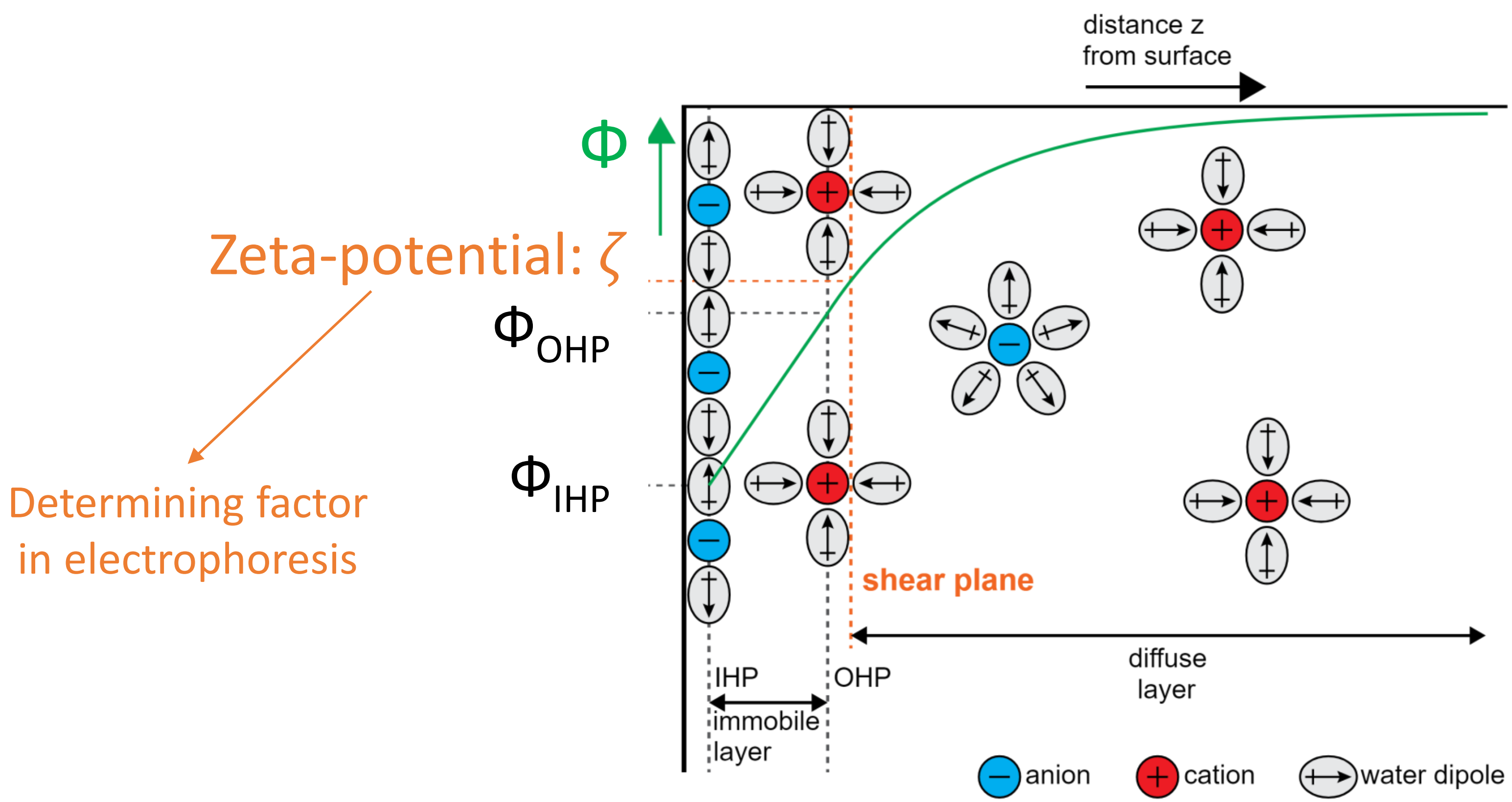
5 – Morphology and microstructure of electrodeposits

Effects of electroplating conditions

I) Reminders

1) Electrode in an electrolyte: development of an electrical double layer

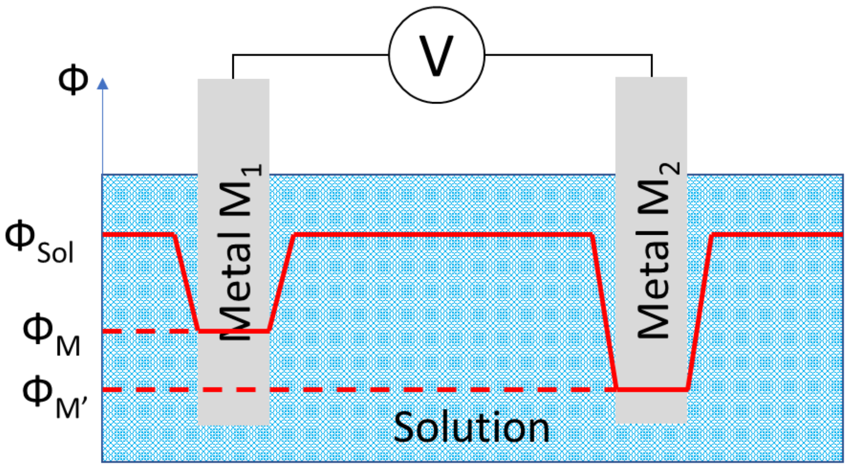


I) Reminders

1) Electrode in an electrolyte: development of an electrical double layer

2) Equilibrium characterized by the Nernst equation

Need an additionnal electrode



$$\Delta \mathrm{E} = \sum \Delta\phi = \phi_M - \phi_{M'} = E_M^{eq} - E_{M'}^{eq}$$

ΔE is the difference of Nernst potentials

$$\Delta \mathrm{E} = \Delta E^0 + \frac{RT}{z_1 F} ln\left[M_1^{z_1+}\right] - \frac{RT}{z_2 F} ln\left[M_2^{z_2+}\right]$$

I) Reminders

1) Electrode in an electrolyte: development of an electrical double layer

2) Equilibrium characterized by the Nernst equation

3) At equilibrium, there exists an exchange current

$$i_0 = zF\beta_{Red}[Red] \cdot exp^{\frac{-\Delta G^*_{\chi,\,Red}}{RT}} \cdot exp^{\frac{-\alpha zF\Delta\phi_{eq}}{RT}} = zF\beta_{Ox}[Ox] \cdot exp^{\frac{-\Delta G^*_{\chi,\,Ox}}{RT}} \cdot exp^{\frac{(1-\alpha)zF\Delta\phi_{eq}}{RT}}$$

I) Reminders

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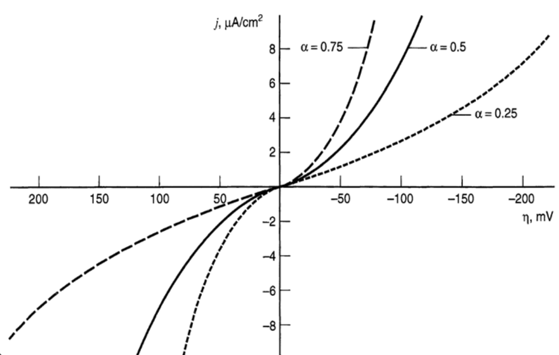
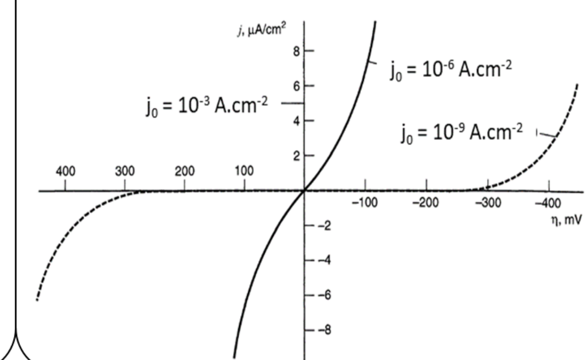
3) At equilibrium, there exists an exchange current

4) If the electrode potential is forced to a value $E < E^{eq}$ then electrons will be transfered from the cathode to metal cations → electrodeposition

Effect of the transfer coefficient α



Effect of the exchange current i_0



Out of equilibrium: $\Delta\phi = \Delta\phi_{eq} + \eta$

$$i = i_0 \left(exp^{\frac{(1-\alpha)zF\eta}{RT}} - exp^{\frac{-\alpha zF\eta}{RT}} \right)$$

Butler-Volmer equation

I) Reminders

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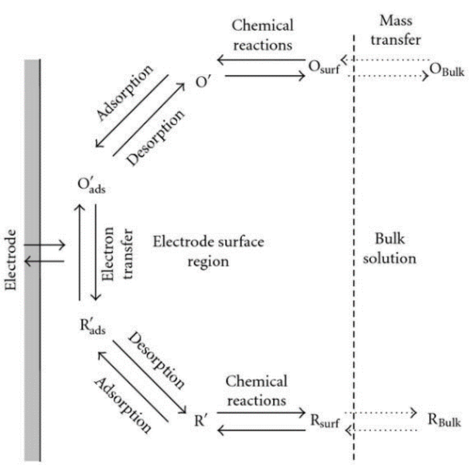
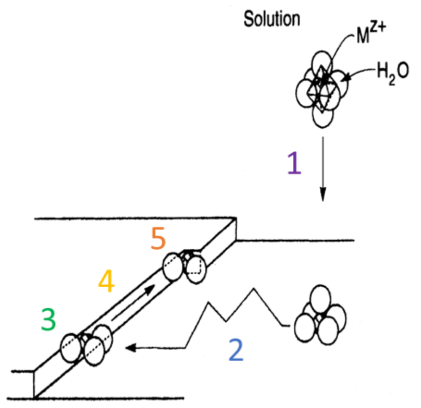
5) Electrodeposition may involve five steps:

- Mass transfer to the interphase
- Chemical reactions
- Adsorption on planar surfaces
- Adion diffusion and dehydration
- Charge transfer/electrocrystallization





I) Reminders

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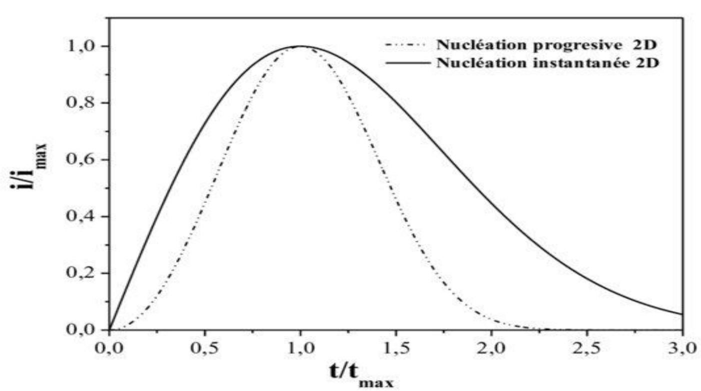
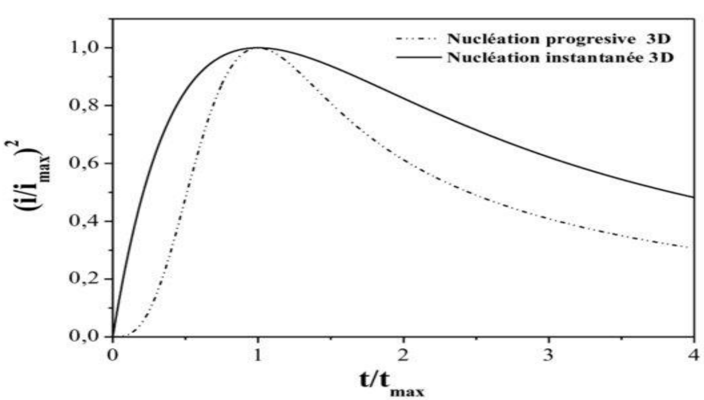
5) Electrodeposition may involve five steps

6) 3D or 2D Nuclei can be formed instantaneously or progressively:

3D/2D related to the interplay between η and Δσ

Density of nuclei N(t) related to η and the density of surface defects





I) Reminders

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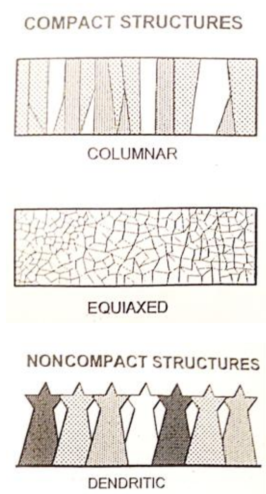
6) 3D or 2D Nuclei can be formed instantaneously or progressively

7) Deposit characteristics result from nucleation and growth regime

low η: low nuclei density, coarse grain compact coating

medium η: high nuclei density, fine grain structure

high η: oriented growth (dendrites) or powdery deposit



II) Effect of electroplating parameters

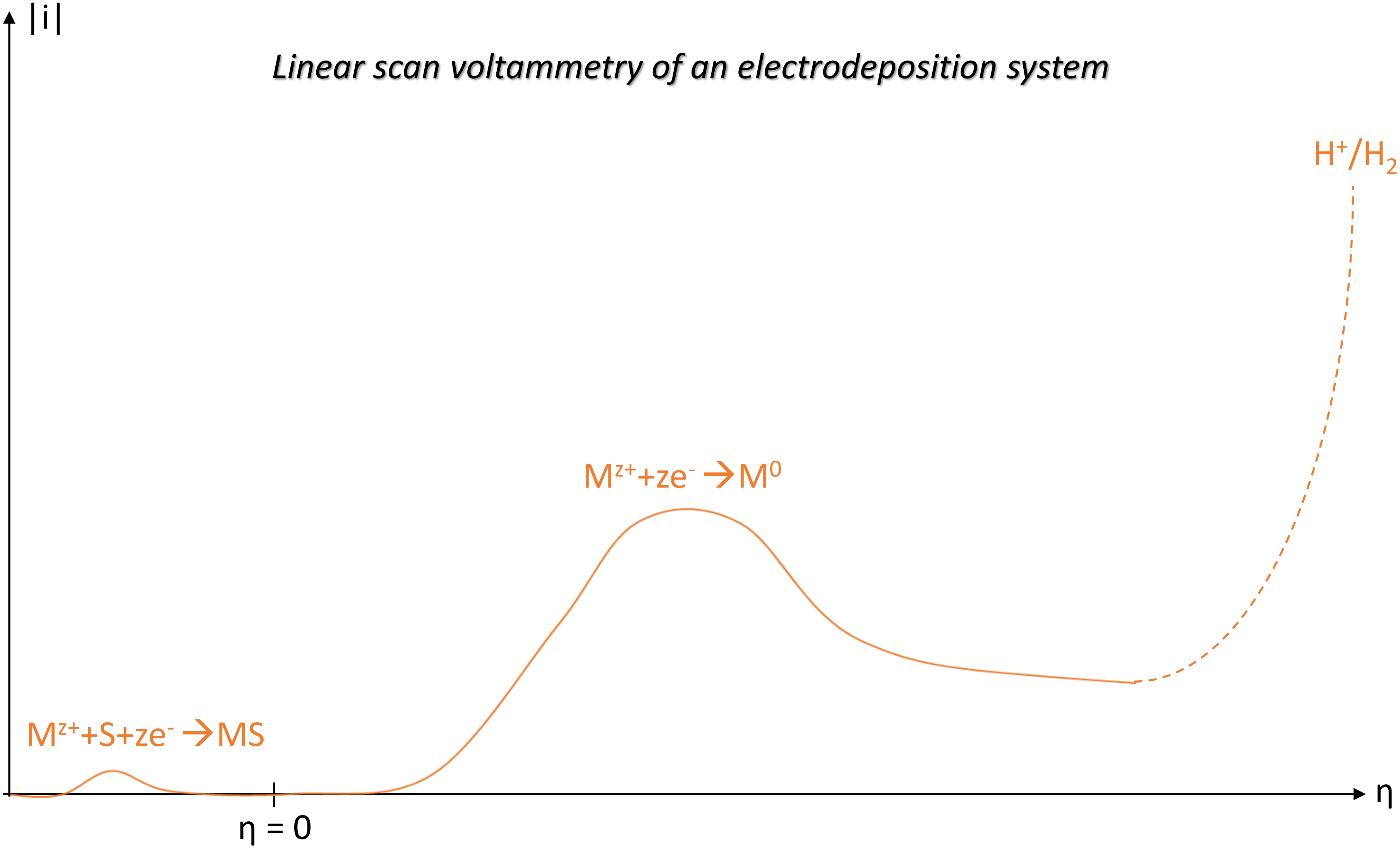
Effect of the overpotential

Final morphology and microstructure is determined by:

- Nucleation rate and nucleation mechanism
- Growth rate and growth orientation

II) Effect of electroplating parameters

Effect of the overpotential



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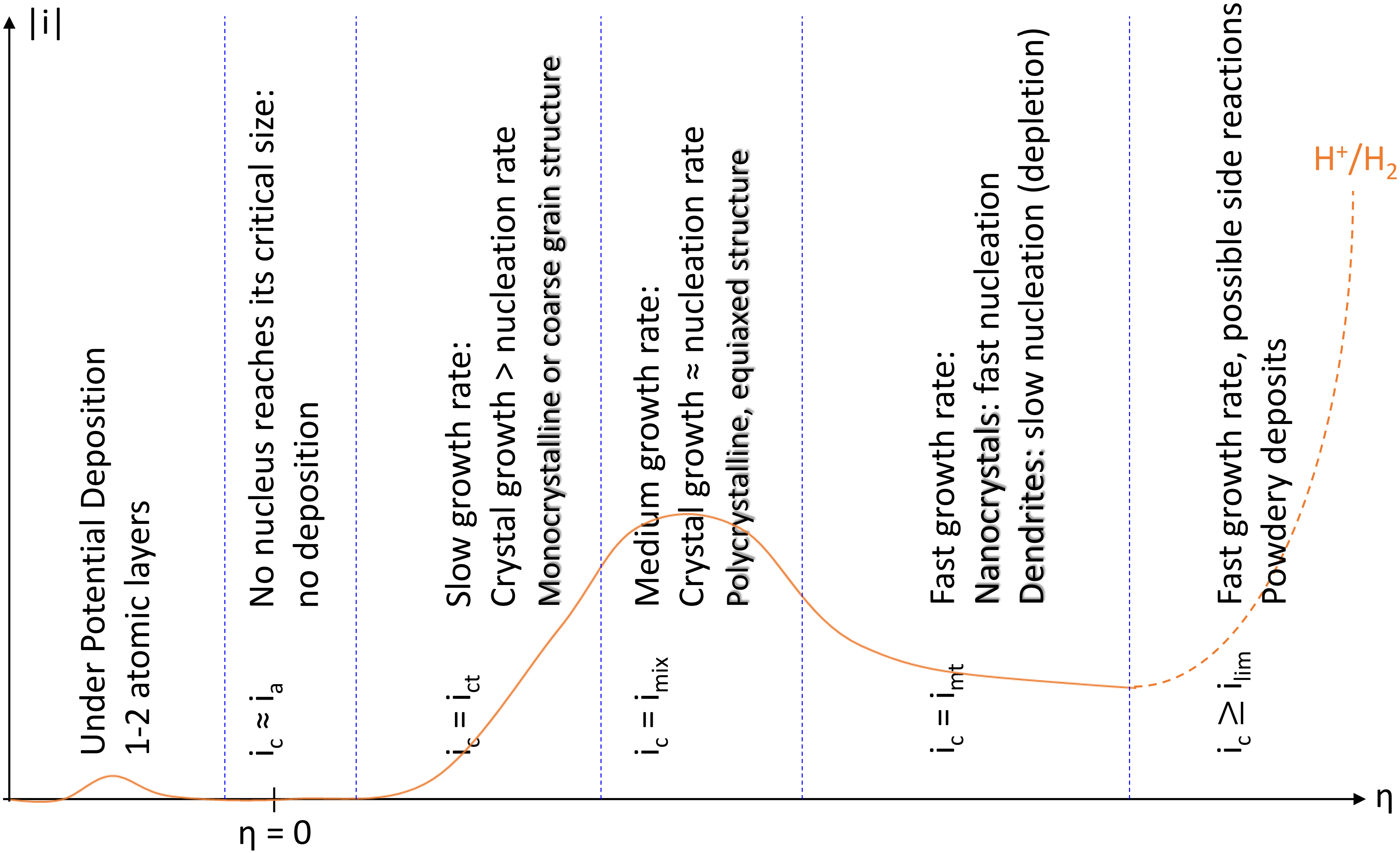


II) Effect of electroplating parameters

Influencing parameters

Polarization

Current density

M^{z+} concentration

Agitation

Temperature

Supporting electrolyte

} Affects electrocrystallization kinetics
Affects j/j_{lim}

Additives _ _ _ _ _ _ _ _ _ _ _ _ Inhibits or accelerates electrocrystallization

Dopants _ _ _ _ _ _ _ _ _ _ _ _ _ Modify the electrodeposit properties

Substrate _ _ _ _ _ _ _ _ _ _ _ _ Induction process, adhesion, epitaxy

pH _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ Ion type and solvation, ionic conductivity, surface tension

Others: sound waves, electromagnetic waves, magnetic field

II) Effect of electroplating parameters

Influencing parameters

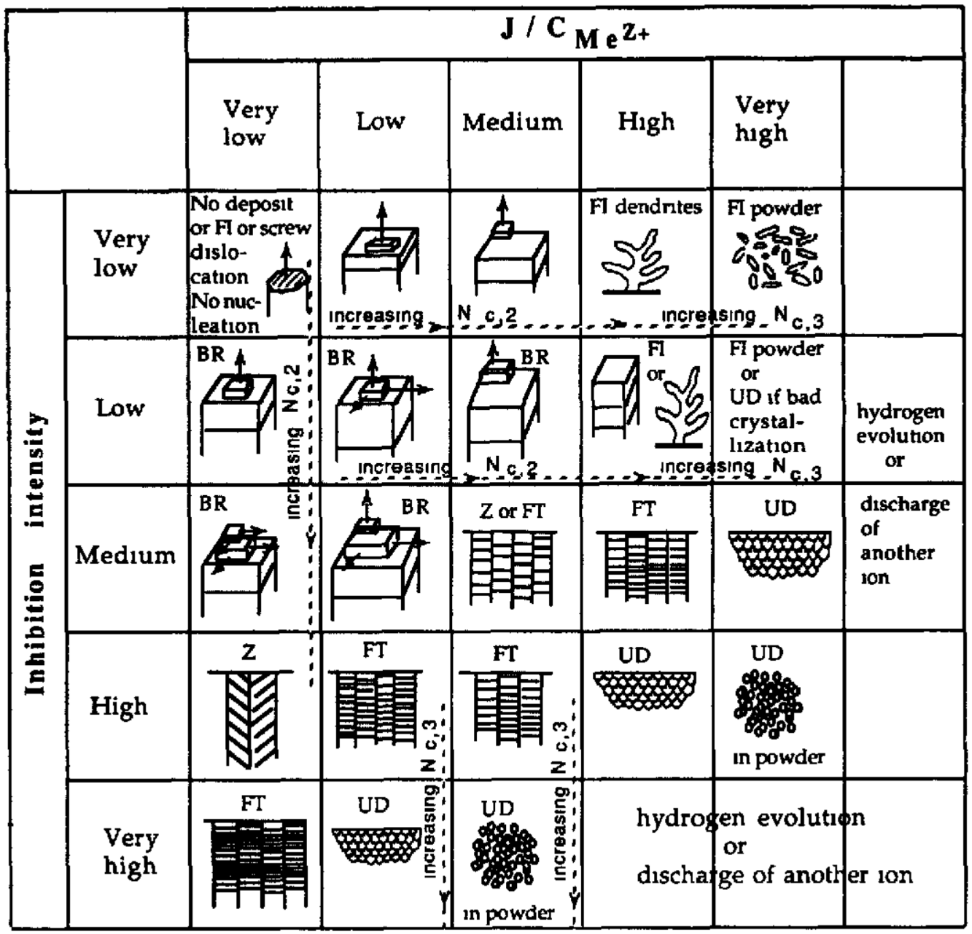


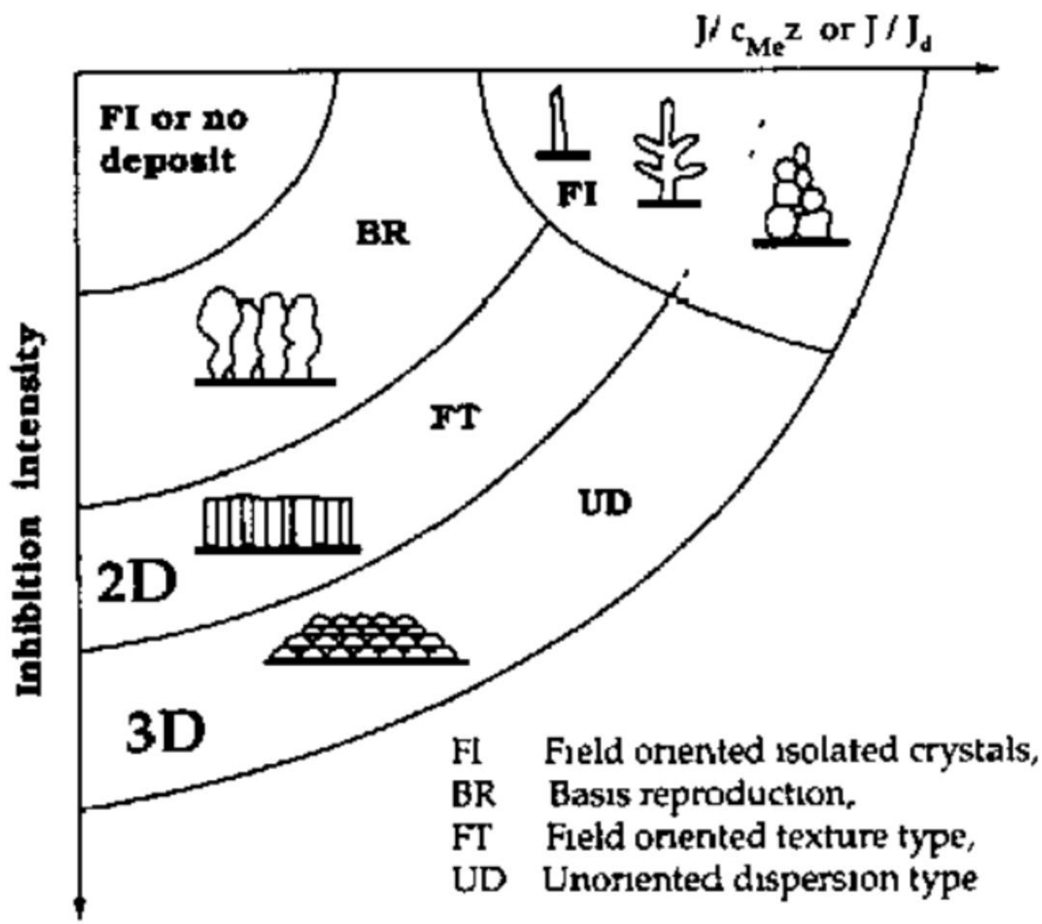
Fig 1 Detailed diagram showing different possible types of polycrystalline electrodeposits as a function of $J/C_{Me^{z+}}$ and inhibition intensity

(1) field orientated isolated crystals type (FI),
(2) basis-orientated reproduction type (BR),
(3) twinning intermediate type (Z),
(4) field orientated texture type (FT),
(5) unorientated dispersion type (UD)

Simultaneous effects of inhibition and current density

II) Effect of electroplating parameters

Influencing parameters



In abscissa: mass transfer characterized by $J/c_{Me}z_{+}$ or J/J_d
- J current density
- $c_{Me}z_{+}$ bulk concentration of metal ion to be discharged
- J_d diffusion limiting current density

In ordinate: inhibition intensity
- 2D bidimensional nucleation
- 3D tridimensional nucleation

Fig 2 Simplified diagram showing different possible types of polycrystalline electrodeposits as a function of J/C_{Mez^+} and inhibition intensity

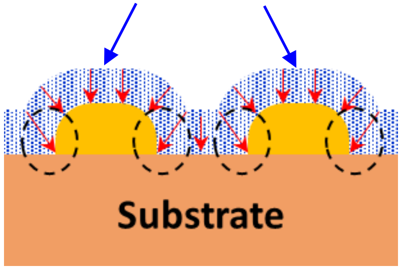
Simplified diagram

II) Effect of electroplating parameters

Additives: Brighteners

✓ **Brighteners:** weak inhibitors → increases micro-throwing power

Adsorb and inhibit low overpotential regions

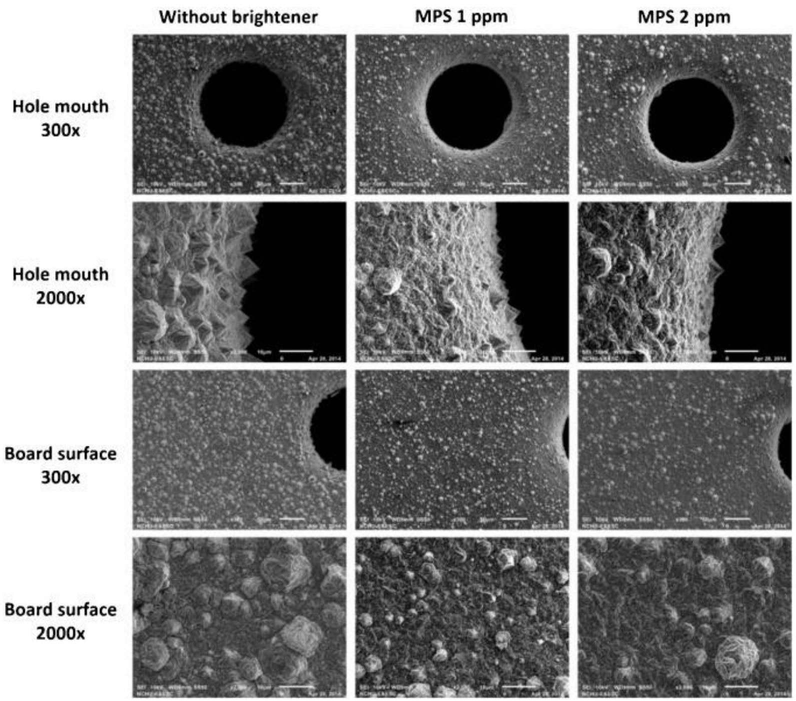


Micro-leveling: reduces surface roughness
Grain refining: hardness but tensile stress

Organosulfur molecules

(e.g. thioethers, phenolsulfonic acid)

2-Methylsulfanylethyl sulfite: $C_3H_7O_3S^{2-}$

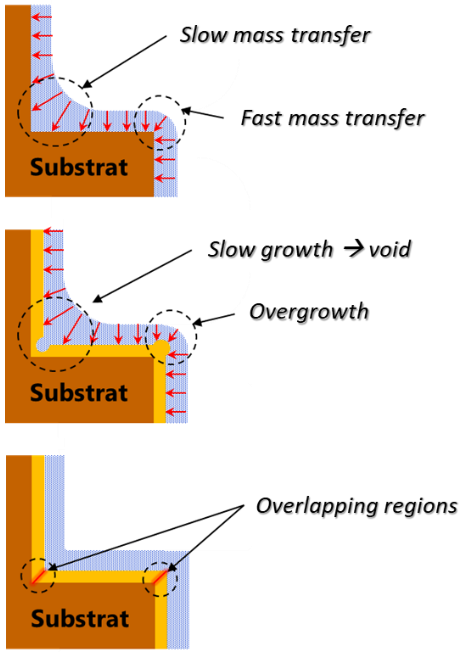


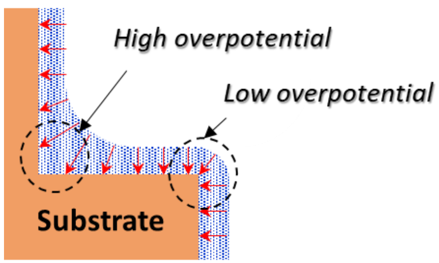
II) Effect of electroplating parameters

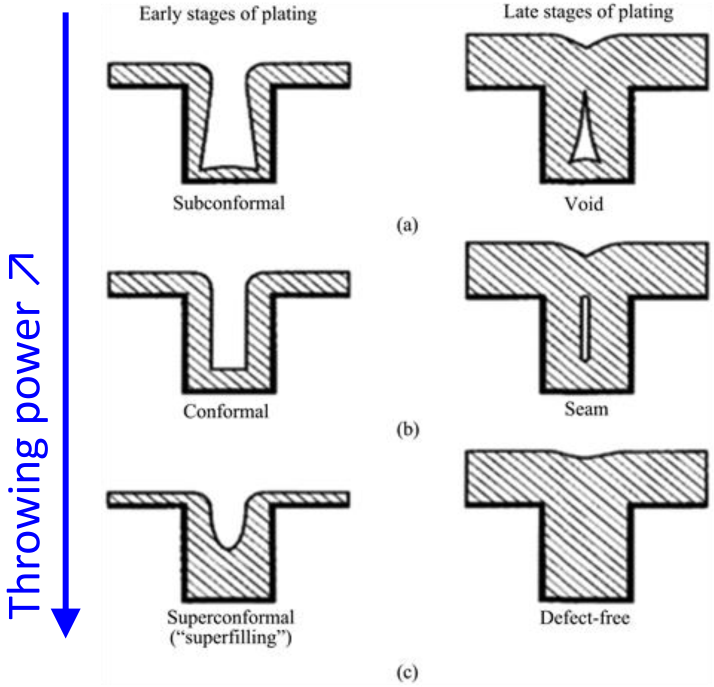
Additives: Levelers

✓ **Levelers:** strong inhibitors → increases macro-throwing power

Adsorb on low overpotential regions, the lower the potential the stronger the inhibition







Quaternary amines, amino compounds, macro molecules (e.g. polyvinylpyrrolidone)

II) Effect of electroplating parameters

Additives: Wetting agents

- ✓ **Wetting agents:** decreases the surface tension

Ensure a good wetting of the substrate

Prevent trapping of gas bubbles (e.g., H_2 evolving at the cathode)

Reduces the compressive stress in ultra-thin coatings

Typically, anionic and non-ionic surfactants (e.g., SDS, polyethylene glycol)

II) Effect of electroplating parameters

Additives: Accelerators & Suppressors

- ✓ **Accelerators:**

Decreases the electrochemical activation energy via intermediate states

Catalysts

- ✓ **Suppressors:**

Increases the electrochemical activation energy by stabilizing cations

Complexing agents (e.g., EDTA, citrates)

II) Effect of electroplating parameters

Additives: Stress suppressors

✓ **Stress suppressors:**

Chemisorption and incorporation in the metal lattice — induce compressive stress

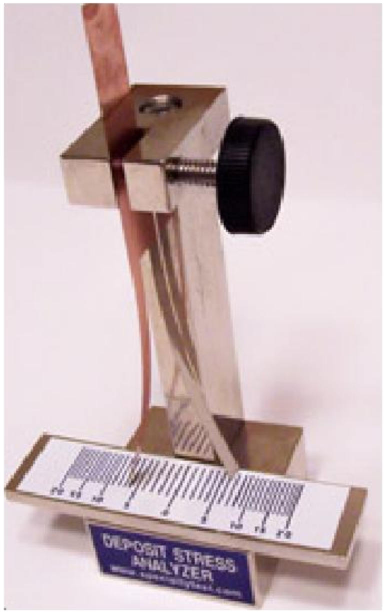
Compensate for tensile stress

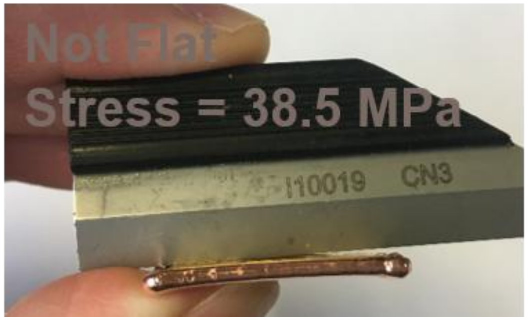
Typically, saccharine, acetates, salicylates…

But also inorganic additives

II) Effect of electroplating parameters

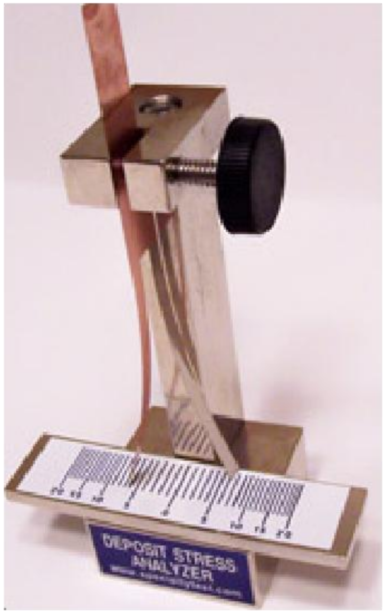
Origin of internal stress

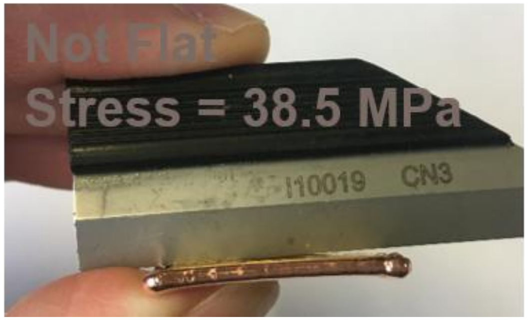




II) Effect of electroplating parameters

Origin of internal stress





Primary contributions to internal stress:

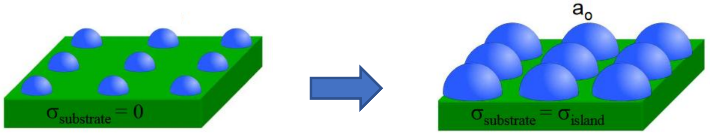
Heterogeneous nucleation – substrate-deposit interactions

- Difference of lattice parameters:

$a_s > a_d$
Compressive

$a_s < a_d$
Tensile

- Capillary forces:



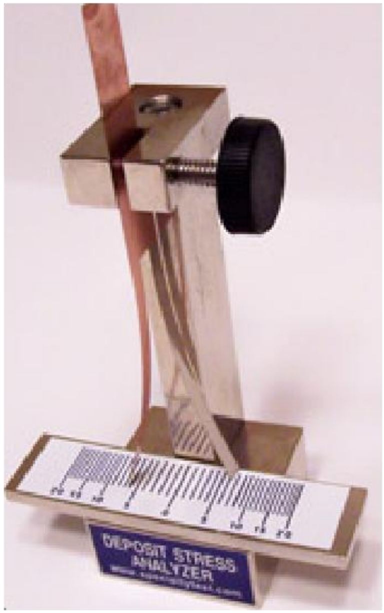
Compressive

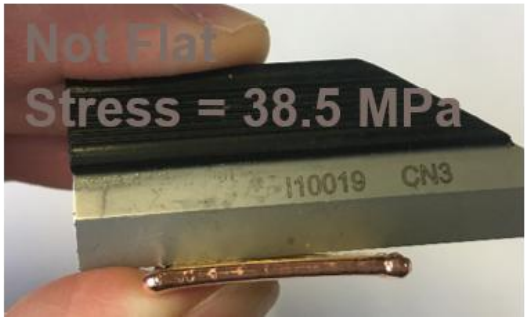
Less compressive

Prevailing for ultrathin deposits

II) Effect of electroplating parameters

Origin of internal stress

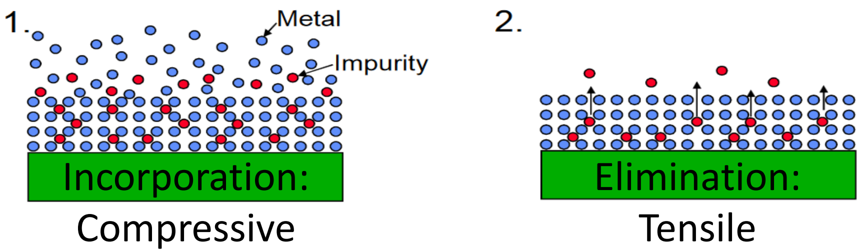




Secondary contributions to internal stress:

Growth – internal structure of the deposit

- Interstitial incorporation/elimination:



- *Grain overlapping (tensile)* ∝ *N(t)* (Nuclei density)
- *Thermal expansion/contraction*
- *Other point and plane defects*

Prevailing for thick deposits

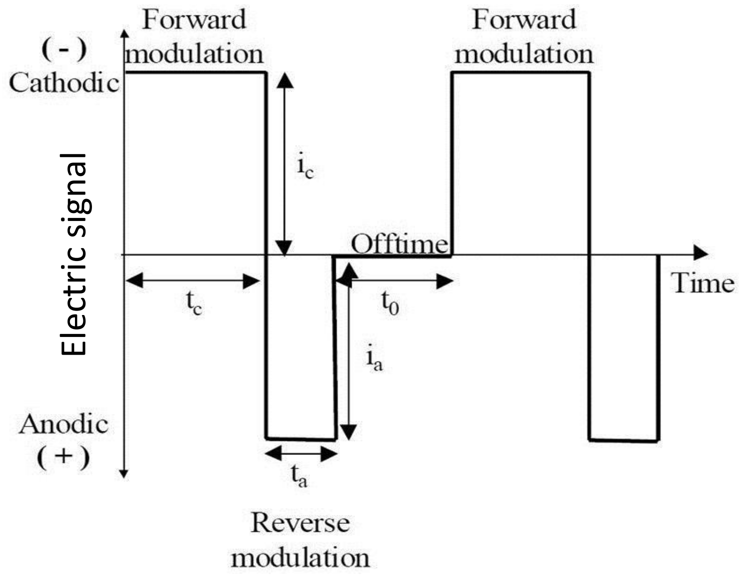
II) Effect of electroplating parameters

Pulse and reverse pulse plating

Application of a periodic electrical signal between two electrodes

Typically: a succession of rectangular pulses in the millisecond-second ranges

Alternatively: any other type of wave shapes (e.g., square, triangular, sine, steps)



Some important characteristics

Frequency: $f = (\sum_i t_i)^{-1}$

Duty cycle: $\gamma = f \cdot t_c$

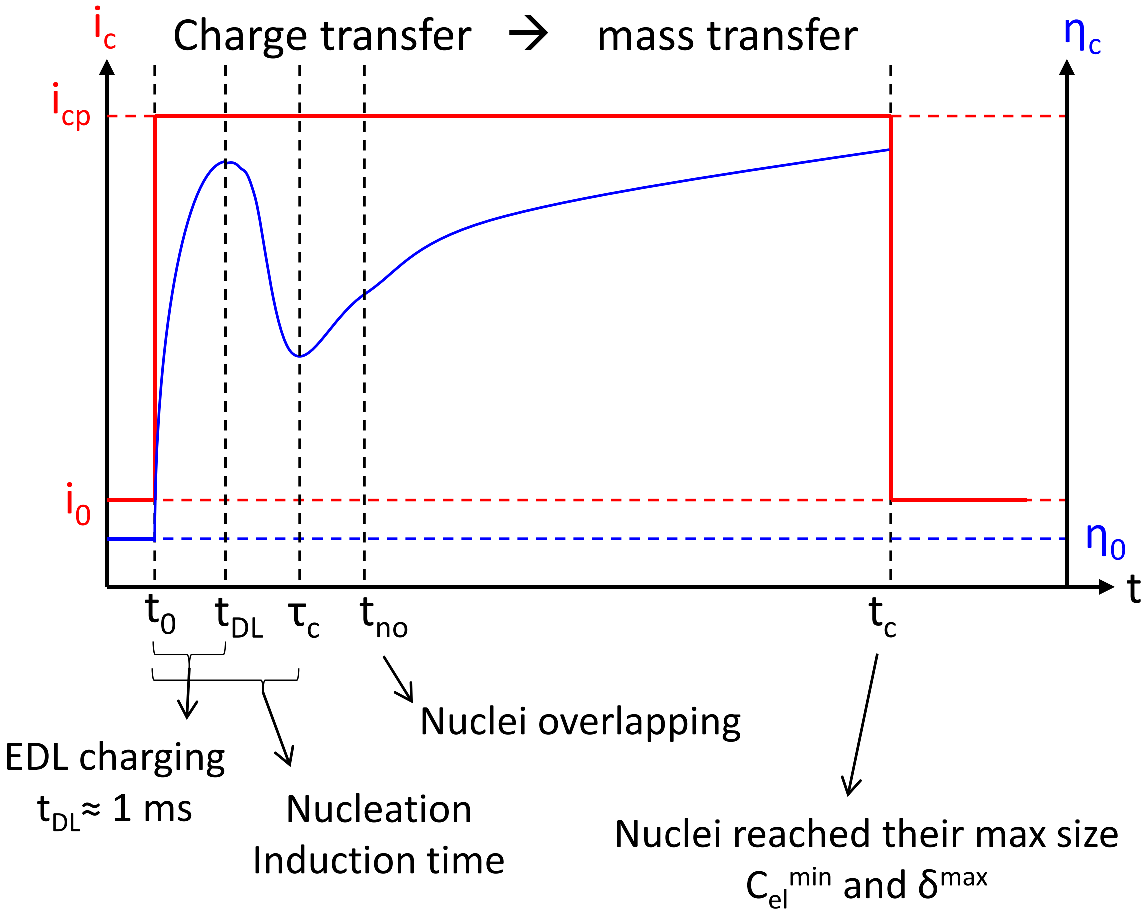
Average I: $I_A = \left(\sum_i \int I_i(t)\, dt\right) \cdot \gamma$

Average η: $\eta_A = \left(\sum_i \int \eta_i(t)\, dt\right) \cdot \gamma$

II) Effect of electroplating parameters

Pulse and reverse pulse plating

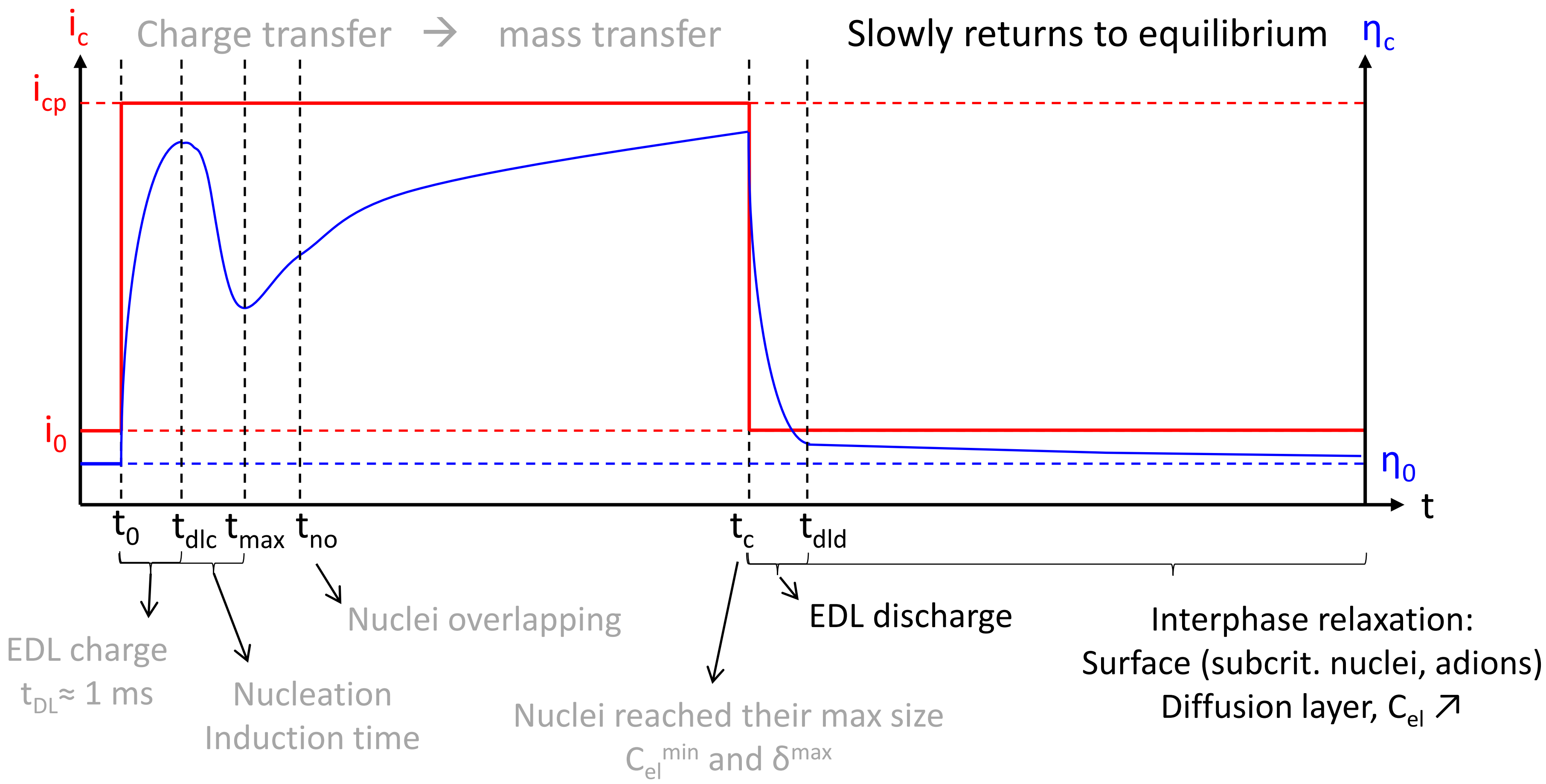
What happens during a cathodic pulse?



II) Effect of electroplating parameters

Pulse and reverse pulse plating

What happens during the off-time?



II) Effect of electroplating parameters

Pulse and reverse pulse plating

Effect of pulse parameters

Off-time:

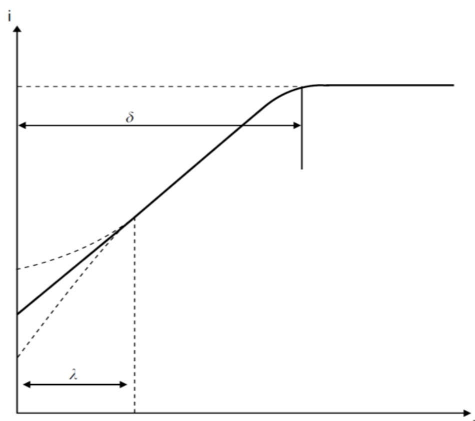
- long: $\delta \longrightarrow 0$ and $E \longrightarrow E_{eq}$ very slow growth rate
- short: Interphase is only partially relaxed

Cathodic peak current density or overpotential:

- high: instantaneous nucleation: $N_c = N_0$ for $t = \tau$
  short transition between charge, mix, and mass control
- low: progressive nucleation: $N_c(t) = N_0 k_n t$
  deposition is controlled by charge transfer

Cathodic pulse time:

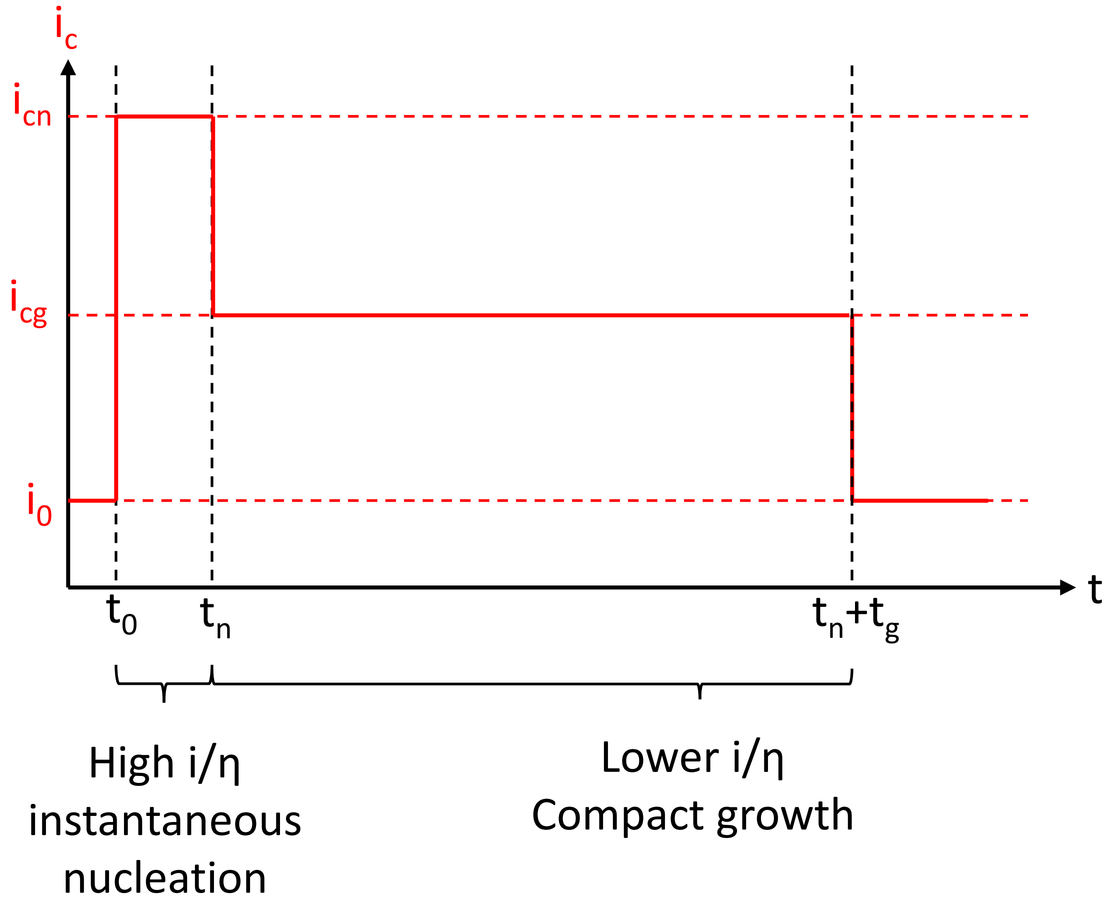
- long: $N_c \longrightarrow N_0$ and/or $\delta \longrightarrow \sqrt{\pi D t}$
- short: $C_{el} \lesssim C_{sol}$ and/or $N_c < N_0$
- $t_c < \tau$: no critical nuclei is formed → no deposition



II) Effect of electroplating parameters

Pulse and reverse pulse plating

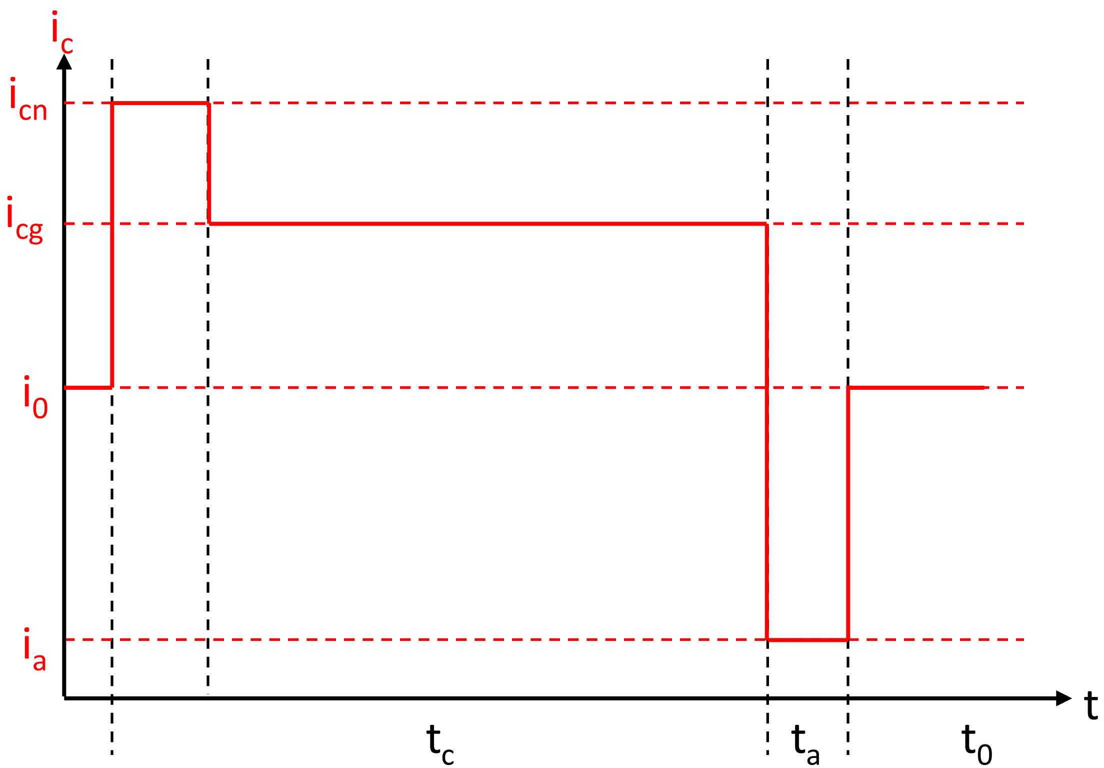
Two consecutive cathodic pulses:



II) Effect of electroplating parameters

Pulse and reverse pulse plating

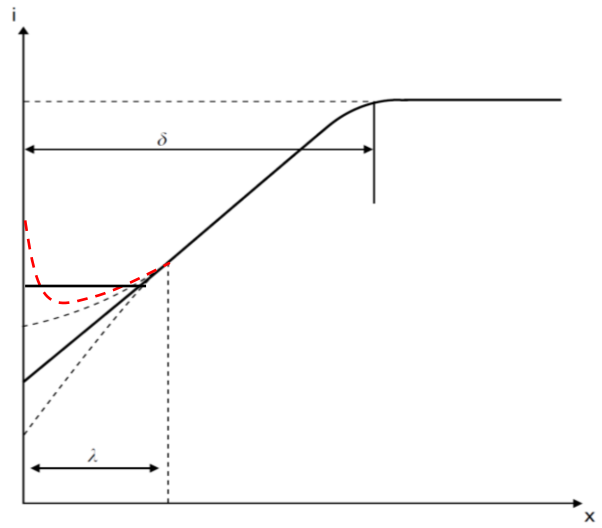
Reverse pulse plating:



Electrocrystallization

Relaxation

Electrodissolution → *overgrowth (edges and apex)*



II) Effect of electroplating parameters

Pulse and reverse pulse plating

Advantages of pulse plating:

More parameters to control the morphology and microstructure

Possible to tune the micro- and macrothrowing powers: **leveling without levelers**

A way to simultaneously control grain size and internal stress

Drawbacks of pulse plating:

More parameters = more complexity

Slow electrodeposition

Lower efficiencies