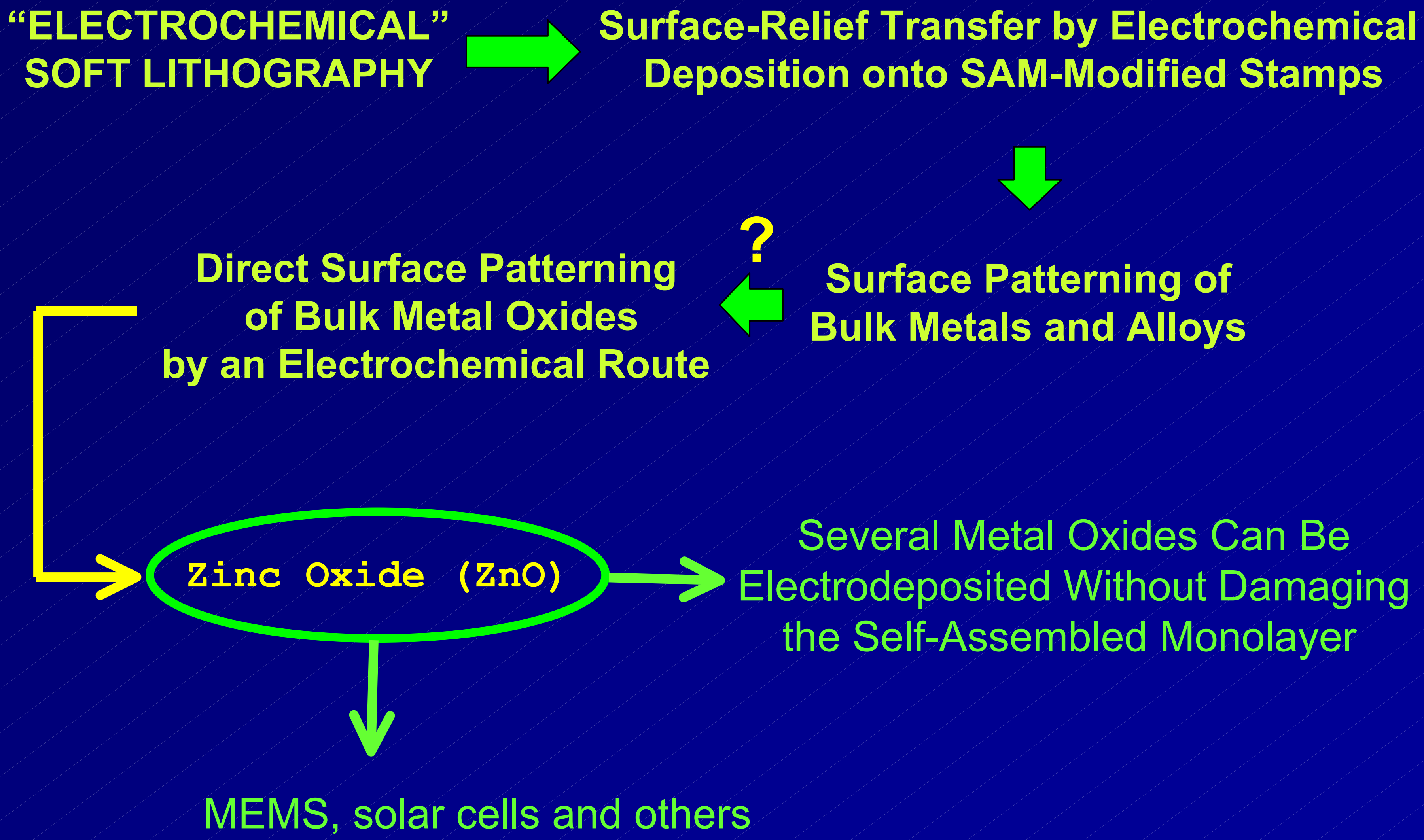
SAM-modified Nanostructured Gold Electrode





Electrochemically-Nanomolded Cu Surface

AFM Images (800 x 800 nm^2)



"ELECTROCHEMICAL"
SOFT LITHOGRAPHY

Surface-Relief Transfer by Electrochemical
Deposition onto SAM-Modified Stamps

Surface Patterning of
Bulk Metals and Alloys

?

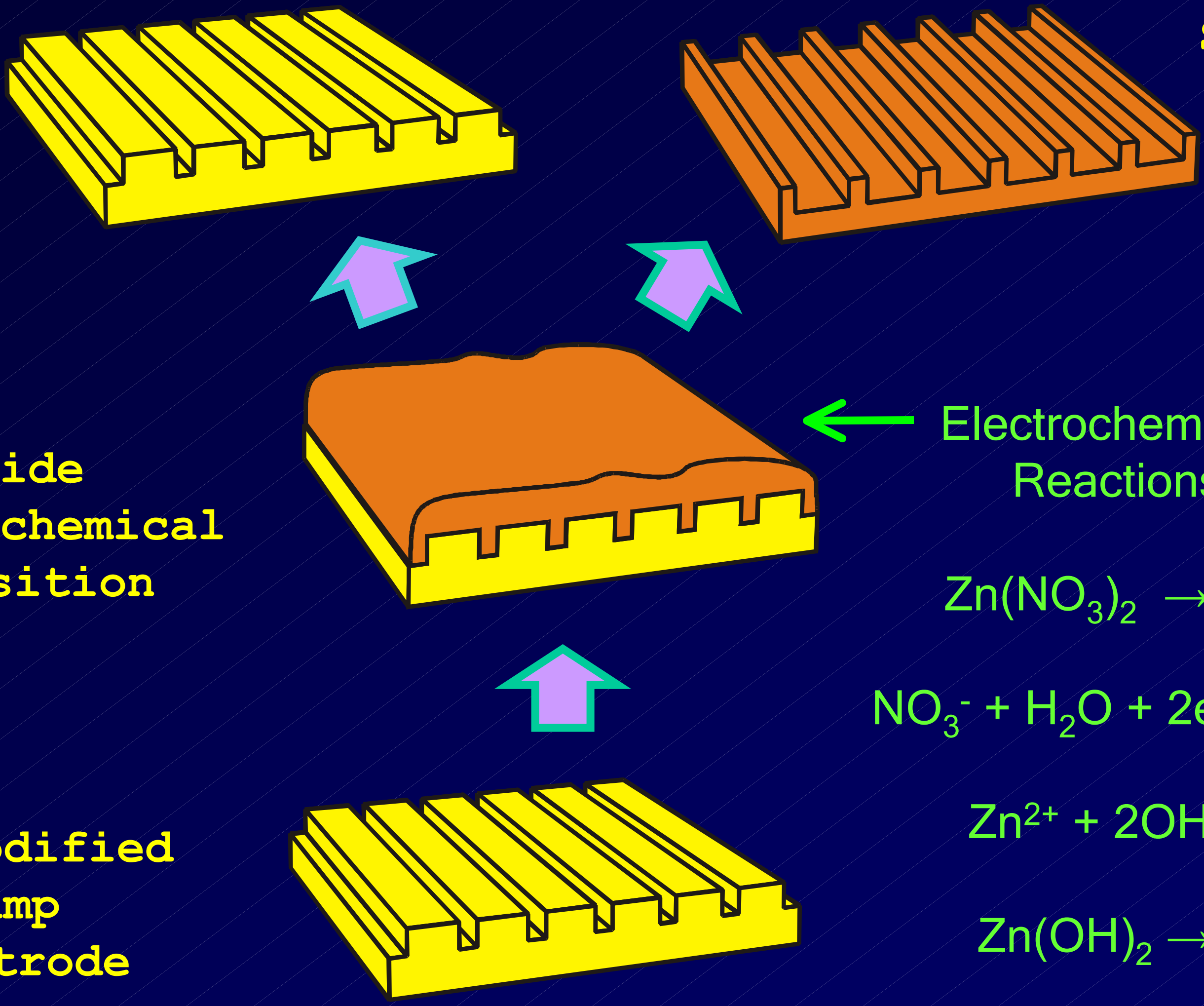
Direct Surface Patterning
of Bulk Metal Oxides
by an Electrochemical Route

Zinc Oxide (ZnO)

Several Metal Oxides Can Be
Electrodeposited Without Damaging
the Self-Assembled Monolayer

MEMS, solar cells and others

Surface Patterning of Metal Oxides by ”Electrochemical” Soft Lithography



Patterned ZnO Surface

Oxide Electrochemical Deposition

Electrochemical/Chemical Reactions on SAMs

SAM-modified Stamp Electrode

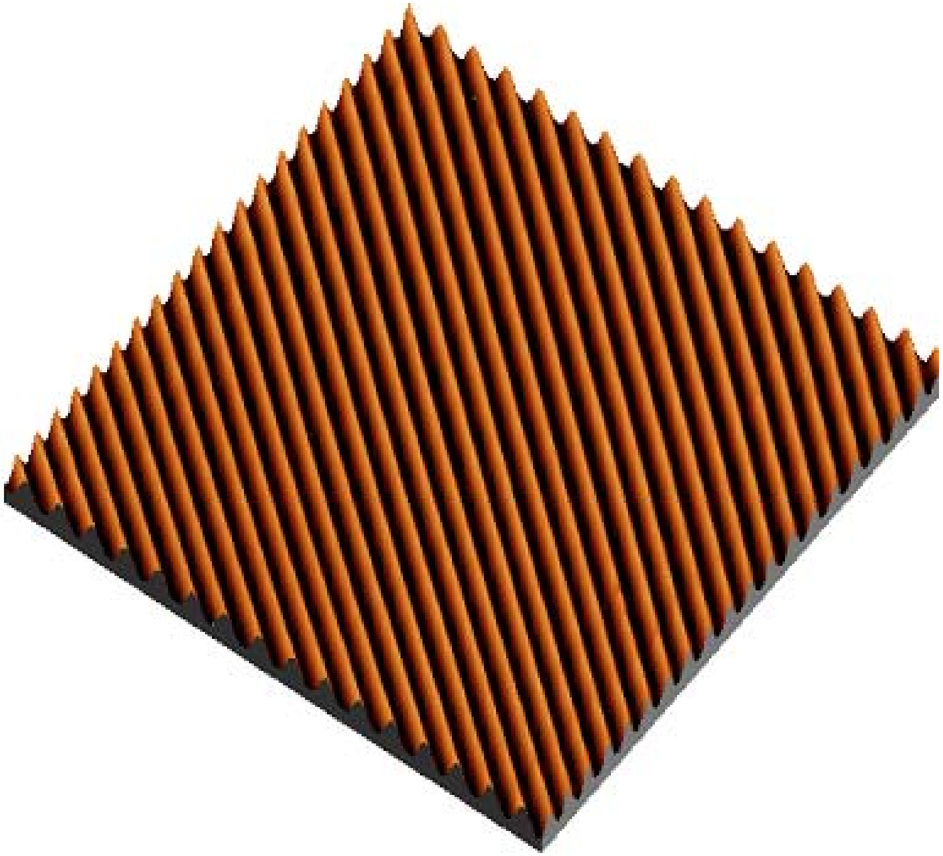
$Zn(NO_3)_2 \rightarrow Zn^{+2} + 2NO_3^-$

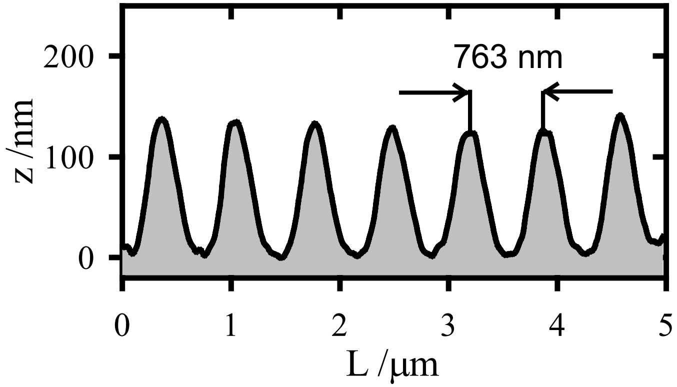
$NO_3^- + H_2O + 2e \rightarrow NO_2^- + 2\ OH^-$

$Zn^{2+} + 2OH^- \rightarrow Zn(OH)^2$

$Zn(OH)_2 \rightarrow ZnO + H_2O$

Copper Stamp





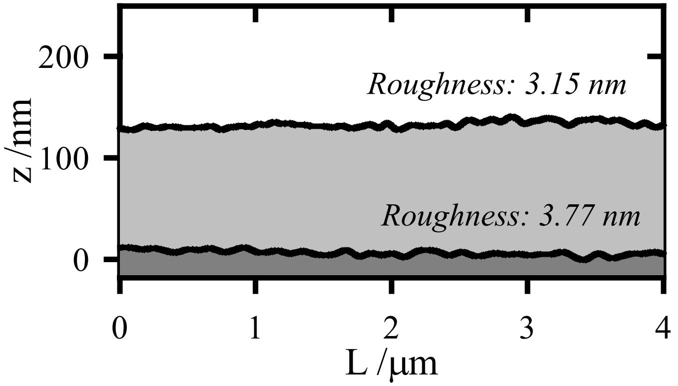
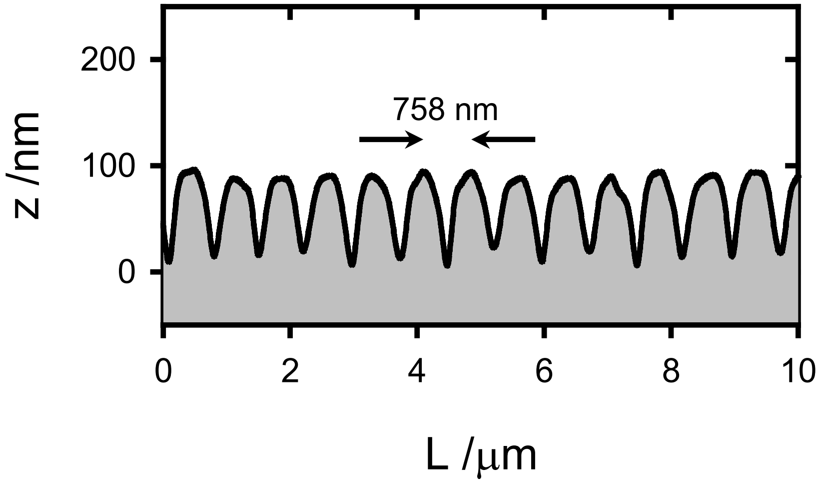
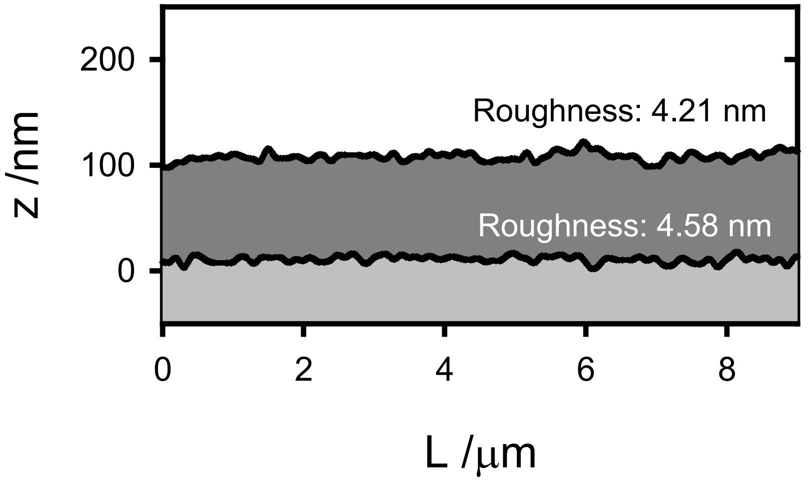


Imagen AFM (20 x 20 μm^2)

Patterned Zinc Oxide (ZnO) Surface
Micromolded by “Electrochemical” Soft Lithography

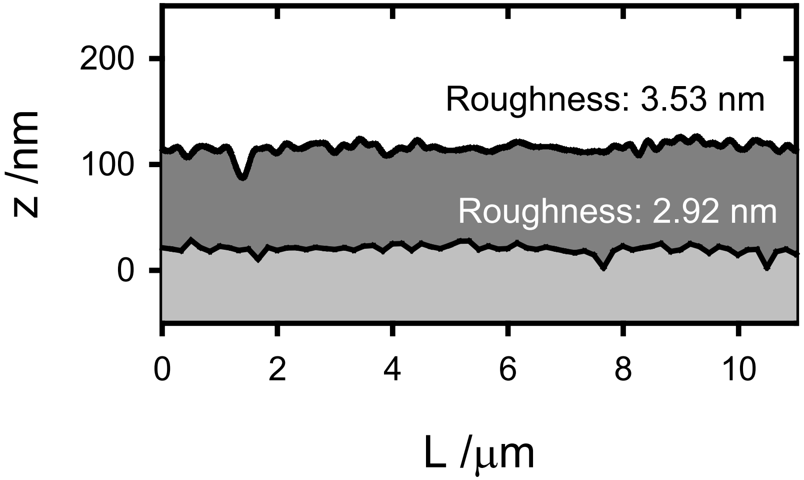
AFM Image (9 x 9 μm^2)

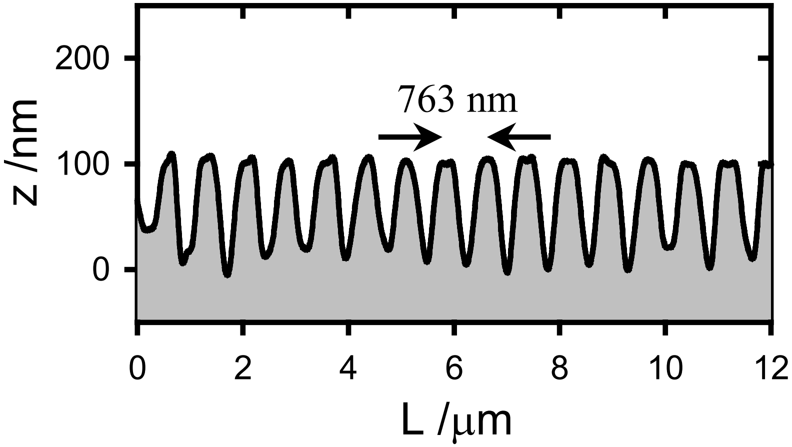




“Electrochemical” Soft Lithography – Metal Oxides Surface Patterned Bulk Cuprous Oxide (Cu_2O)

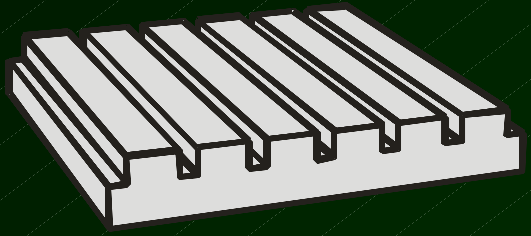
AFM Image (12 x 12 μm²)





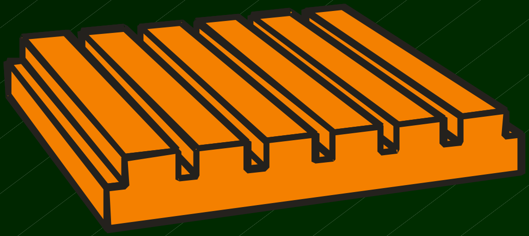
SOFT LITHOGRAPHIC TECHNIQUES

Non-Conductive Stamps



PDMS,
Silicon
or Quartz

Conductive Stamps



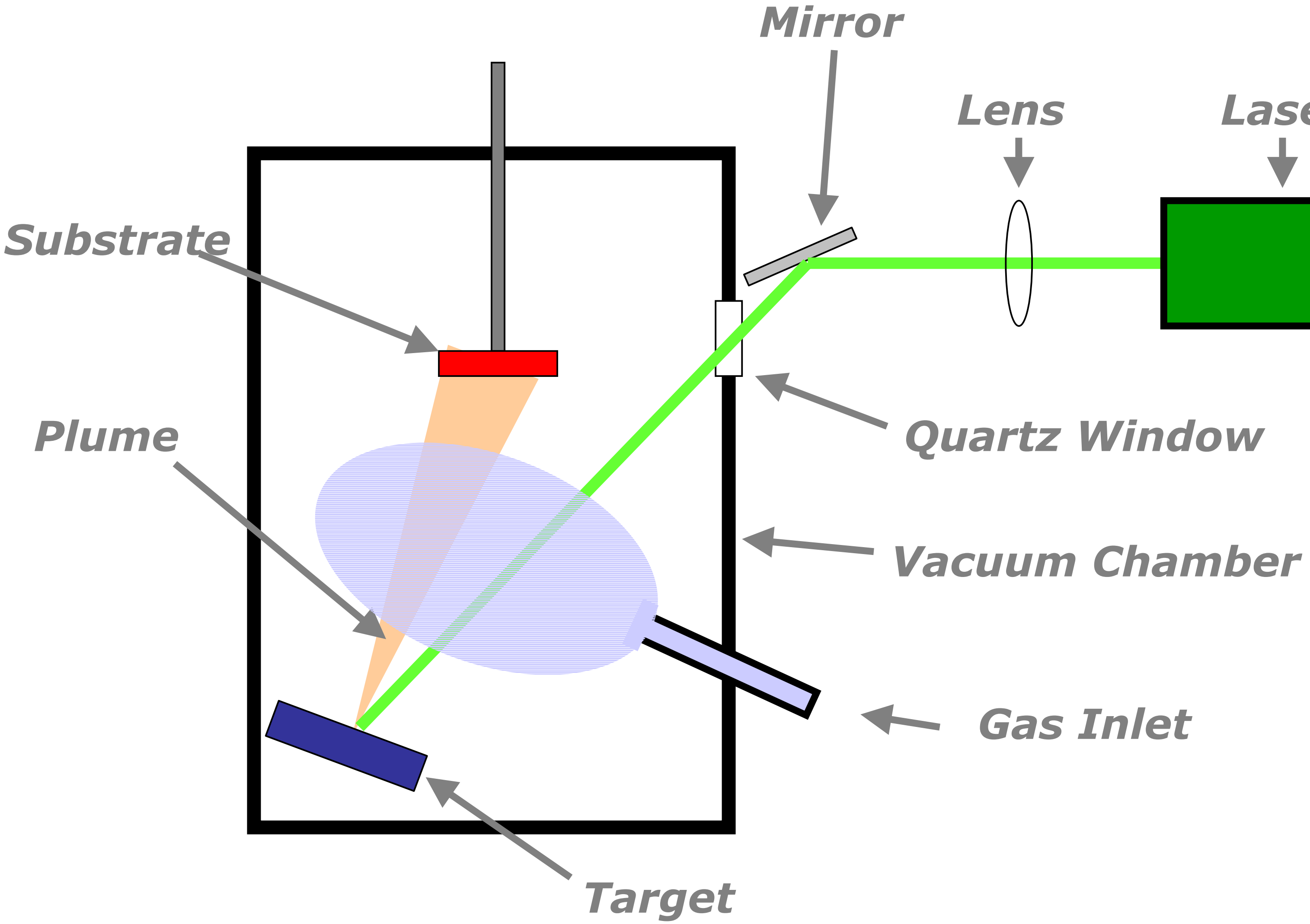
Metal

"ELECTROCHEMICAL"
SOFT LITHOGRAPHY

Direct Surface Patterning of
Metals, Alloys, Semiconductors

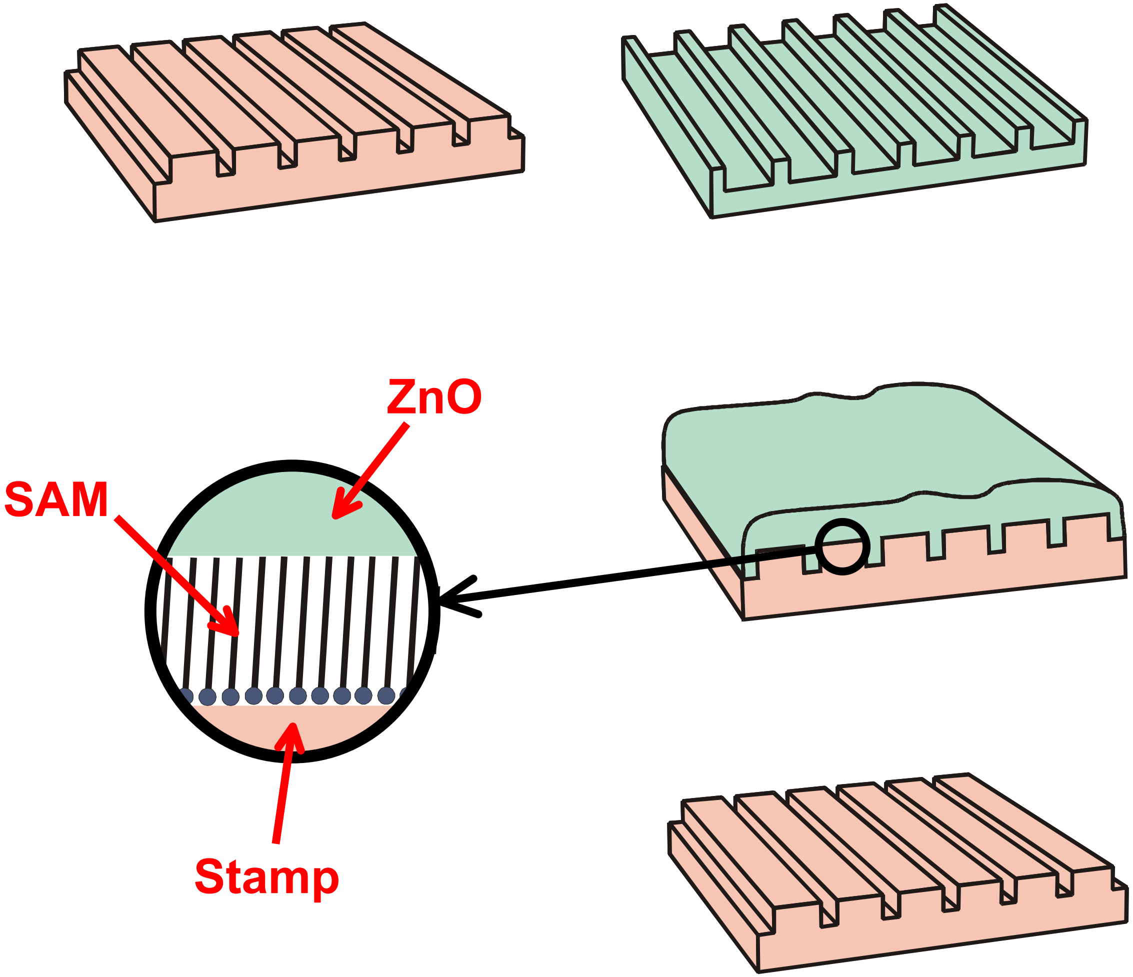
Is it possible to the use SAM-modified metallic stamps in combination with other deposition techniques different from the electrodeposition?

Pulsed-Laser Deposition of Zinc Oxide (ZnO) Films



Dr. Carlos Zaldo – Department of Ferroelectric Materials
Instituto de Ciencia de Materiales de Madrid (Spain)

Molding Surface-Relief Patterns on ZnO Surfaces Deposited by Pulsed-Laser Ablation



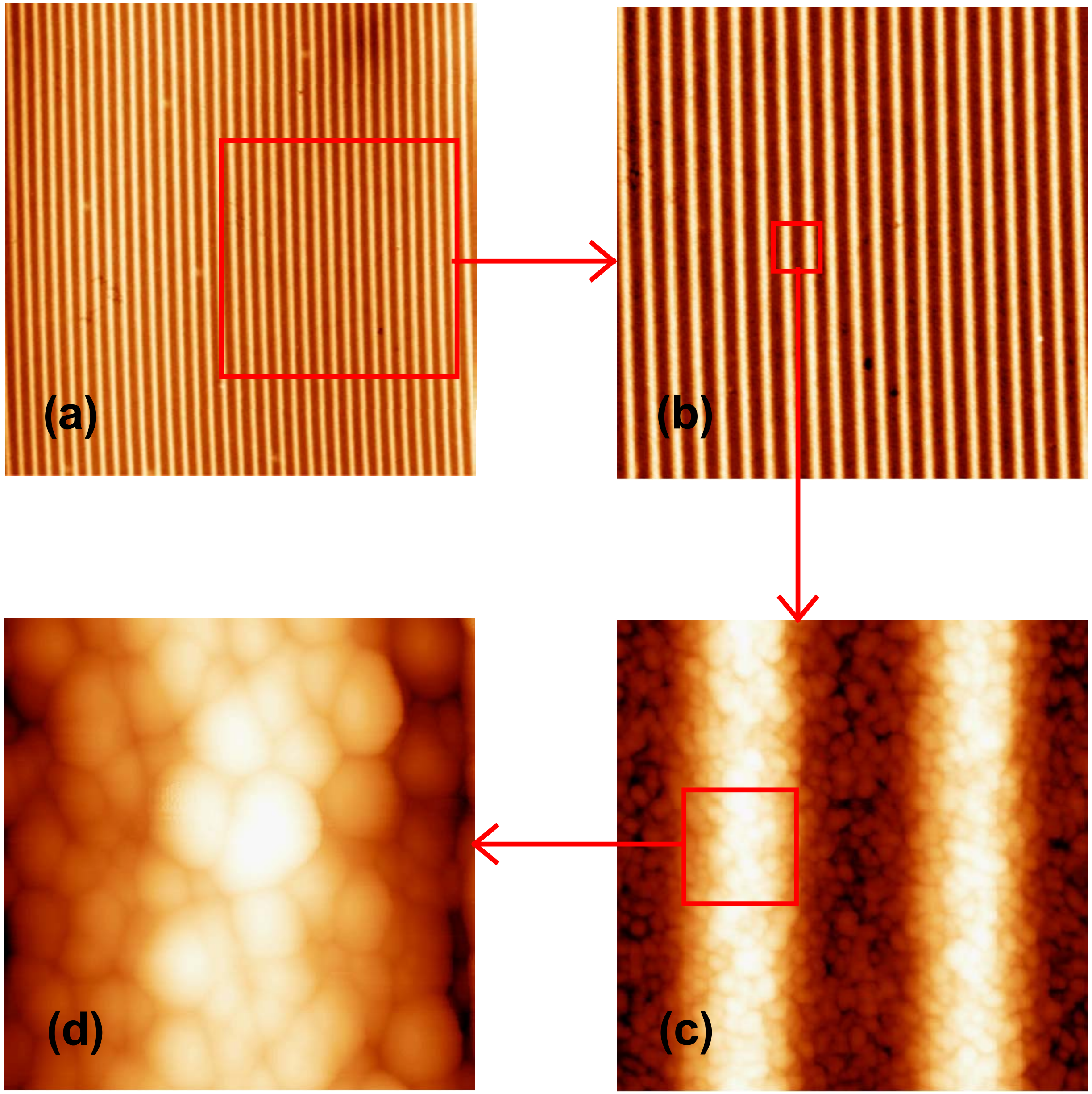
Release Step

Pulsed-Laser Deposition onto the SAM-Modified Stamp

SAM-Modified Stamp

Patterned Zinc Oxide (ZnO) Surfaces

AFM Images



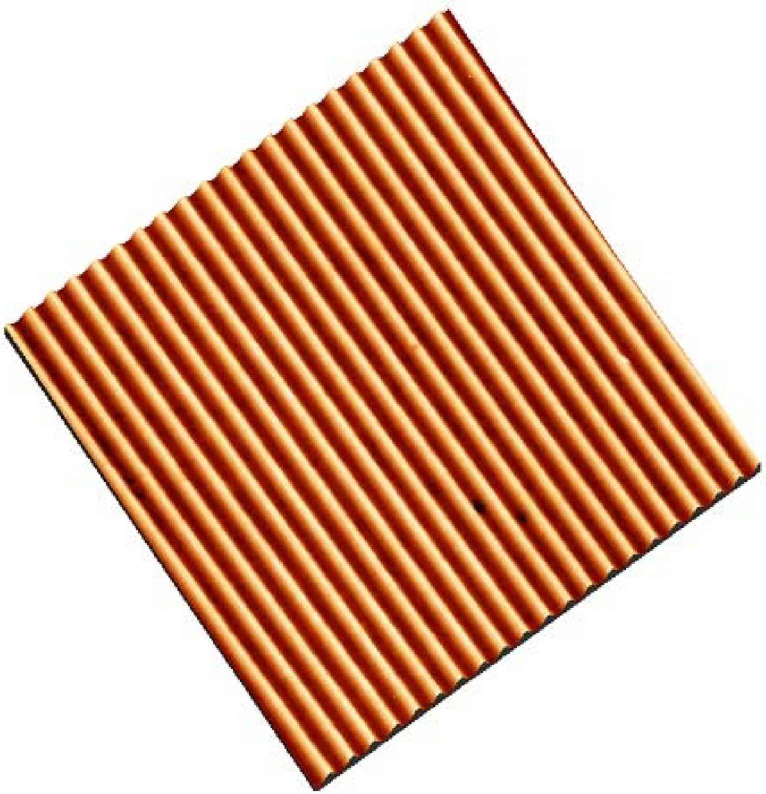
25 x 25 μm²

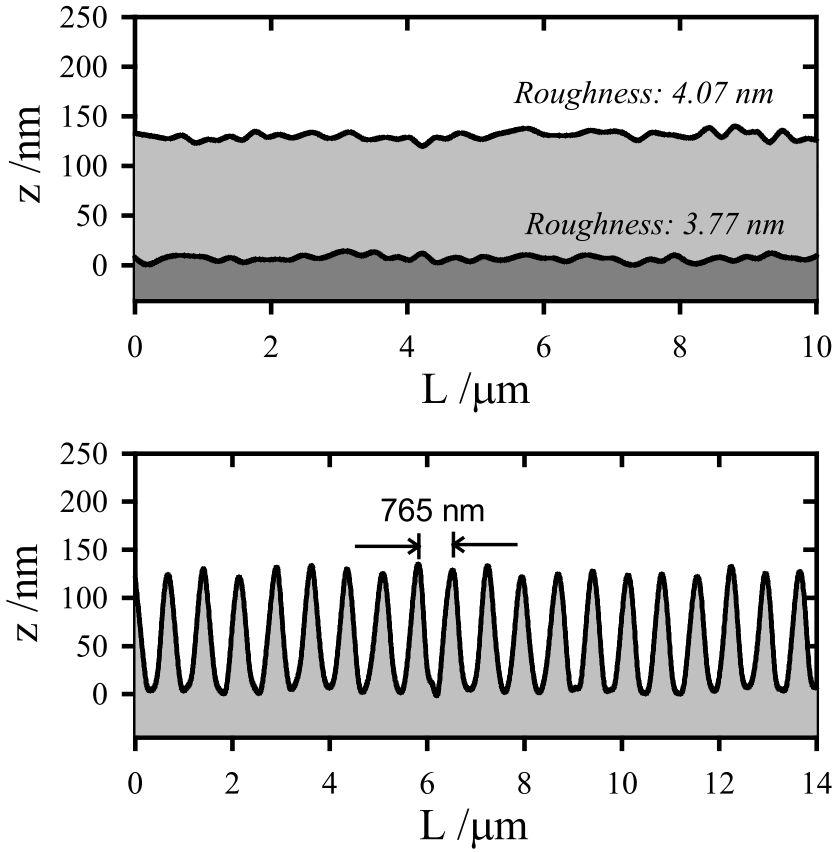
15 x 15 μm²

1,5 x 1,5 μm²

500 x 500 nm²

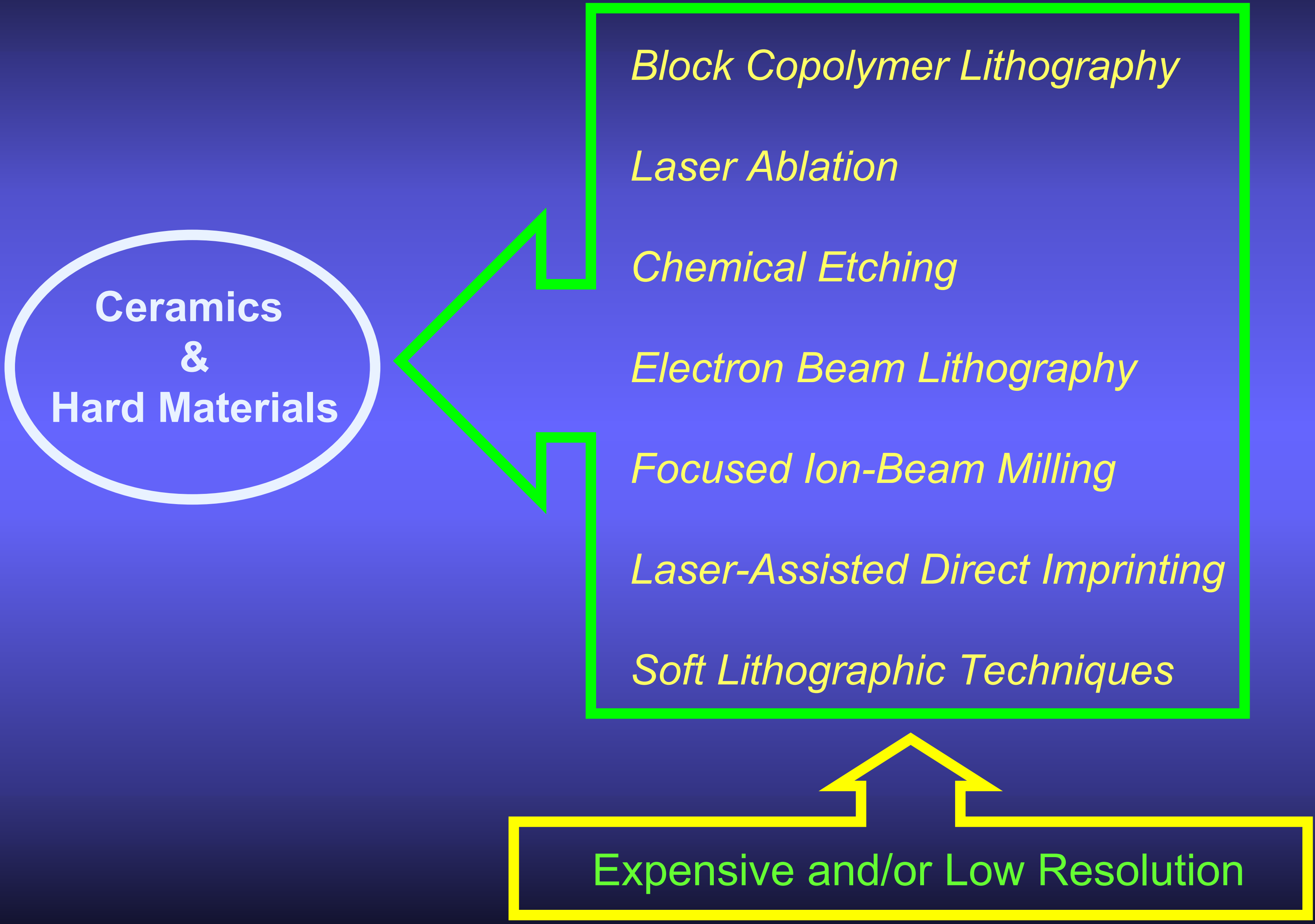
Micromolded Pulsed-Laser Deposited ZnO Surface





AFM image (15 x 15 μm²)

Common Strategies for Patterning Ceramics and Hard Materials



Ceramics
&
Hard Materials

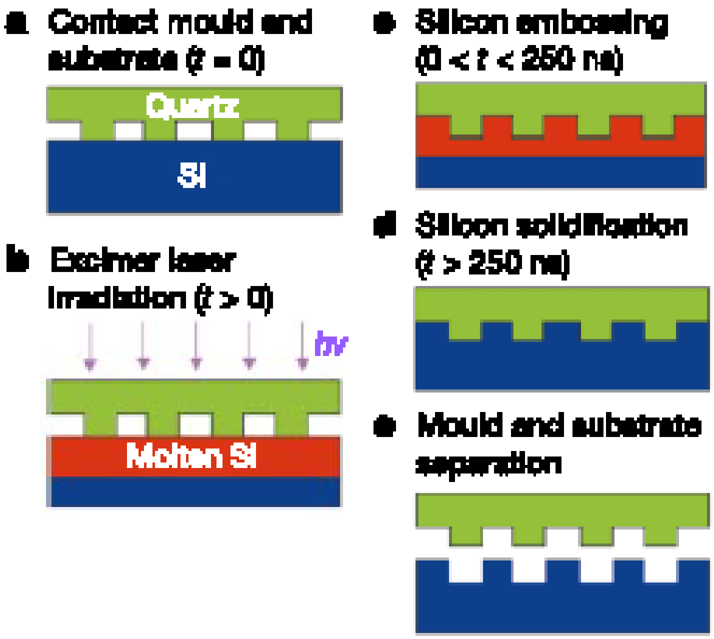
- *Block Copolymer Lithography*
- *Laser Ablation*
- *Chemical Etching*
- *Electron Beam Lithography*
- *Focused Ion-Beam Milling*
- *Laser-Assisted Direct Imprinting*
- *Soft Lithographic Techniques*

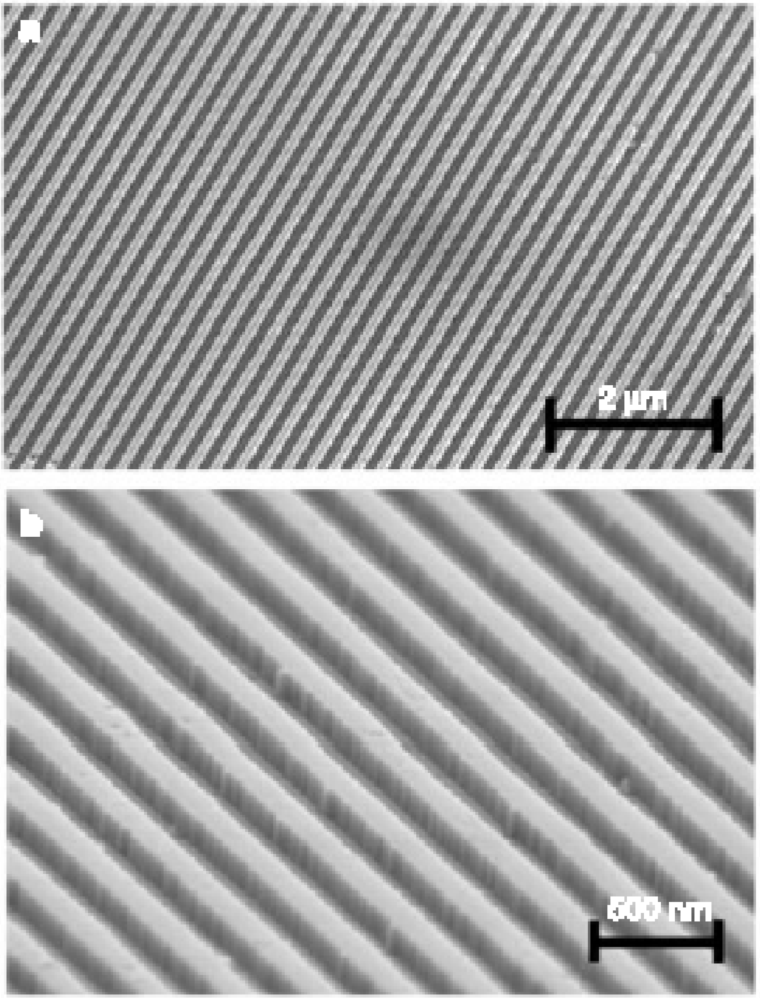
Expensive and/or Low Resolution

Ultrafast and direct imprint of nanostructures in silicon

Stephen Y. Chou*, Chris Keimel & Jian Gu

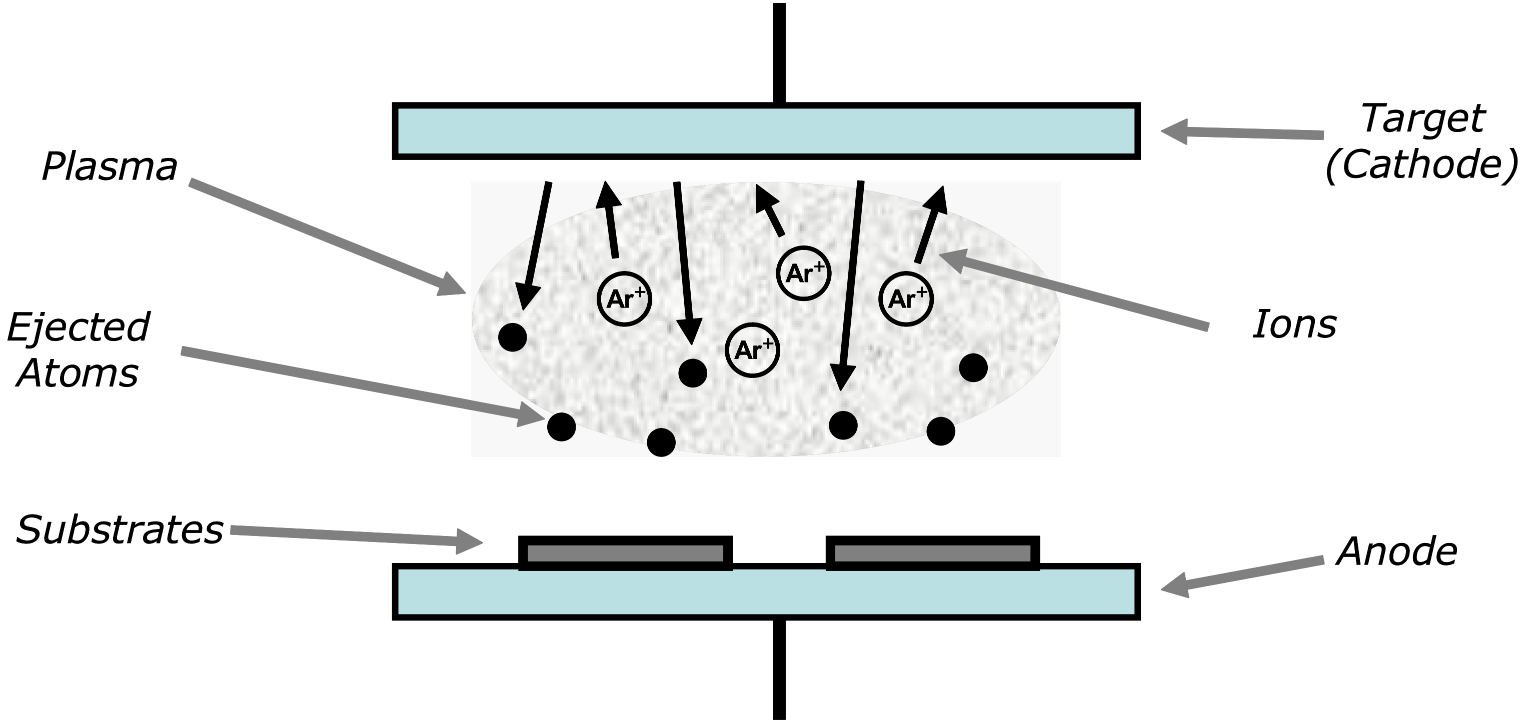
NanoStructure Laboratory, Department of Electrical Engineering,
University, Princeton, New Jersey 08544, USA





Nature, **417** (2002) 835

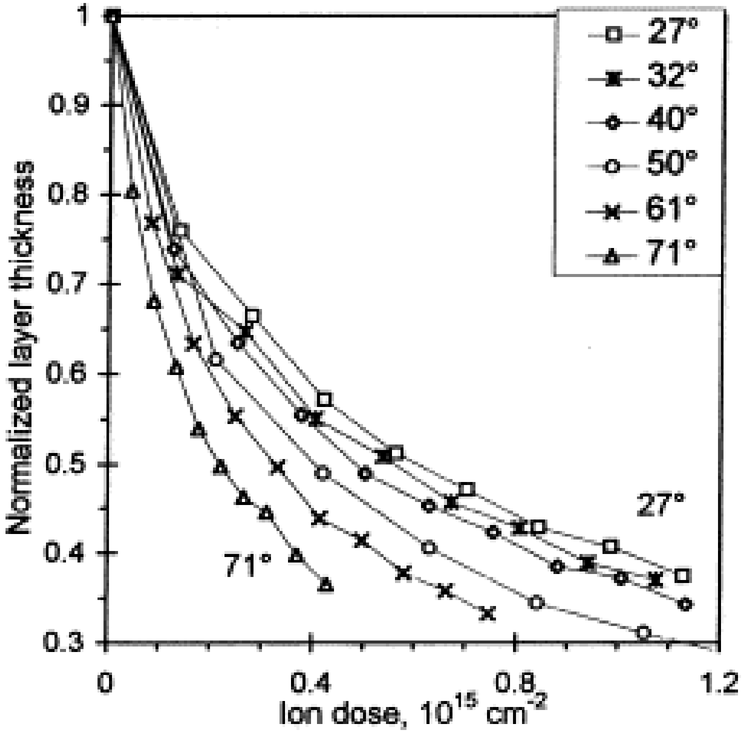
Ceramic Films Deposited by Reactive Sputtering

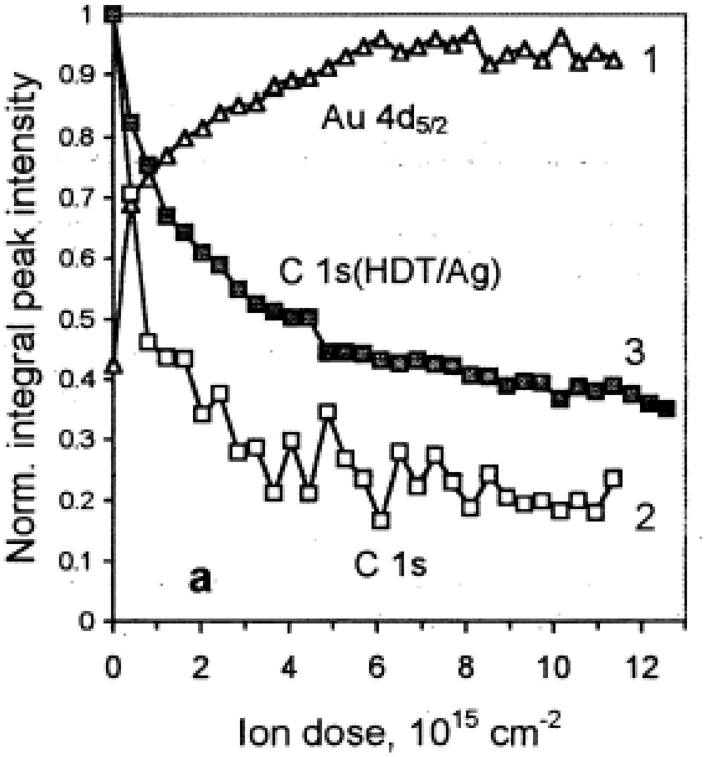


Prof. J.M. Albella and Dr. L. Vázquez
Department of Physics and Surface Engineering
ICMM - Spain

Sputtering of self-assembled monolayers

Collision of energetic species damages severely the self-assembled molecular film.





Chenakin *et al.* Surf. Sci. **436** (1999) 131

Reactive Sputtering Deposition Onto Self-Assembled Monolayers

What Kind of Precautions Do We Have to Take Into Account ?

Energetic Sputtered Species Colliding on the Substrate Could Damage Severely the Self-Assembled Monolayer

Increase the Substrate-Target Distance And Thermalize the Sputtered Species with the Inert Gas

Reactive Magnetron Sputtering Conditions:

Planar Configuration → Target-Substrate Distance: ~~65 mm~~ 265 mm

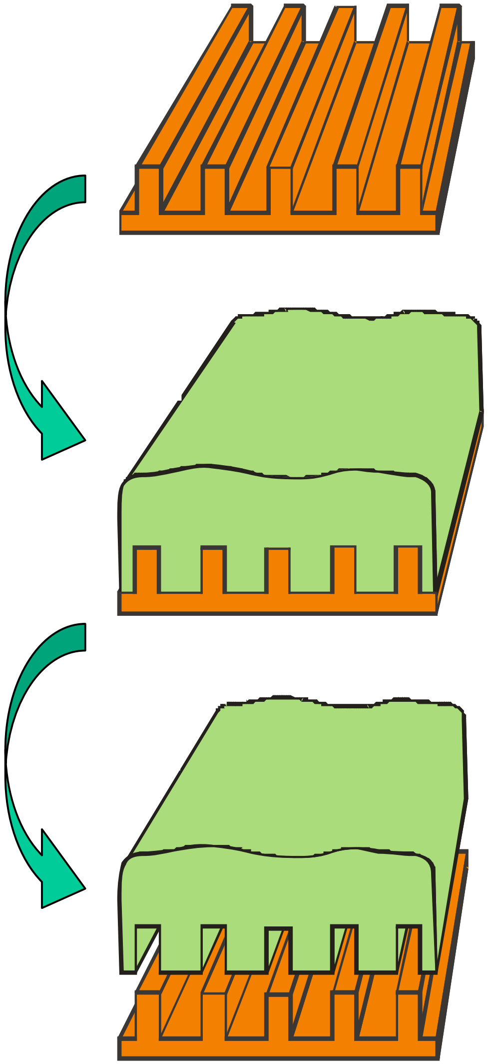
Titanium Nitride (TiN)

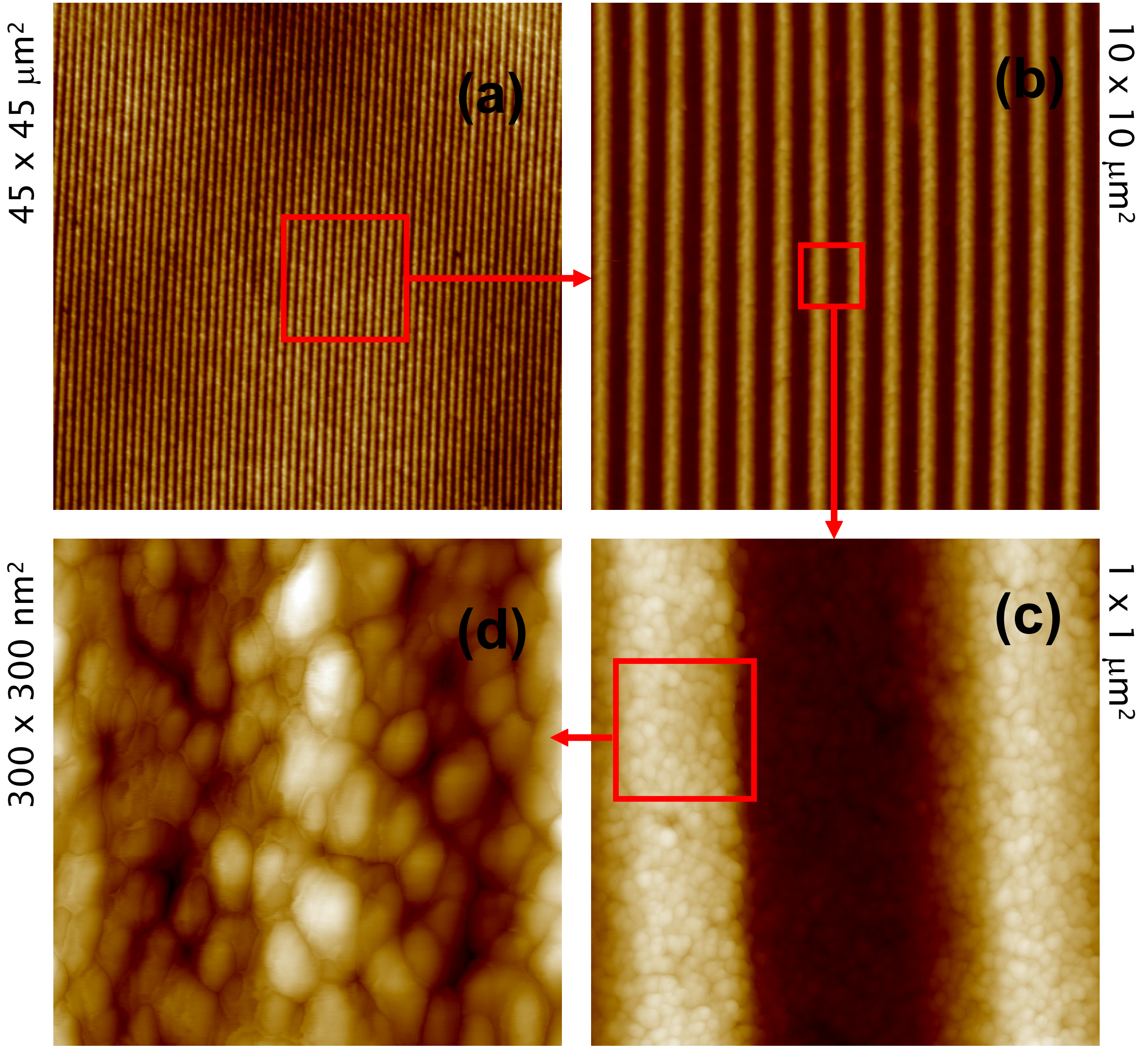
Gas Flow (Ar + N_2) = 11 sccm (93 % Ar + 7 % N_2)
Stoichiometric Ratio (N/Ti) = 0.992
Total Pressure (P_{Ar} + P_{N2}) = 2.10^{-3} mbar

Aluminum Nitride (AlN)

Gas Flow (Ar + N_2) = 29.5 sccm (20 % Ar + 80 % N_2)
Stoichiometric Ratio (N/Al) = 0.987
Total Pressure (P_{Ar} + P_{N2}) = 4.10^{-3} mbar

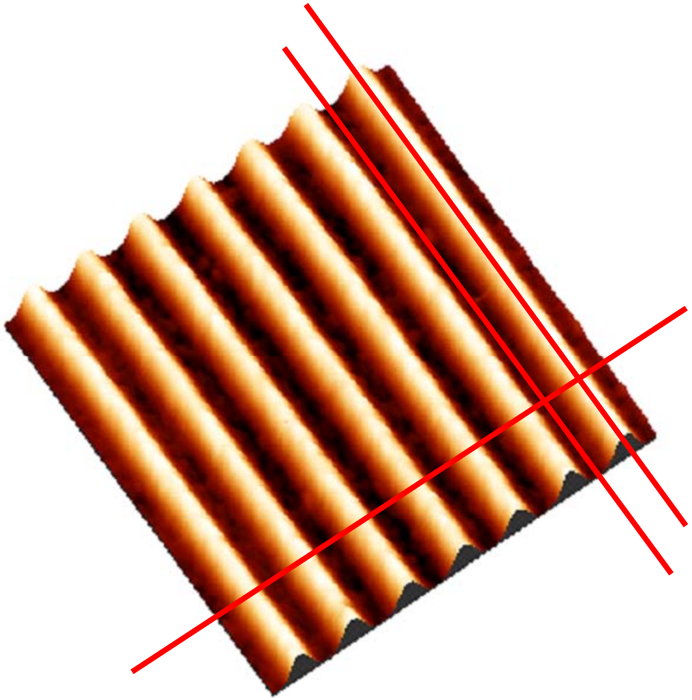
Micromolded Titanium Nitride (TiN) Surface





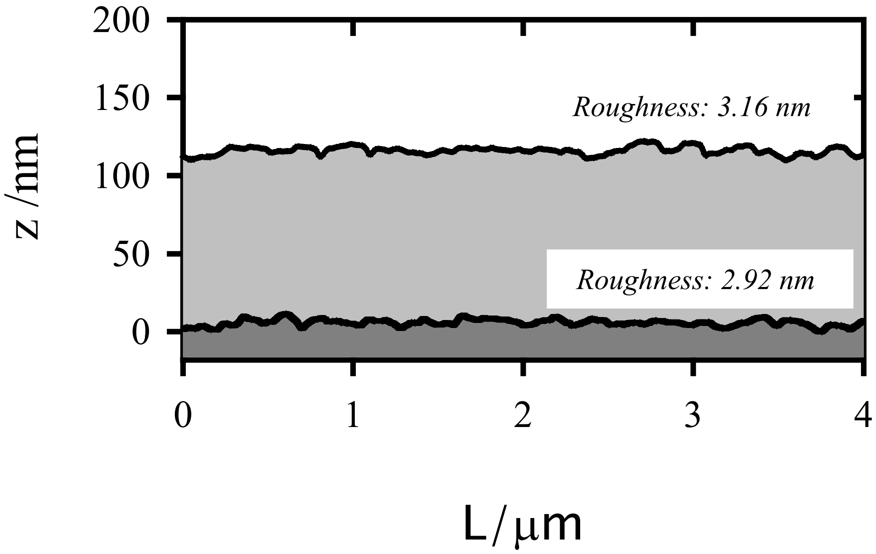
TM-AFM Images

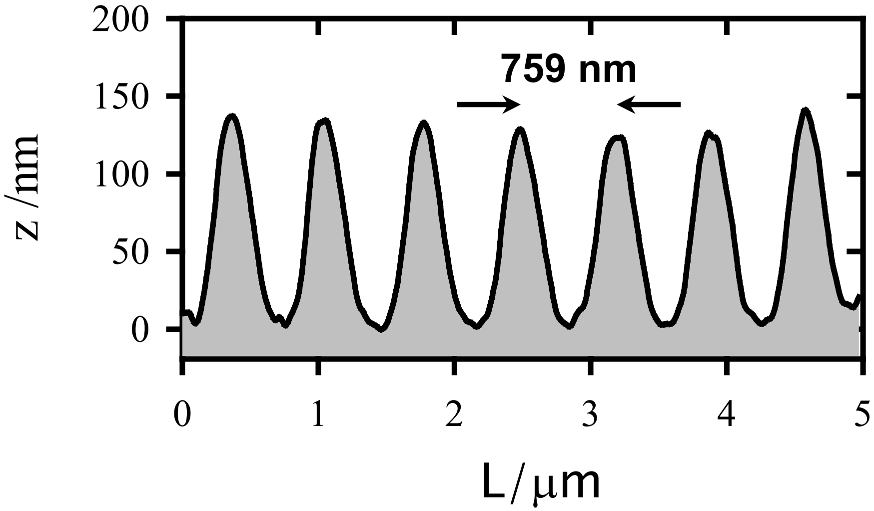
Titanium Nitride



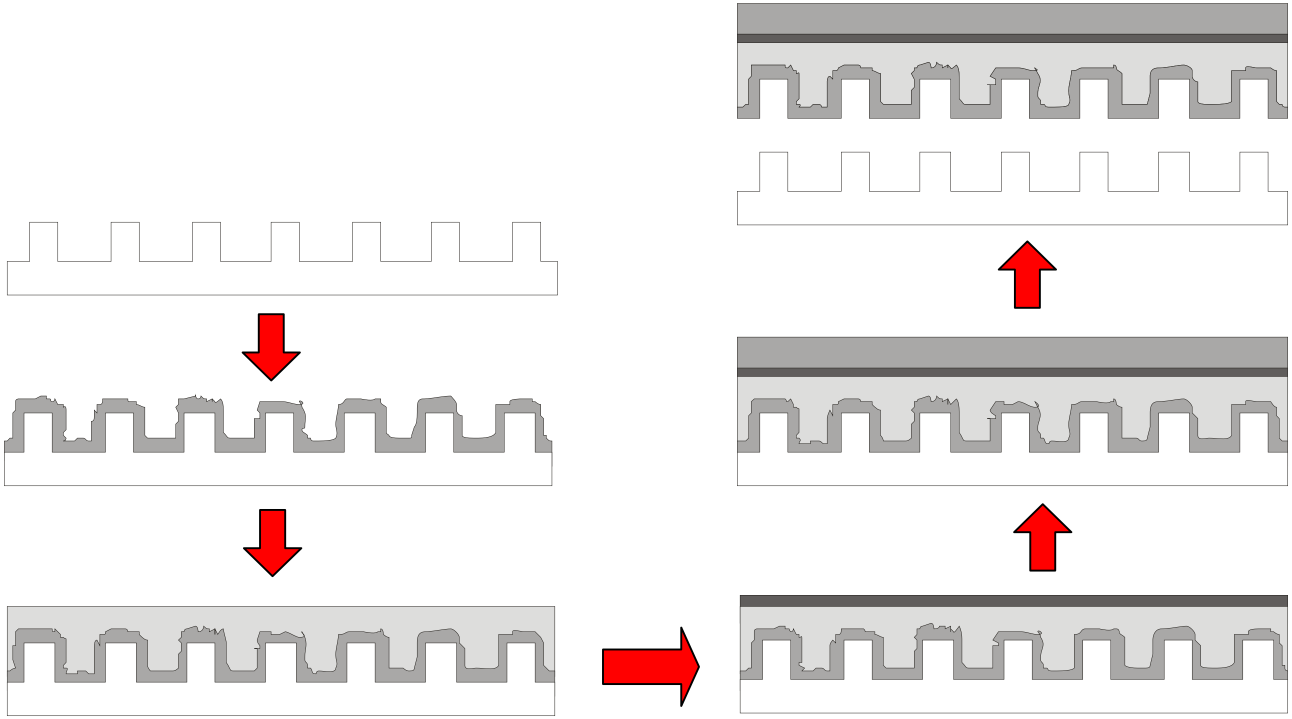
14-15 GPa

AFM image (5 x 5 μm^2)





Fabrication of a TiN–made “Imprinting Stamp”



Release

SAM-Modified
Patterned Surface

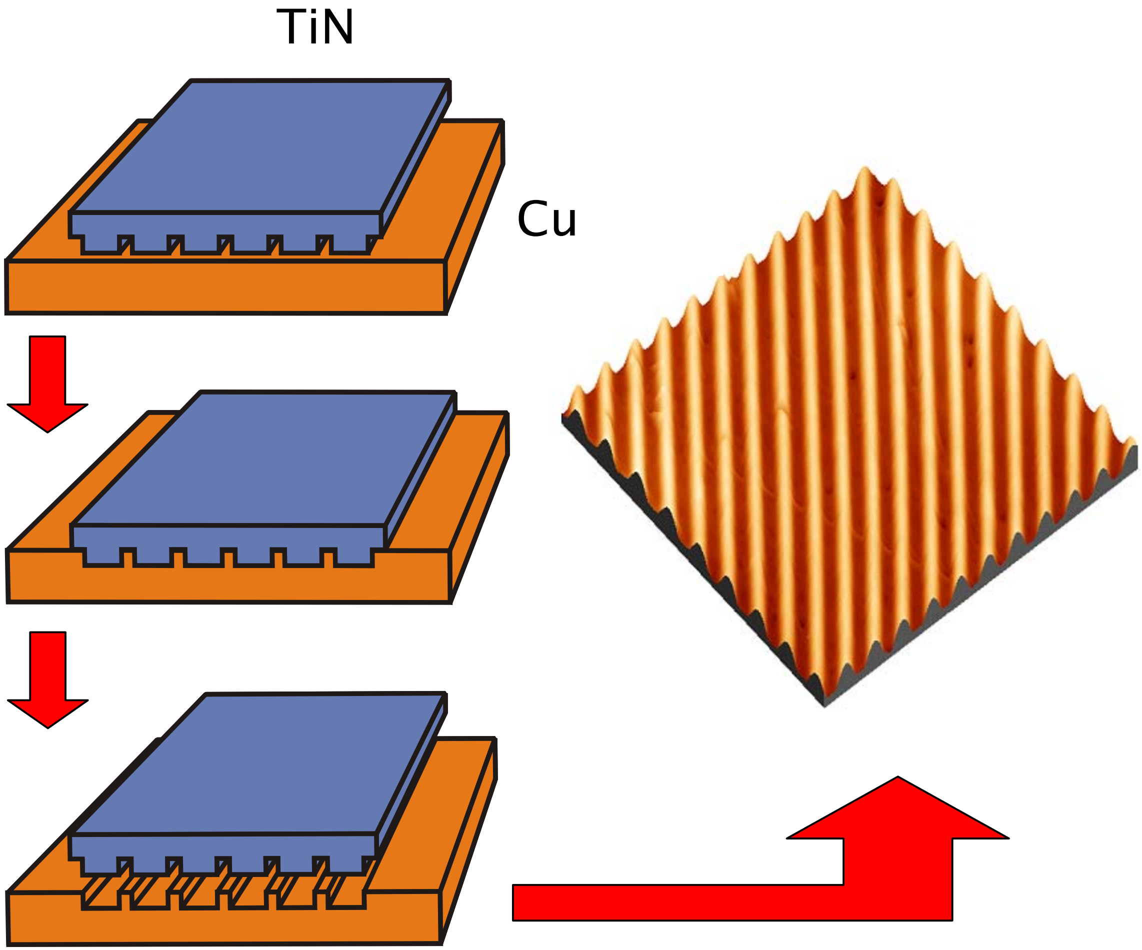
Metal
Electrodeposition

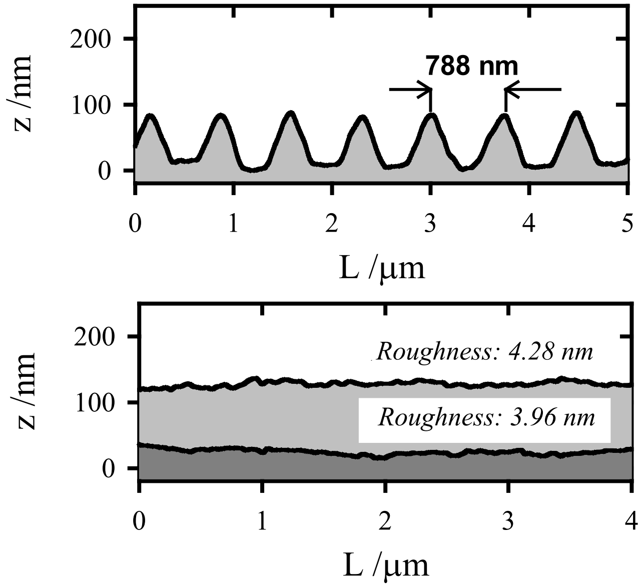
Reactive Sputtering
Deposiion of TiN

Sputtering
Deposition of Ti

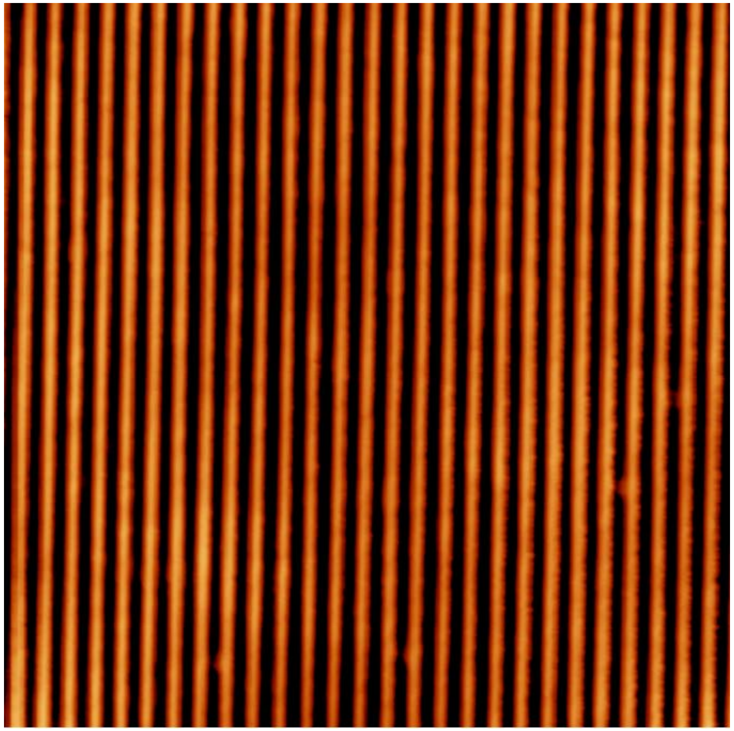
Thin-Film Metal
Evaporation

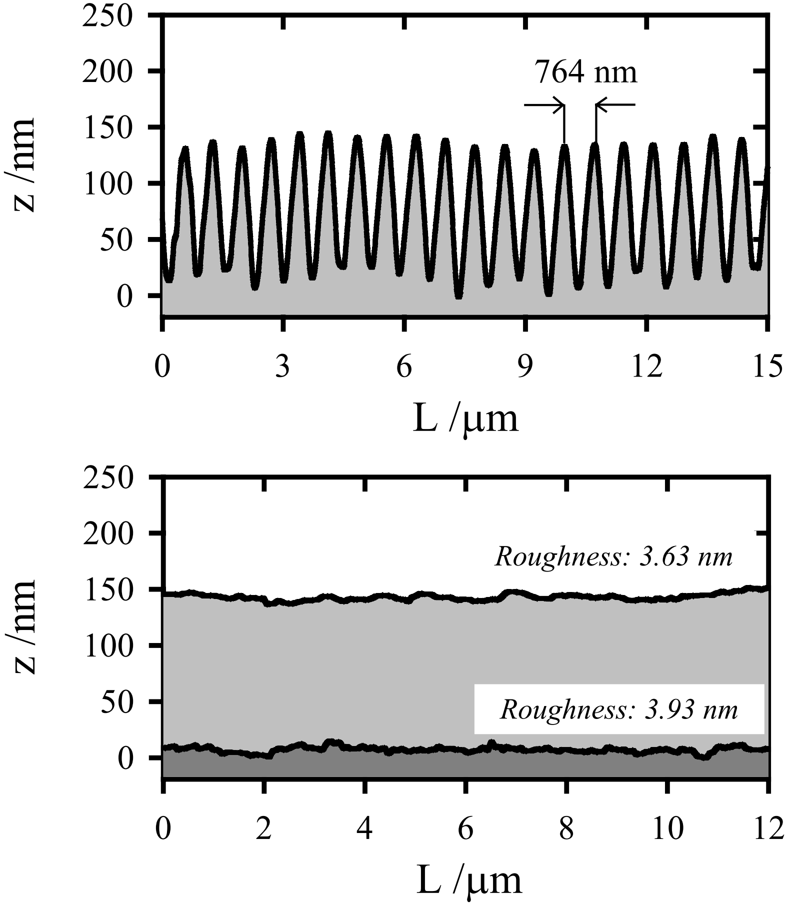
Patterned Ceramic Surfaces as Imprinting Tools





Micromolding of Aluminum Nitride (AlN) Surfaces



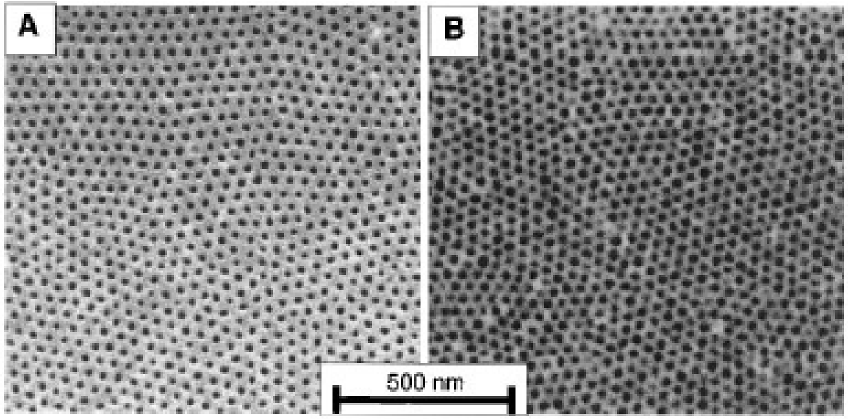


AFM image (20 x 20 μm²)

Strategies for Nanostructuring Ceramic Surfaces
Patterning with Nanoscale Accuracy

Block Copolymer Lithography: Periodic Arrays of $\sim 10^{11}$ Holes in 1 Square Centimeter

Miri Park, Christopher Harrison, Paul M. Chaikin,
Richard A. Register, Douglas H. Adamson

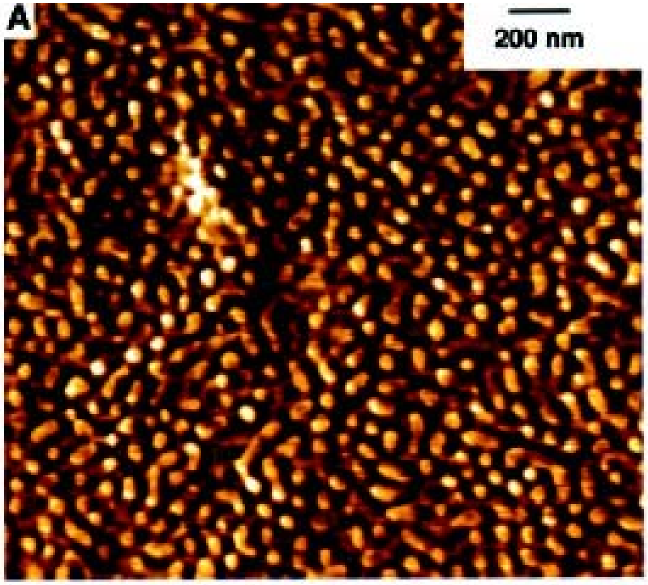


Silicon Nitride

Science, **276** (1997) 1401

Ordered Bicontinuous Nanoporous and Nanorelief Ceramic Films from Self Assembling Polymer Precursors

Vanessa Z.-H. Chan,[1] James Hoffman,[2] Victor Y. Lee,[3]
Hermis Iatrou,[4] Apostolos Avgeropoulos,[4] Nikos Hadjichristidis,[4]
Robert D. Miller,[3] Edwin L. Thomas[1]*



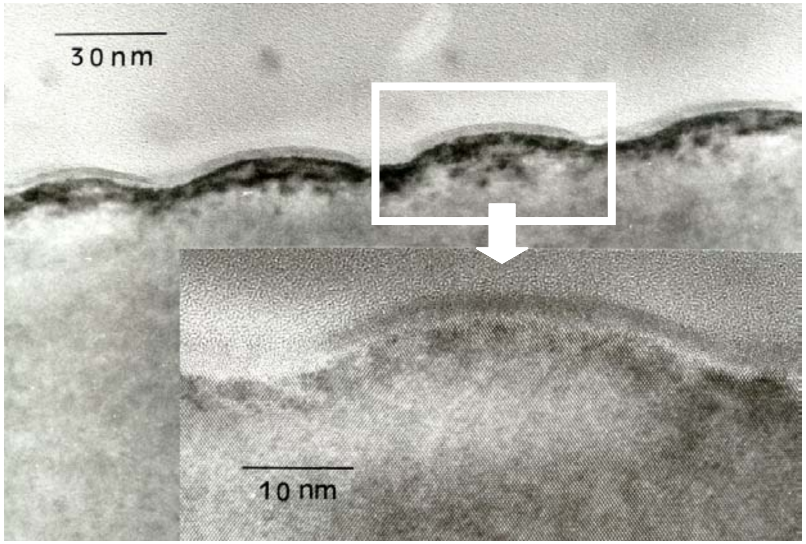
Silicon Oxycarbide

Science, **286** (1999) 1716

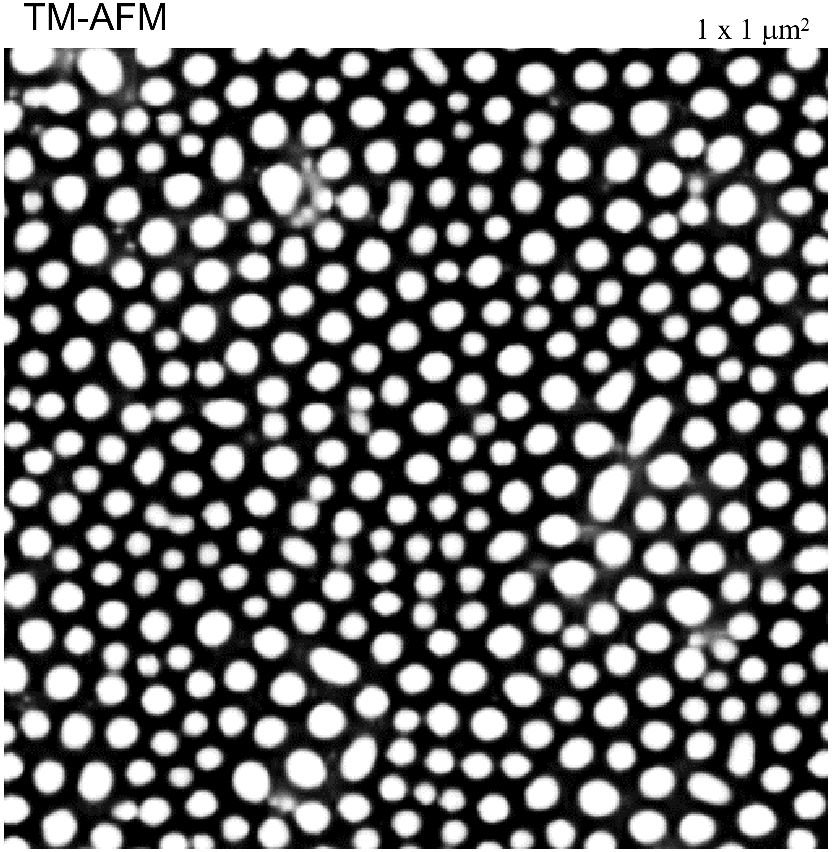
Master Nanofabrication by Low-Energy Ion-Beam Sputtering

n-type Si(100) substrates
Ar^+ bombardment (normal incidence)
at 1 keV and 0.24 mA

TEM

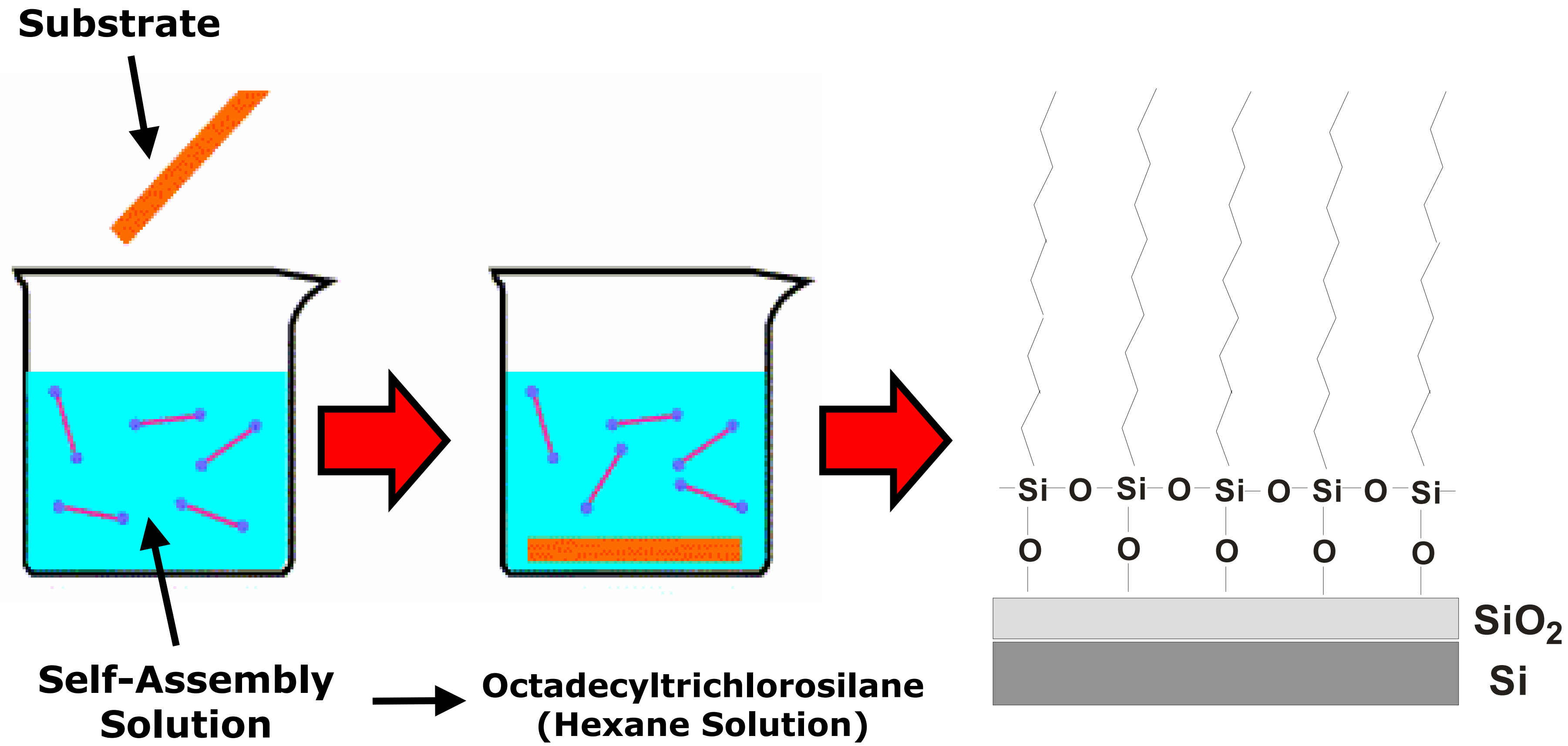


TM-AFM



Department of Physics and Surface Engineering – ICMM – Spain

Long-Chain Silane Self-Assembled Monolayers as Anti-Sticking Molecular Coatings



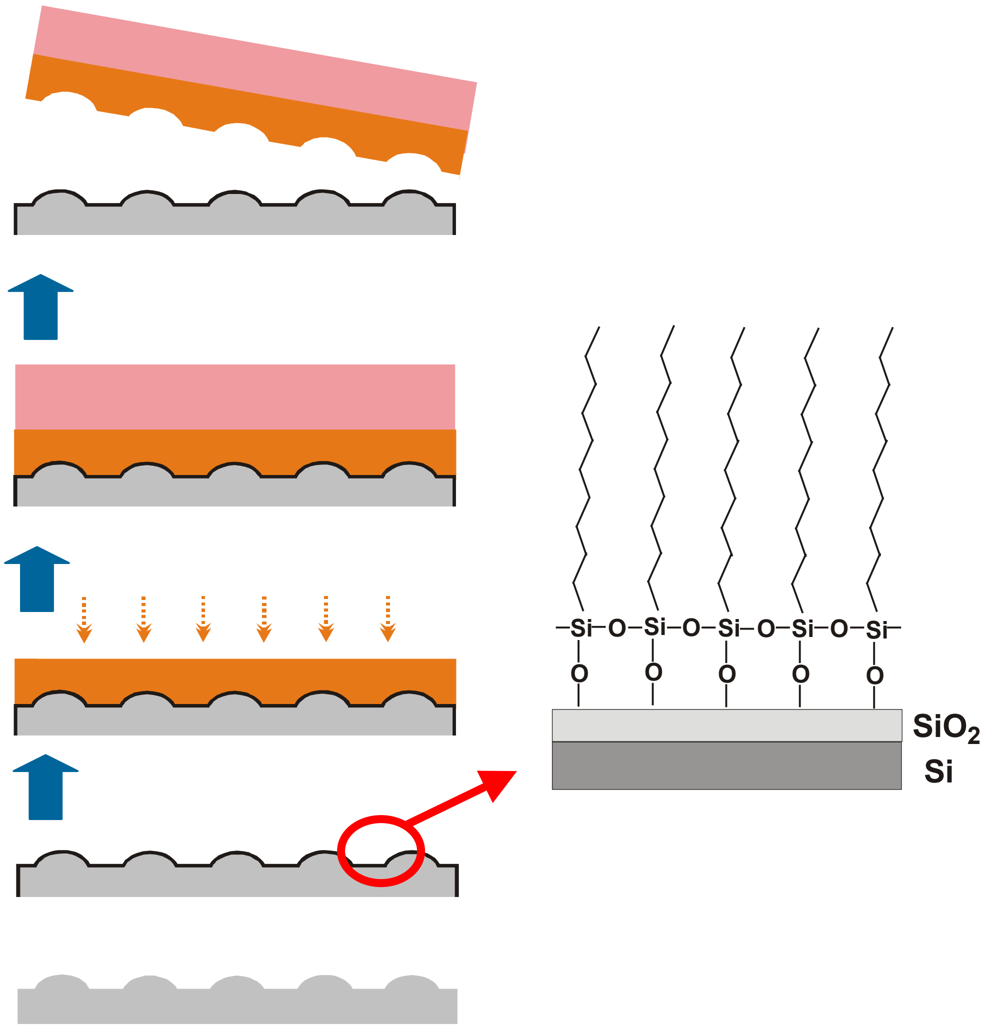
Substrate

Self-Assembly
Solution

→ Octadecyltrichlorosilane
(Hexane Solution)

Replication at the nanometer scale.

Building-up the metal nanomolds by thermal evaporation



Release of the Nanostructured Metal Film

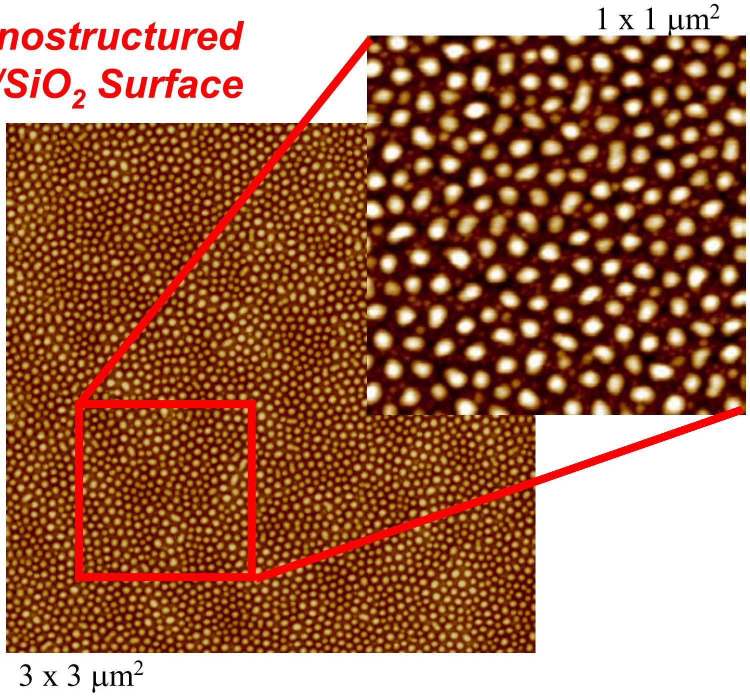
Electrochemical Deposition of a Thick Metal Film

Evaporation of a Thin Metal Film (100-200nm)

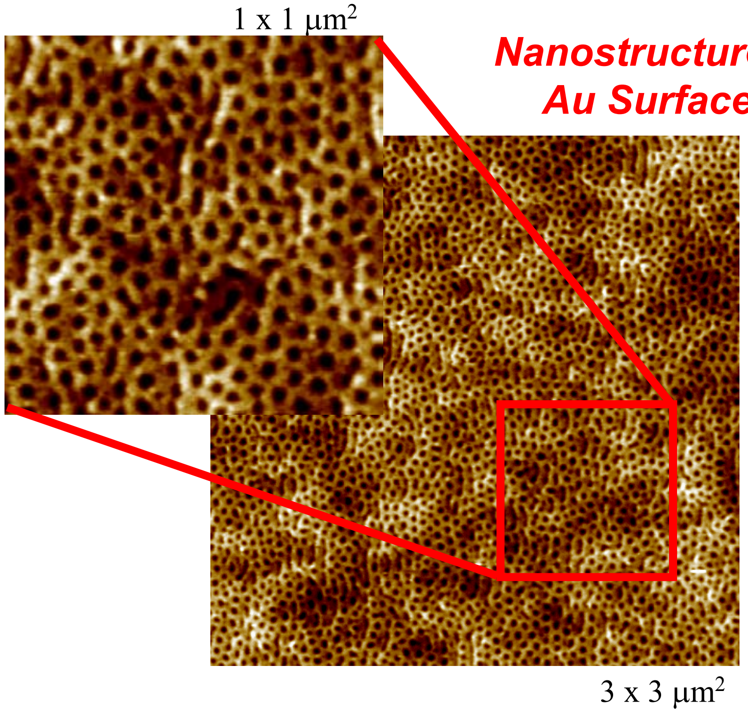
Surface Modification by Octadecyltrichlorosilane Self-Assembled Monolayer

Nanostructured Si/SiO_2 Substrate

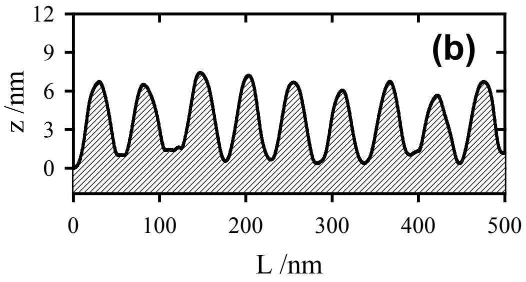
Fabrication of Metal Nanomolds

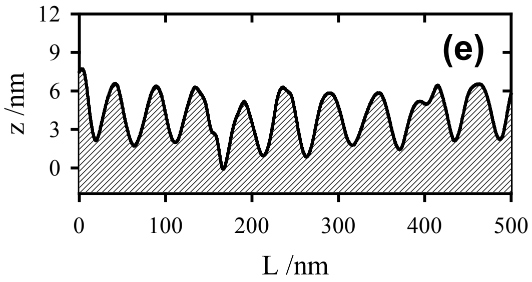


Nanostructured Si/SiO$_2$ Surface



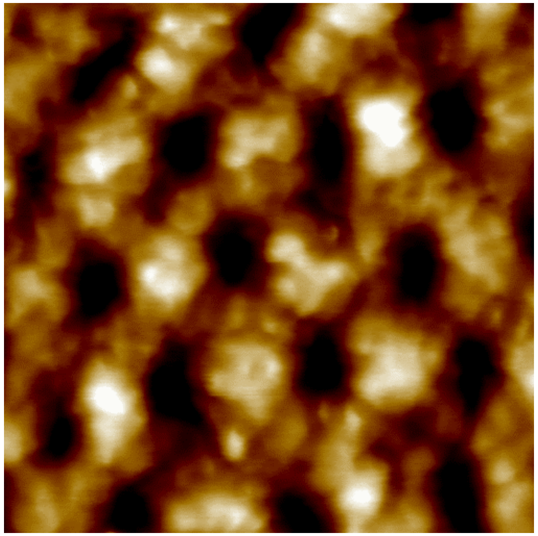
Nanostructured Au Surface

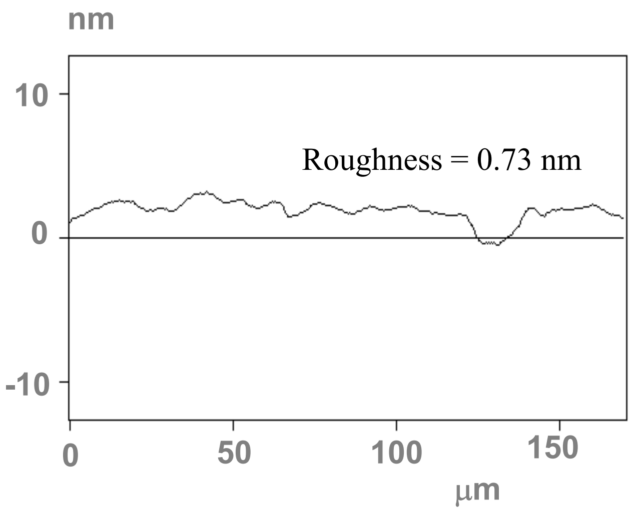




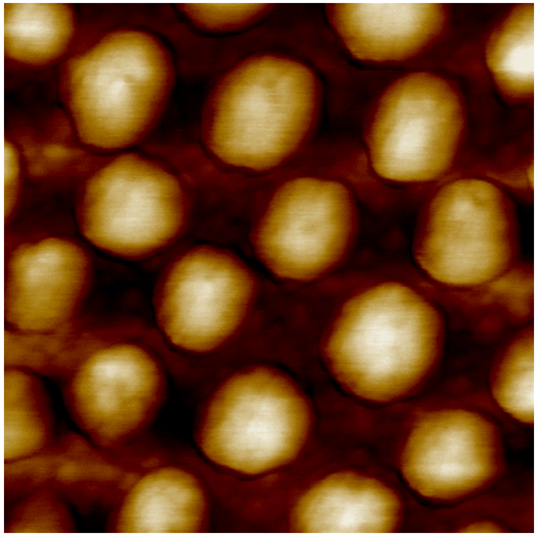
O.Azzaroni, M. Fonticelli, G. Benítez, P.L. Schilardi, R. Gago, I. Caretti, L. Vázquez and R.C. Salvarezza, Adv.Mater. 16 (2004) 405

TM-AFM 200 x 200 nm²

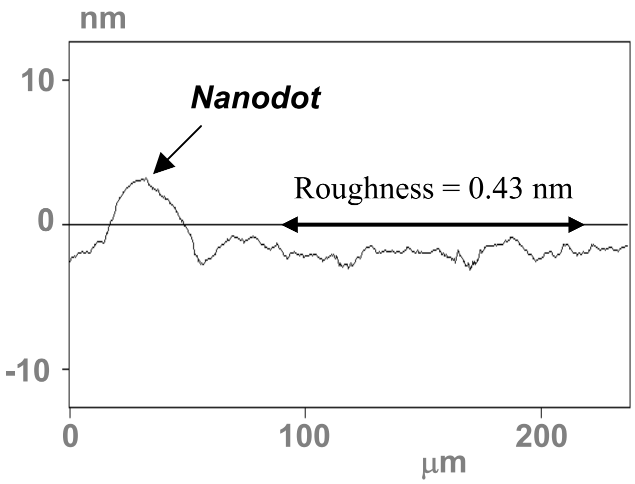




Au



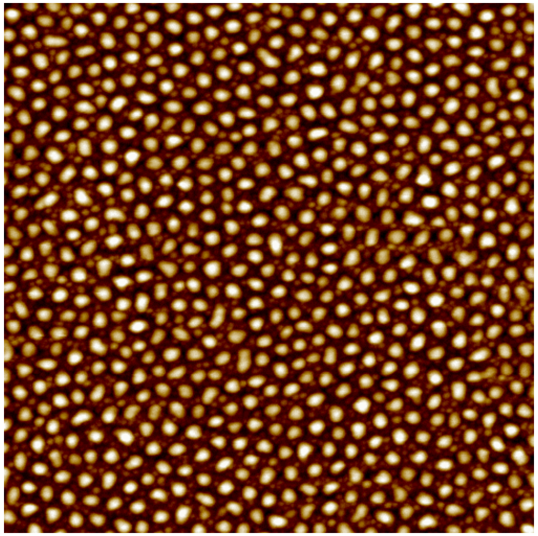
TM-AFM 200 x 200 nm²



Si/SiO_2

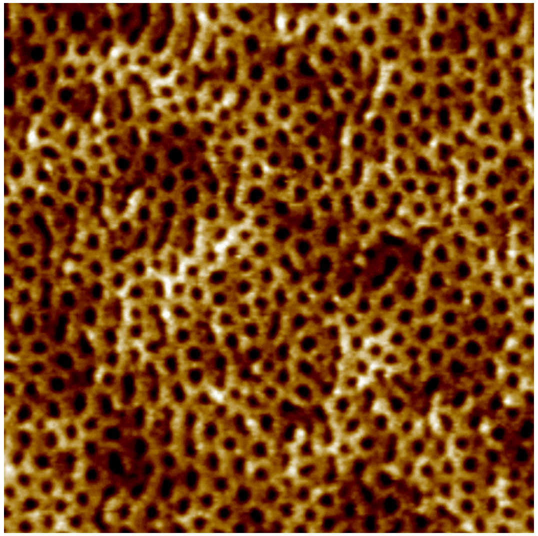
O. Azzaroni, M. Fonticelli, P.L. Schilardi, R. Gago, L. Vázquez and R.C. Salvarezza, Nanotechnology 15 (2004) S197

Nanoscale Replication on Ceramic Materials



1 x 1 μm^2

Nanostructured
Si/SiO_2 Master Surface

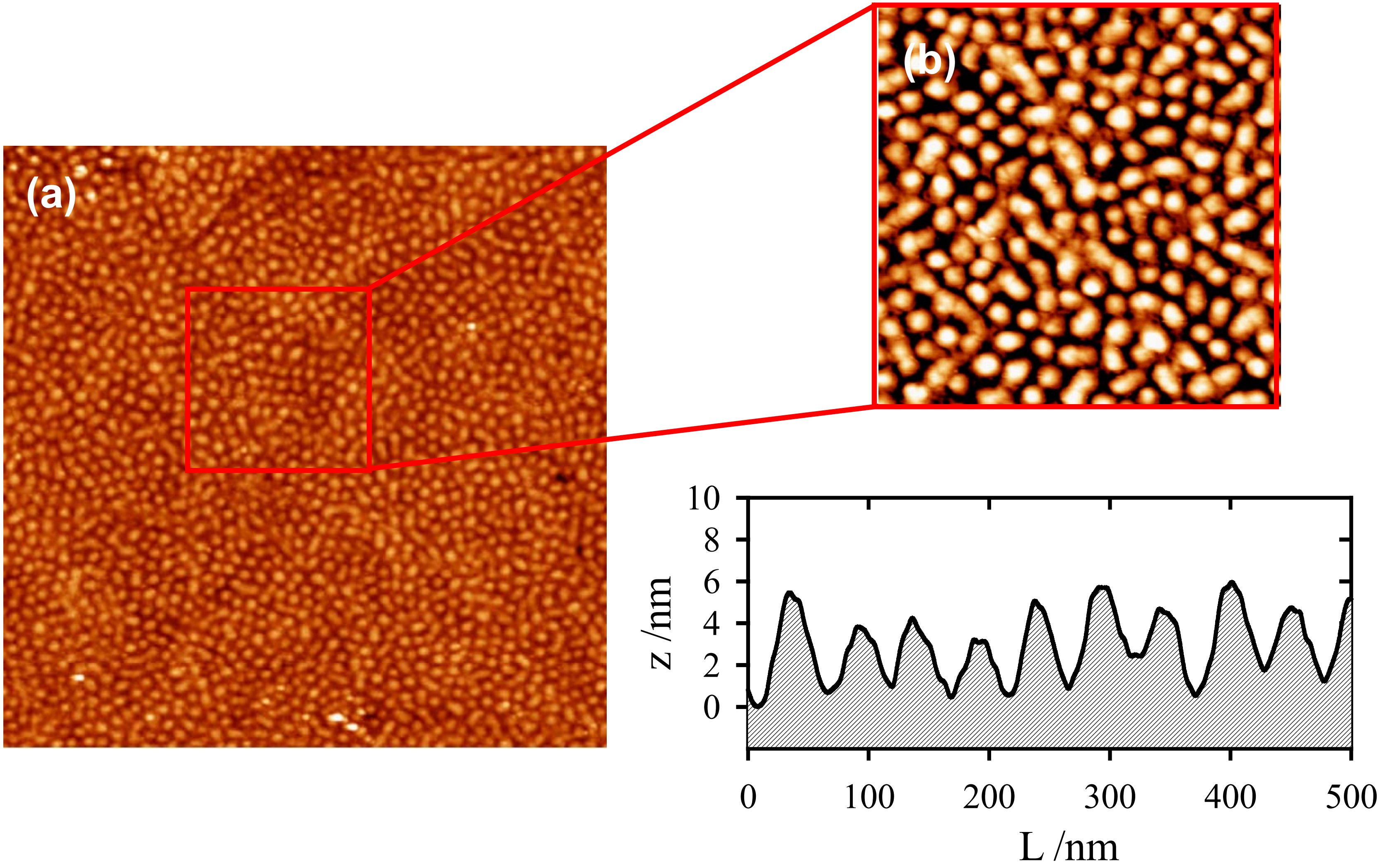


1 x 1 μm^2

Gold-Made Nanomold

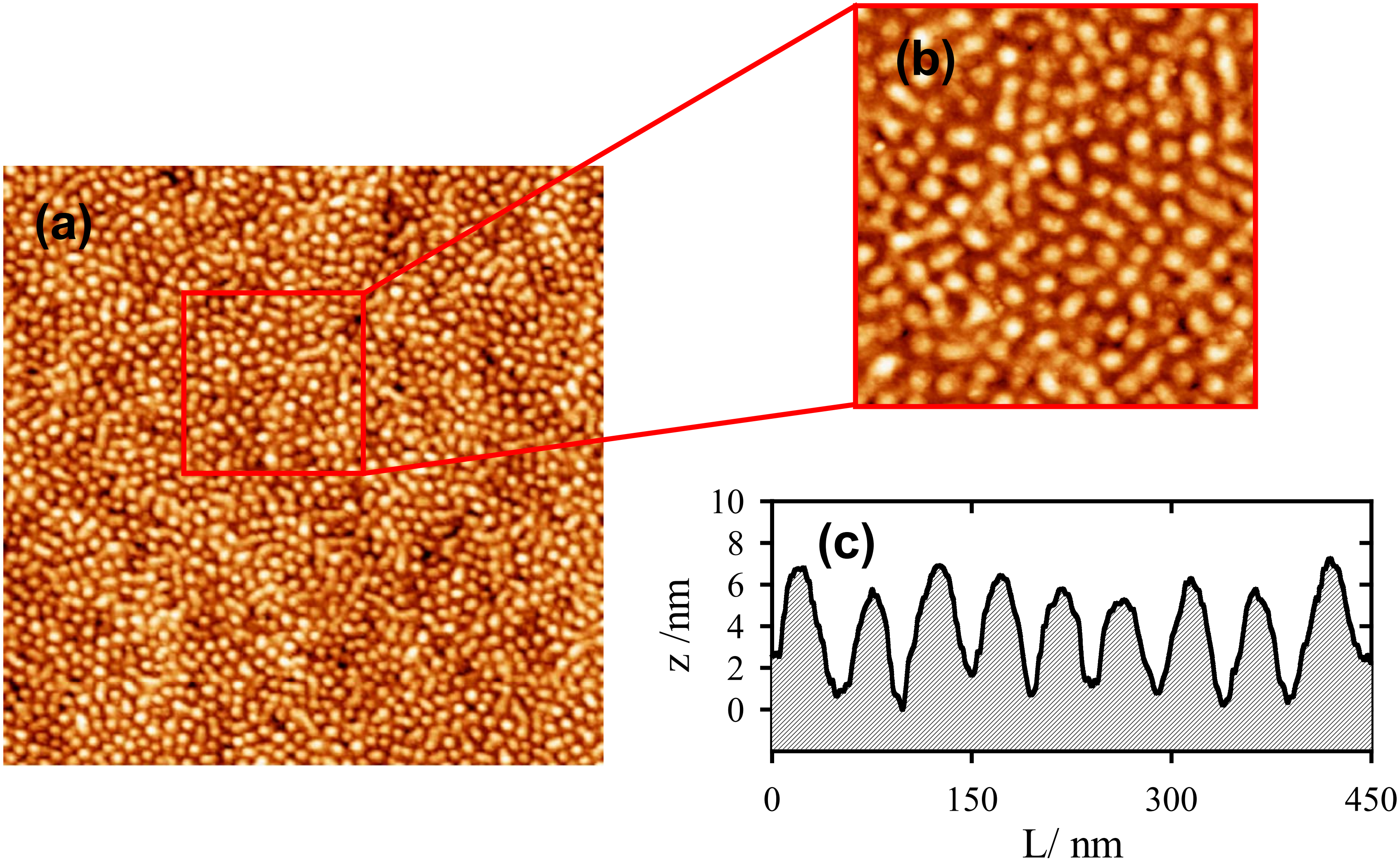
?

Nanoreplicated Ttanium Nitride (TiN) Surface



AFM Images: (a) 2 x 2 μm² (b) 600 x 600 nm²

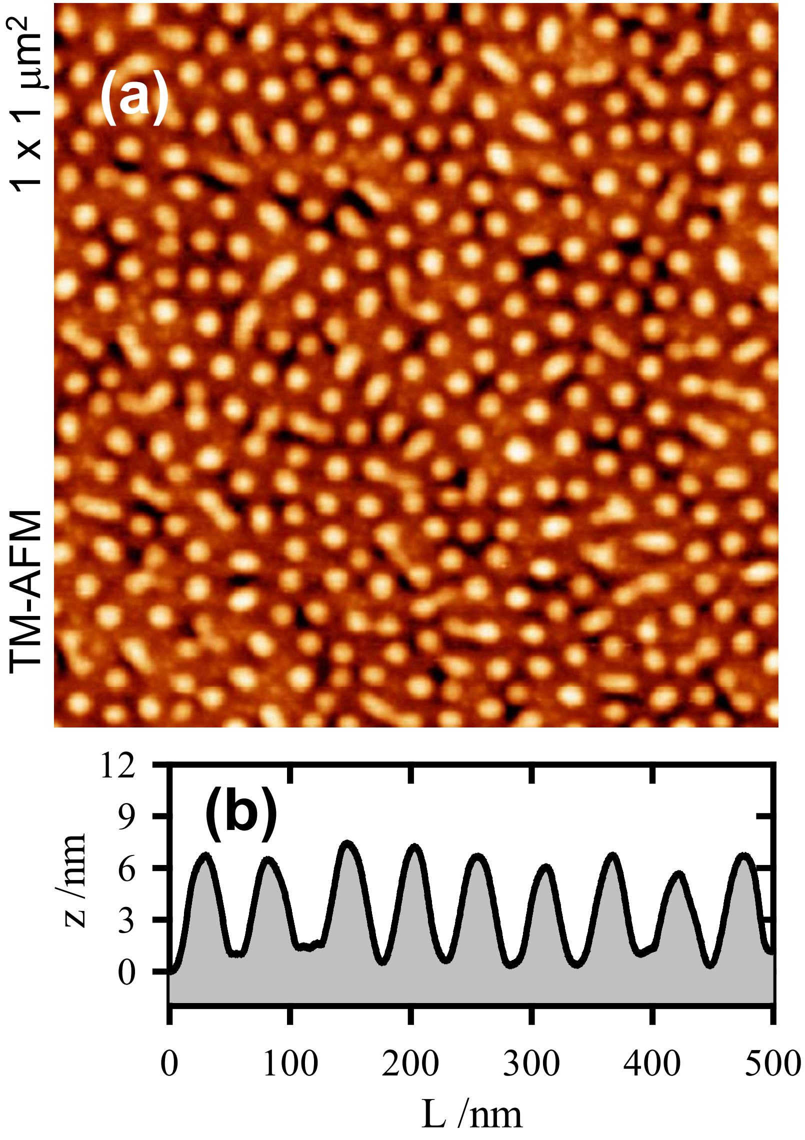
Nanoreplicated Aluminum Nitride (AlN) Surface



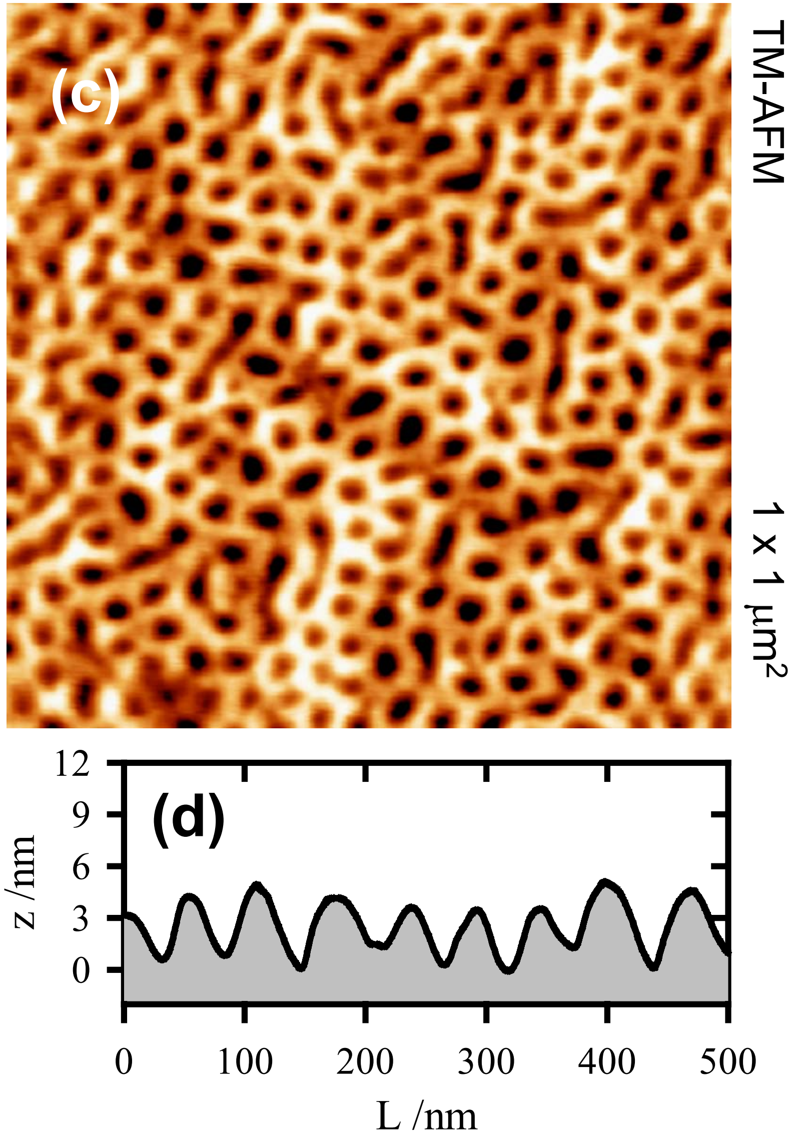
AFM Images: (a) 2 x 2 μm^2 (b) 600 x 600 nm^2

Direct Molding of Nanostructured Ceramic Surfaces

SiO_2/Si



Titanium Nitride



Conclusions

* Molding and replication techniques, commonly used for patterning polymeric materials, can be succesfully extended to a wide range of materials.

* By using conductive “stamps” is possible to exploit the advantages of soft lithographic techniques for patterning materials that can be electrodeposited.

* Molding and replication techniques can be used for transferring surface-relief patterns onto different materials, from metals to ceramics, with nanoscale resolution.

* When dealing with “electrochemical” soft lithography using conductive stamps, the self-assembled monolayer plays a key role as “release agent” during the replica-molding process. Its electrochemical stability determines the feasibility of the process.

* The same SAM-modified conductive “stamps” can be used for patterning other materials that can be deposited by pulsed laser ablation or reactive sputtering.

* Deposit grain size is a variable that influences the fidelity of the molding process, and it must be taken into account when the deposition technique is chosen.

Acknowledgements

INIFTA – CONICET – ARGENTINA
Roberto Salvarezza (SPM & Surface Chemistry Laboratory Director)
Patricia Schilardi
Mariano Fonticelli
Federico Castez

Instituto de Ciencia de Materiales de Madrid – SPAIN
Department of Physics and Surface Engineering – Luis Vázquez
Department of Ferroelectric Materials – Carlos Zaldo

Financial Support

Fundación Antorchas (Argentina)

Consejo Nacional de Investigaciones Científicas y Técnicas (Argentina)

Agencia Nacional de Promoción Científica y Tecnológica (Argentina)