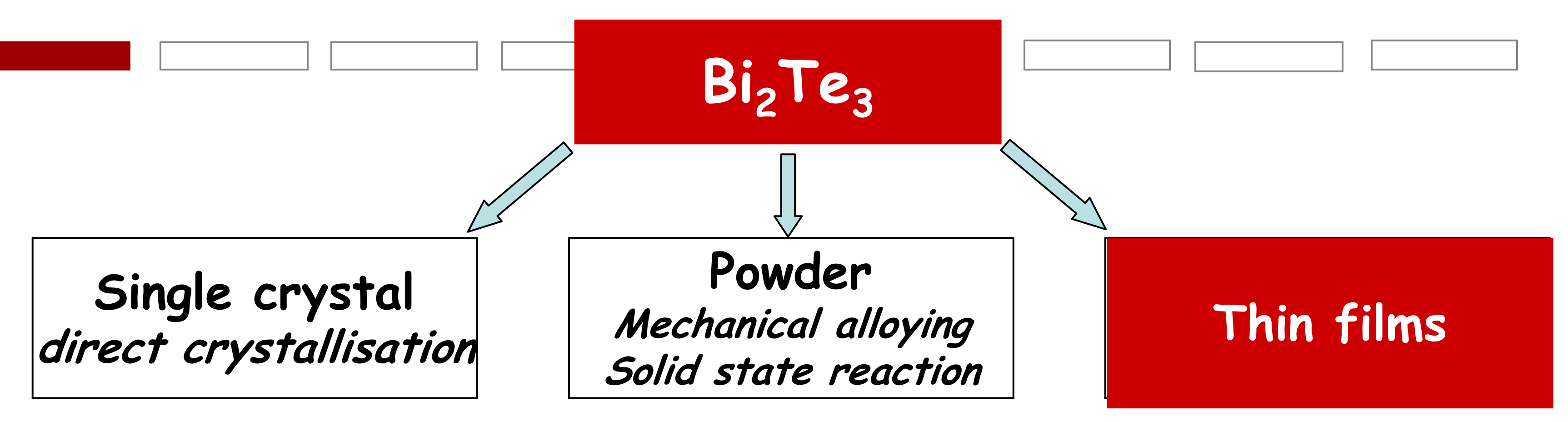
Influence des conditions d'électrodéposition pulsée sur la nucléation, la morphologie et les propriétés de films de tellurures de bismuth

C. Boulanger, V.Richoux, S. Diliberto, N. Stein

Elaboration



<u>Miniaturization, microelectronic</u>

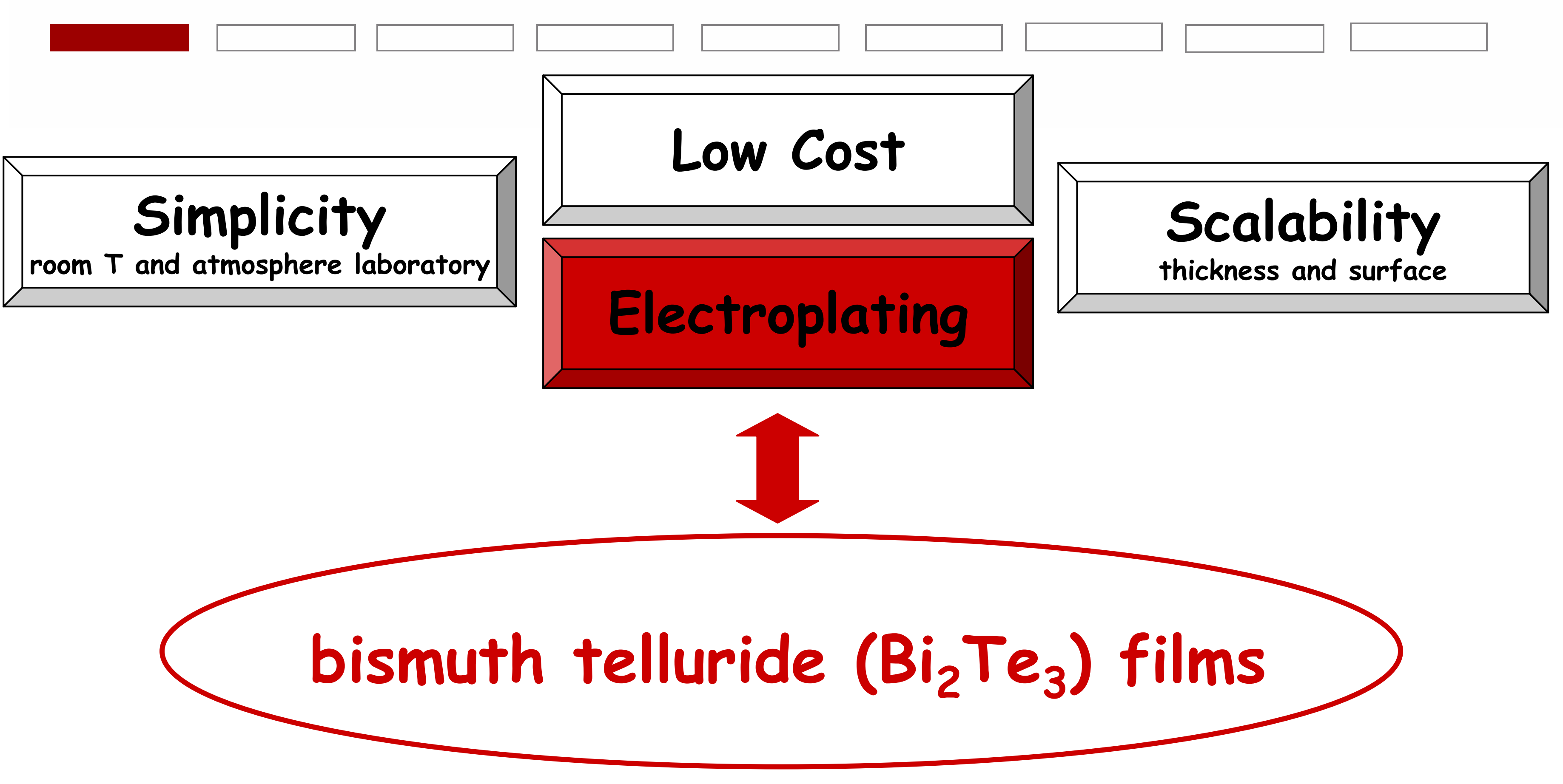
atomic monolayers several nm < **Thickness of thin films** < Several tens of µm

<u>Growth methods</u>

- Flash evaporation
- MOCVD
- Molecular beam epitaxy
- Pulsed laser deposition
- Sputtering

} Thickness of deposit < 1 µm → **Electrodeposition**

Elaboration



Electroplating

❖ Definition of protocols

n-type SC

Binaries

p-type SC

$Bi_{2-x}Te_{3+x}$

$Bi_{2+x}Te_{3-x}$

Journal of Materials Chemistry, 6, 5, 1996 P. Magri et al
Journal of Crystal Growth, 277, 2005, S. Michel et al.
Journal of The Electrochemical Society, 152, 10, 2005 A. Zimmer et al
Journal of Crystal Growth 296, 2006, S. Michel et al
Electrochimica Acta, volume 52, 14, 2007, A. Zimmer et al
Electrochimica Acta 52, 2007 V. Richoux et al

Ternaries

$n\text{-}Bi_2Te_{2.7}Se_{0.3}$

Journal of Appl Electrochem, 33, 1, 2003 S. Michel et al.
Journal of Solid State Electrochem. , 2007 S. Michel et al.

$p\text{-}Bi_{0.5}Sb_{1.5}Te_3$

Thin Solid Films, 483, 2004, D Del Frari et al
Journal of Applied Electrochemistry, 36, 4, 2006 Del Frari et al

Electroplating concept

HNO_3 1M

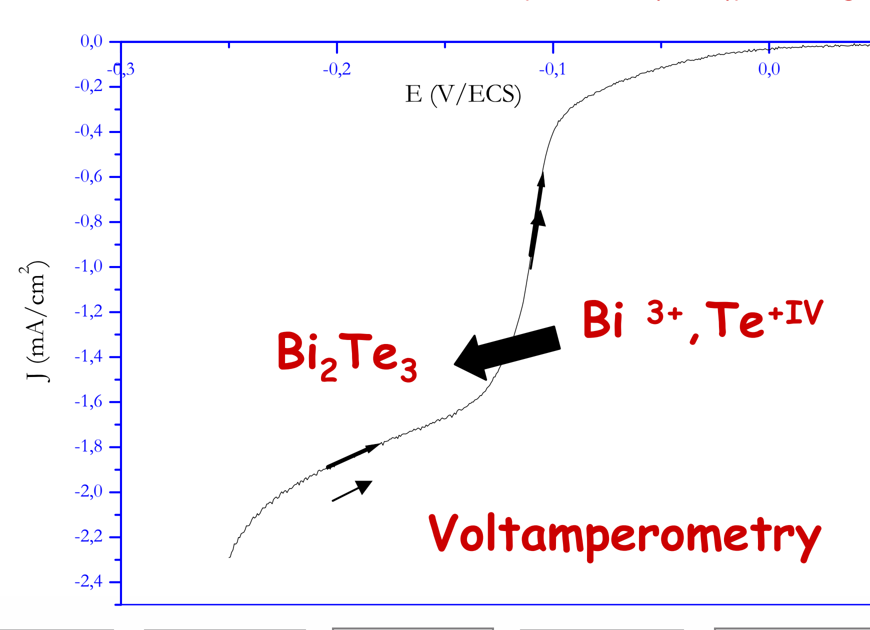
$2Bi^{3+} + 3xTe^{+IV} + 18\ e^- \rightarrow Bi_2Te_3$

$2Bi^{3+} + 3xTe^{+IV} + 3(1-x)Se^{4+} + 18\ e^- \rightarrow Bi_2(Te_xSe_{1-x})_3$

$HClO_4$ 1M + Tartaric Acid 0.1 M

$2(1-x)Sb^{3+} + 2xBi^{3+} + 3Te^{+IV} + 18\ e^- \rightarrow (Sb_{1-x}Bi_x)_2Te_3$

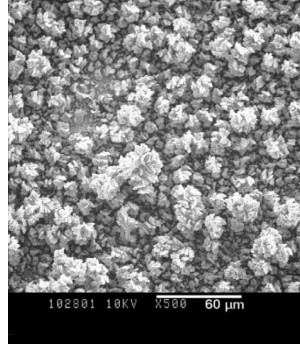
- Experimental parameters
  - Chemical conditions : concentration, ratio of cations
  - Deposition mode :
    E, J



Pulsed electrodeposition

$Bi_{0.5}Sb_{1.5}Te_3$

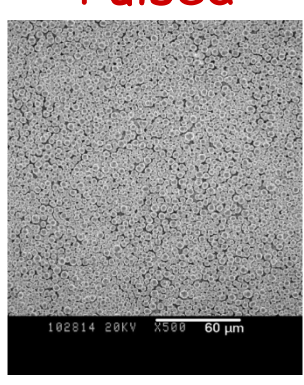
Direct

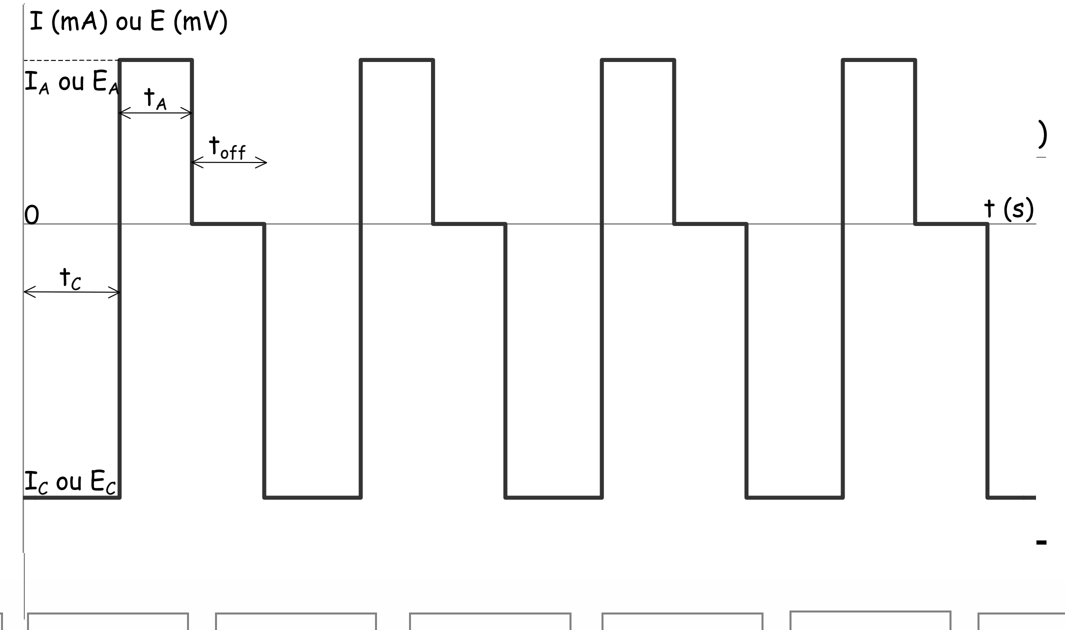


Technique used in order to:

- improve the morphology of electroplated films

- modify the nucleation, grain size





Experimental conditions

- Electrolyte : HNO_3 1M, [Te] = 2.10^{-2}M, Bi/Te = 1, 2 or 3

- Substrates: Stainless steel or gold plates

- Electrochemistry:
  - Voltamperometric and chronopotentiometry studies

- Characterizations:
  - EPMA, XFS (composition)
  - XRD (cristallography)
  - SEM (morphology)
  - Hall effect, Van der Pauw (transport properties)
  - Seebeck effect

Determination of nucleation type

Aim : a morphology with small grains and dense layers

→ optimization of the deposit conditions

theoretical models of nucleation

Instantaneous nucleation :
immediate activation of all reaction sites and constant number of nuclei

Progressive nucleation :
increase of nuclei number during the growth process

$$\ln\left(\frac{i}{t}\right) = a - bt^2$$

2D

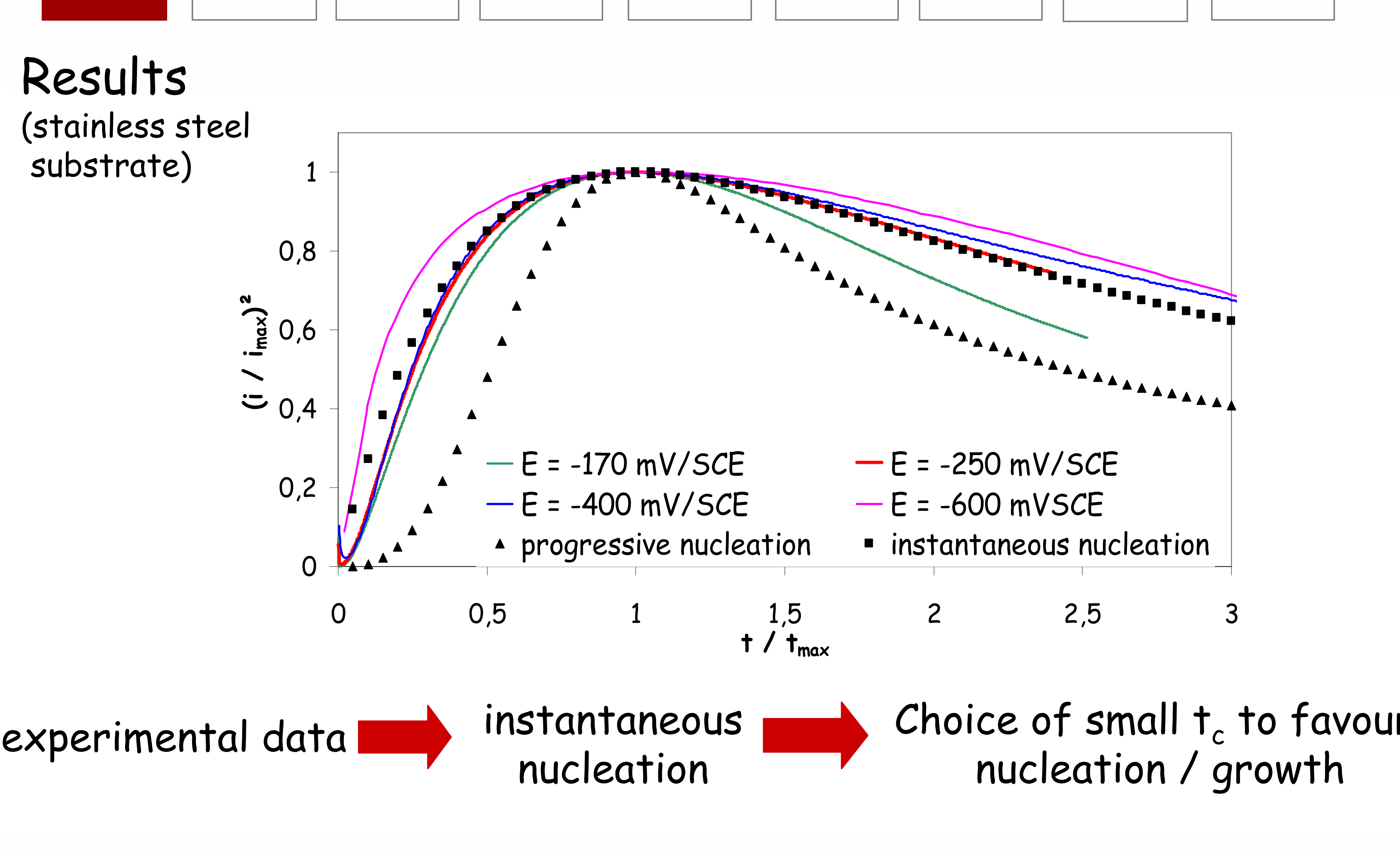
$$\ln\left(\frac{i}{t^2}\right) = c - dt^3$$

$$\left(\frac{i}{i_{max}}\right)^2 = \frac{1.9542}{t/t_{max}}\left(1 - \exp\left[-1.2564\left(\frac{t}{t_{max}}\right)\right]\right)^2$$

3D

$$\left(\frac{i}{i_{max}}\right)^2 = \frac{1.2254}{t/t_{max}}\left(1 - \exp\left[-2.3367\left(\frac{t}{t_{max}}\right)^2\right]\right)^2$$

B. Scharifker, G. Hills, Electrochem. Acta, 7, 1983, 879


Determination of nucleation type
Results
(stainless steel
substrate)
(i / i_max)²
1
0,8
0,6
0,4
0,2
0
0
0,5
1
1,5
2
2,5
3
t / t_max
E = -170 mV/SCE
E = -250 mV/SCE
E = -400 mV/SCE
E = -600 mVSCE
progressive nucleation
instantaneous nucleation
experimental data
instantaneous
nucleation
Choice of small t_c to favour
nucleation / growth
Juillet 2008
GDR Thermoélectricité

Determination of nucleation type

From the values of i_{max} and t_{max}

Calcul of nuclei density (N_0)

$$N_0 = 0.0652 \frac{1}{(8\pi C M/\rho)^{1/2}} \frac{(zFC)^2}{i_{max}^2 t_{max}^2}$$

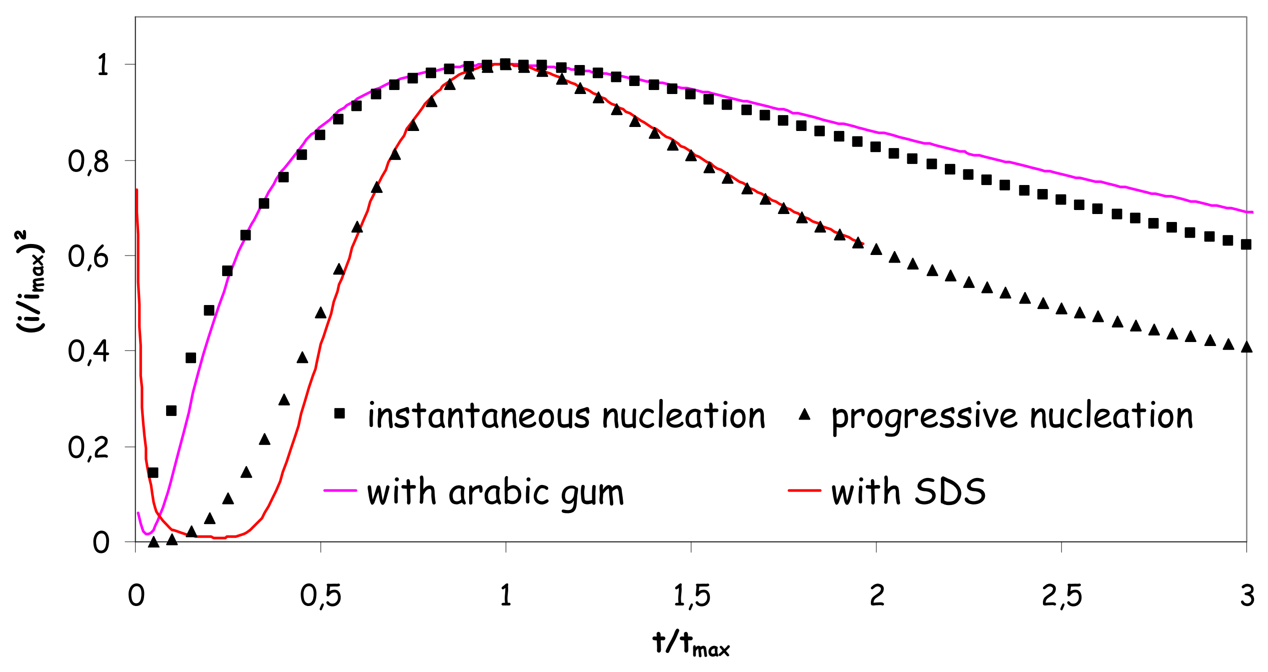
E (mV)	nuclei density N_0 (.cm^{-2})
-170	$1.50.10^6$
-250	$1.24.10^7$
-400	$6.53.10^7$
-600	*$2.77.10^8$*

Increase of N_0 with the potential

Determination of nucleation type

<u>Addition of surfactants : 0.02 w %</u>

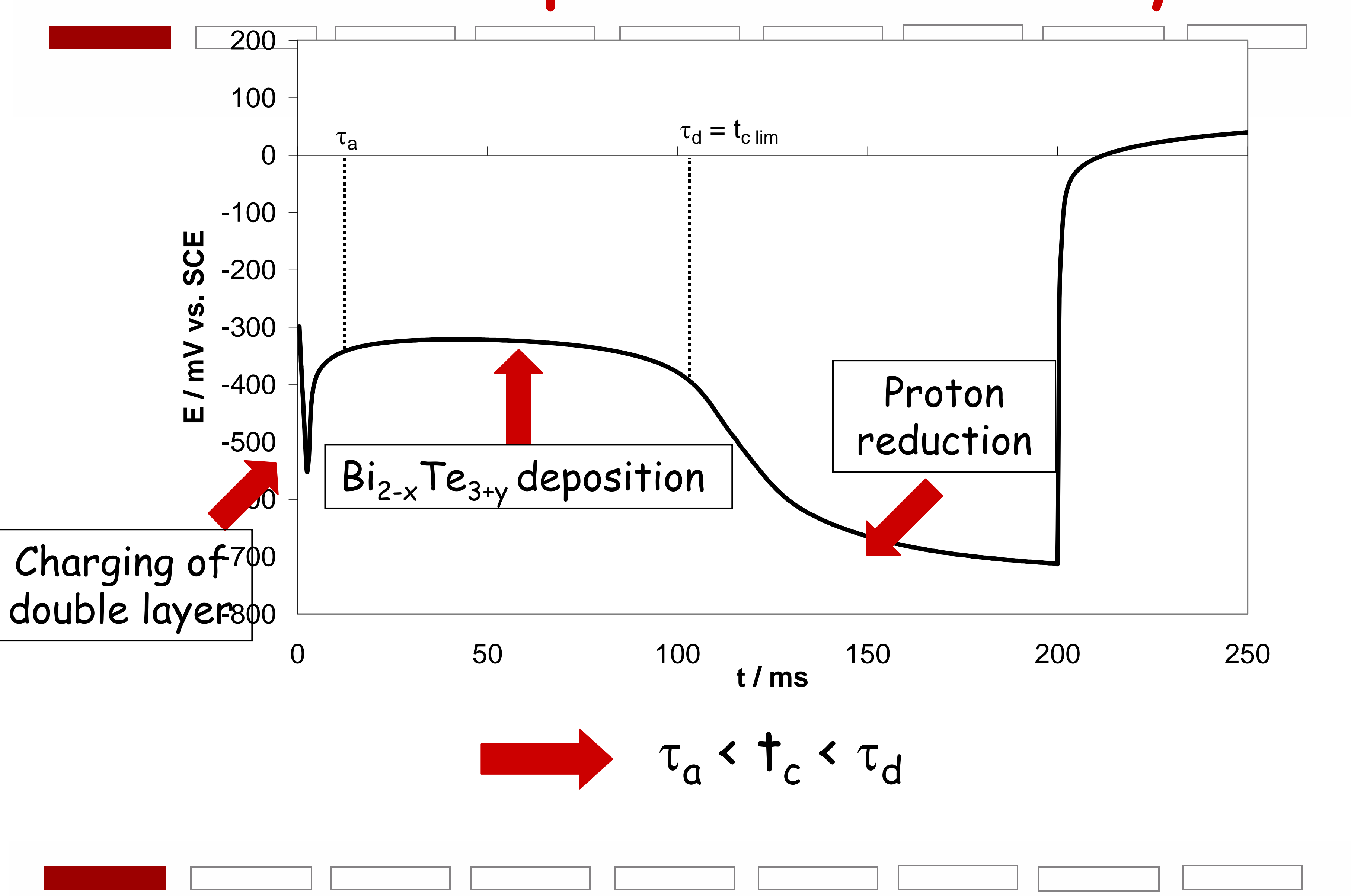
E = -250 mV, substrate stainless steel



- Arabic gum
- SDS sodium dodecylsulfate

- Instanteneous nucleation
- Progressive nucleation

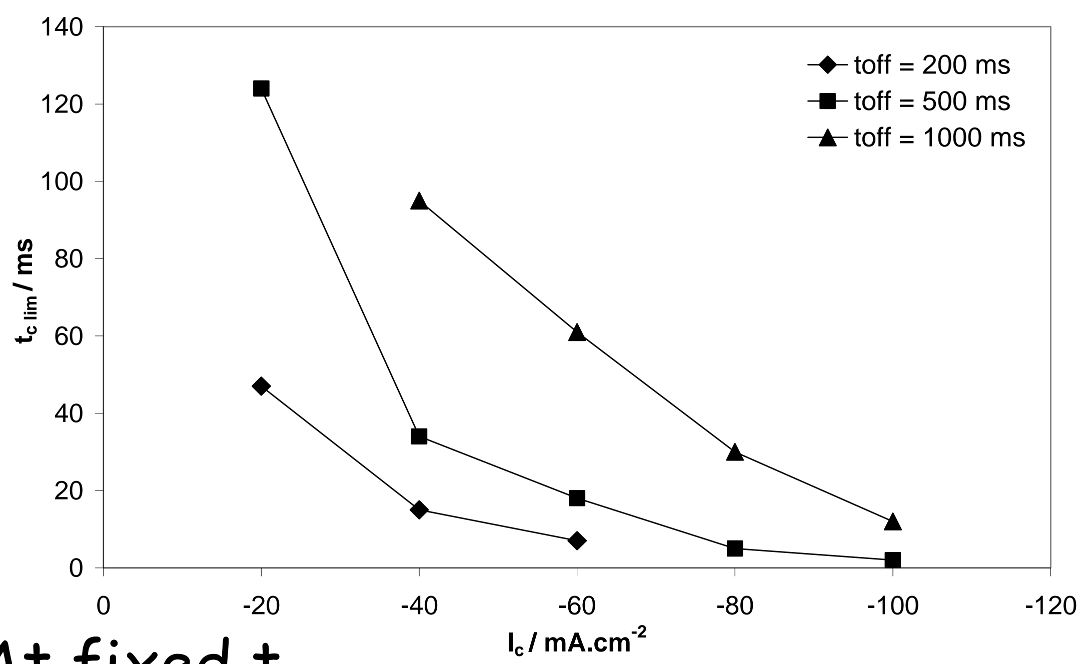
Chronopotentiometric study



$\tau_a < t_c < \tau_d$

Chronopotentiometric study

Determination of $t_{c\,lim}$ = time where proton reduction is observed



<u>At fixed t_{off}</u>
Increase of J_c

shorter $t_{c\,lim}$

<u>At fixed J_c</u>
Increase of t_{off}

longer $t_{c\,lim}$

Relations between pulsed parameters

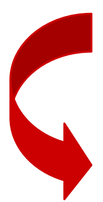
- Litterature: empirical relation : $J_m < J_{\text{limit in direct mode}}$

J.C. Puippe, F. Leaman, American Electroplaters and surface Finished Society, 1986

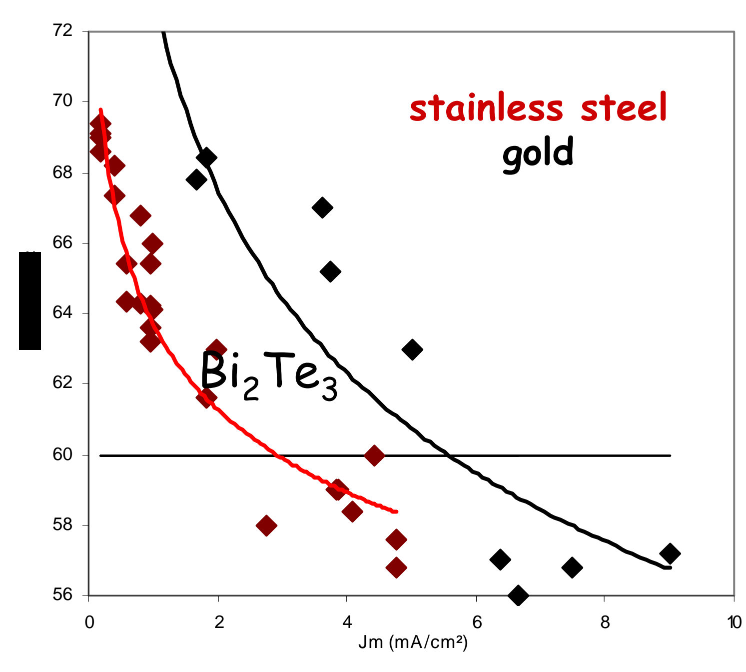
$-3\ mA.cm^{-2} < J_{lim\ direct} < -4\ mA.cm^{-2}$ in the case of Bi_2Te_3

- Definition of a medium current density: J_m

$$J_m = J_c \times \frac{t_{on}}{t_{on} + t_{off}}$$

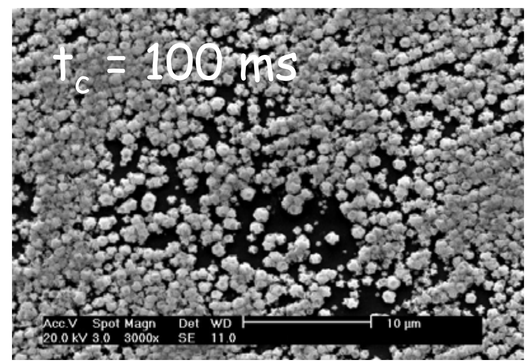


Our results verify the relation

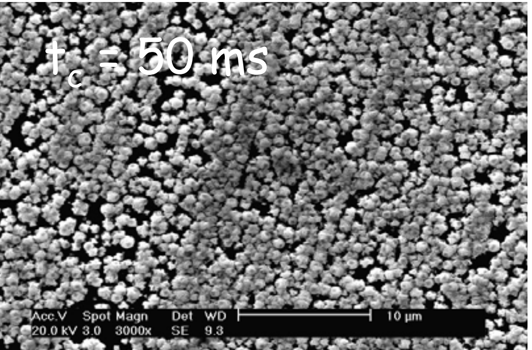


Influence of t_c on growth and morphology

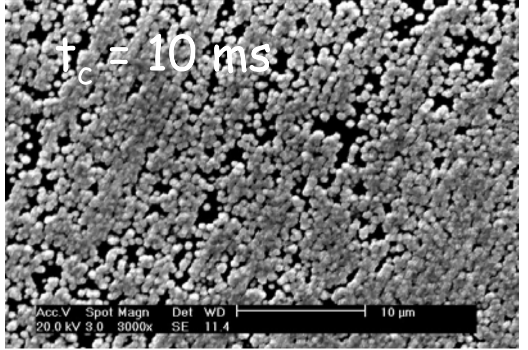
J_c = -20 mA.cm^{-2} et t_{off} = 1s, [Te] = 2.10^{-2}M, Bi/Te = 1



Agregates : 900 nm
Coverage : 75%
$Bi_{1.9}Te_{3.1}$



Agregates : 700 nm
Coverage : 81%
$Bi_{1.83}Te_{3.17}$



Agregates : 650 nm
Coverage : 87%
$Bi_{1.53}Te_{3.47}$

Decrease of t_c

- better coverage
- smaller agregates
- increase of Te content

Small t_c = best morphology but necessary improvement of stoichiometry

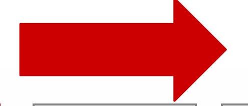
Effect of J_c on growth and morphology

t_c = 10 ms and t_{off} = 1s, [Te] = 2.10^{-2}M, Bi/Te = 1

$J_c/mA.cm^{-2}$	Coverage percentage	agregate size	stoichiometry
-20	62%	600 nm	$Bi_{1.79}Te_{3.21}$
-60	65%	450 nm	$Bi_{1.82}Te_{3.18}$
-100	82%	350 nm	$Bi_{1.89}Te_{3.11}$

Increase of J_c

- better coverage
- smaller agregates
- decrease of Te content

 High current density = optimal J_c

Influence of Bi/Te ratio on stoichiometry

$[Te] = 2.10^{-2}M$, Bi/Te = 1, 2 or 3

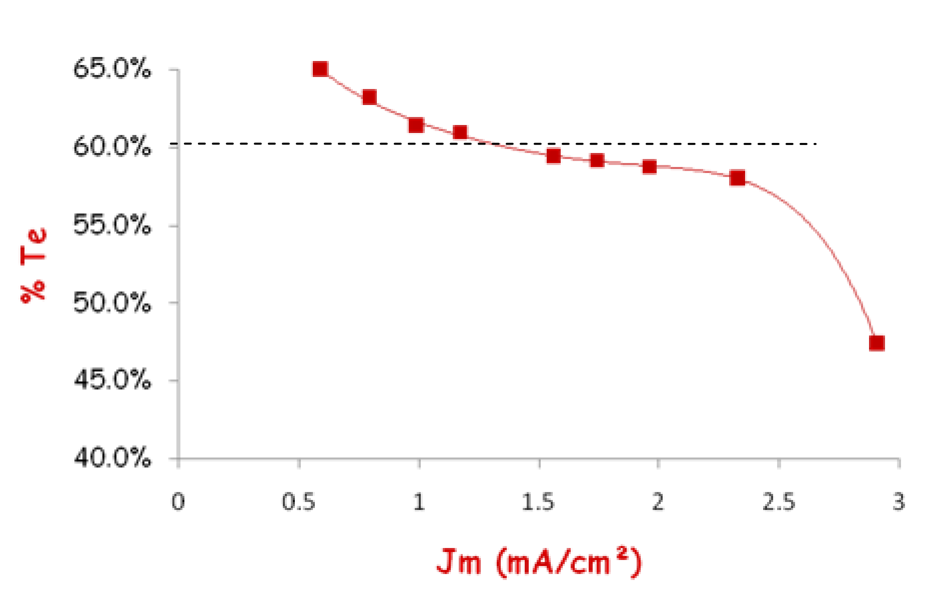
Pulse parameters	Bi/Te = 1	Bi/Te = 2	Bi/Te = 3
t_{on} = 10ms $J_c = -60mA.cm^{-2}$	$Bi_{1.82}Te_{3.18}$	$Bi_{1.91}Te_{3.09}$	$Bi_{1.90}Te_{3.10}$
t_{on} = 10ms $J_c = -100mA.cm^{-2}$	$Bi_{1.89}Te_{3.11}$	$Bi_{1.99}Te_{3.01}$	$Bi_{2.08}Te_{2.92}$

Increase of Bi/Te ratio

Decrease of Te %

Compositions obtained with [Bi]/[Te] = 2

Experimental conditions	Stoichiometry
t_{on} = 10ms, J = -60mA/cm ^{2}	$Bi_{1.75}Te_{3.25}$
t_{on} = 10ms, J = -80mA/cm ^{2}	$Bi_{1.84}Te_{3.16}$
t_{on} = 10ms, J = -100mA/cm ^{2}	$Bi_{1.99}Te_{3.01}$
t_{on} = 20ms, J = -60mA/cm ^{2}	$Bi_{1.95}Te_{3.05}$
t_{on} = 20ms, J = -80mA/cm ^{2}	$Bi_{2.03}Te_{2.97}$
t_{on} = 20ms, J = -100mA/cm ^{2}	$Bi_{2.06}Te_{2.94}$
t_{on} = 30ms, J = -60mA/cm ^{2}	$Bi_{2.04}Te_{2.96}$
t_{on} = 30ms, J = -80mA/cm ^{2}	$Bi_{2.10}Te_{2.90}$
t_{on} = 30ms, J = -100mA/cm ^{2}	$Bi_{2.63}Te_{2.37}$



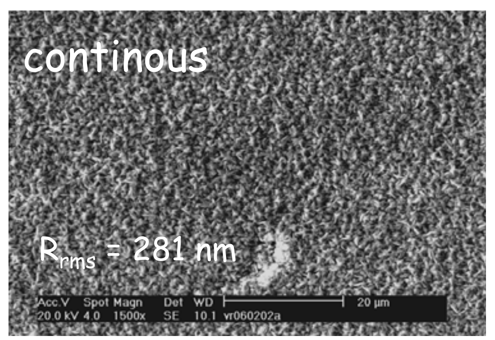
t_{off} = 1s, $[Te^{IV}]$ = 2.10^{-2}M, [Bi]/[Te] = 2, HNO_3 1M

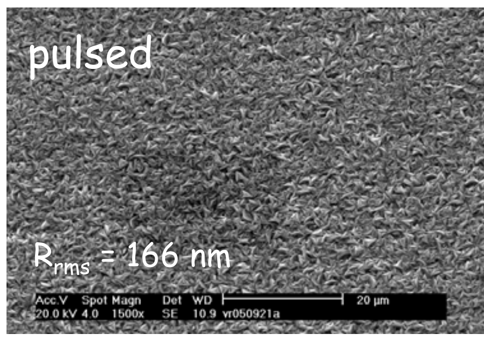
Comparison between methods: roughness

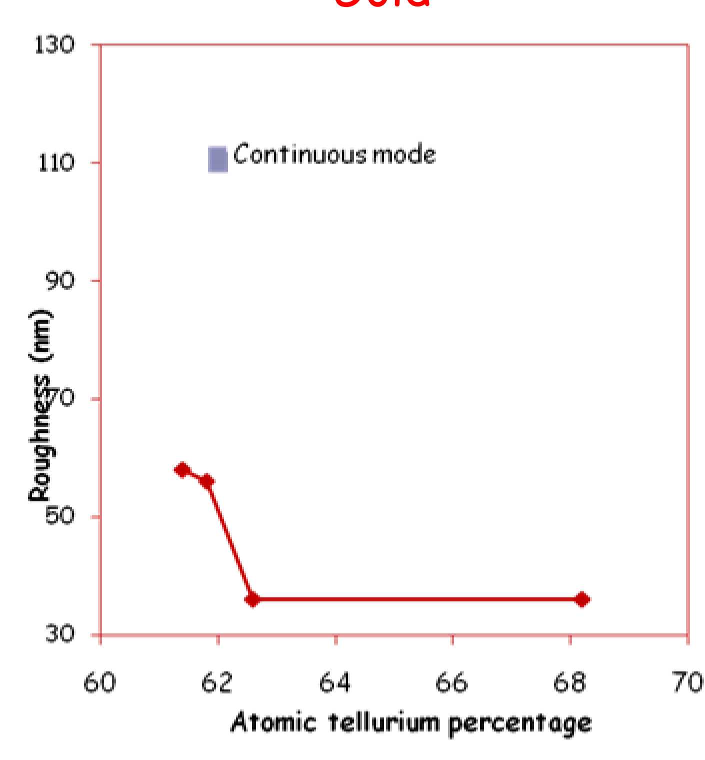
Bi_2Te_3 films electrodeposited for both methods

Stainless steel

Gold

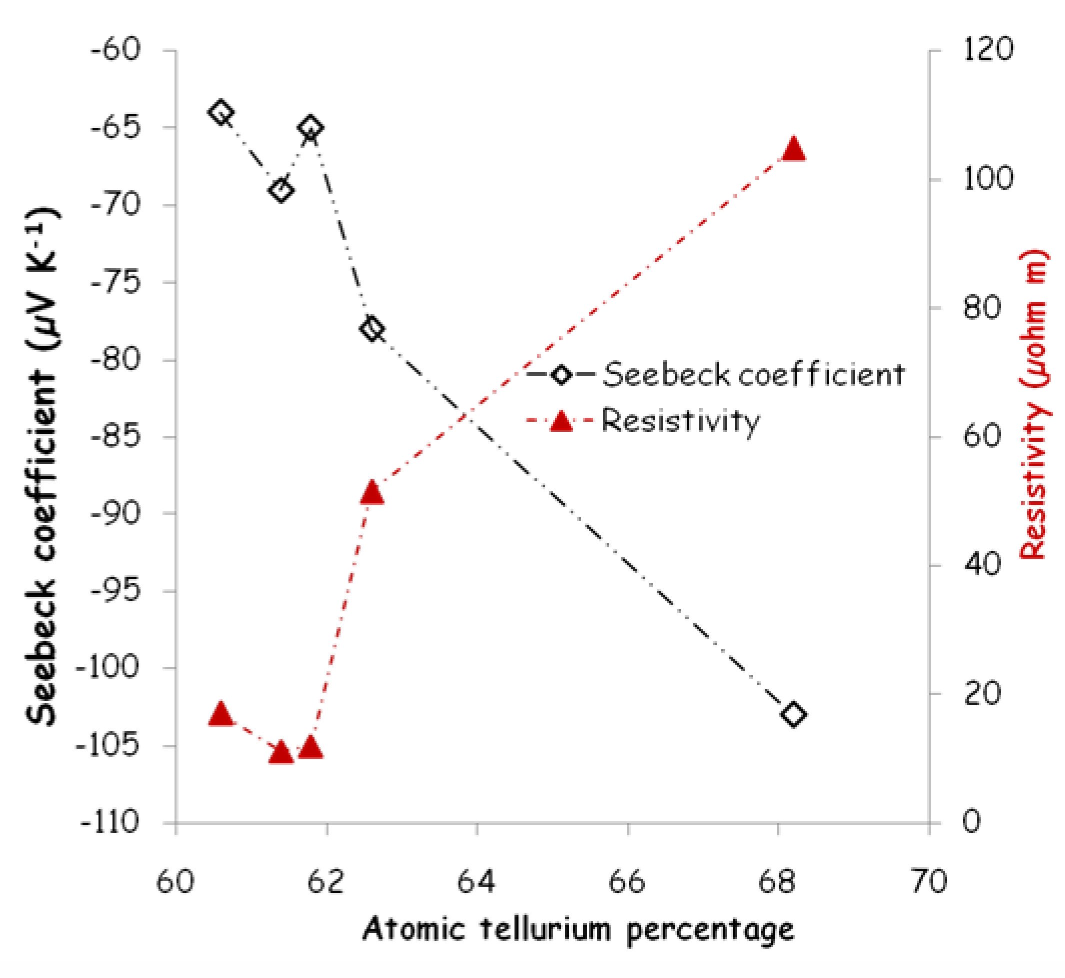




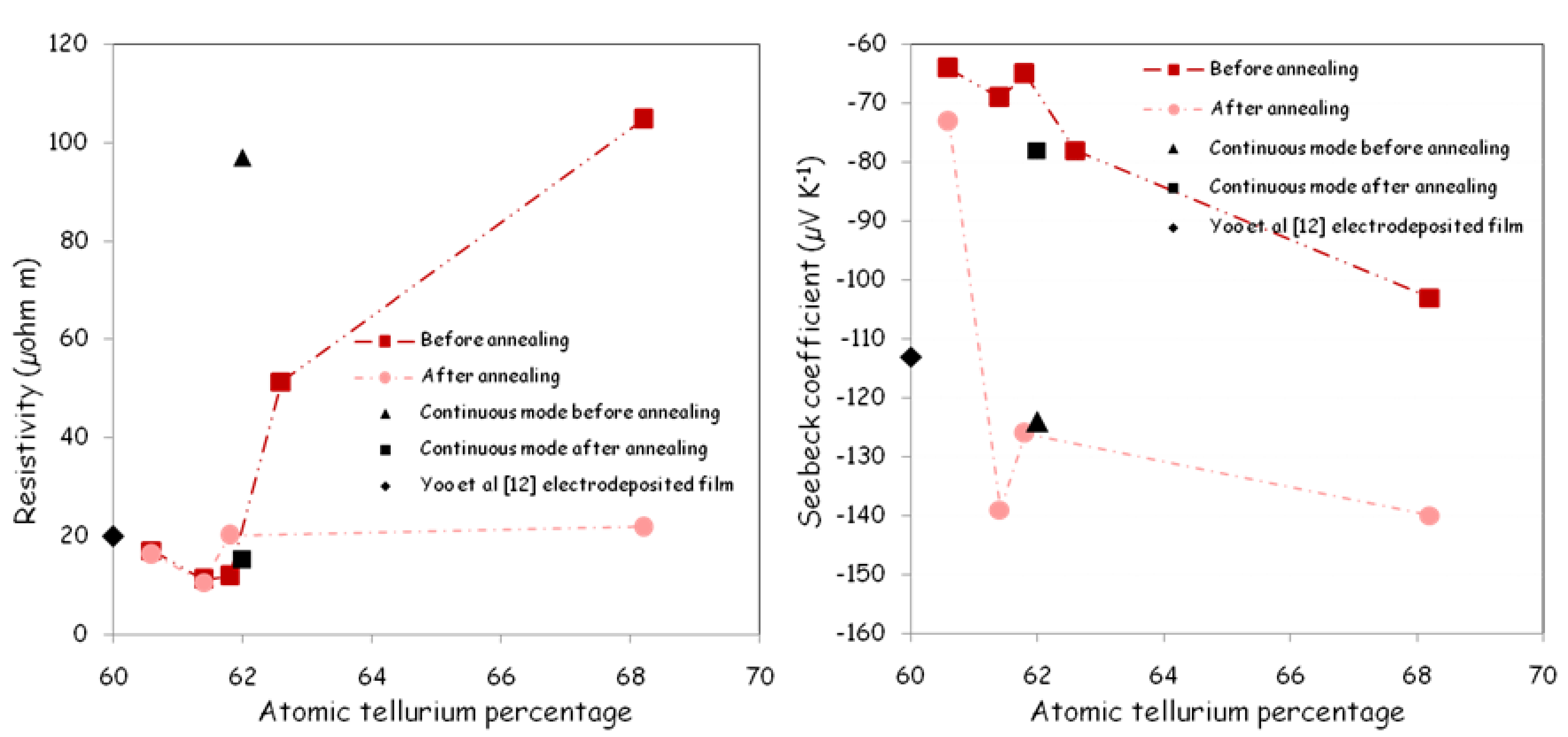


Pulsed films → Smaller roughness and grains, better adhesion

Seebeck coefficient and resistivity



Comparison between methods: physical properties



Annealing : T=150 °C - t =15 h and T = 300 °C - t=3 h

Comparison between methods: physical properties

Pulsed electroplating

Direct electroplating

	Binary ($Bi_{1.9}Te_{3.1}$)	Antimony ternary ($Bi_{0.5}Sb_{1.5}Te_{3.0}$)
Seebeck coefficient (µV/K)	- 65 -124	108 190
Resistivity (µΩ.m)	12 97	9 545
Power factor (µW/K^2.m)	356 159	**1350** 66

Conclusion

- Pulse Electroplating of Bi_2Te_3
- Instantaneous 3D nucleation
- Best parameters :
  - small t_c ($\approx$ 10 ms)
  - high J_c ($\approx$ -100 mA.cm^{-2})
  - t_{off} (1s)
- Improvement of morphology and roughness
- Promising Seebeck coefficient and power factor/ternary