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Electrosynthesis of nanostructures for energy

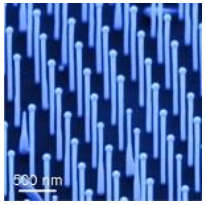
N. STEIN

Electrochemistry of Materials Research Group

thematic school of the GDR NAME

ELaboration of NANOmaterials for the recovery, conversion, transport and storage of energy

11-16 June 2023



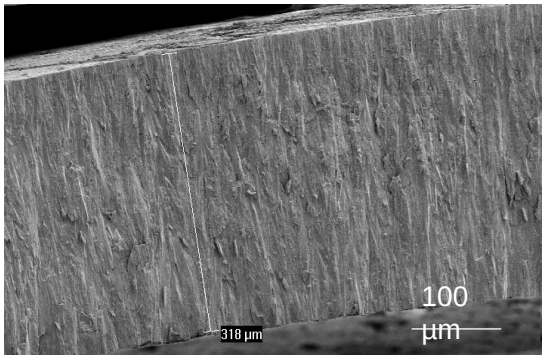
NAME

GDR NAnoMaterials for Energy applications

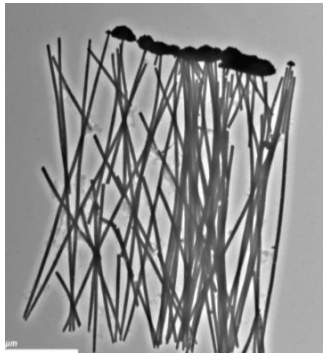
Electrochemistry of Materials Research group: *Scientific objectives*

- Analytic study of chemical and electrochemical systems for optimized processes
- **Synthesis and processing of functional materials by electrolysis …**

Thermoelectric materials



Electroplated thick film of bismuth telluride for Peltier modules



Bundle of electroplated Bismuth telluride nanowires

Contents

1. Electrosynthesis of films
    a) Basics
    b) Example : Bismuth Telluride
2. The synthesis of nanostructures by electrosynthesis
    a) Low dimensional films (2D)
    b) Focus on the 1D nanostructures

Contents

Basics of electrosynthesis

Electrosynthesis : WIKIPEDIA The Free Encyclopedia

« synthesis of chemical compounds in an electrochemical cell »

Products of the reaction on the electrode = **electrodeposition**

- **direct reduction** of chemical compound at an electrode assisted by external electrical source
  - **Cathodic reaction** : $Cu^{2+} + 2e^- \rightarrow Cu°$

- ***direct oxidation*** of chemical compound at an electrode assisted by external electrical source
  - **Anodic reaction** : synthesis of manganese dioxyde

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^- \ (overall\ reaction)$$

Basics of electrosynthesis

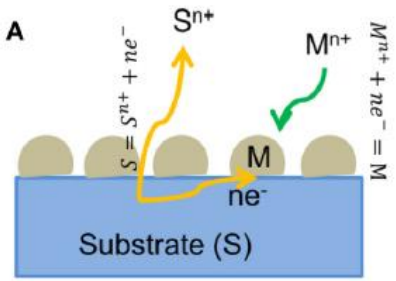
- **Indirect synthesis** induced by anodic or cathodic reaction assisted by external electrical source

1/ $$\frac{1}{2}O_{2\,(aq)} + H_2O_{(l)} + 2\ e^- \rightarrow 2\ OH^-{}_{(aq\ and\ ads)}$$

2/ $$Zn^{2+}{}_{(aq)} + 2\ OH^-{}_{(ads)} \rightarrow Zn(OH)_{2(s)} \rightarrow ZnO_{(s)}$$

- **from a chemical reductor** (electroless deposition) No external source, more difficulty to control the thickness and uniformity of the deposits

Exposing a less noble metal containing solution (S) to a more noble metal (M)



$$S = S^{n+} + ne^-$$
$$M^{n+} + ne^- = \mathrm{M}$$

Galvanic displacement reaction

- Examples : GaSb, Bi_2Te_3…

Manzano, CRITICAL REVIEWS, 2022, VOL. 47, NO. 5, 772–805
Lahiri, February 2019 | Volume 7 | Article 85

Basics of electrosynthesis

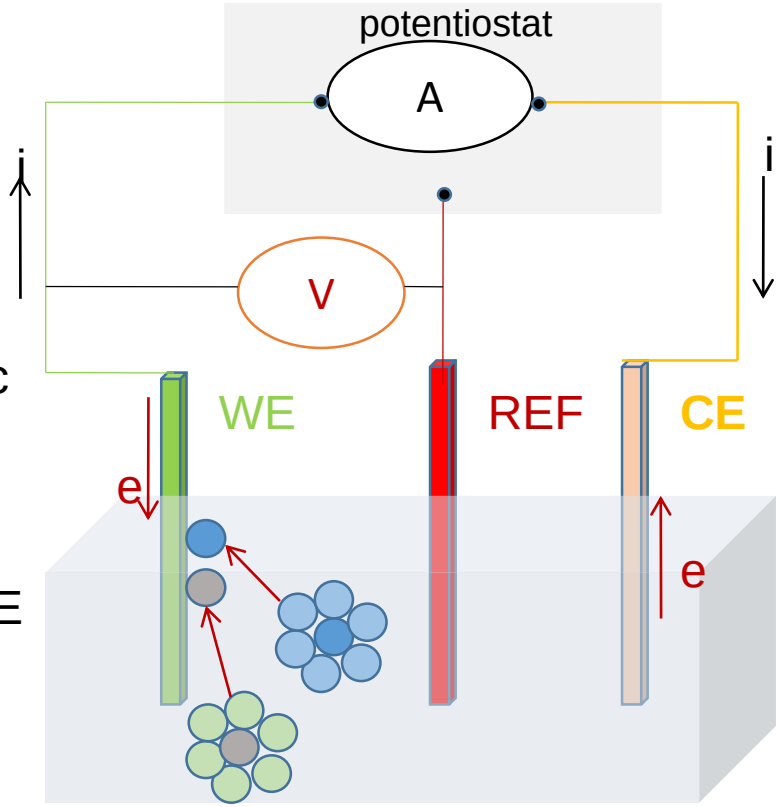
Experimental setup

external source
Potentiostat E_{fixed}
Galvanostat I_{fixed}
Waveform generator

Working electrode
Exposed area for the deposition

Reference electrode
Define the thermodynamic voltage V_{WE}-V_{Ref}

Counter electrode
Reverse reaction of the WE



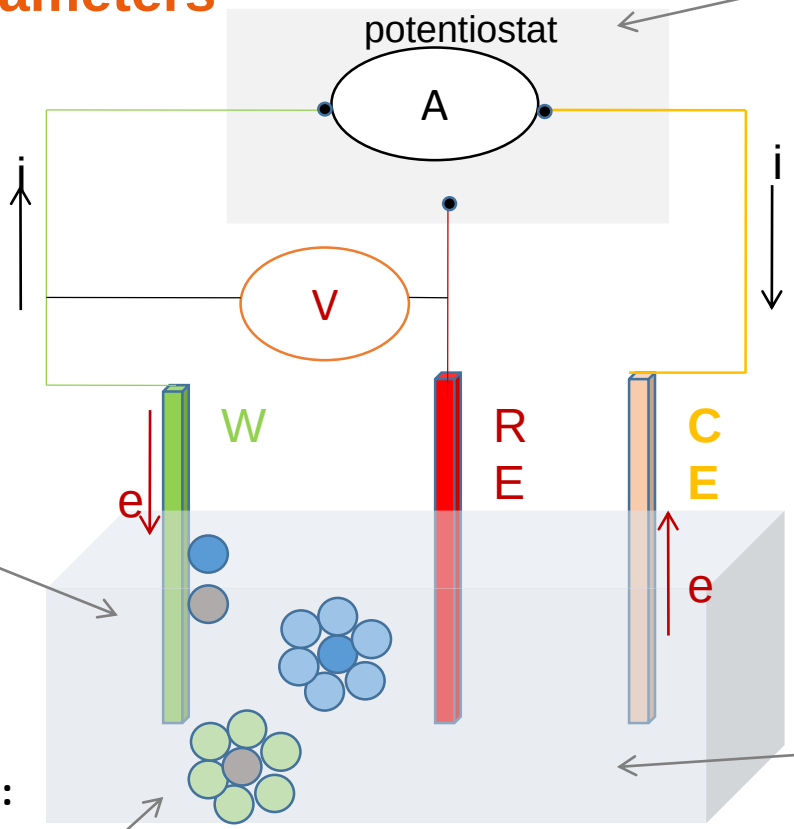
Electrolyte solution
aqueous, non aqueous, ionic liquids, or molten salts

$M^{n+} + ne^- \rightarrow M°$

Basics of electrosynthesis

Experimental parameters

Electrical parameters:
- E potential
- I current density
- Q consumed charge



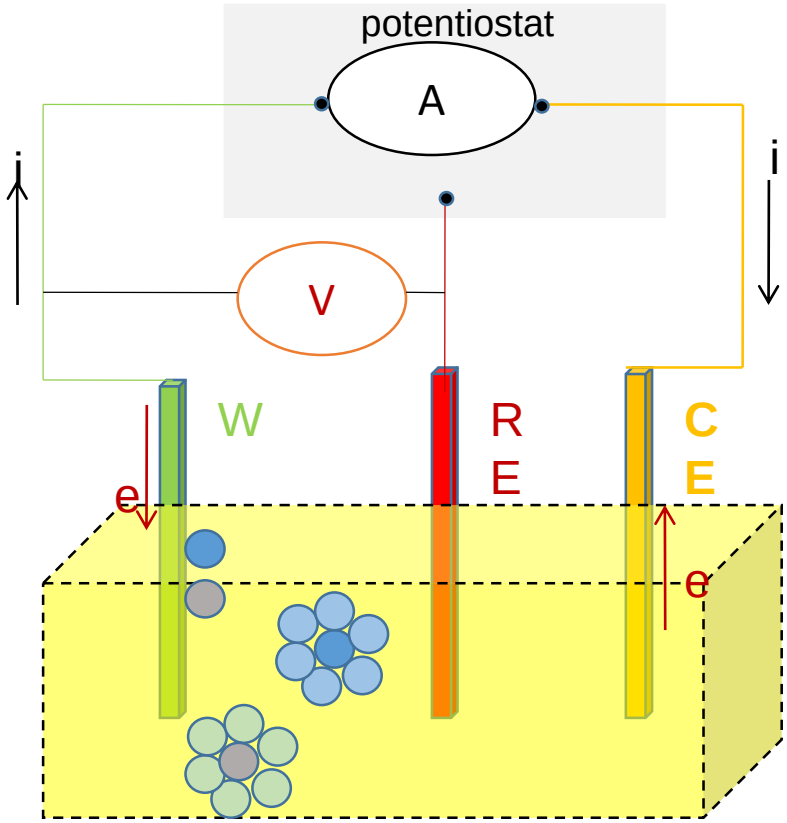
Electrode parameters:
- Type of substrate
- Geometry
- Surface roughness

Electrolyte parameters:
- Nature and Concentration of the precursors
- Supporting electrolyte
- Additives
- Temperature

Mass transfer parameters:
- Mode: diffusion, convection Hydrodynamic conditions

Basics of electrosynthesis

Chemical parameters



Type and concentration of precursors
Solubility of the precursors
solvent : aqueous or not aqeuous medium
Complexing agents = electrochemistry
additives = morphology
Temperature = mass transport
Viscosity = mass transport

Side reactions
Hydrogen evolution Reaction
electroactivity domain

Basics of electrosynthesis

Chemical parameters : the importance of the electrolyte solution

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	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub		Uuq				

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

Electrodeposited metal in **aqueous medium**

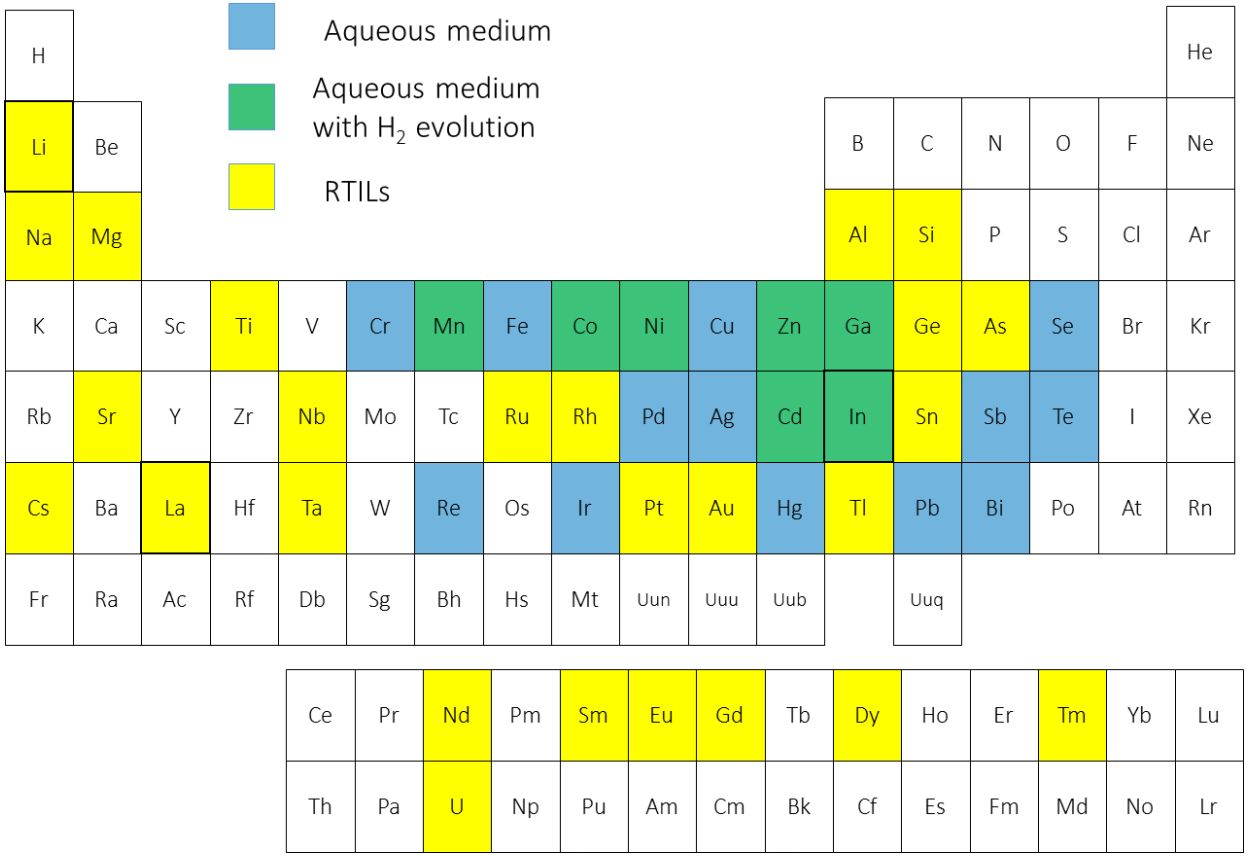
Limitation by hydrogen evolution

(E~-1.2 V) $H_2O + 1e^- \rightarrow \frac{1}{2} H_2 + OH^-$

Reduction reaction	E° (V *vs.* SHE)
$Mn^{2+} + 2e^- \rightarrow Mn$	−1.19
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.45
$Co^{2+} + 2e^- \rightarrow Co$	−0.28
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.26
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$Rh^{3+} + 3e^- \rightarrow Rh$	+0.76
$Pd^{2+} + 2e^- \rightarrow Pd$	+0.95
$Ag^{+} + e^- \rightarrow Ag$	+0.80
$Ir^{3+} + 3e^- \rightarrow Ir$	+1.16
$Pt^{2+} + 2e^- \rightarrow Pt$	+1.18
$Au^{3+} + 3e^- \rightarrow Au$	+1.50

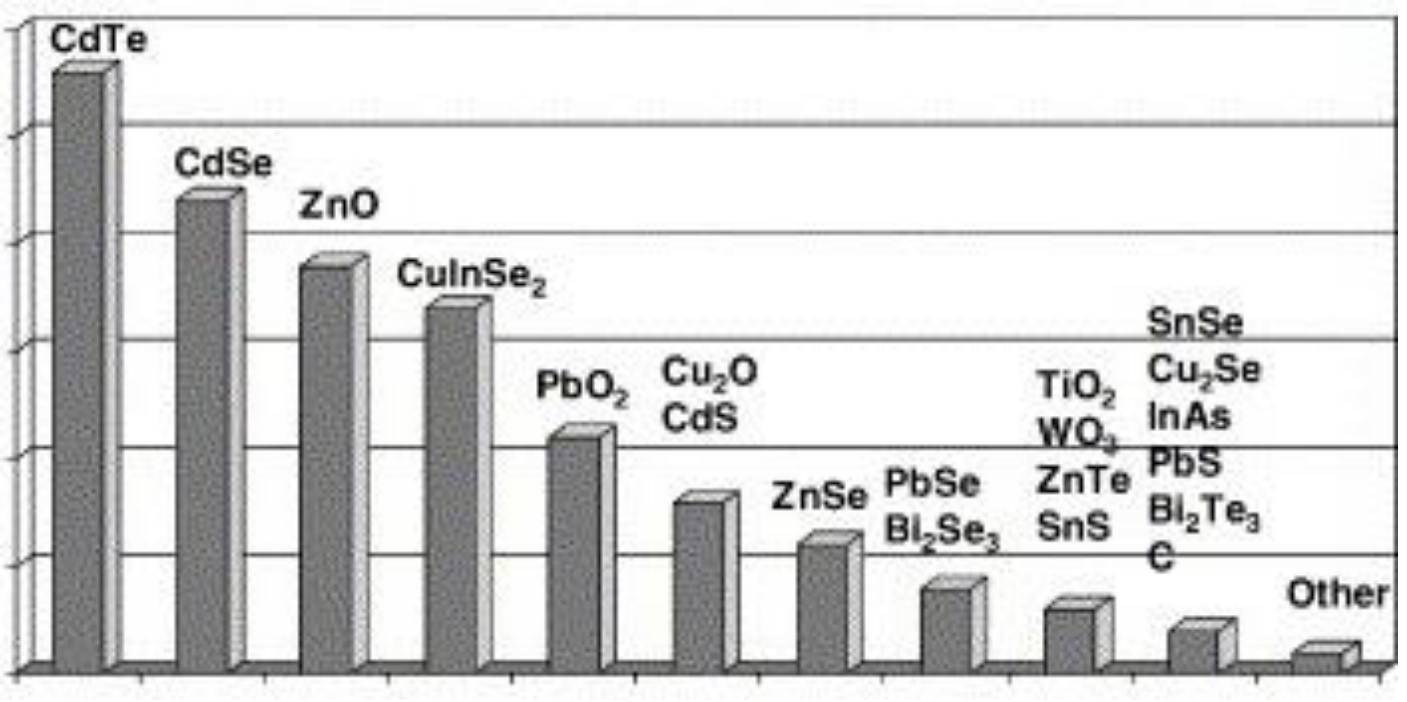
Basics of electrosynthesis

Chemical parameters : the importance of the electrolyte solution



Limitation by the electroactivity domain of the solvent

Electrodeposition of semiconductors

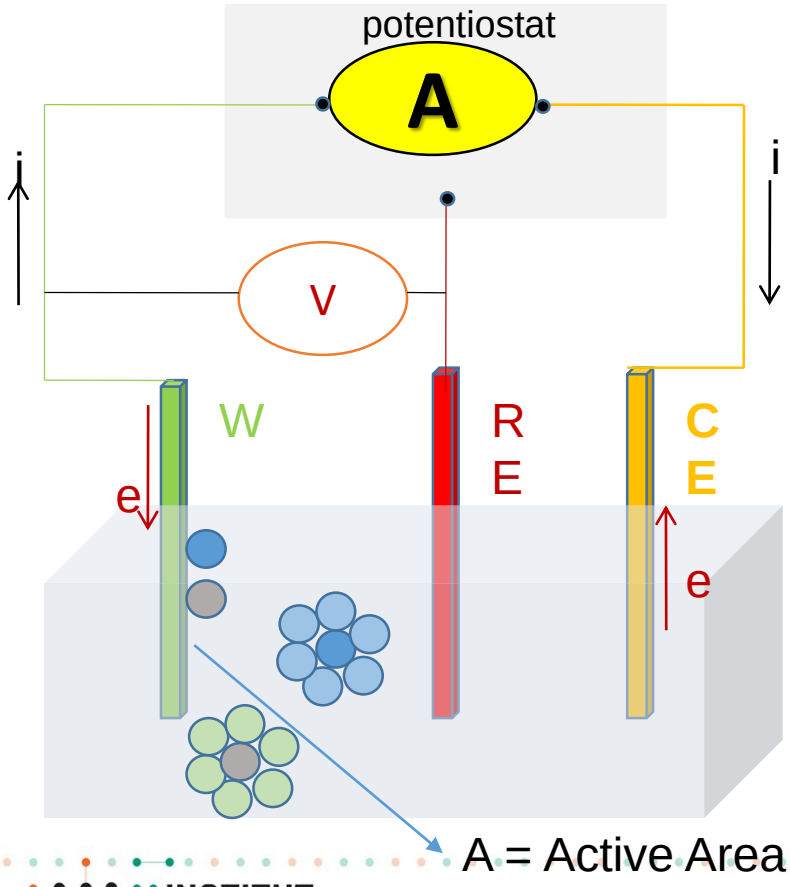


Number of published papers from Current Contents data base (2002) as a function of the nature of the semiconductor

D. Lincot, "Electrodeposition of semiconductors," Thin Solid Films, Proceedings Paper vol. 487, no. 1-2, pp. 40-48, Sep 2005.

Basics of electrosynthesis

Electrical parameters = I current density and Q consumed charge



$M^{n+} + ne^- \rightarrow M°$

Reaction speed = v_c

$$v_c = \frac{\partial \xi}{\partial t} = \frac{\partial n_M}{\partial t} = -\frac{1}{n}\frac{\partial n_{e^-}}{\partial t}$$

$$\boldsymbol{v_c = -\frac{i}{nF}} = -\frac{1}{nF}\frac{\partial Q}{\partial t}$$

$$Q = \int i dt = n_{e^-}F = \frac{m}{M}F = \frac{\rho e A}{M}F$$

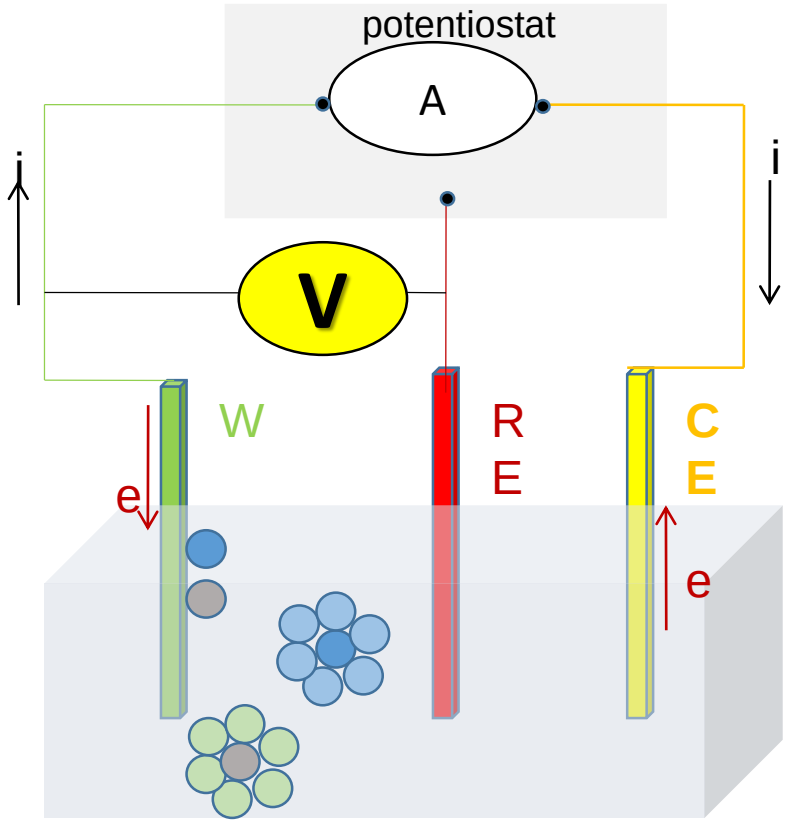
Avogadro's constant *F*

Mass of deposits *m*
Thickness *e*

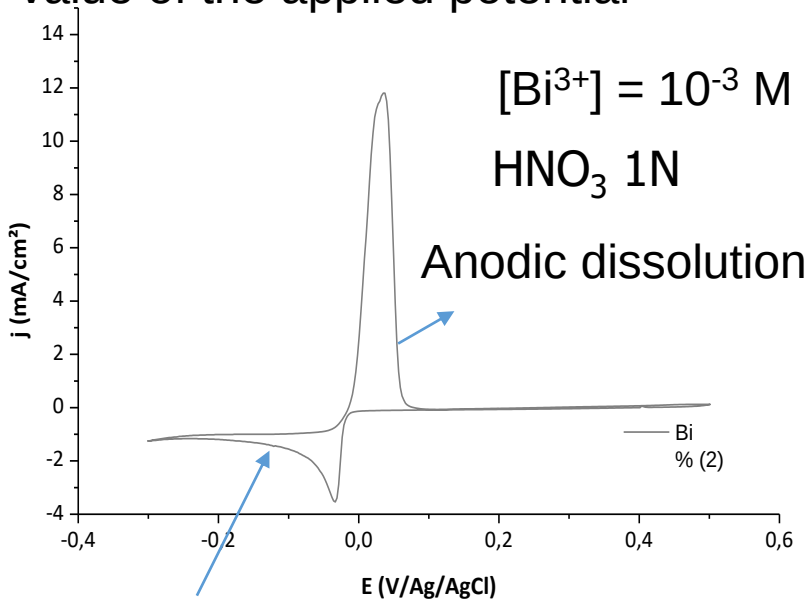
Faradic Yield $FY(\%) = \frac{e_{exp}}{e_{th}}$

Basics of electrosynthesis

Electrical parameters : E potential



The cyclic voltametry a tool to define the value of the applied potential



$[Bi^{3+}] = 10^{-3}$ M

HNO_3 1N

Anodic dissolution of Bi

Potential window

Selectivity of the targeted cathodic reaction

$$Bi^{3+} + 3e \longrightarrow Bi°$$

Side reactions

Hydrogen evolution Reaction

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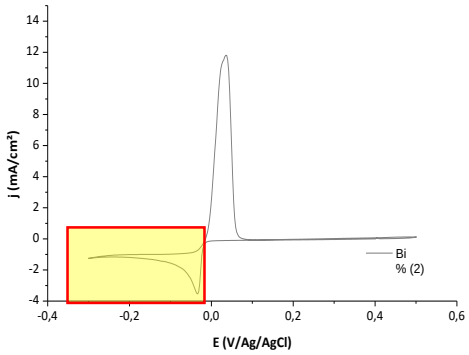
Basics of electrosynthesis

Electrical parameters : E potential



$$E_{eq} = E^{0}_{M^{n+}/M^{0}} + \frac{RT}{nF} Ln \frac{a_{M^{n+}}}{a_{M^{0}}}$$

potential

E_{eq}

$i = i^{o}\,(nF/RT)\eta$

linear region

exponential region

$$i = i^{o} e^{\frac{(1-\alpha)nF\eta}{RT}}$$

$M^{\circ} \leftarrow M^{n+} + ne^{-}$

Mixed control

Charge and mass transfer

$I_{lim} = f(|M^{n+}|_{sol})$

Mass transfer control

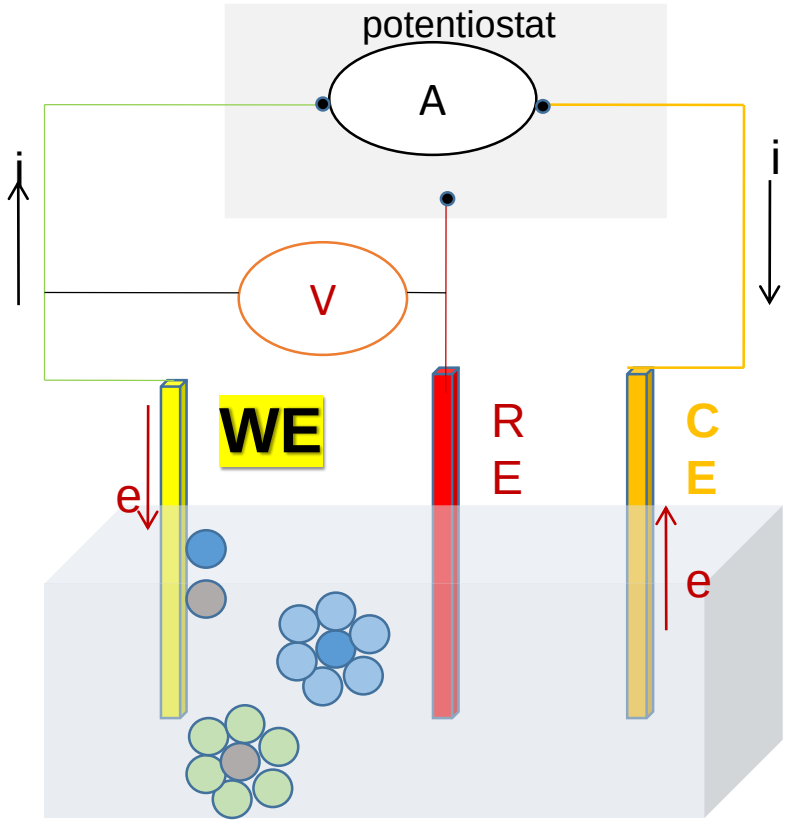
Limiting current density region

Charge transfer control

current density

Basics of electrosynthesis

Nature of the electrode



electronic substrate

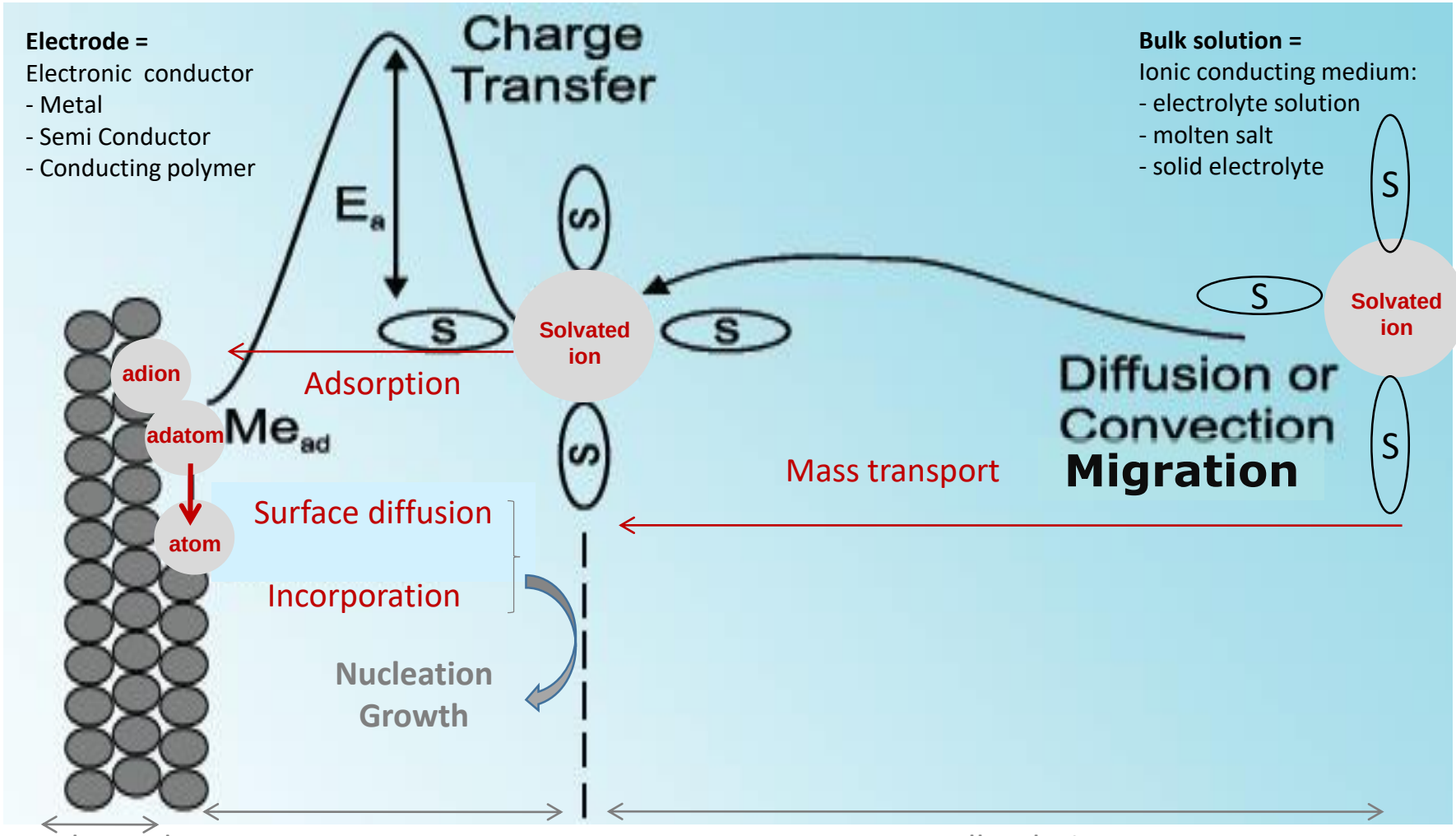
•Charge transfer

•Geometry

• surface roughness

=> **electrocrystalization process**

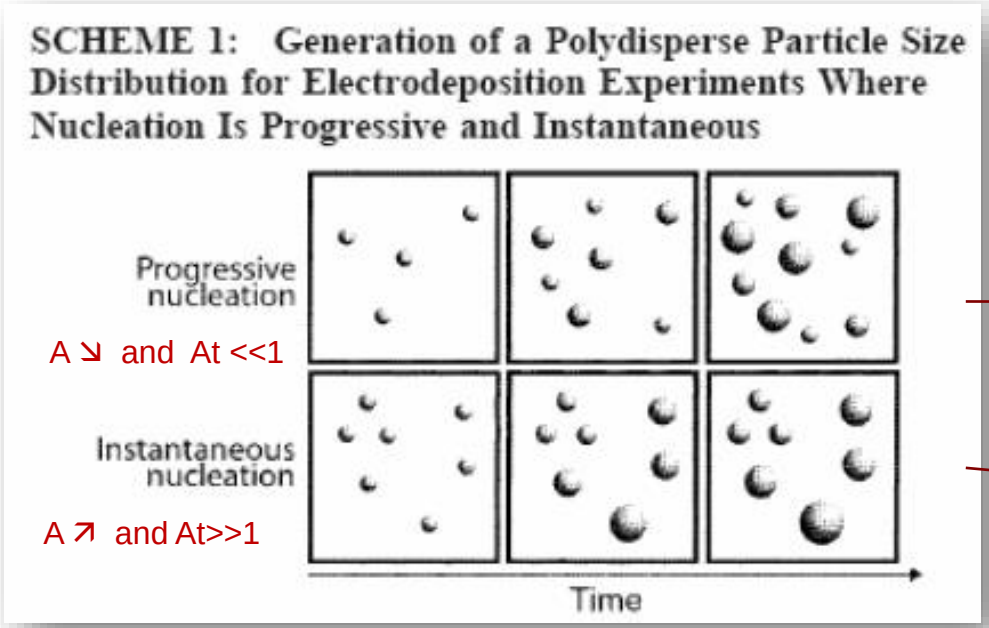
Basics of electrosynthesis



Basics of electrosynthesis

Growth

defects on crystal face ➔ nucleation sites for electrodeposition



$N = N_0[1- \exp(-At)]$

N_0 = total number of sites

(maximum possible number of nuclei per unit surface)

A = nucleation rate constant

→ $N \approx N_0 At$

increase of nuclei number during the growth process

→ $N \approx N_0$

immediate activation of all reaction sites and constant number of nuclei

Nucleation – growth

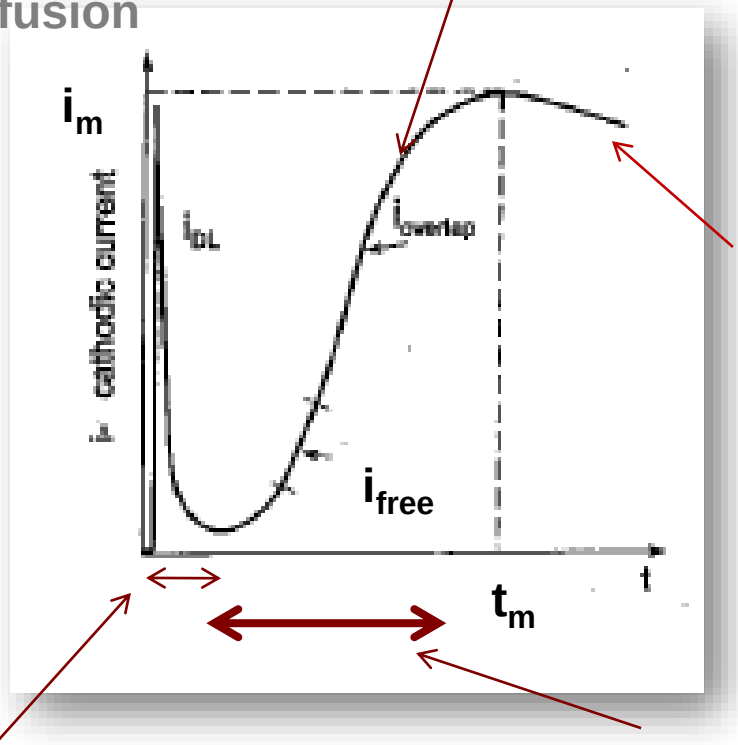
Electrochemist point of view

current-time transients i=f(t)

Example of 3D nucleation limited by diffusion

Z_3 =overlap of nuclei

Slowing down of nucleation and current ↘



Z_4 = diffusion of ions in solution

Limiting current

Z_1 =double layer charging current

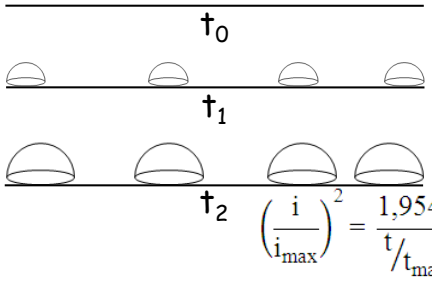
Z_2 = i↗

- growth of independant nuclei
- increase in nb of nuclei

Current time transients

theoretical models of nucleation

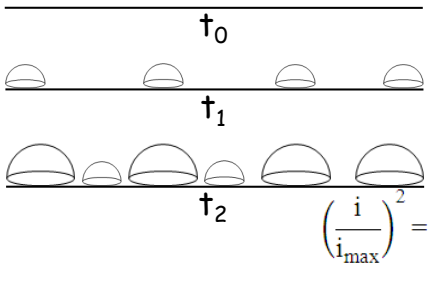
3D Nucleation



Instantaneous nucleation

immediate activation of all reaction sites and constant number of nuclei

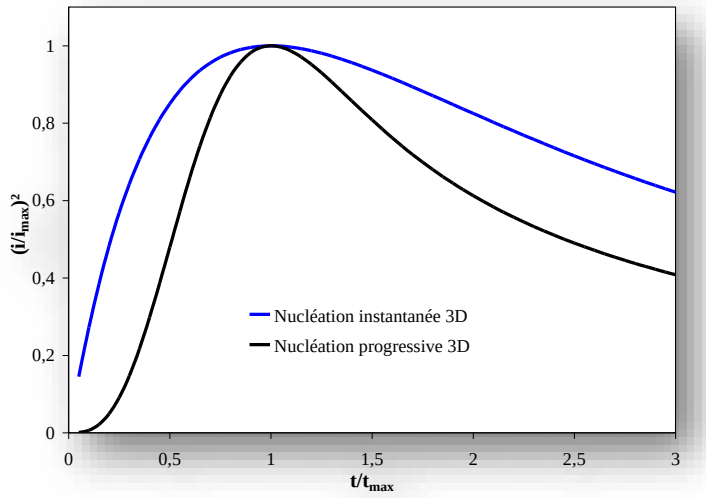
$$\left(\frac{i}{i_{max}}\right)^2 = \frac{1{,}9542}{t/t_{max}}\left(1\text{-}\exp\left[-1{,}2564\left(\frac{t}{t_{max}}\right)\right]\right)^2$$



Progressive nucleation

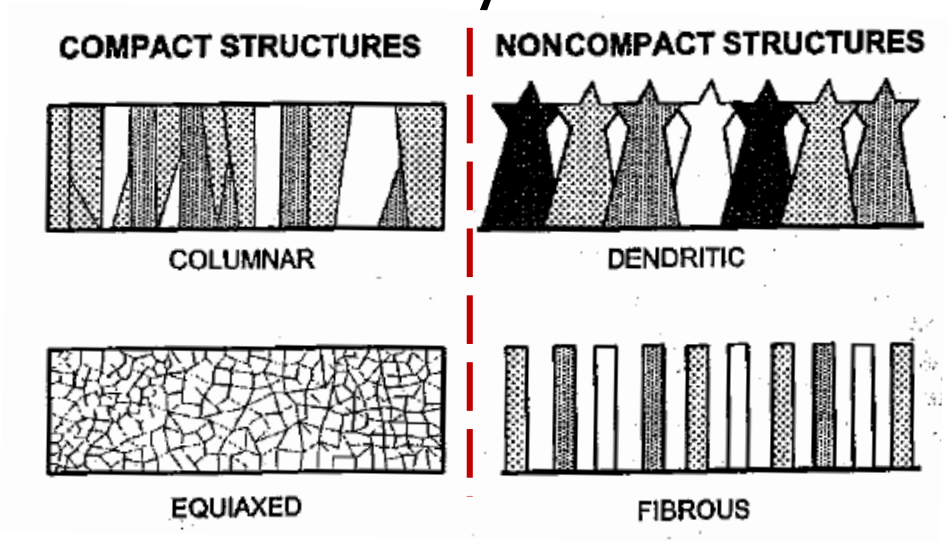
increase of nuclei number during the growth process

$$\left(\frac{i}{i_{max}}\right)^2 = \frac{1{,}2254}{t/t_{max}}\left(1\text{-}\exp\left[-2{,}3367\left(\frac{t}{t_{max}}\right)^2\right]\right)^2$$



B. Scharifker, G. Hills, Electrochim. Acta 28 (1983) 879.

Electrocrystallization



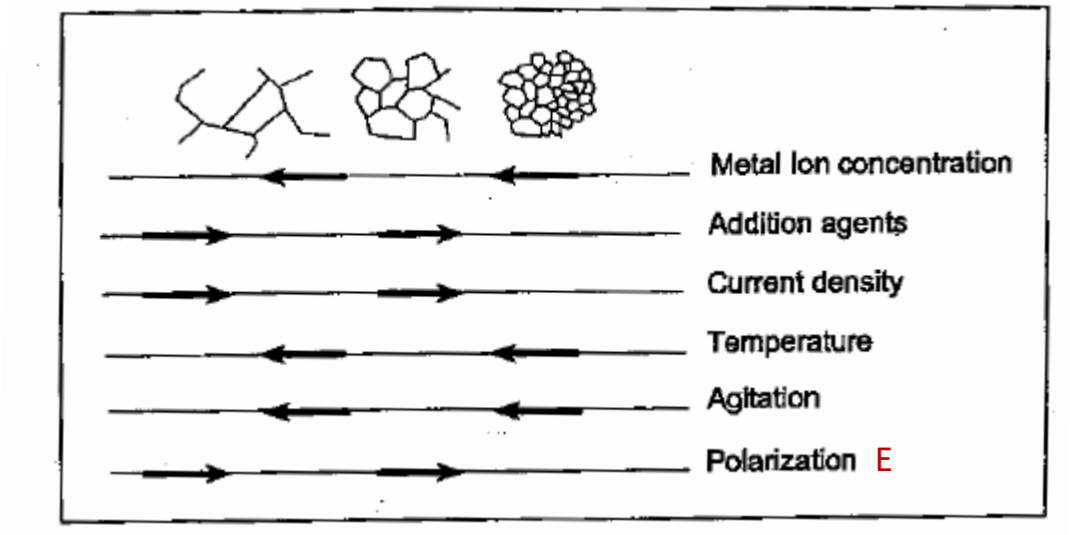
Schematic présentation

of grain structures of electrodeposited films

Operating conditions over electrodeposit structure

***Arrow**: increase of the given parameter in determining grain sizes*

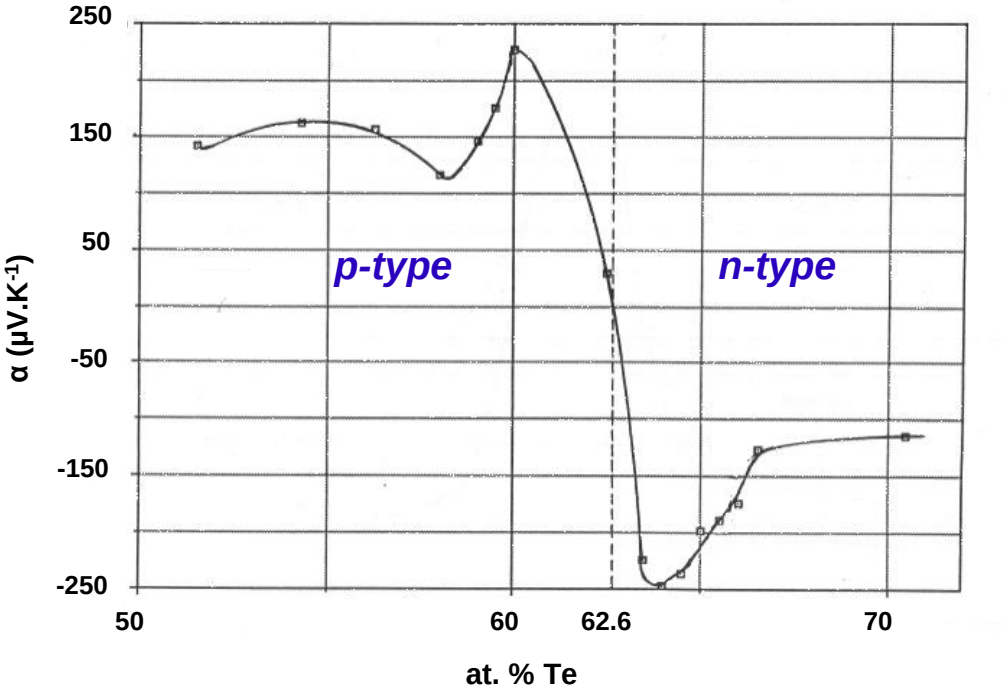
But also
- Chelates
- Other C^+ et A^-
- Substrate
- pH
- Adsorbed species



Contents

Example : electrodeposition of Bismuth Telluride

Thermoelectric material



A textbook case !

Bi excess → **p-type** (ZT^{300K} = 0.54 for $Bi_{2.1}Te_{2.9}$)

Te excess → **n-type** (ZT^{300K} = 0.65 pour $Bi_{1.78}Te_{3.22}$)

Conductivity transition : $Bi_{1.88}Te_{3.12}$

High dependence of chemical composition on the transport properties of the compound
Necessary to monitor the composition of Bi_2Te_3

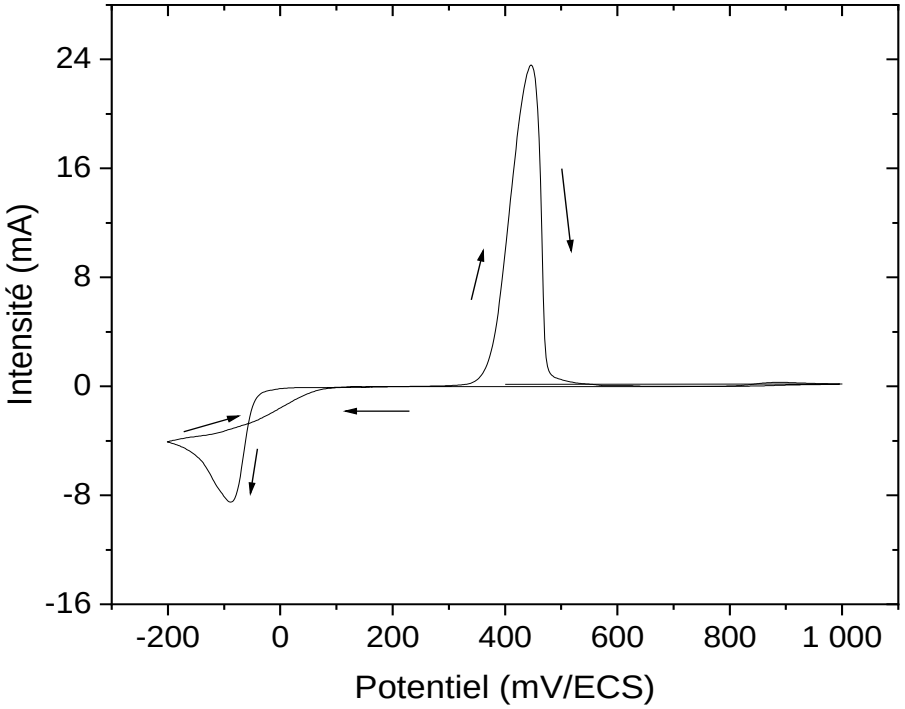
Example : electrodeposition of Bismuth Telluride

Setting of the electrodeposition setup

Electrolyte solution
HNO_3 1M
$[Bi^{3+}]=[HTeO_2^+] = 10^{-3}$ M

Cathodic reaction
$2Bi^{3+}+3HTeO_2^+ +18\ e^- +9H^+ \rightarrow Bi_2Te_3+6H_2O$

Mechanism
Coreduction or precipitation ?

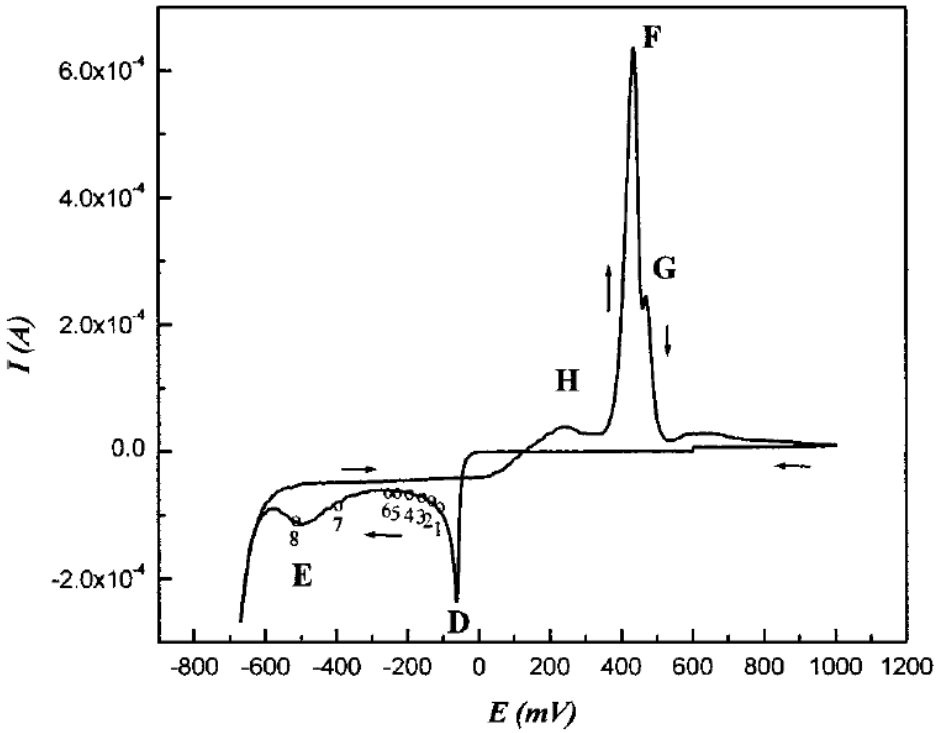


Single phase in acidic Medium

Michel Journal of Crystal Growth 2005, 277, (1-4), 274-283.

Example : electrodeposition of Bismuth Telluride

Setting of the electrodeposition setup



Several anodic peaks

=>Bi-Rich deposits at more cathodic potentials
(E peak = Bi reduction)

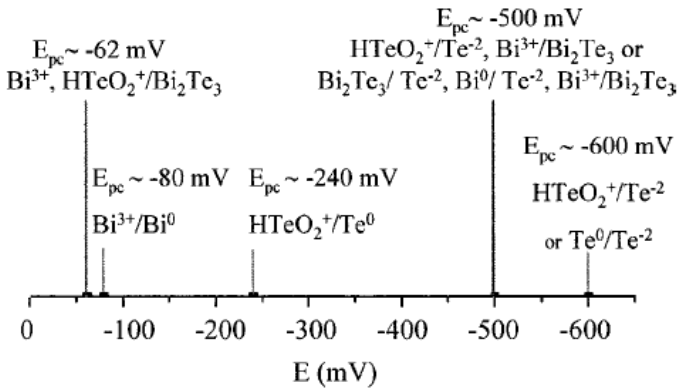
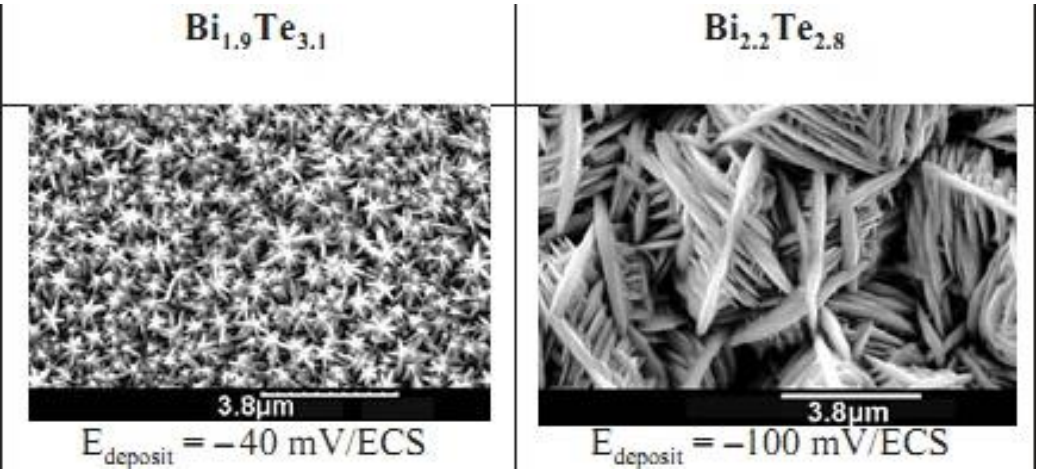


Figure 8. Summary of the reduction potentials observed as determined by the cyclic voltammogram studies.

Martin-Gonzalez, M.; Prieto, A. L.; Gronsky, R.; Sands, T.; Stacy, A. M., Insights into the electrodeposition of Bi2Te3. Journal of the Electrochemical Society 2002, 149 (11), C546-C554.

Example : electrodeposition of Bismuth Telluride

Influence of the applied potential



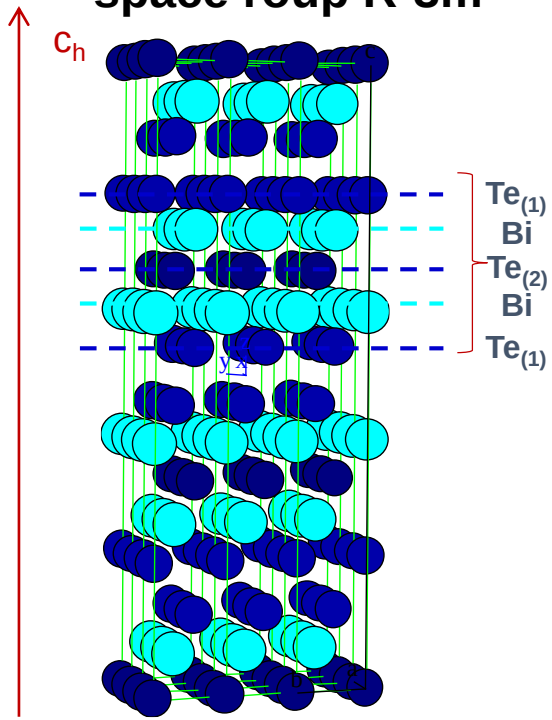
at more cathodic applied potentials
- Bi enrichment
- Coarser grains

Michel Journal of Crystal Growth 2005, 277, (1-4), 274-283.

Example : electrodeposition of Bismuth Telluride

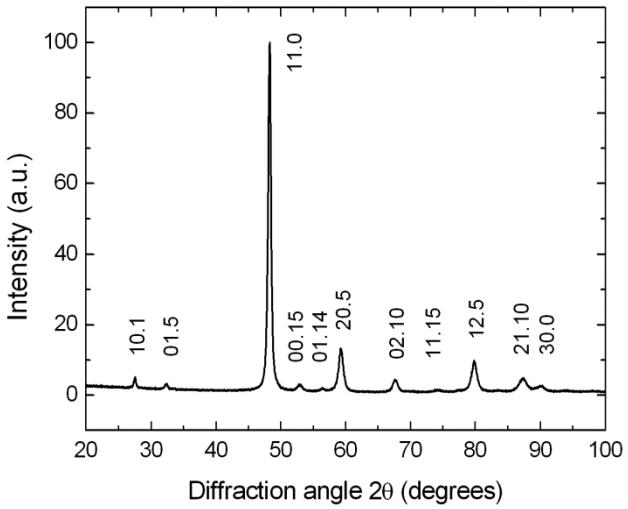
Influence of the applied potential

rhomboedral space roup R-3m



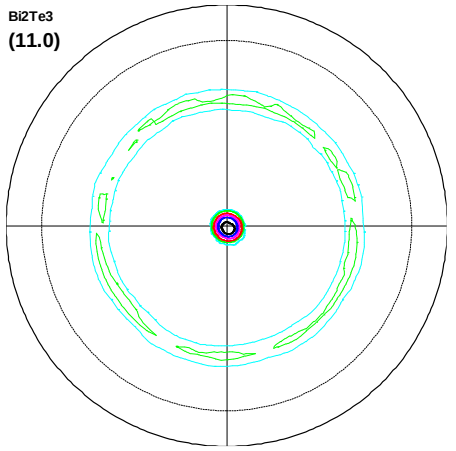
Lamellar symmetry

XRD analysis



Preferential growth direction perpendicular to (110)

Pole figure analysis



fiber texture

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Michel, Journal of Crystal Growth 2006, 296, (2), 227-233.

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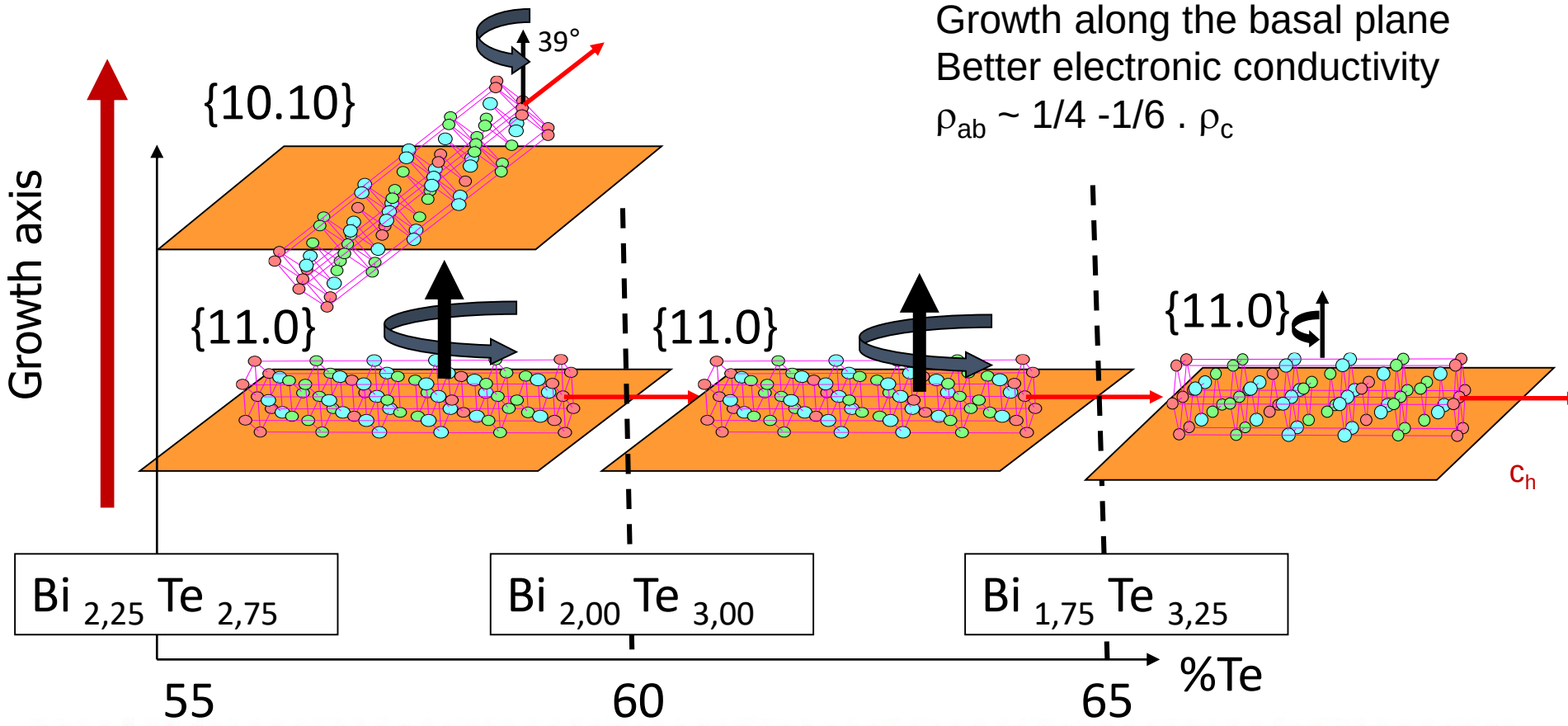
Example : electrodeposition of Bismuth Telluride

Influence of the applied potential



Michel, Journal of Crystal Growth 2006, 296, (2), 227-233.

Example : electrodeposition of Bismuth Telluride

Influence of the additive on the roughness

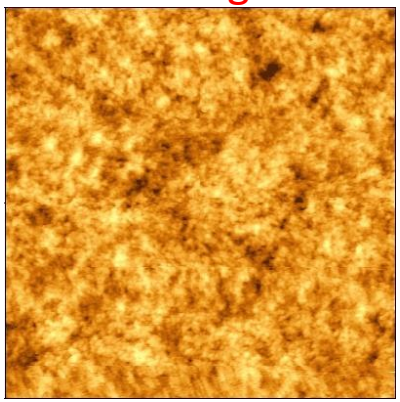
Without gum

AFM (10x10 µm²)

569 nm — 51 nm

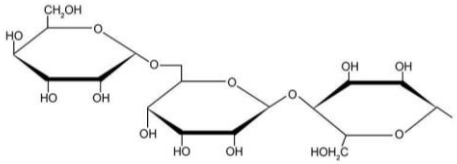
0 nm — 0 nm

With gum



RMS = 92 nm

RMS = 9,4 nm



Arabic gum 0,01 wt. %

[Bi]/[Te] = 1 [Te] = 10^{-2} M

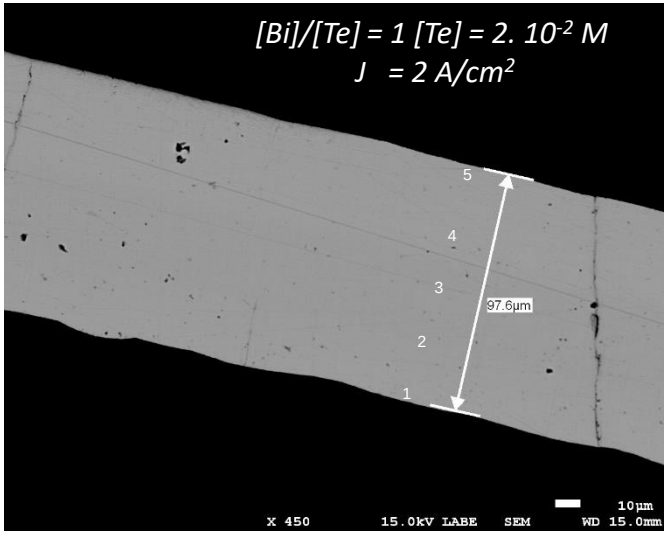
$-0.25A/dm^2 < J < -0.10A/dm^2$

	$Bi_{1,8}Te_{3,2}$	$Bi_{2,0}Te_{3,0}$	$Bi_{2,2}Te_{2,8}$
S (µV/K) without gum	-75	-65	-50
S (µV/K) with Arabic gum	-167	-115	-56

Michel, Journal of Crystal Growth 2006, 296, (2), 227-233.

Towards application

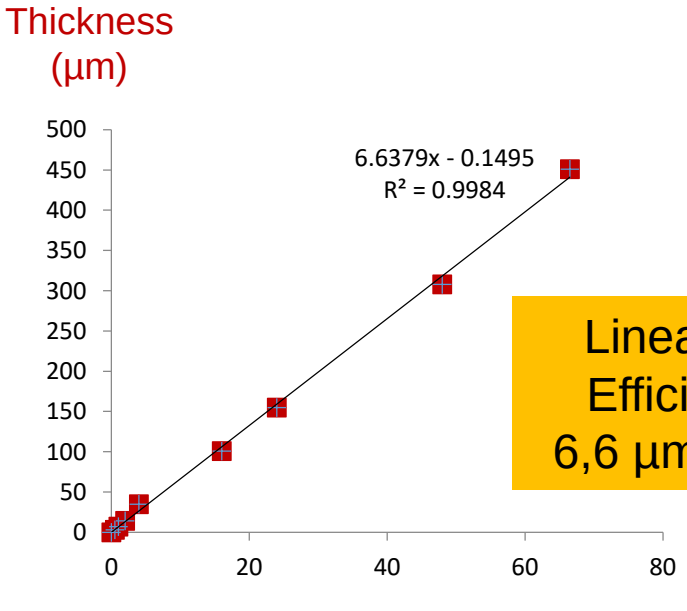
- Interest of anode to maintain the concentration of cations in the electrolyte
- No modification of the electrolyte concentration even after 100 h
- Constant stoichiometry = f(t) = f(thickness)



Cross section composition for one film:

1 : 37,96%Bi ; 62,04%Te
2 : 38,00%Bi ; 62.00 %Te
3 : 36,58%Bi ; 63,42%Te
4 : 37,83%Bi ; 62,17%Te
5 : 37,58%Bi ; 62,43%Te

average : 37,38%Bi ; 62,62%Te
± 0,82

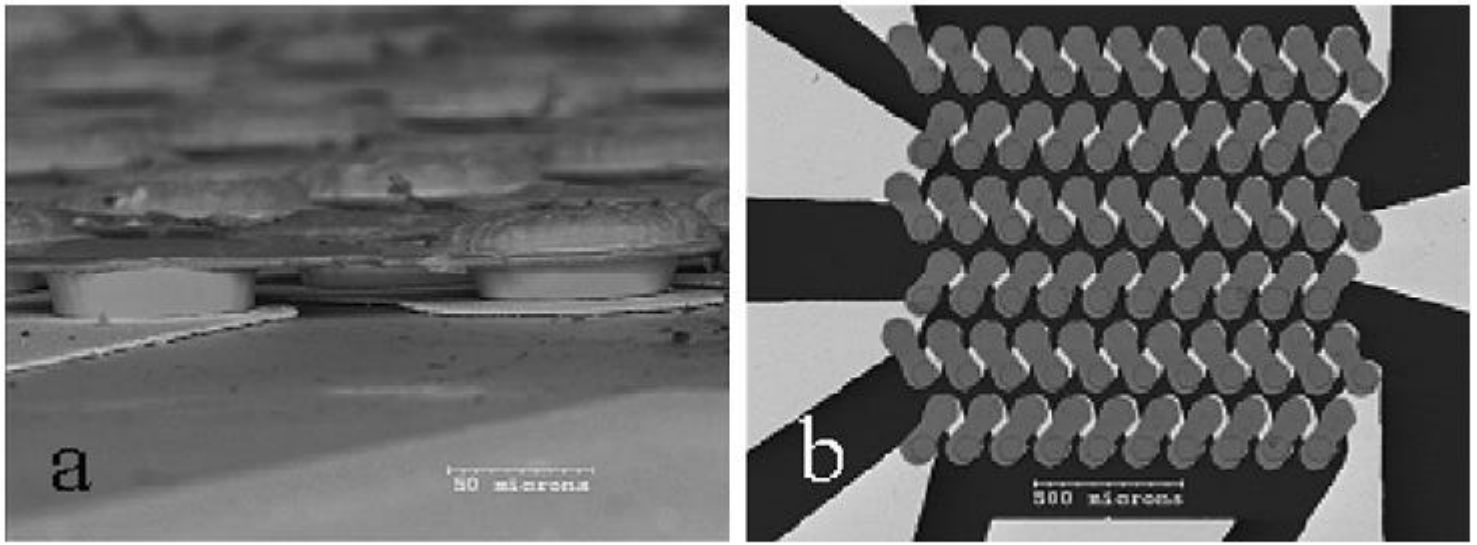


Linear growth rate
Efficiency ~100 %
6,6 µm/h → 450 µm

Maas *Journal Electronic Materials* **2014,** 43, (10), 3857-3862.

Electroplating of Bi_2Te_3 layers

microdevice fabricated by a MEMS-like electrochemical process.



. (a) SEM image of a completed p-/n-type couple (~20 μm height); (b) SEM overview of entire completed mircodevice. Reprinted with permission from ref. [128].

Snyder, Nature Materials 2003, 2 (8), 528-531.

Electrodeposition of films

Take-home message

Low cost synthesis (low temperature, absence of vacuum, no advanced equipment)
High growth rate 1µm/h 50µm/h
Thickness control by monitoring the consumed charge
Easy control by applied potential or current
Limited interdiffusion and chemical reaction
Scalability (large or small areas)
Conformal method

Selectivity
Polycristalline state
Thickness = From tens of nm to hundreds of µm
Weak epitaxial relationship
chemical elements accessible depend mainly on the solvent
large range of chemical and electrochemical parameters (electroanalytical study)
Need for electronic substrate

Contents

The synthesis of nanostructures by electrosynthesis

Low dimensional films (2D)

interaction energies between substrate and metal ad-atoms

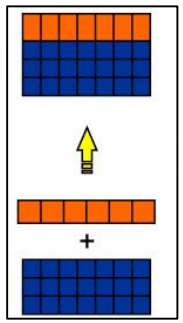
$$\Psi_{Me_{ads}-S} < \Psi_{Me_{ads}-Me}$$

3D growth independent of the substrate/deposit lattice matching (Volmer-Weber-type growth)

Nucleation favored over any crystallographic inhomogeneity (dislocations, etc.) or surface inhomogeneity (grain boundaries, etc.).

Over Potential Deposition OPD

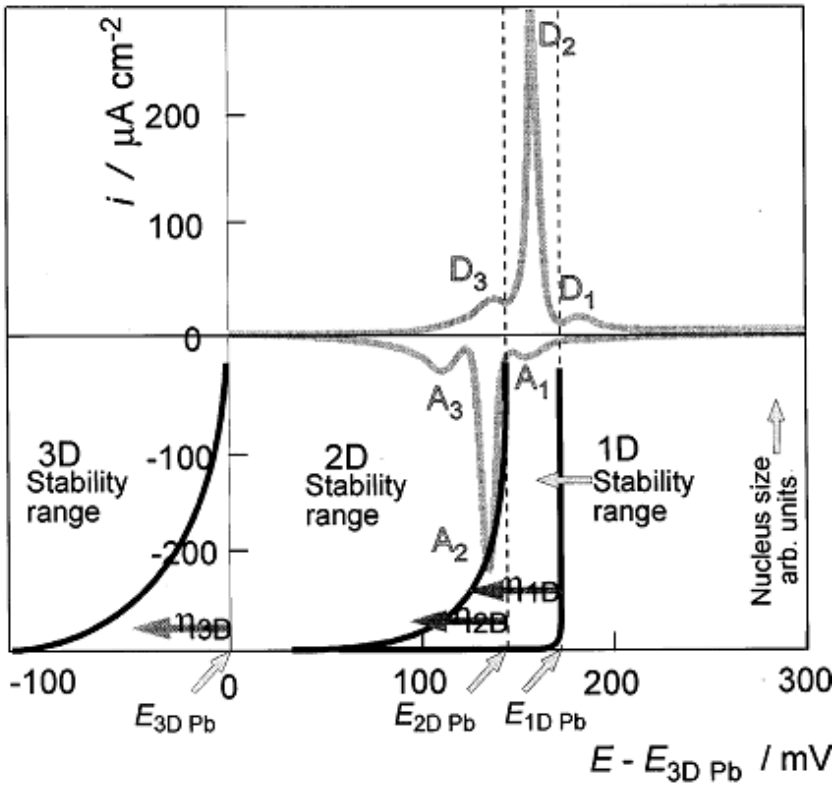
$$\Psi_{Me_{ads}-S} > \Psi_{Me_{ads}-Me}$$



Possibility of low-dimensional 2D deposits…
on perfect atomic surface
Under Potential Deposition UPD

The synthesis of nanostructures by electrosynthesis

Low dimensional films (2D) : Under Potential Deposition



Example Ag(111)/Pb^{2+}

Typical ***An*** Cathodic Adsorption peaks

Dn anodic desorption Peaks

Black curve = sizes of the respective 1D, 2D and 3D nucleus as function of overpotential

Formation of more stable adsoption layer of Pb on single crystal of silver (111)

Growth at more positive potentials than bulk deposition (3D)

The synthesis of nanostructures by electrosynthesis

Low dimensional films (2D) : Under Potential Deposition

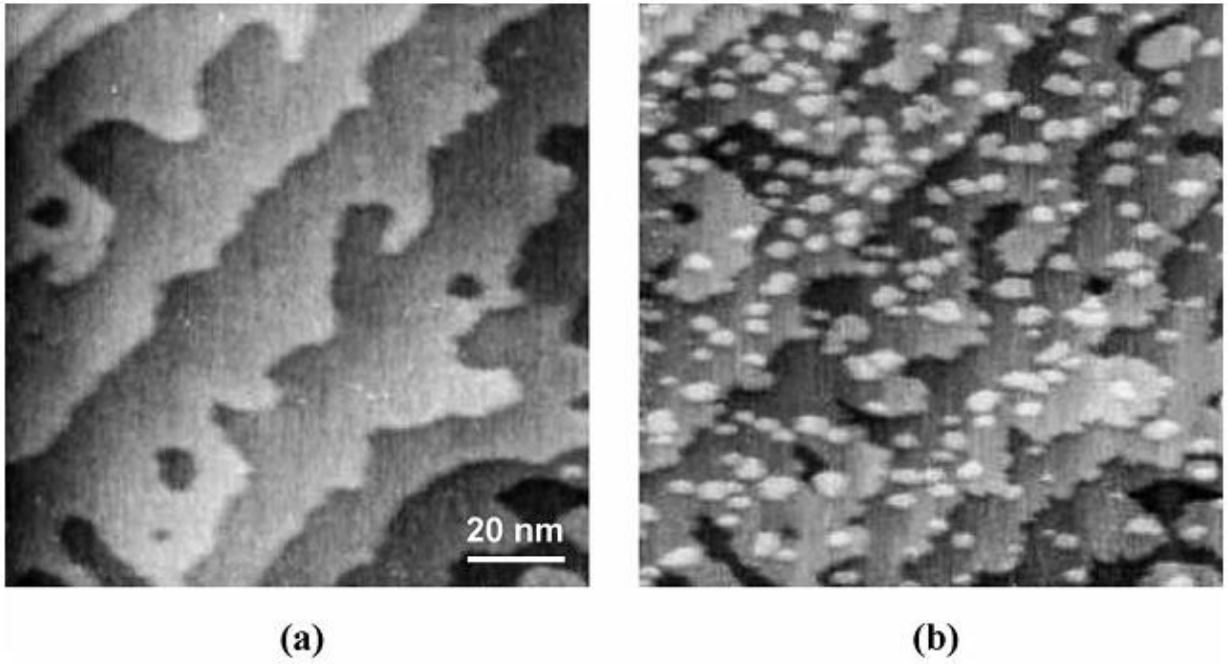


Figure 1.8. UPD of Ag on a stepped Au(100) substrate. Electrolyte: 5 mM Ag_2SO_4 + 0.1 M H_2SO_4 (T = 298 K). (a) *in situ* STM image of the substrate surface at underpotential $E - E_{\infty} = 400$ mV. (b) *in situ* STM image showing the formation of a condensed Ag monolayer at underpotential $E - E_{\infty} = 15$ mV.

Example of Ag on a stepped Au (100) substrate

In Situ STM image

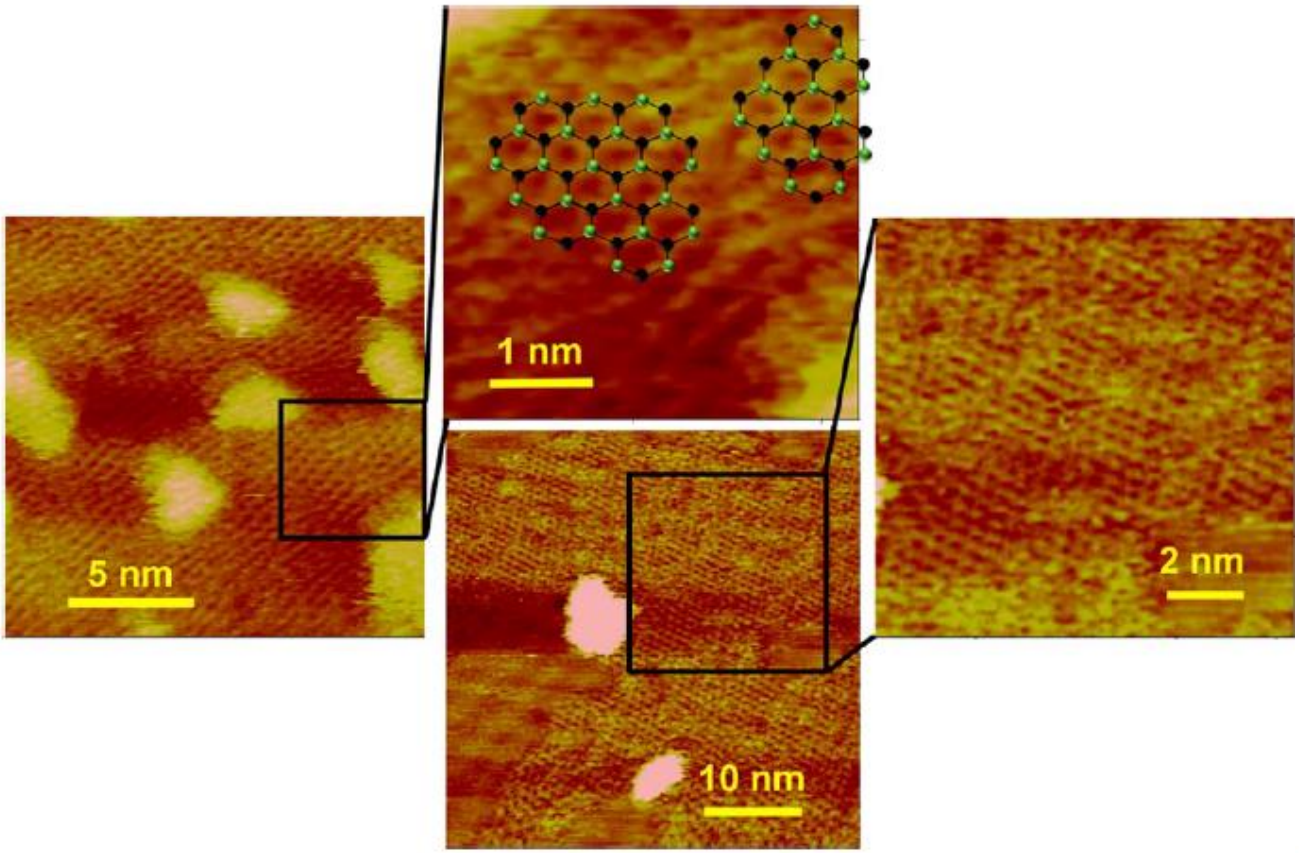
Formation of a Ag monolayer at UPD

INSTITUT JEAN LAMOUR

UNIVERSITÉ DE LORRAINE

The synthesis of nanostructures by electrosynthesis

Low dimensional films (2D) : Under Potential Deposition



Example of a 2D material = Germanene on Au (111)

- electrodeposition in an aqueous $HGeO3^-$ solution at pH 9.
- in situ EC-STM image
- distinct honeycomb structure
- Initial germanene nucleated at defects in the Au(111) herringbone (HB) reconstruction.

Bui, ACS Nano 2017, 11, 9481−9489

The synthesis of nanostructures by electrosynthesis

Low dimensional films (2D) :
ECALE electrochemical atomic layer epitaxy

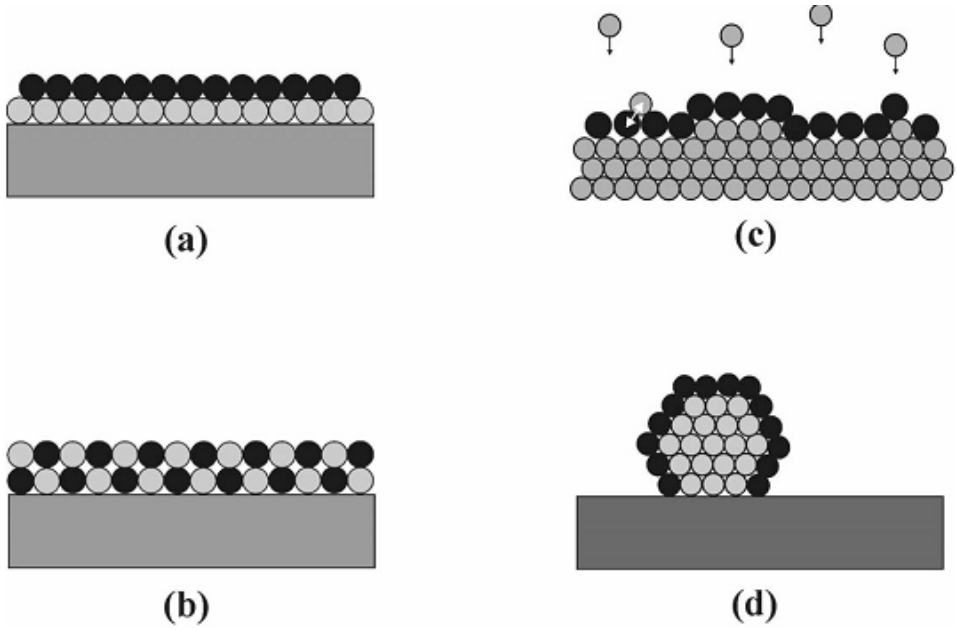


Figure 1.10. Possible applications of UPD in nanotechnology (a schematic representation). (a) deposition of superlattices and multilayers, (b) deposition of ultrathin alloy and compound films, (c) electrochemical surfactant mediated growth, (d) monolayer modification of nanoparticles.

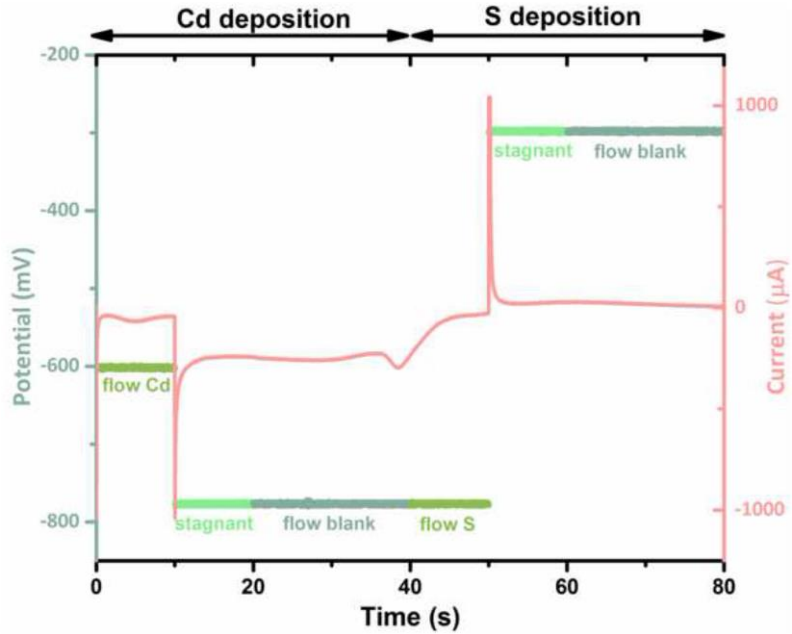
Possible applications of UPD in nanotechnology for duplex nanostructures

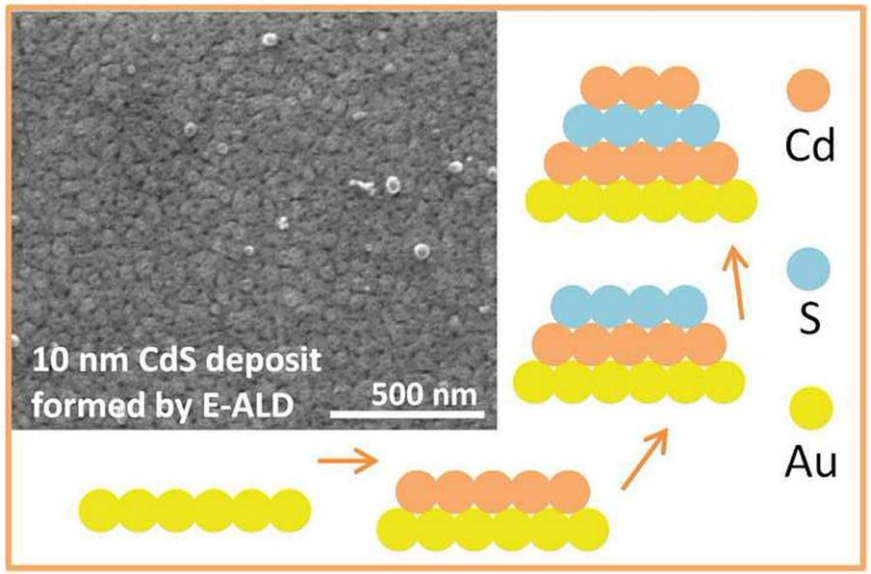
- a) superlattices and multilayers
- b) deposition of ultrathin alloy and compound films
- c) and d) Monolayer modification of nanoparticles or films

The synthesis of nanostructures by electrosynthesis

Low dimensional films (2D) :
ECALE electrochemical atomic layer epitaxy

Formation of CdS thin film using electrochemical atomic layer deposition by **sequential** underpotential deposition



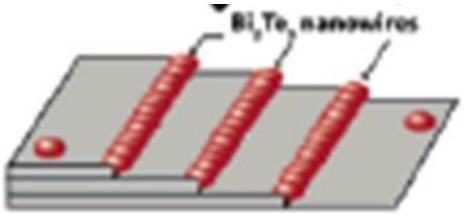


Shen, Electrochimica Acta 271 (2018) 19 26

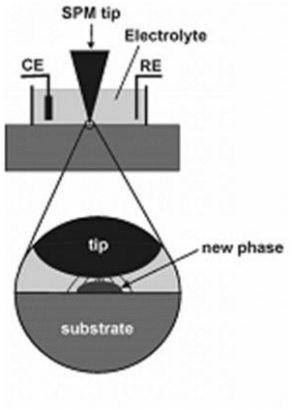
Contents

Electrodeposition of nanowires

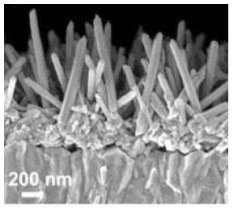
Synthesis strategies



- Electrochemical Step Edge Decoration

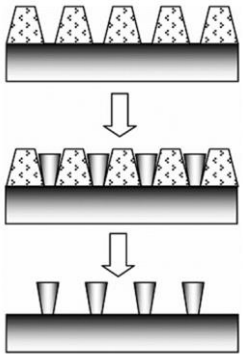


- Assisted by Scanning Probe Microscope



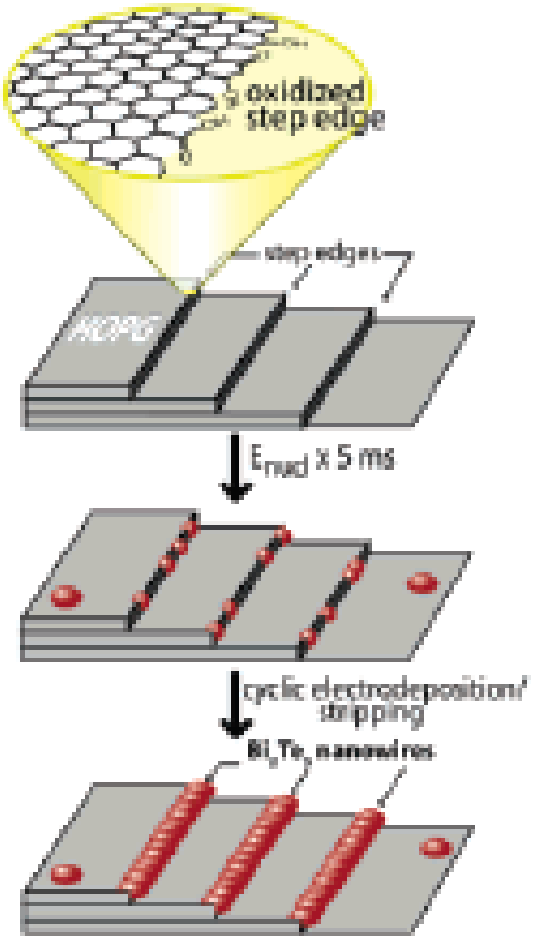
- Self-assembly synthesis

- Template Synthesis



Electrodeposition of nanowires

Electrochemical Step Edge Decoration



Substrate = Highly Oriented Pyrolitic Graphite

Electrodeposition preferred along the edges of the substrate

Presence of crystalline defects along steps with high charge transfer kinetics

Electrodeposition of nanowires

Electrochemical Step Edge Decoration

Example of Copper Nanowires

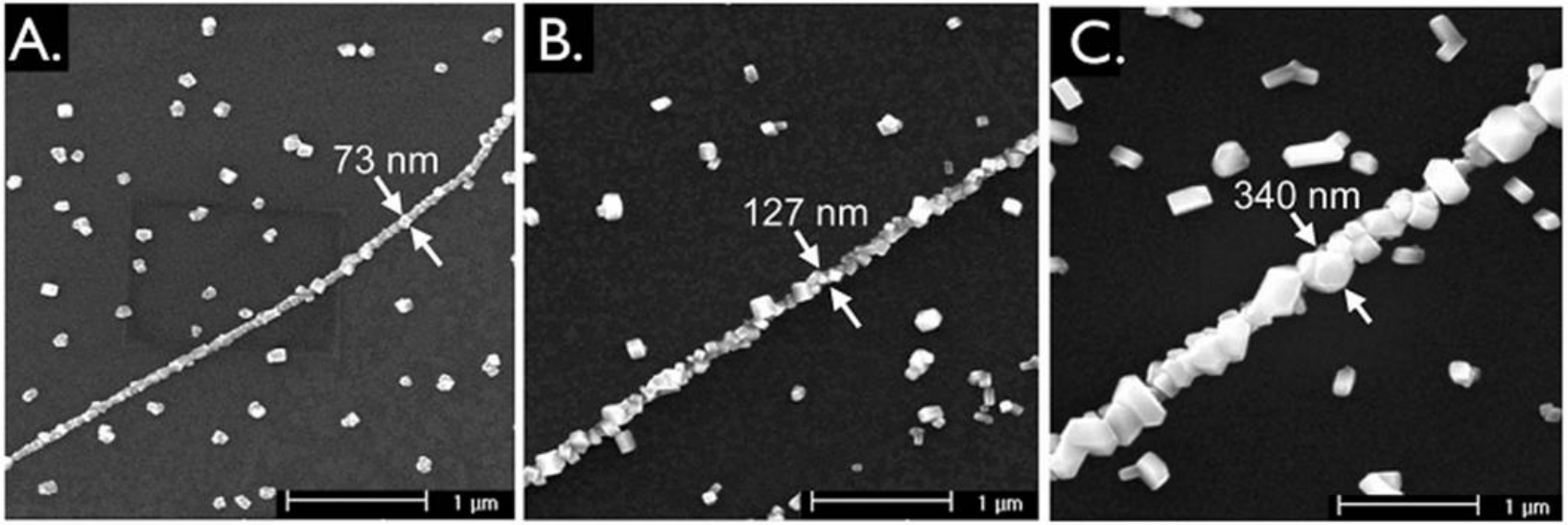


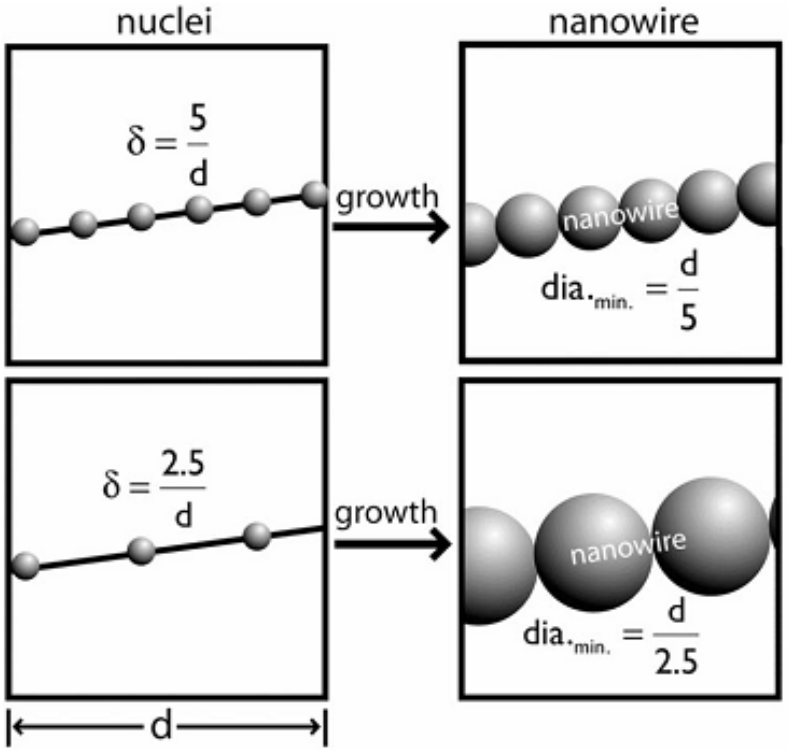
Figure 9.5. Scanning electron micrographs of copper nanowires. These nanowires were electrodeposited from an 2.0 mM $CuSO_4$ $5H_2O$, 0.1 M Na_2SO_4 using $E_{nucl} = -800$ mV_{SCE} and $E_{grow} = -5$ mV_{SCE}. The growth times employed in each experiment were: A, 120 s; B, 600 s; C, 2700 s.

Menke, *Nano Letters* **2004,** 4, (10), 2009-2014.

Electrodeposition of nanowires

Electrochemical Step Edge Decoration

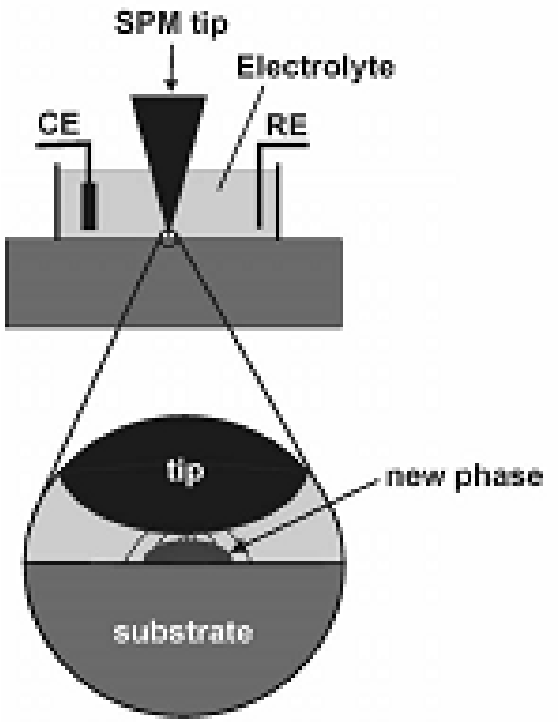
Reciprocal relationship between the nucleation density and minimum nanowire diameter



Material	ESED Method	Wire diameter (nm)	Functional properties evaluated
Mo	E/C[a]	1000–15	electrical
MoO_2	direct	1250–20	none
MnO_2	direct	150–40	none
Pd	direct	500–50	electrical, hydrogen sensing
Ag	direct	1000–200	electrical, ammonia sensing
Pt, Cu	direct	750–60	electrical
Ag_xO	direct	1100–700	electrical, ammonia sensing
Au	direct + EO[b]	300–50	none
Sb	direct + EO	300–30	none
Bi_2Te_3	cyclic ED/S[c] + EO	300–30	electrical, thermoelectric power generation
CdSe	cyclic ED/S	300–30	photoluminescence
CdS	E/C	116–550	photoluminescence, photoconductivity
MoS_2	E/C	800–50 (w) × 3–100 (h)	optical absorbance
SiO_2	CVD[d]	80 (w) × 20–40 (h)	none

Electrodeposition of nanowires

SPM-assisted nanostructuring



Localized electrodeposition between the tip and the substrate

$R_{electrolyte} / R_{polarisation} >> 1$

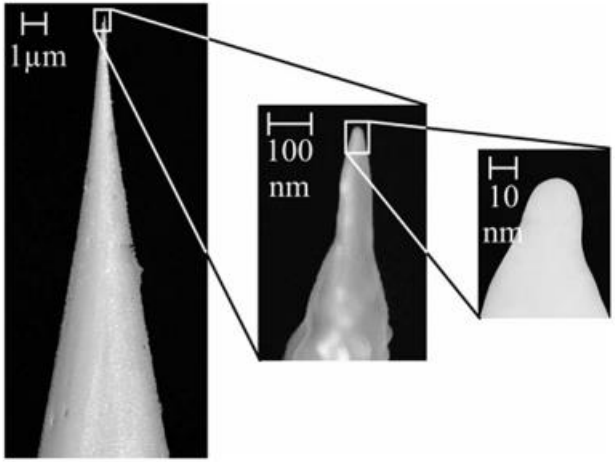
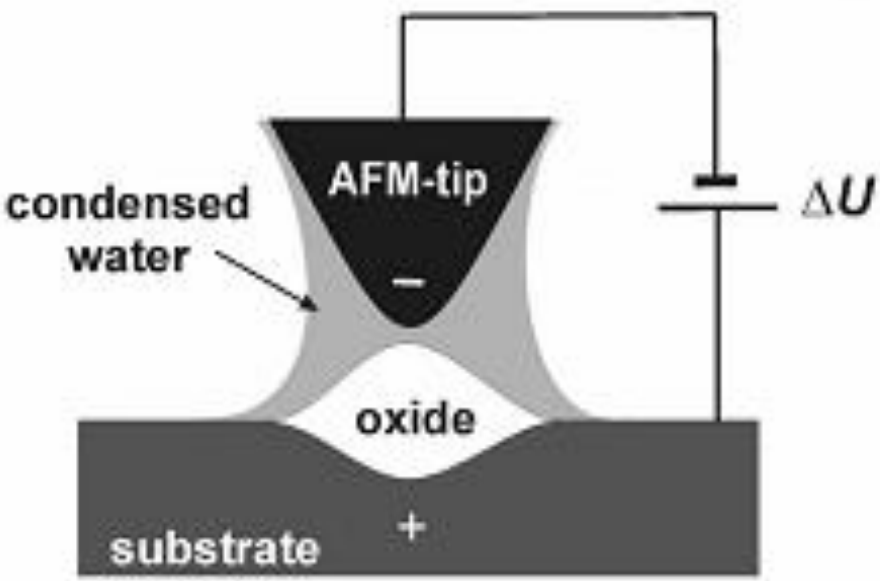


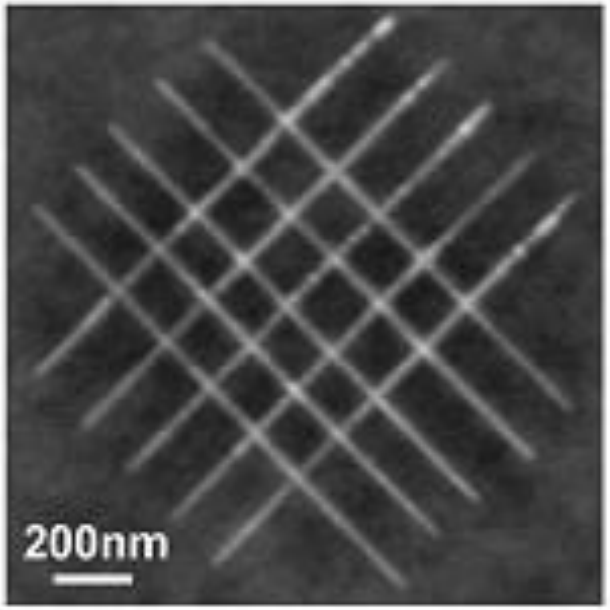
Figure 6.9. Scanning and transmission electron images of Au STM tips, as prepared with the combined field emission/sputtering technique. The diameter of the STM tip apex is approximately 20 nm.

Electrodeposition of nanowires

SPM-assisted nanostructuring

Localized anodic oxidation induced by the AFM tip
SiO_2 pattern fabricated by lo tip-induced oxidation of p-Si(111) substrate
Relative humidity 3%





Teichert, Physics Reports 365 (2002) 335 – 432

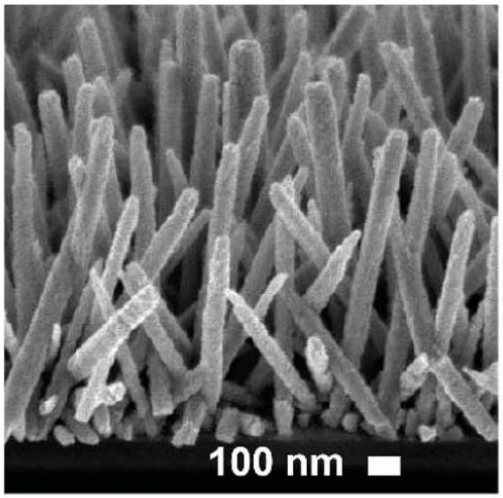
Electrodeposition of nanowires

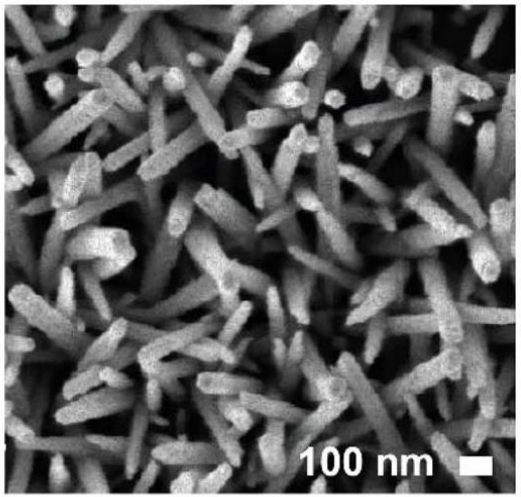
Self-assembly synthesis : in aqueous medium

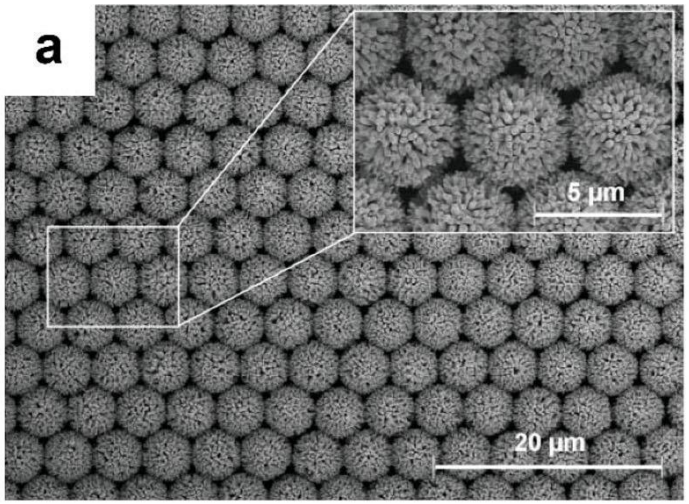
Template less synthesis of single crystalline ZnO nanowires
single crystalline ZnO nanowires

$$Zn^{2+}_{(aq)} + 2\ OH^{-}_{(ads)} \rightarrow Zn(OH)_{2(s)} \rightarrow ZnO_{(s)}$$

Source of hydroxide ions : Molecular oxygen, Nitrate ions, Hydrogen peroxide







FE-SEM micrographs of ZnO nanowires deposited on copper and on polystyren spheres (bioinspired sea urchins)

Manzano, CRITICAL REVIEWS, 2022, VOL. 47, NO. 5, 772–805

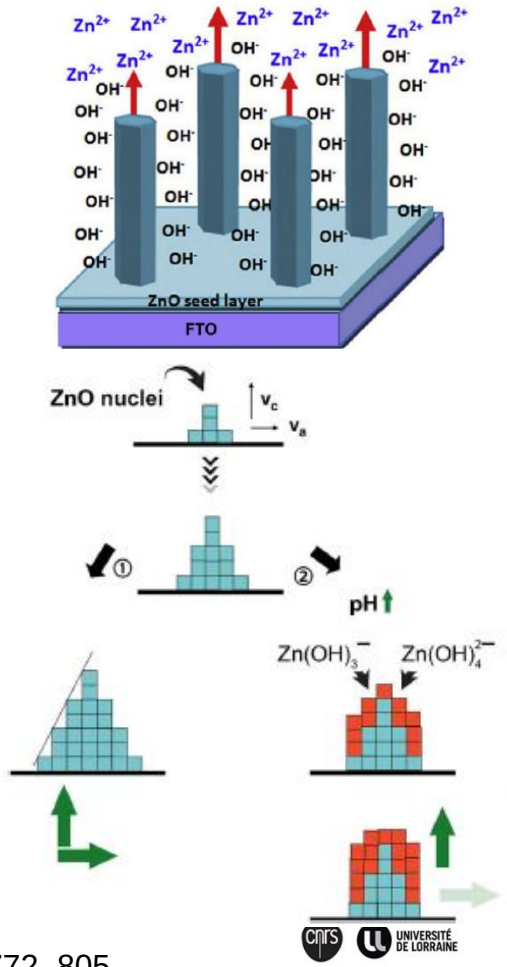
Electrodeposition of nanowires

Self-assembly synthesis : in aqueous medium

Template less synthesis of single crystalline ZnO nanowires rapid growth along the longitudinal axis :

- Diffusion rate of Zn(II) species is significantly less than the rate formation of the hydroxide ions

- Adsorption of the negatively charged Zn(II) species as well as the hydroxide ions on the top Zn-terminated (0001) polar plane of the hexagonal ZnO crystals,



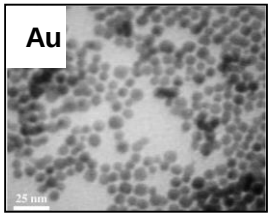
Manzano, CRITICAL REVIEWS, 2022, VOL. 47, NO. 5, 772–805

Electrodeposition of nanowires

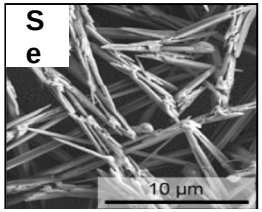
Self-assembly synthesis : in ionic liquid

Materials containing only ions
T_{melt} < 100°C
Some are liquid at Room Temperature : RTILs

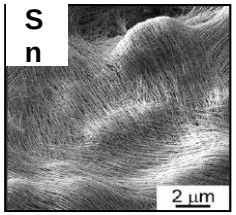
✚ Low vapor pressure	⇨	Low inflammability, low volatility
✚ Wide electrochemical window	⇨	Electrodeposition of reactive elements
✚ High thermal stability	⇨	High cristallinity of materials
✚ Capping agents	⇨	**Template-free nanostructures synthesis**



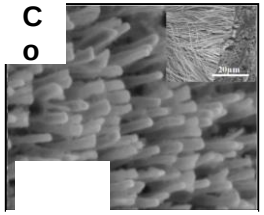
Absalan et al., *Coll. Surf. A* (2015)



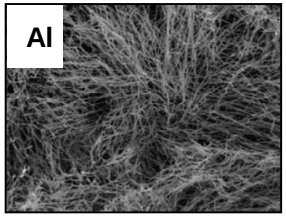
Steichen et al., *Electrochem. Comm.* (2011)



Al-Salman et al., *Chem. Mater* (2015)



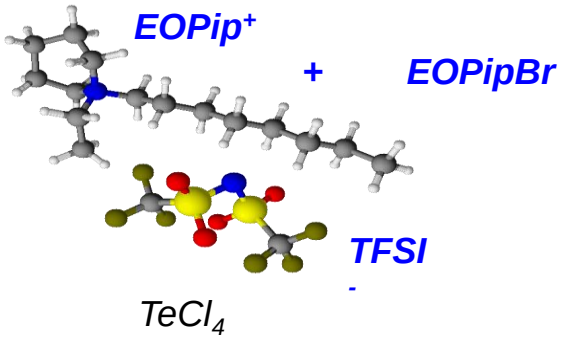
Hsieh et al., *Electrochim Acta* (2014)



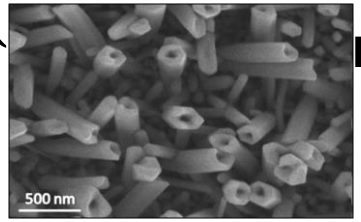
Su et al., *Electrochem Comm* (2013)

Electrodeposition of nanowires

Self-assembly synthesis : in ionic liquid

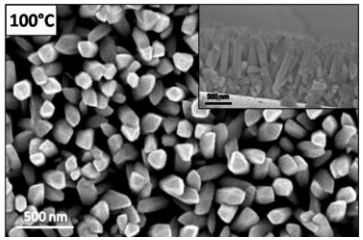


overpotential ↑



Hollow nanostructures

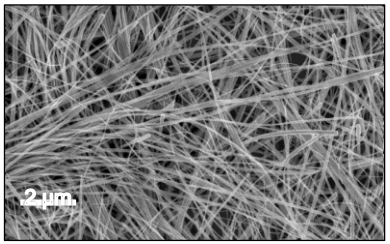
AR ≈ 10



Nanorods

Aspect Ratio ≈ 13

Te^{IV} speciation
[Br^-]



Hair-like nanowires

L = 70 ± 10 µm
Ø = 50 ± 20 nm

AR ≈ 1800

Thiebaud et al., *Electrochimica Acta 197* (2016)

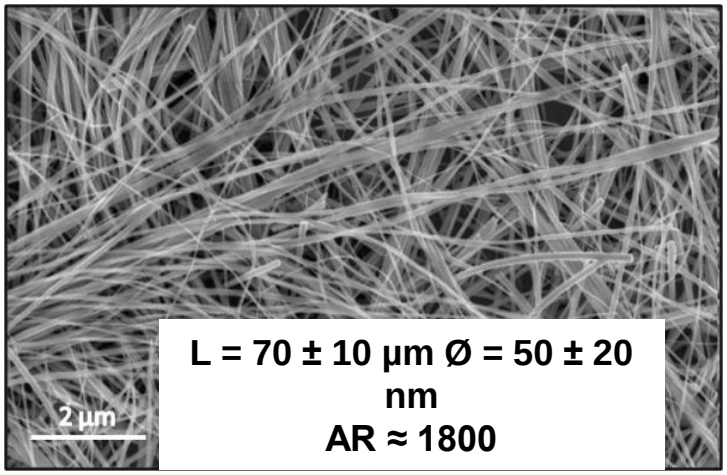
Electrodeposition of nanowires

Self-assembly synthesis : in ionic liquid

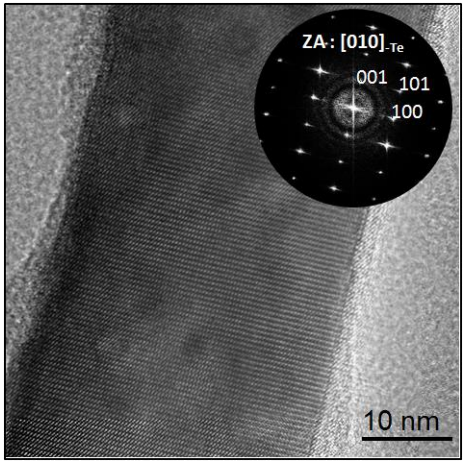
T = 100°C
$|Te^{IV}|$ = 5 mM, Ep
% Br = 0,2 %

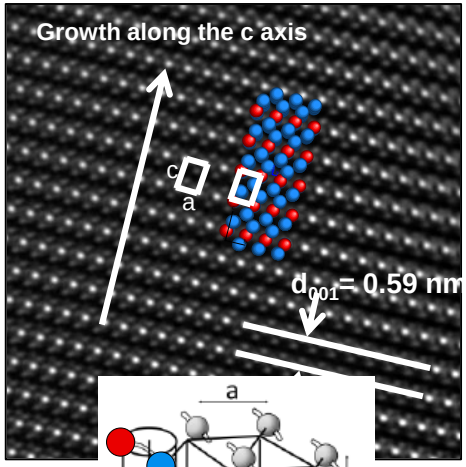
0.2 % EOPipBr

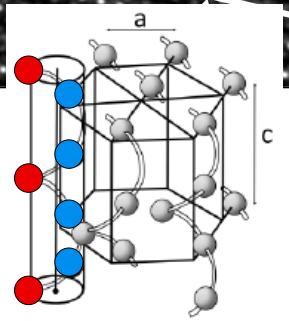
HRTEM analysis

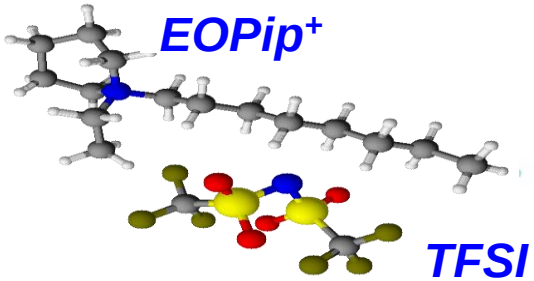


L = 70 ± 10 µm Ø = 50 ± 20 nm
AR ≈ 1800









Bis(trifluorométhylsulfonyl)imidure

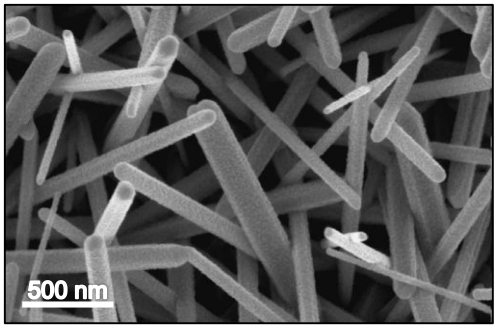
Specific mass transport (viscosity)
Anistropic structure of Te

Thiebaud et al., *Electrochimica Acta 197* (2016)

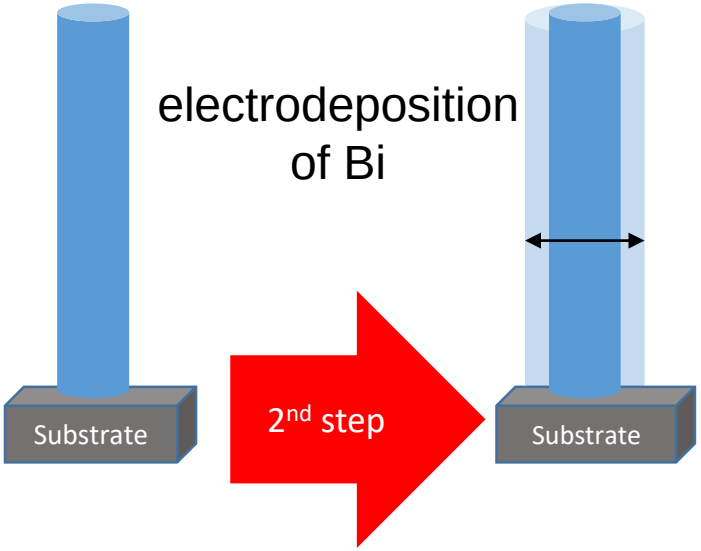
Electrodeposition of nanowires

Self-assembly synthesis :
2 step synthesis of core@shell NWs

Te nanowires

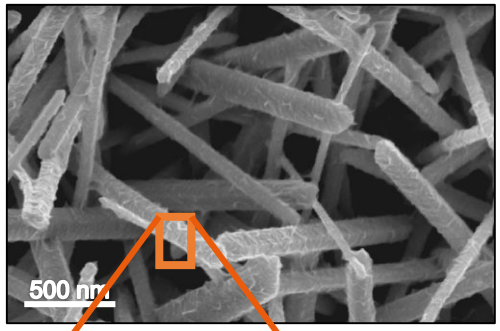


EOPipTFSI/Br
$TeCl_4$

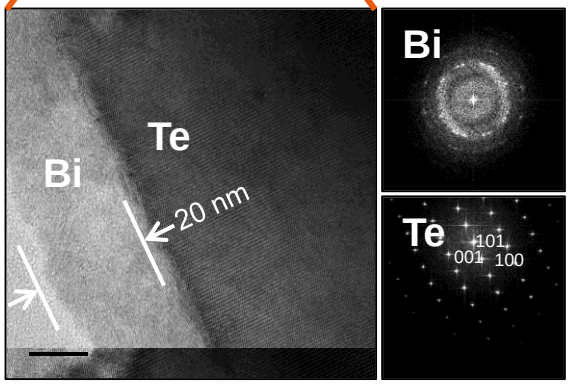


$Bi^{3+} + 3e^- \rightarrow Bi°$

Te@Bi nanowires



*$|BiBr_3|$ = **5 mM**, C_1"*
EOPipTFSI T = 100°C



Single crytalline Te nanowire

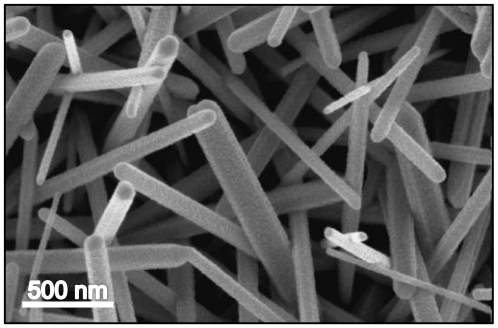
Te@Bi Core@Shell nanowire

L. Thiebaud, Electrochemistry Communications, 86 (2018) 30-33.

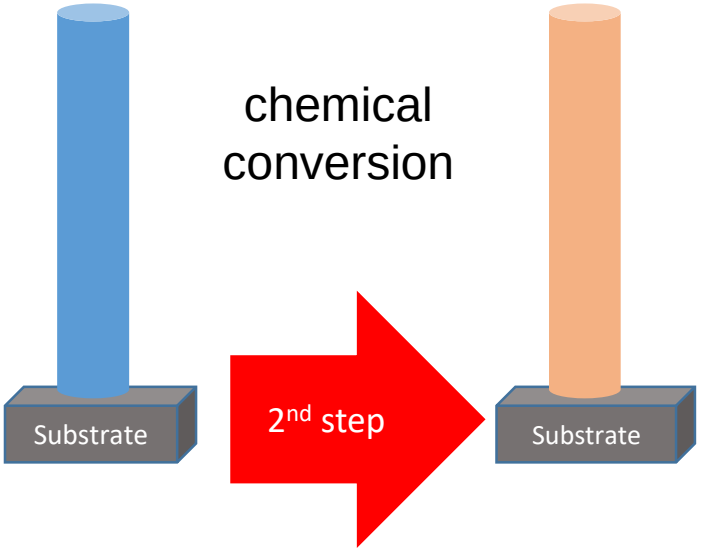
Electrodeposition of nanowires

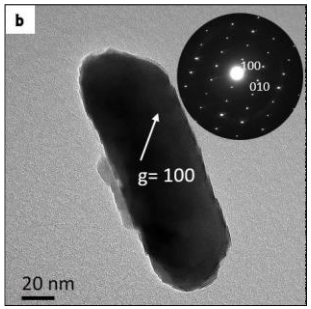
Self-assembly synthesis :
2 step synthesis of binary compounds

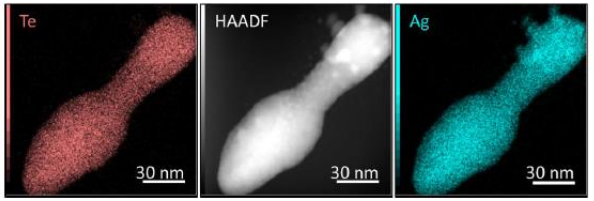
Te nanowires



EOPipTFSI/Br
$TeCl_4$







$$4Ag(I) + 3Te(0) \rightarrow 2Ag_2Te + Te(IV)$$

Single crytalline Te nanowire

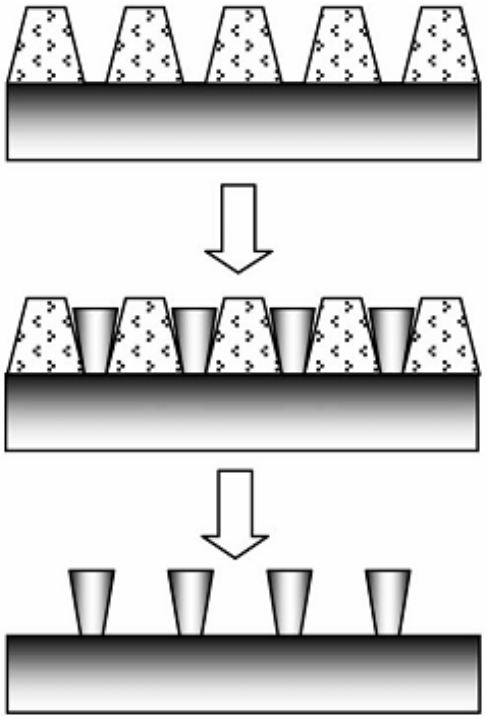
Single crystalline Ag_2Te nanowire

Al Hokayem Materials Chemistry and Physics 289 (2022) 126487

Electrodeposition of nanowires

The template synthesis

- **bottom-up approach**



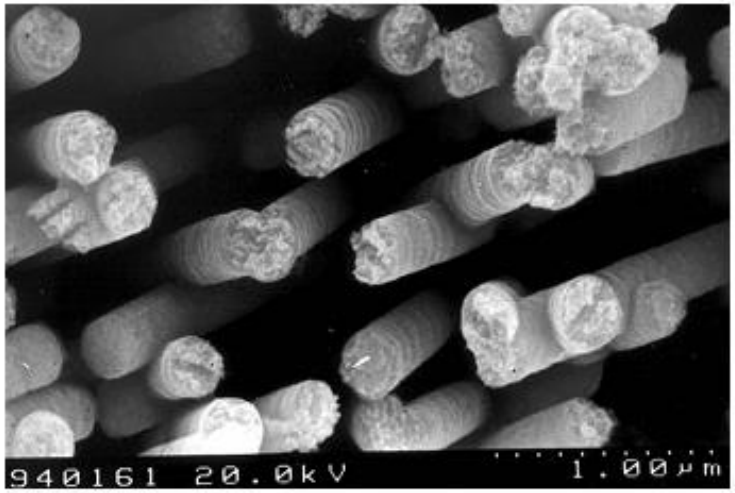
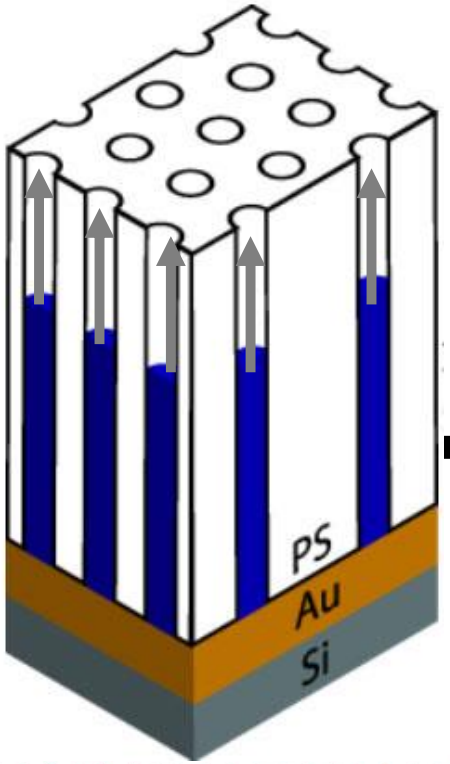


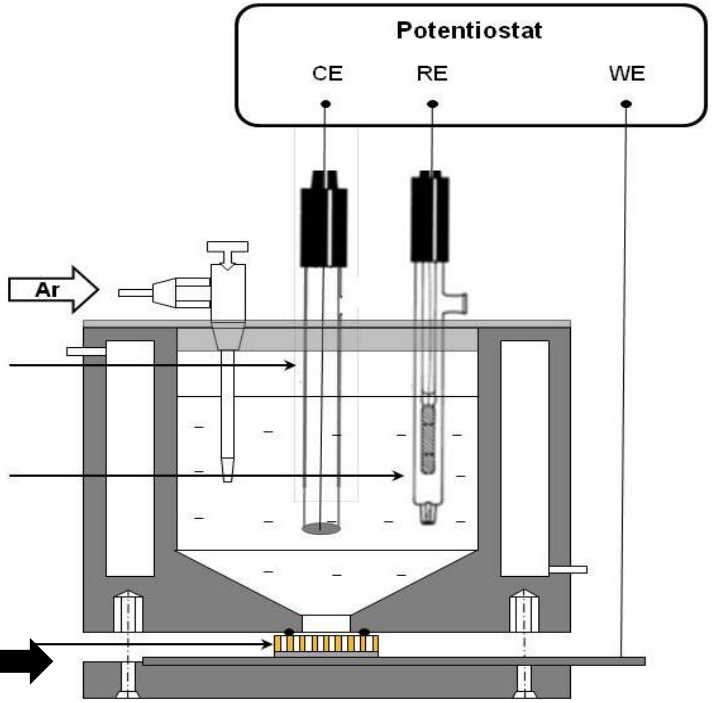
Figure 3.3. Single crystalline gold nanowires in a poly-carbonate track-etched (PCTE) membrane template after dissolution of the template [13].

Martin, C. R. Science 1994, 266, (5193), 1961-196

Electrodeposition of nanowires

The template synthesis



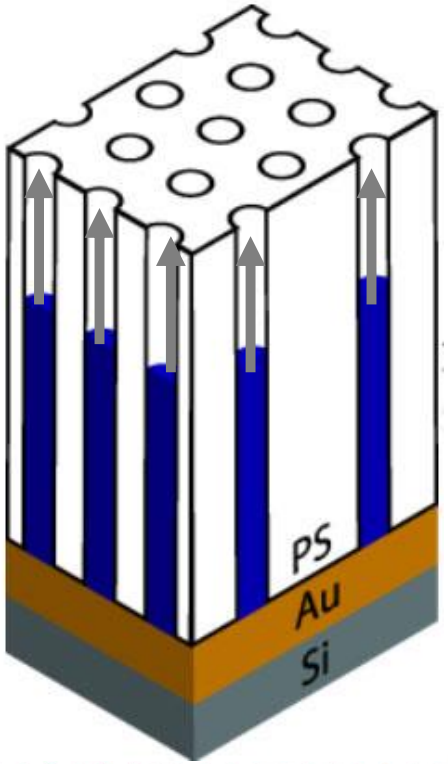


Exposed area : 0,785 cm²

- ✓ Membrane = array of ultra-microelectrodes
- ✓ Filling = Cathodic reduction $M^{n+} + ne^-$ → M°

Electrodeposition of nanowires

The template synthesis : 1/the membrane



- **Dimensions of nanowires directly linked to those of membrane pores**
  - Nanowires 1D nanostructures
  - Length : 1 - 100µm
  - Diameter : 10 – 200 nm
  - High diameter/length ratio

- **Physical properties of the template**
  - insulating (electronic and thermal conductivity)
  - mechanical resistance
  - temperature resistance

Electrodeposition of nanowires

The template synthesis : 1/ the membrane
porous AAO anodized aluminium oxide films

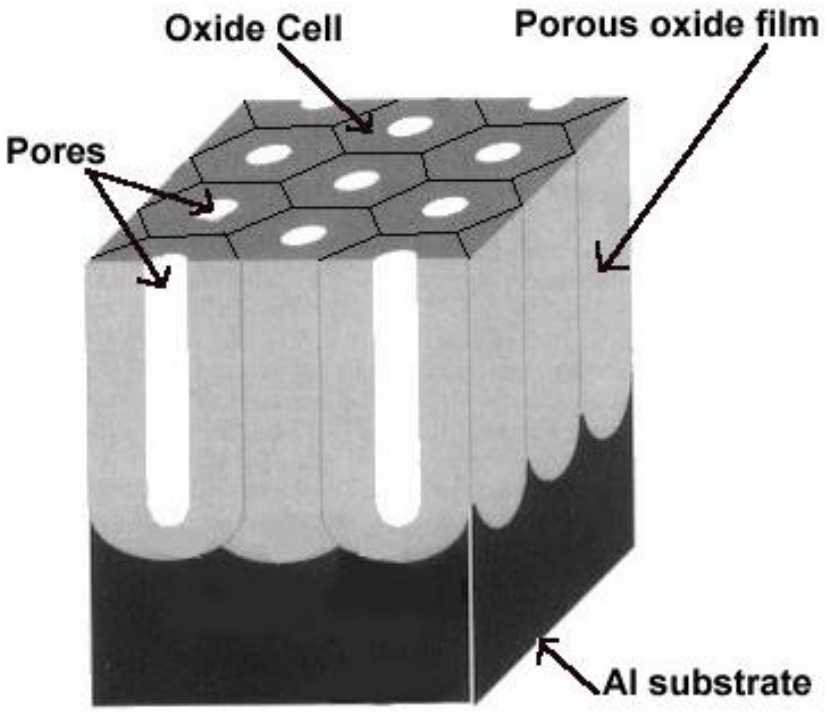
✓**Anodization of high purity aluminium** in mineral acid

✓uniform spatial distribution of vertical pores in honeycomb cells (hexagonal symmetry)

✓Presence of insulating, dense oxide layer (called **barrier layer**) separating the Al substrate and the porous oxide film

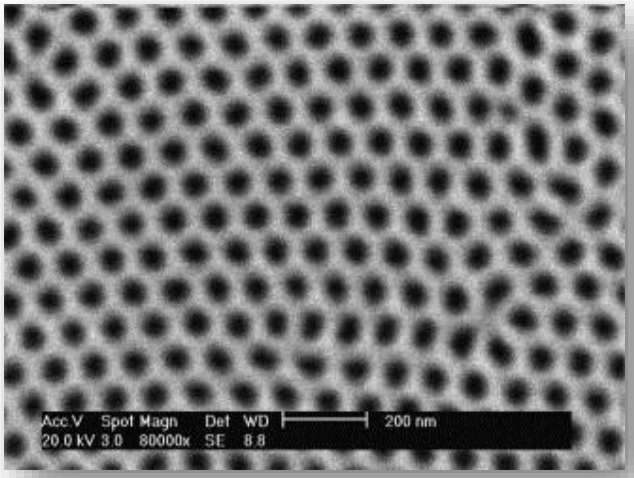
➢*thinning the barrier layer**

✓**Geometric parameters** (pores size, radius, density) linked to anodization parameters (electrolyte, anodizing voltage)

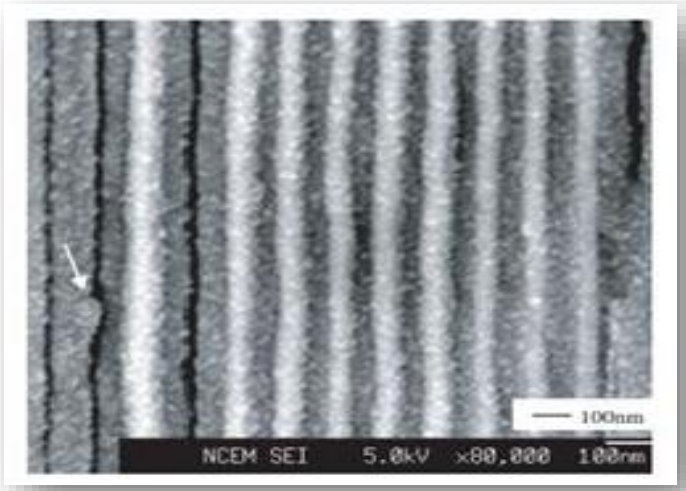


Electrodeposition of nanowires

Template synthesis : : 1/ the membrane
porous AAO anodized aluminium oxide films



Top view



Cross section

- ✓ Porous structure ~ a honeycomb array
- ✓ High pore density > 10^9 pores/cm²
- ✓ Range of thickness = 10 – 100 µm
- ✓ Commercial products (filtration) = interconnection between nanopores

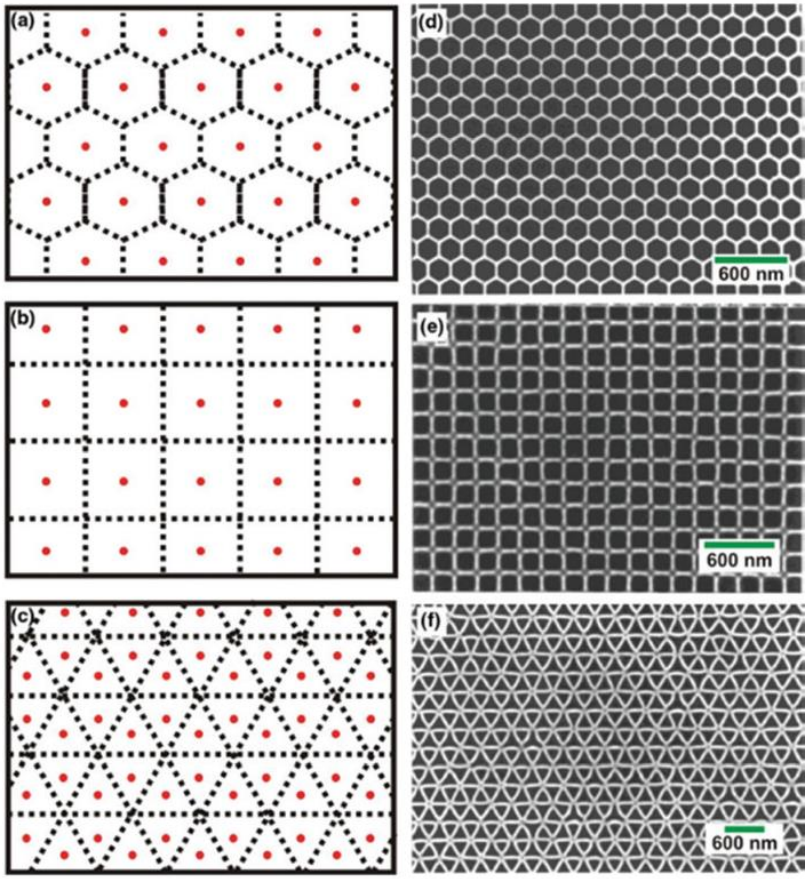
The most popular template in the literature (possibility of annealing)

Sander. Advanced Materials 2002, 14, (9), 665-667.

Electrodeposition of nanowires

Template synthesis : : 1/ the membrane
porous AAO anodized aluminium oxide films

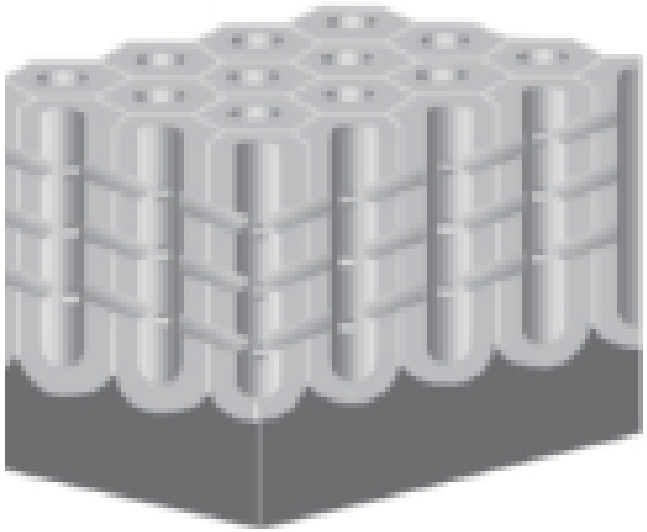
Cell representations and SEM images of
prepatterned AAO in three exemplary geometries.



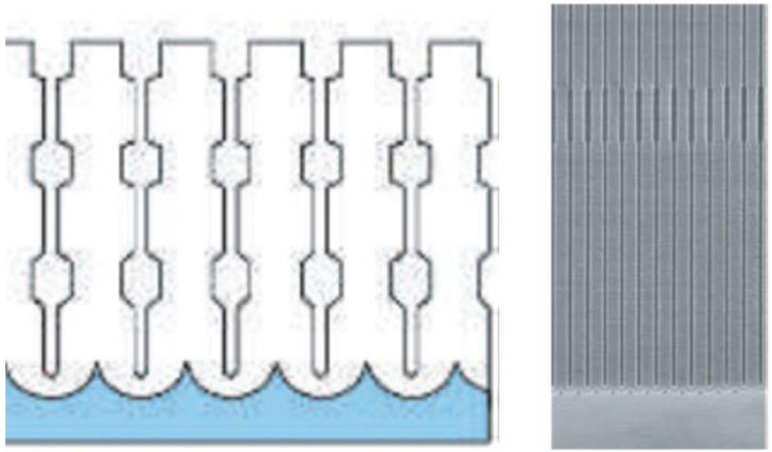
Electrodeposition of nanowires

Template synthesis : : 1/ the membrane
porous AAO anodized aluminium oxide films

3D anodic porous alumina template



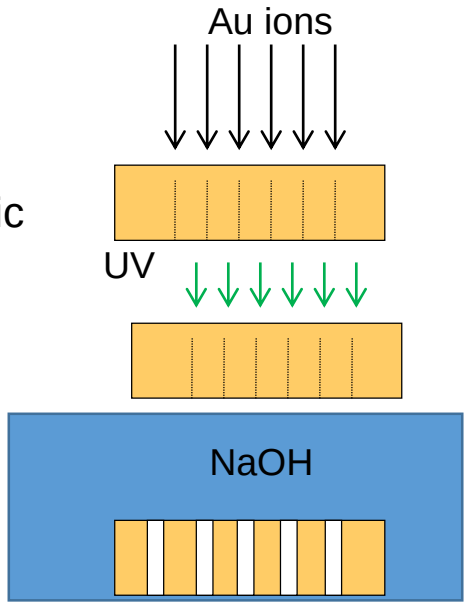
Schematic and SEM image of a **diameter modulated** AAO membrane.



Caballero-Calero, O.; Martín-González, M.
Scripta Materialia 2016, 111, 54-57.

Electrodeposition of nanowires

Template synthesis : : 1/ the membrane
ion-track etched polymeric membranes ITEP



Synthesis of ITEP membranes

1. **Irradiation** of polymeric foils with single Au ions of 11.4 MeV/u specific kinetic energy at heavy ion linear accelerator
2. **Exposition to UV** light for 1 h
3. **Etching of the nanopores** in aqueous NaOH

Polymers

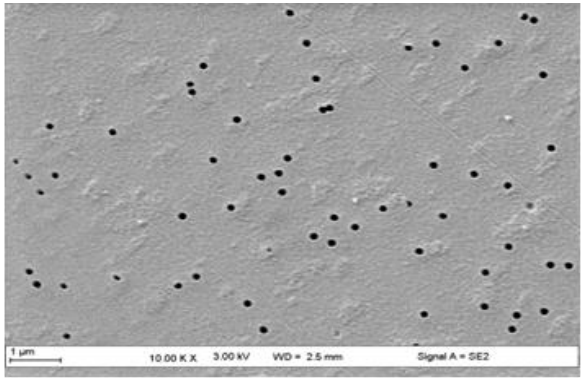
polycarbonate, polyethylene terephthalate, polymide

Electrodeposition of nanowires

Template synthesis : : 1/ the membrane
ion-track etched polymeric membranes ITEP

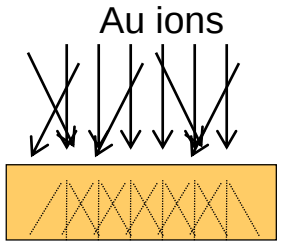
Typical dimensions

Low pore density: 10^8 –10^9 pores/cm²,
thickness 5 – 50 µm
maximum aspect ratio 1 / 1000
Potential defects: twin pore
Tunable dimensions by chemical post etching



Top view
Pore density 3 10^9 cm^{-2}

3D nanowire network prepared in ion-track etched membranes



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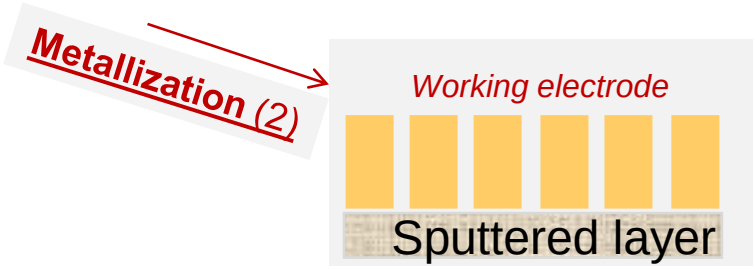
Caballero-Calero Scripta Materialia 2016, 111, 54-57.

cnrs UNIVERSITÉ DE LORRAINE

Electrodeposition of nanowires

Template synthesis : 2/ the metallization step



Adjustment of the sputtering parameters

- homogenous surface
- high electrochemical reactivity at the bottom of **each** pore
- High quality of the electrical contact for lowest internal resistances
- Adhesion
- Influence of metal layer on the electrochemical behavior
- Sealing of pores : thickness > diameter
- Problem of coating along the pore walls

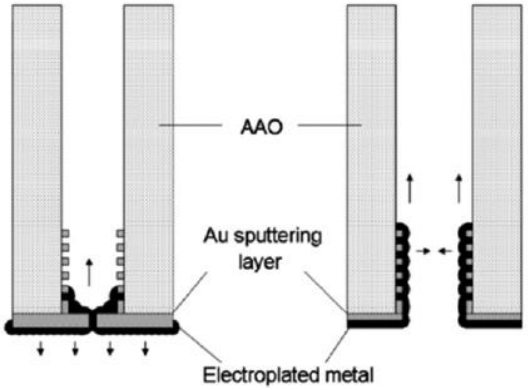
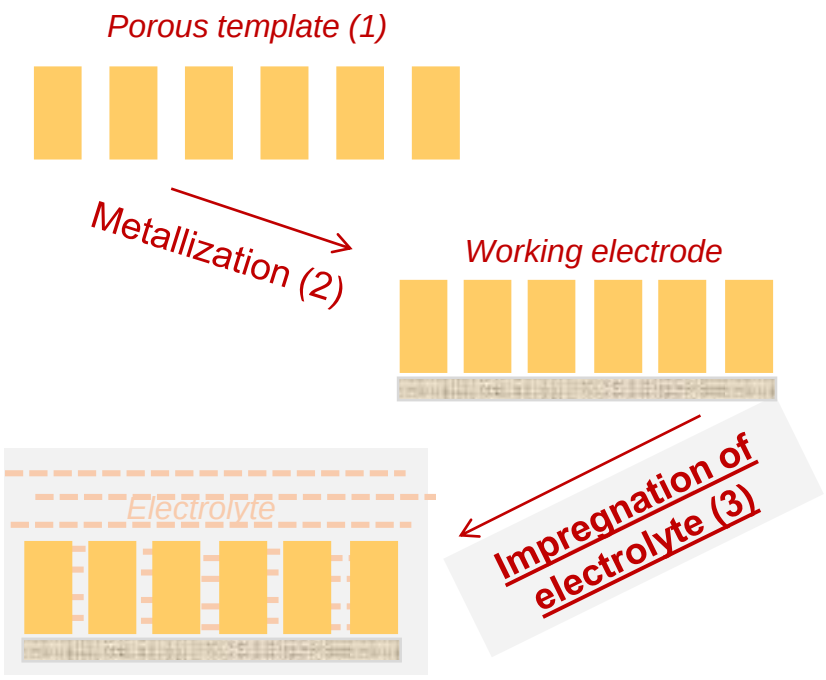


Fig. 6 (A) Influence of the contact sputtering process of a blocked and unblocked membrane onto the seed formation and the following electrodeposition of nanomaterials. (B) SEM images of the resulting CoPt nanotubes and nanowires. Reproduced with permission from J. Fu, S. Cherevko and C.-H. Chung, *Electrochem. Commun.*, 2008, **10**, 514.[57]

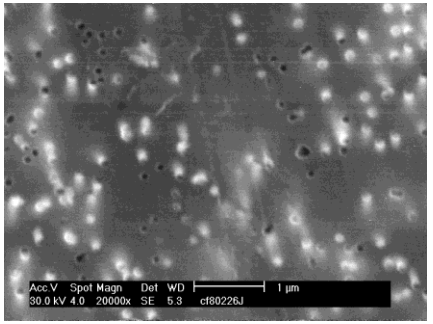
Electrodeposition of nanowires

Template synthesis : 3/ the impregnation step

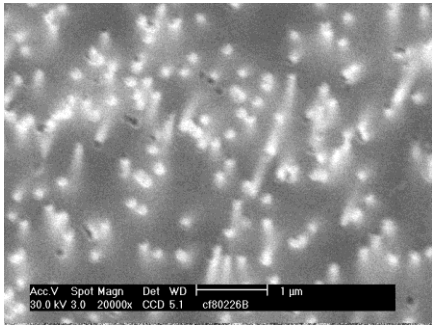


Optimal filling by impregnation whatever the pore sizes = example of polycarbonate membranes

- Pretreatment: sonication of the template in the electrolyte for 2 min



sonication: 0 minute



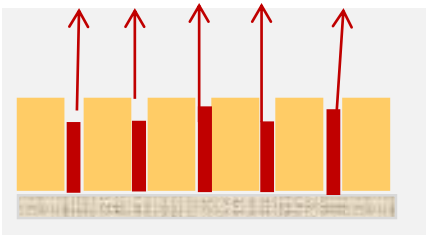
sonication: 2 minutes

- Wetting reagent :addition of DMSO in the electrolyte (50% v/v)

Frantz, Journal of Electronic Materials 2010, 39, (9), 2043-2048.

Electrodeposition of nanowires

Template synthesis : 4/ the electrocrystallization step

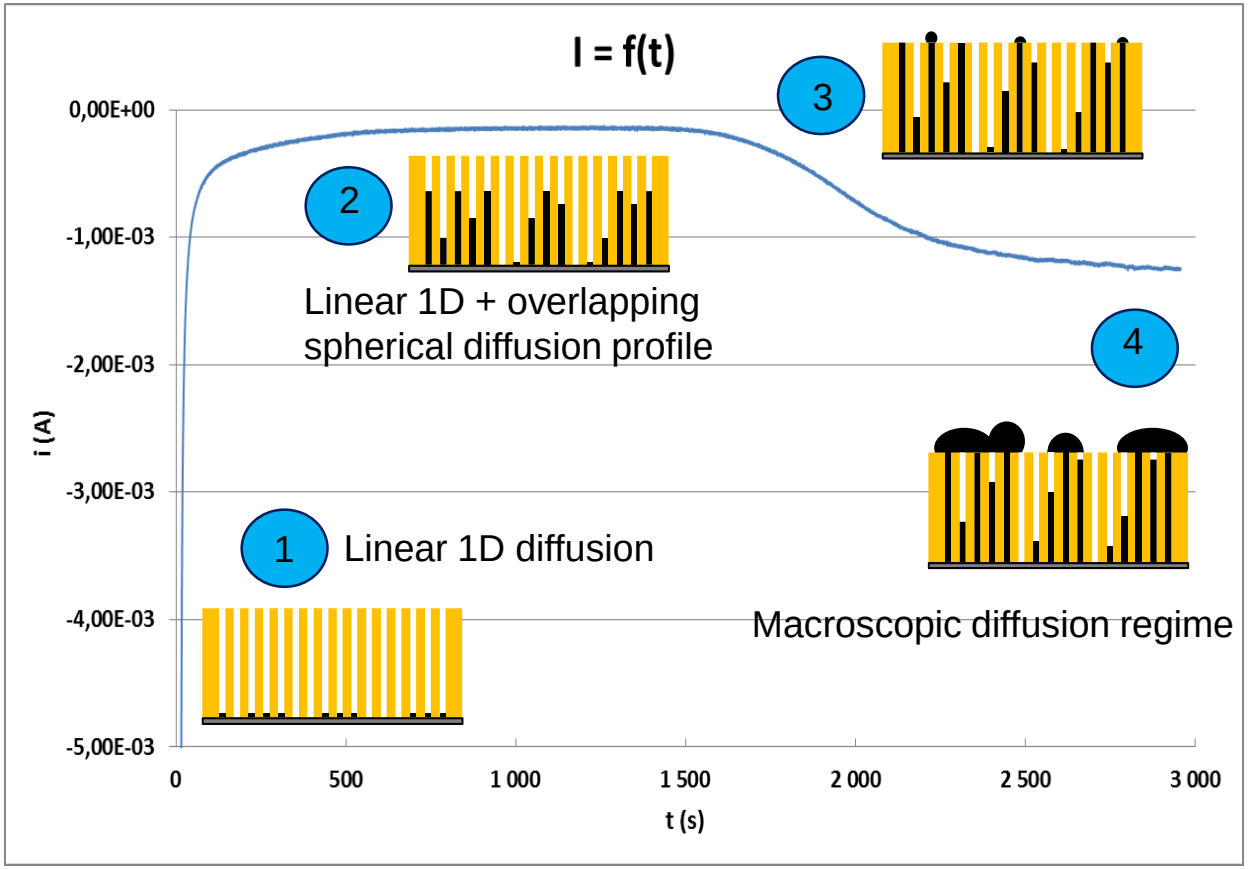


- homogenous filling between the pores ➔ Growth rate
- homogeneous chemical composition along the NWs ➔ Diffusion of ionic species
- growth process ➔ Crystallinity

- No homogenous rate in each pore = filling ratio below 100 %
  - Improvement by lower growth rate (diffusion rate)
  - Improvement by pulse electrodeposition

Electrodeposition of nanowires

Template synthesis : 5/ Growth (chronoamperometric curve)

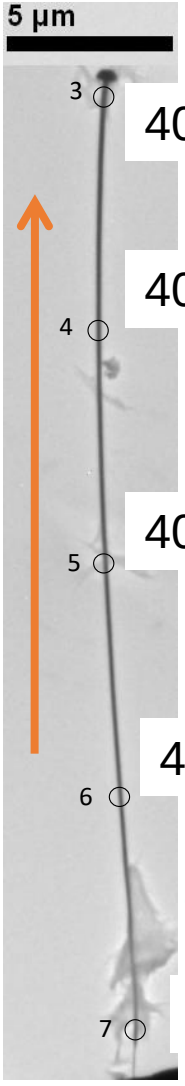


1. Nucleation
2. Growth
3. Filling
4. Coalescence and formation of an upper layer

Specific mass transport regimes

Electrodeposition of nanowires

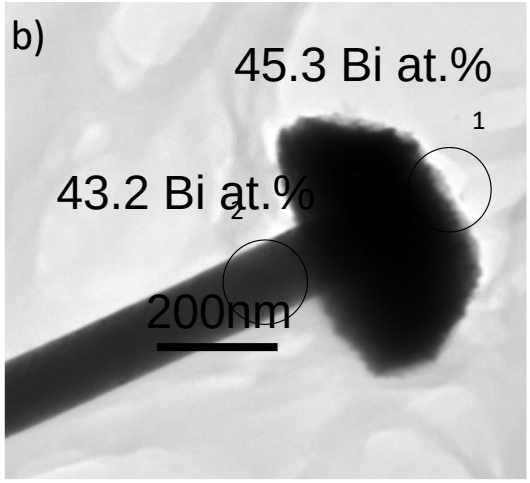
Template synthesis : 5/ Growth



- Example : electrodeposition of Bi_2Te_3 nanowires
- No deviation of the chemical composition along the nanowires

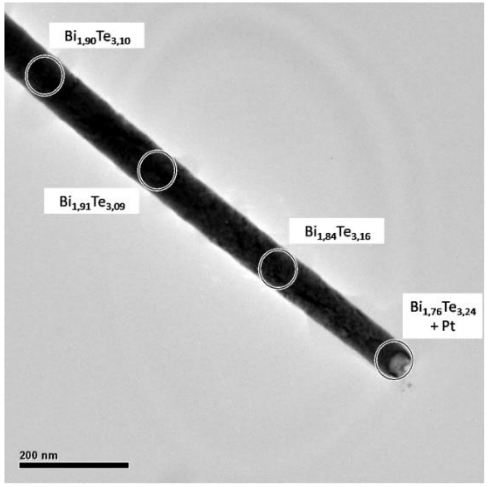
= steady state diffusion regime

Zoom : cap



✓Enrichment of Bi
✓Form texture
✓Change of cation diffusion

Zoom : bottom



✓Enrichment of Te
✓Polyphased state
✓Bi_2Te_3 Te°
✓Poly-crystalline

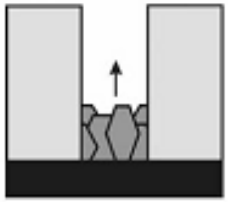
Electrochimica Acta, 69, 2012, 30

Electrodeposition of nanowires

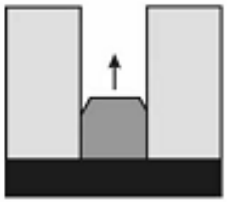
Template synthesis : electrocrystallization

The critical dimension N for a 2D-like nucleus $$N_c = \frac{bS\varepsilon^2}{(Ze\eta)^2}$$

S = surface area occupied by an atom on the surface of a nucleus
ε = surface energy
Z =effective electron number
η= overpotential
B = constant



new grains will grow if the size of an initial cluster exceeds the critical dimension N

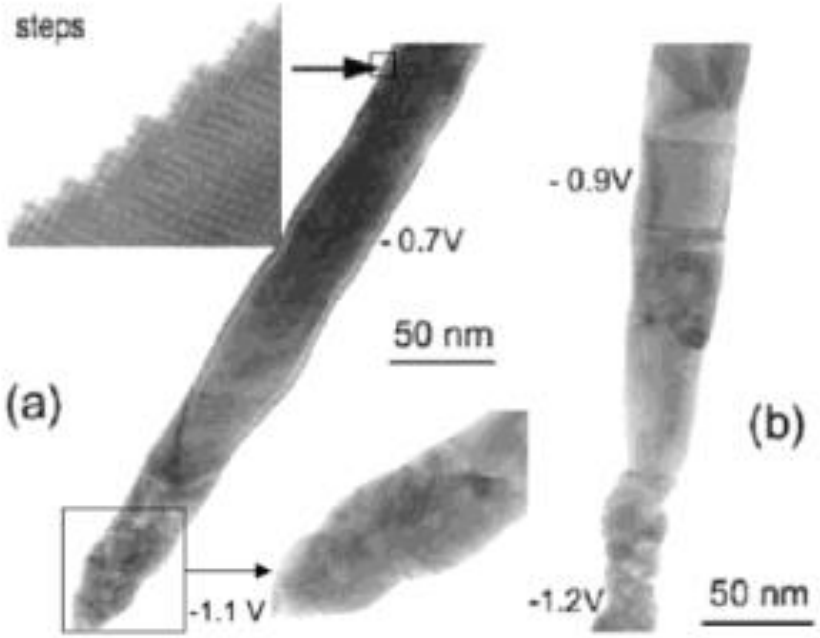


The larger the N is, the more favorable it is for a single crystal to grow from a previously nucleated seed grain.

Electrodeposition of nanowires

Template synthesis : electrocrystallization

$$N_c = \frac{bS\varepsilon^2}{(Ze\eta)^2}$$



Influence of the overpotential η

TEM images of Au nanowires with varying potentials

Tian, M. L.; Wang, J. U.; Kurtz, J.; Mallouk, T. E.; Chan, M. H. W
Nano Lett. ***2003, 3 (7), 919-923.***

Electrodeposition of nanowires

Template synthesis : electrocrystallization

$$N_c = \frac{bS\varepsilon^2}{(Ze\eta)^2}$$

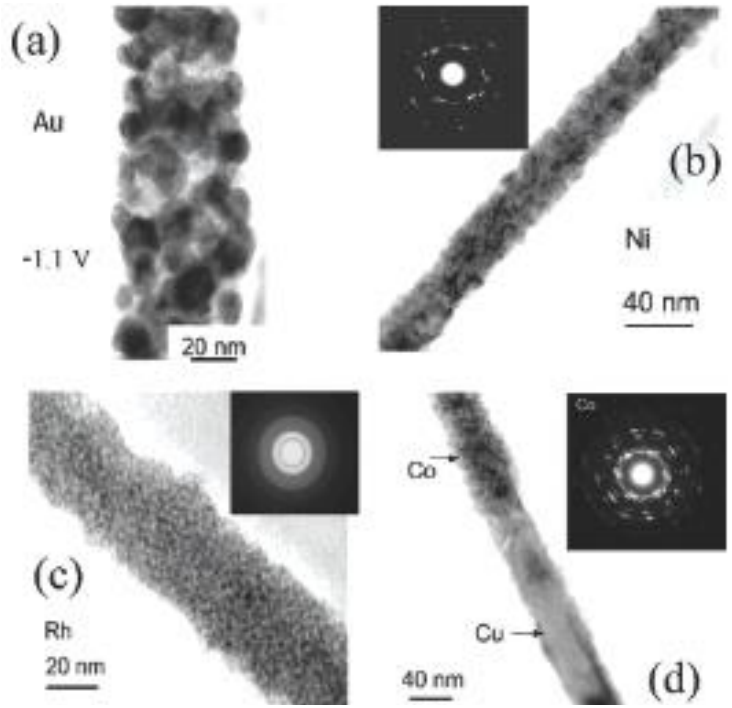


Figure 5. (a–c) TEM images of polycrystalline Au, Ni, and Rh nanowires deposited at $V_{SCE} = -1.1$, -1.1, and -0.25 V, respectively. (d) Junction of a Co/Cu striped nanowire and the ED pattern of a Co wire; single-crystalline Cu and polycrystalline Co were deposited at -0.015 and -1.1 V, respectively. (e)

Influence of the effective electron number Z

TEM images

Co, Ni, Rh	Ag, Au, Cu	Pb, Sn, Bi
Temp Fusion 2700°C 3700°C	Temp Fusion 960°C 1100°C	Temp Fusion 200°C 320°C

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Tian, M. L.; Wang, J. U.; Kurtz, J.; Mallouk, T. E.; Chan, M. H. W
Nano Lett. ***2003, 3 (7), 919-923.***

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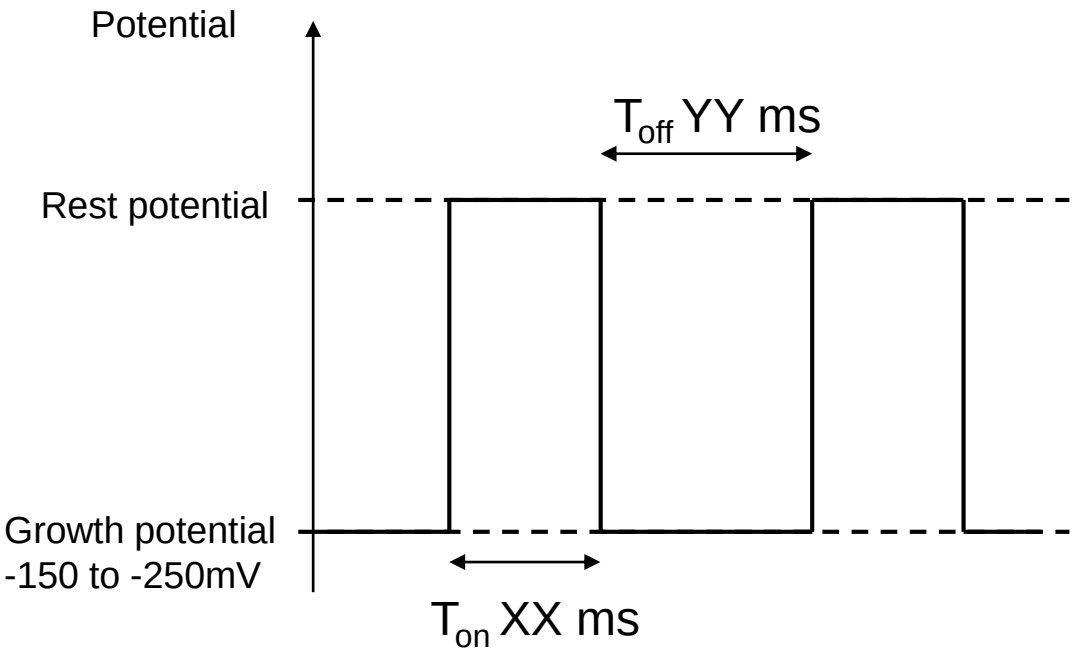
Bi_2Te_3 nanowires

Template synthesis : Pulse electrodeposition



During the relaxation time (toff)

- Recovery and redistribution of the metal ion concentration at the deposition interface
- Atomic surface diffusion

Bi_2Te_3 nanowires

Template synthesis : Pulse electrodeposition

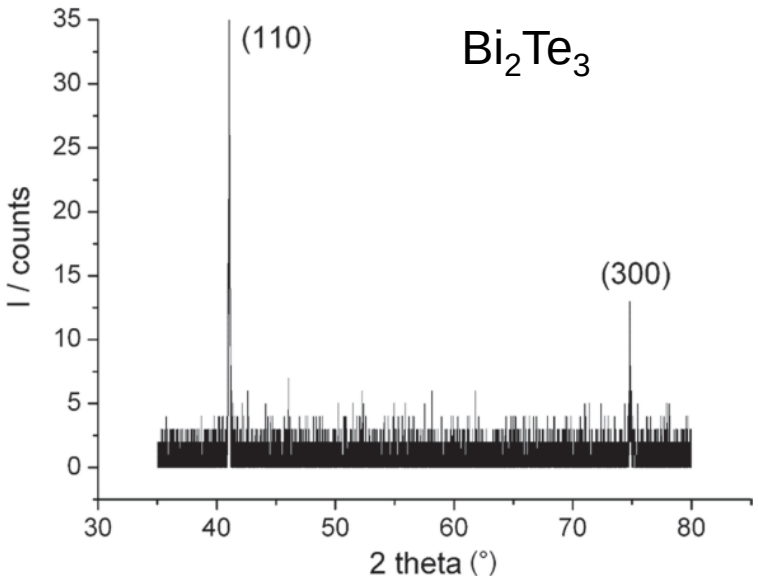


Figure 2. XRD diffraction pattern obtained on a Bi_2Te_3 nanowire array.

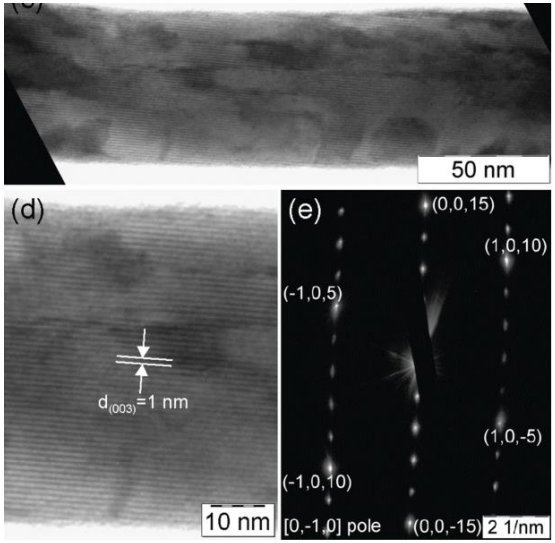
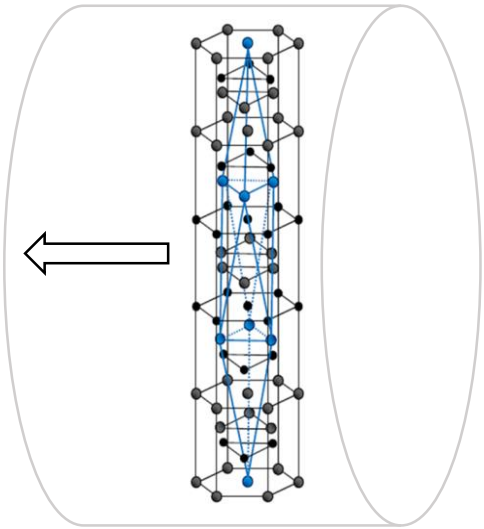


Figure 3. TEM images and electron diffraction pattern obtained in Bi_2Te_3 nanowires: a,b) Dark-field images obtained with two different {015} reflections at a sample region with five nanowires labeled 1 to 5. c–e) HRTEM images and diffraction pattern of a nanowire tilted in [0,–1,0] pole.

Growth direction



the (300) planes are almost perpendicular to the wire axis.
Orientation of c axis ⊥ to wire axis

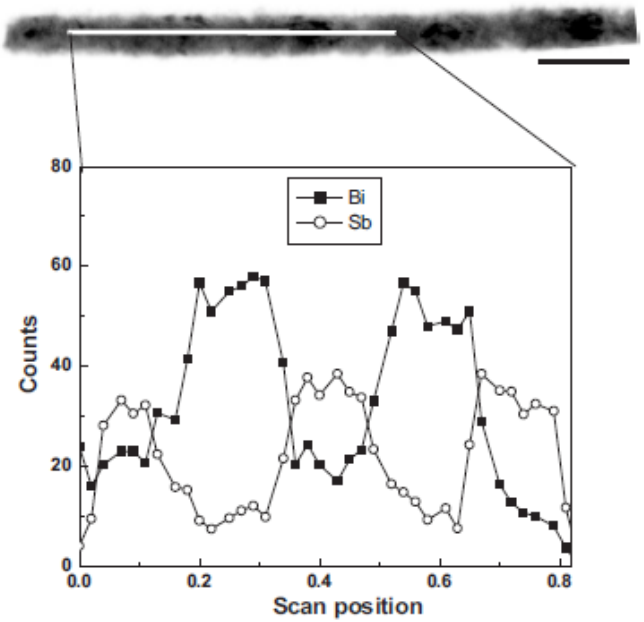
Peranio, N et al.
Advanced Functional Materials 2012, 22, (1), 151-156.

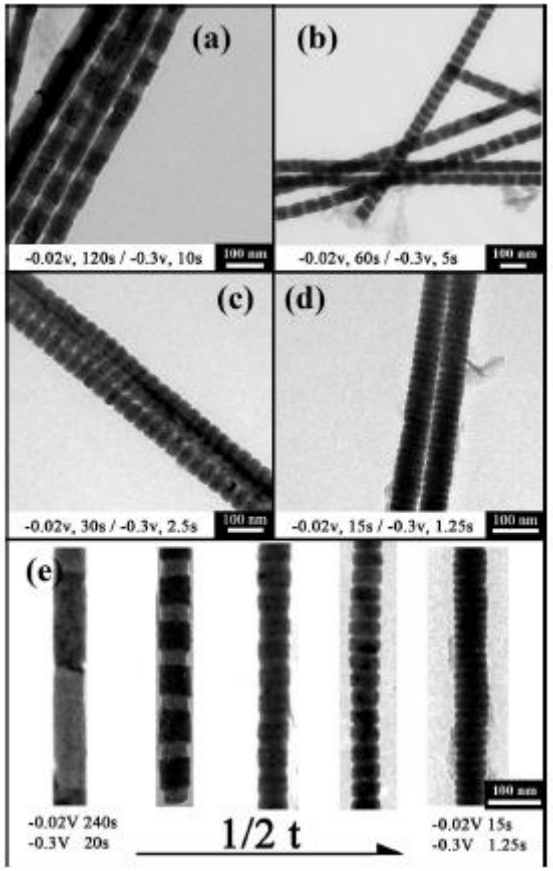
Bi_2Te_3 nanowires

Template synthesis : Pulse electrodeposition

Pulsed deposition in PC membrane:
nanowires $Bi_2Te_3/(Bi_{0.3}Sb._{0.7})_2Te_3$ from a unique solution by adjusting potentials

Pulsed deposition in AAM :
nanowire Bi_2Te_3/Sb
min period: 10 nm





2007 Yoo *Advanced Mater.*
2008 Wang *J. Phys. Chem. C.*

Electrodeposition of nanostructures

✓ **Geometrical engineering at nanoscale**

Large panel of nanostructures : 2D, nanowires, core@shell nanowires, modulated nanowires, nanotubes

✓ **Low cost synthesis (low temperature, absence of vacuum, no advanced equipment**

✓ ***Specific electrochemical systems***

Electrodeposition requires to combine electrochemical analysis and a materials science approach

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Electrosynthesis of nanostructures for energy

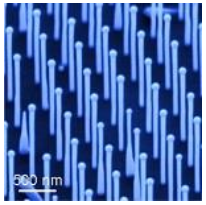
N. STEIN

Electrochemistry of Materials Research Group

thematic school of the GDR NAME

ELaboration of NANOmaterials for the recovery, conversion, transport and storage of energy

11-16 June 2023



NAME

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