



Microscopie STM électrochimique: analyse locale des altérations de surface générées par polarisation

V. Maurice

PSL Research University, CNRS - Chimie ParisTech, Institut de Recherche de Chimie Paris



ParisTech

Microscopie EC-STM

- Dispositif EC-STM

- Préparation pointes STM et surfaces métalliques

Couches d'oxydes à l'interface solution aqueuse/surface métallique

- Adsorption d'ions hydroxydes

- Structure de couches passives 3D

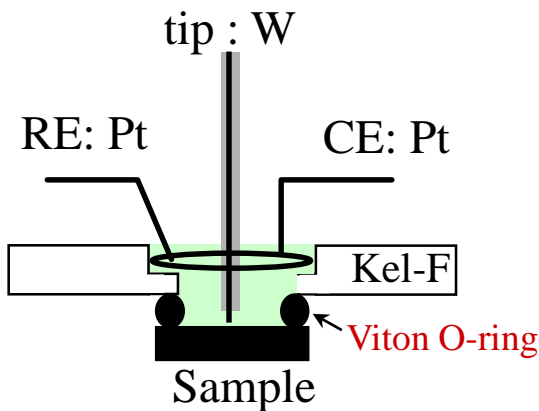
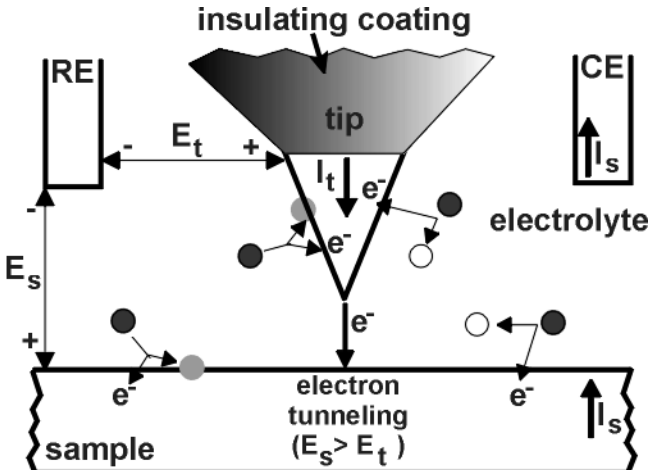
- Réactivité de surfaces passivées

Relation microstructure/réactivité locale

- Dissolution locale des joints de grains

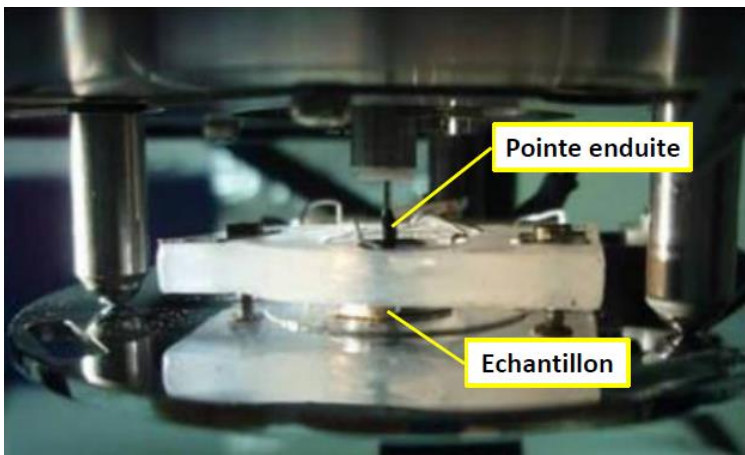
- Caractérisation des joints de grains par couplage EC-STM/EBSD

Dispositif EC-STM



Cellule à 4 électrodes

- pointe enduite
- contrôle indépendant de E_s et $E_t \Rightarrow$ bipotentiostat
- nettoyage rigoureux de la cellule
- électrolyte de hte pureté

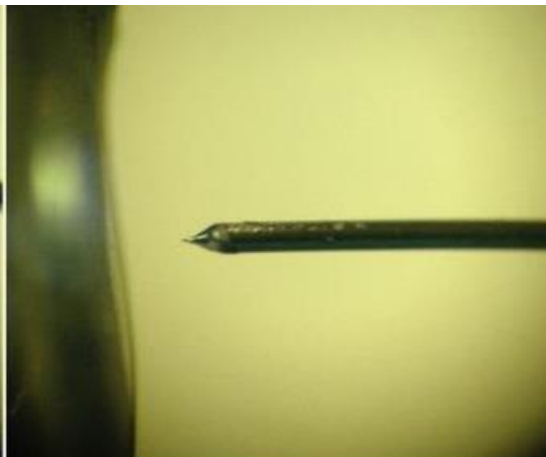
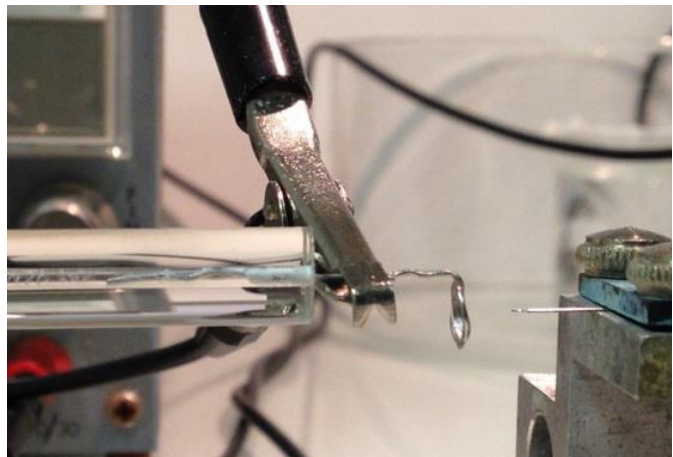


=> Mesures STM avec contrôle électrochimique de l'interface solide/liquide

Tip and surface preparation

Tip preparation (e.g. W)

- From W wire (0.5 mm diameter)
- Etching in NaOH(aq) 3M first at 10V and then 3 V vs Pt CE
- Coating with Apiezon wax



Surface preparation (e.g. Cu)

- Mechanical polishing
 - Diamond paste \rightarrow $\frac{1}{4}$ μm
- Electropolishing
 - H_3PO_4 66%, 1.4 V, 5 min
- HT annealing or not depending on sample
- Transfer to EC-STM cell
 - 0.1 M NaOH(aq), pH 13
 - 0.001 M HCl(aq), pH 3
- In situ reduction of native oxide
 - cathodic pre-treatment by CV from OCP to onset of hydrogen evolution and back
 - CV stopped at required potential for analysis of initial surface

Microscopie EC-STM

Dispositif EC-STM

Préparation pointes STM et surfaces métalliques

Couches d'oxydes à l'interface solution aqueuse/surface métallique

Adsorption d'ions hydroxydes

Structure de couches passives 3D

Réactivité de surfaces passivées

Relation microstructure/réactivité locale

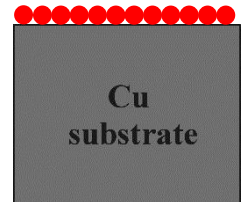
Dissolution locale des joints de grains

Caractérisation des joints de grains par couplage EC-STM/EBSD

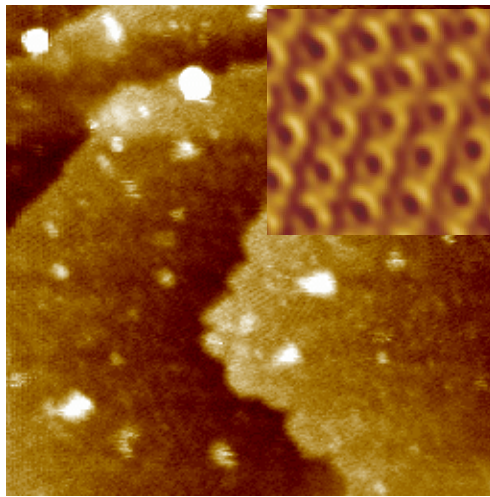
Passivation du Cu

ECSTM ; Cu(111)/NaOH(aq) 0,1M

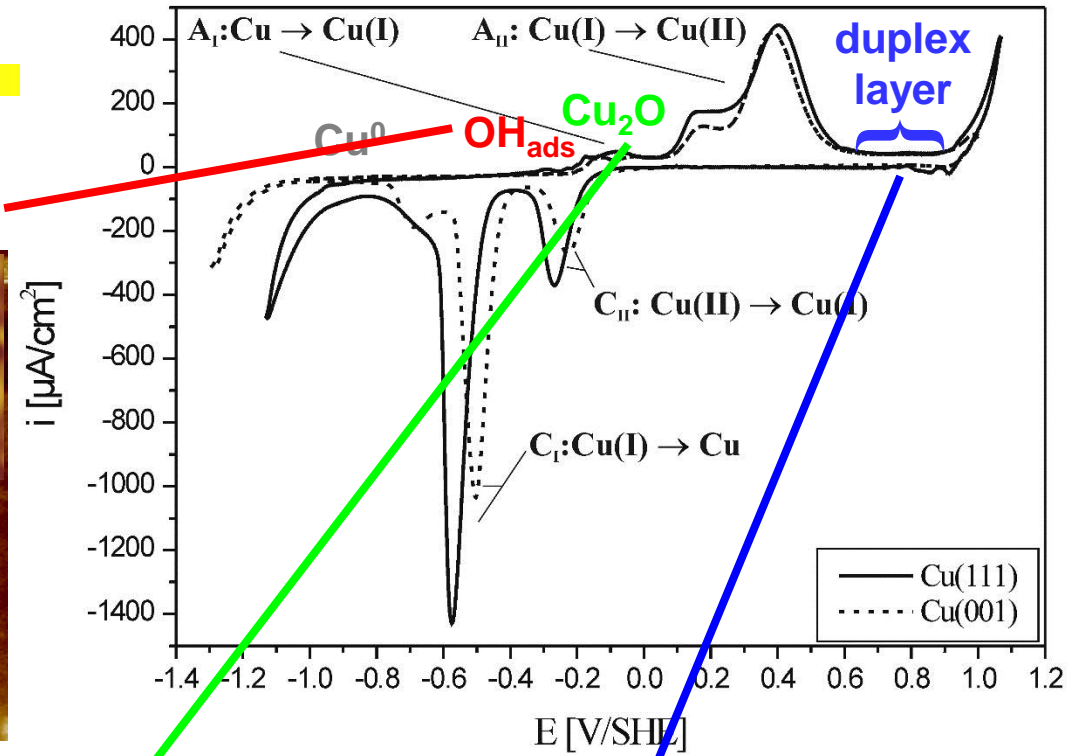
$-0,65 \leq E \leq -0,25V$



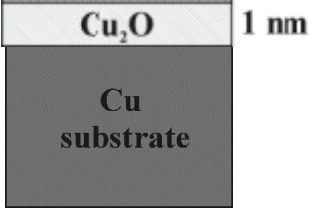
- Adsorption de OH
- Reconstruction induite du Cu
- Formation d'un précurseur de croissance de Cu₂O



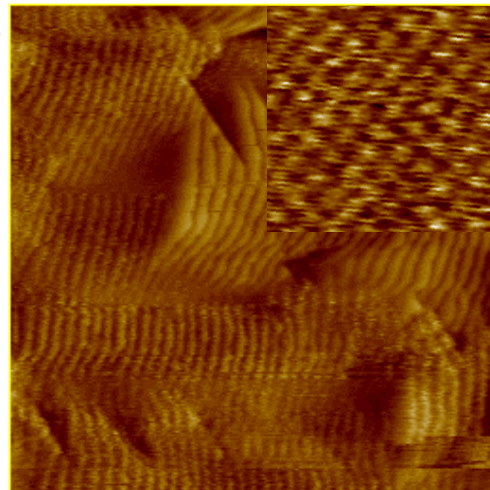
CV's (0.02V/s) for Cu(111) and Cu(001) in 0.1M NaOH



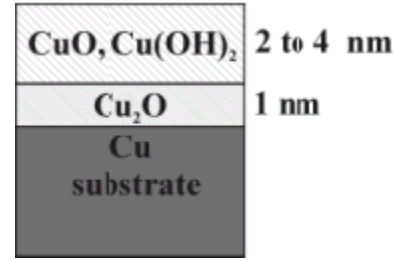
$-0,25 \leq E \leq 0V$



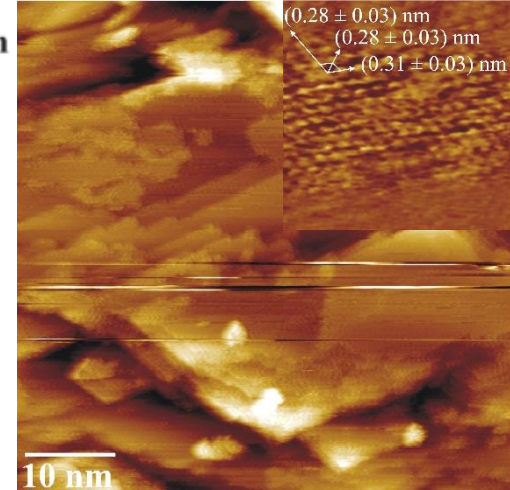
- Couche cristalline
- Cu₂O(111)



$0,4 \leq E \leq 0,9 V$

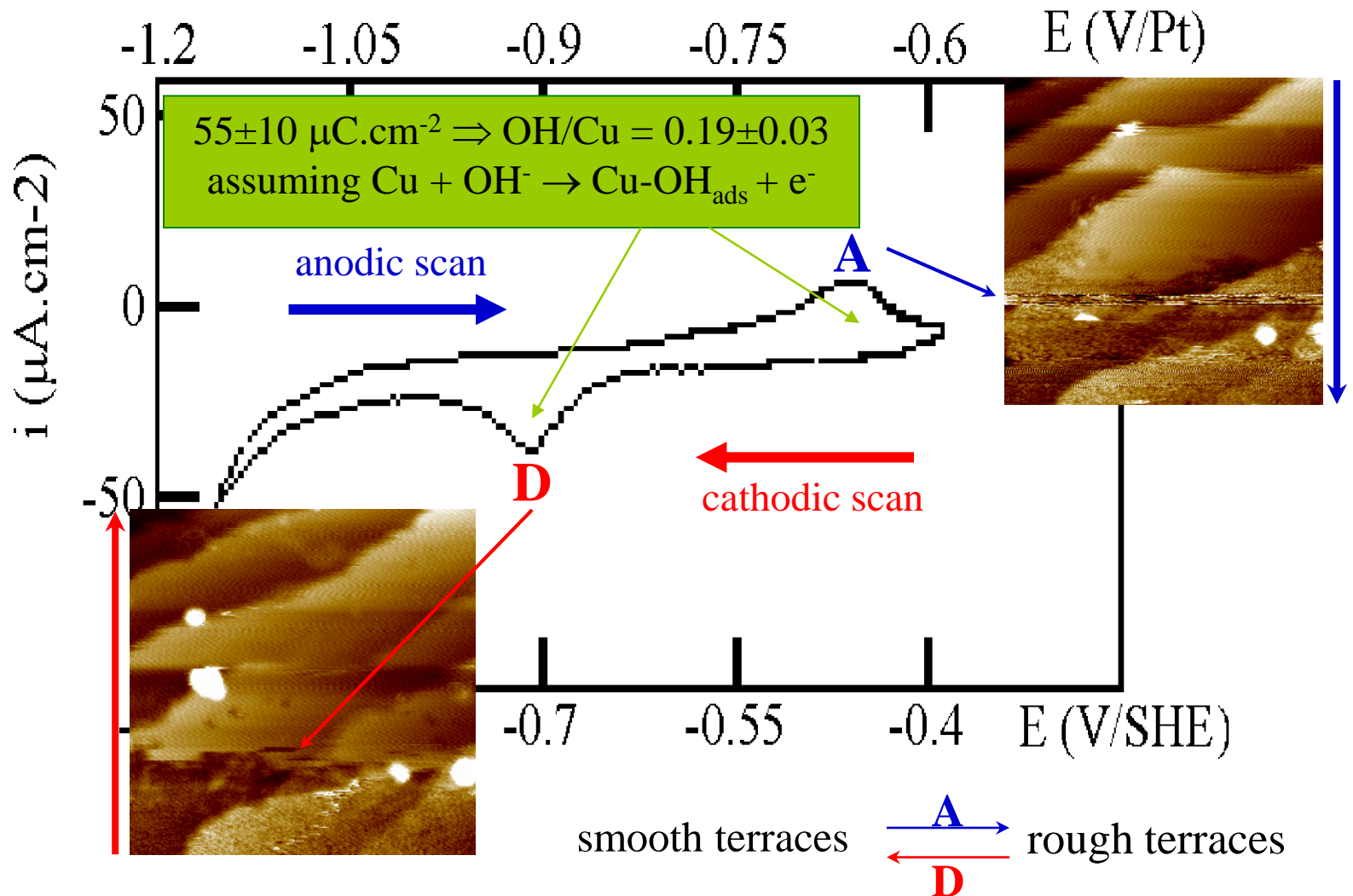


- Couche duplex cristalline
- CuO(001)



Adsorption of OH⁻

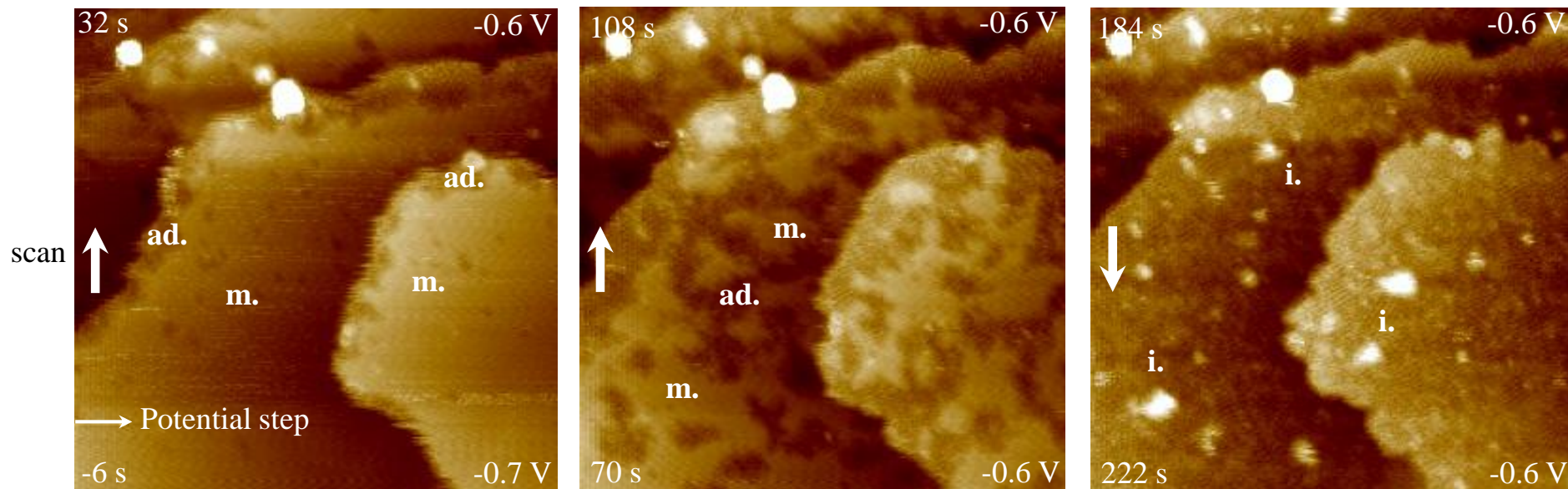
Cu(111) in 0.1M NaOH (20 mV.s⁻¹)
Potential range below oxidation



Croissance 2D et reconstruction

Séquence EC-STM @ -0,6 V (seuil du pic anodique d'adsorption des OH)

38 s/image; X=Y=40 nm; $\Delta Z=1.2$ nm ; $I_t=2$ nA; $E_t=-0.4$ V



- Germination préférentielle de la couche adsorbée aux bords de marches

- Croissance des îlots adsorbés
 - Croissance latérale des terrasses
- ⇒ reconstruction induite

- Saturation par la couche adsorbée
 - Formation d'îlots de Cu
- ⇒ reconstruction induite

Structure des OH_{ads} - reconstruction induite

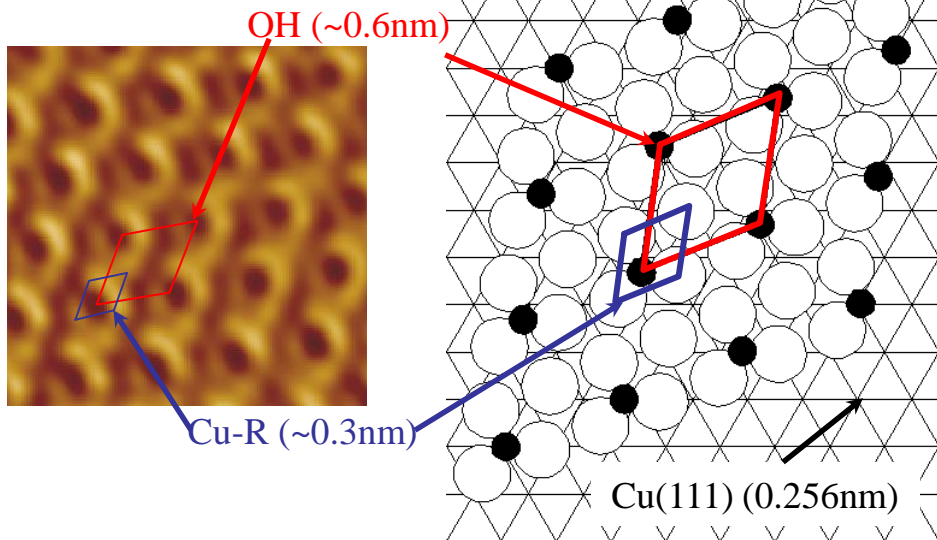
$E = -0.58 \text{ V/SHE}$

$X=Y=5.4 \text{ nm}$

$I_t = 1.3 \text{ nA}$

$E_t = -0.38 \text{ V}$

$Z \text{ range} = 0.2 \text{ nm}$



- maille unitaire : $0.6 \pm 0.02 \text{ nm}$ → recouvrement de 0.19 ($1 \text{ OH}_{\text{ads}}/\text{maille}$), en accord avec les données EC ($\text{Cu} + \text{OH}^- \rightarrow \text{Cu-OH}_{\text{ads}} + e^-$)

- reconstruction induite du Cu(111) → structure moins compacte ($1.28 \times 10^{15} \text{ at.cm}^{-2}$ comparé à $1.76 \times 10^{15} \text{ at.cm}^{-2}$)

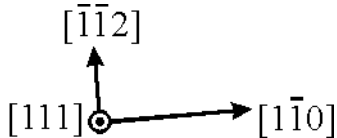
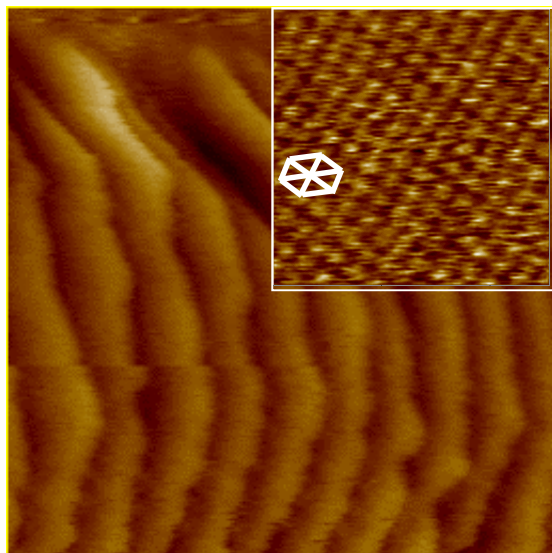
- structure des OH_{ads} : (2x2)

- OH adsorbé en site ternaire creux du plan reconstruit de Cu

- structure des plans OH et Cu-R similaire à celle des plans O et Cu dans $\text{Cu}_2\text{O}(111)$

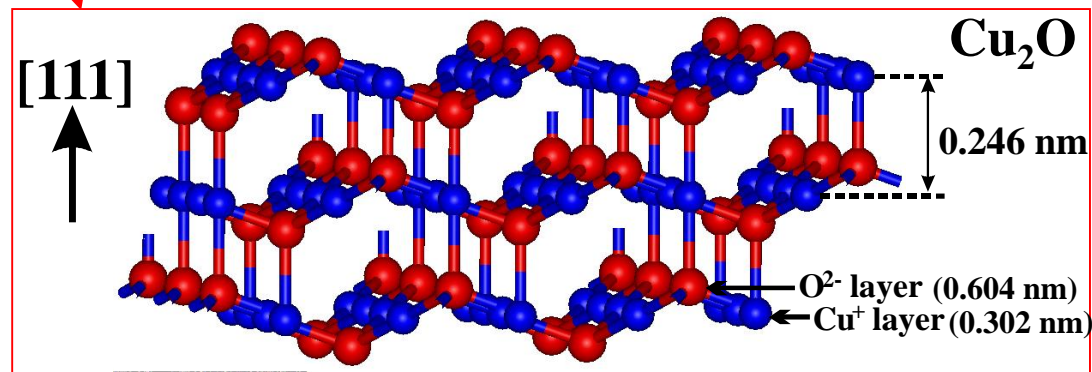
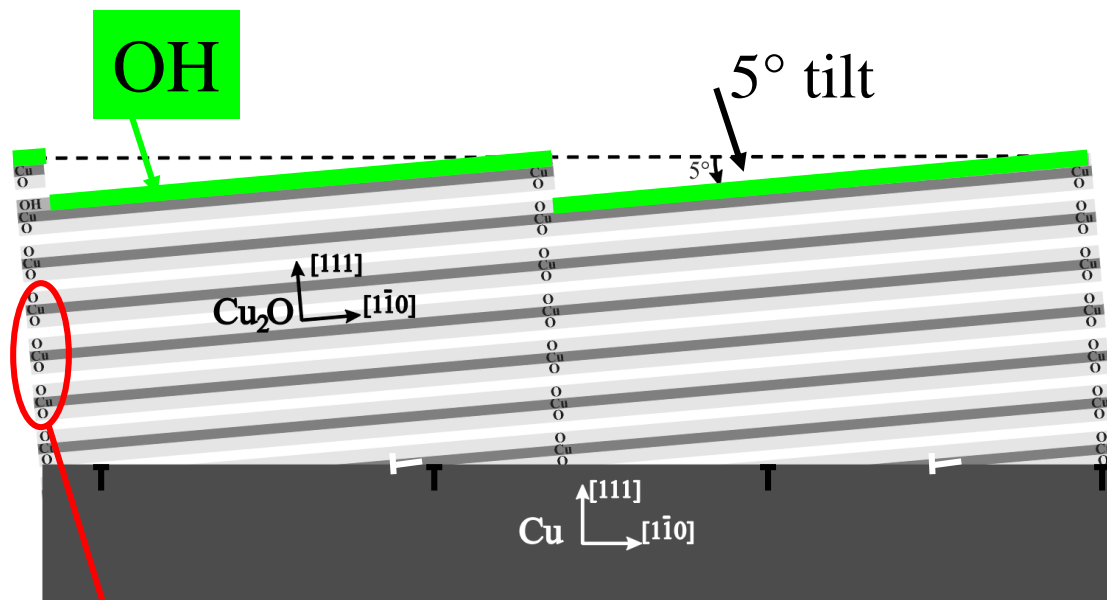
Structure de l'oxyde anodique Cu(I)

$E = -0.2 \text{ V/SHE}$

X=Y= 25nm; Z range = 2nm; I_t 2nA

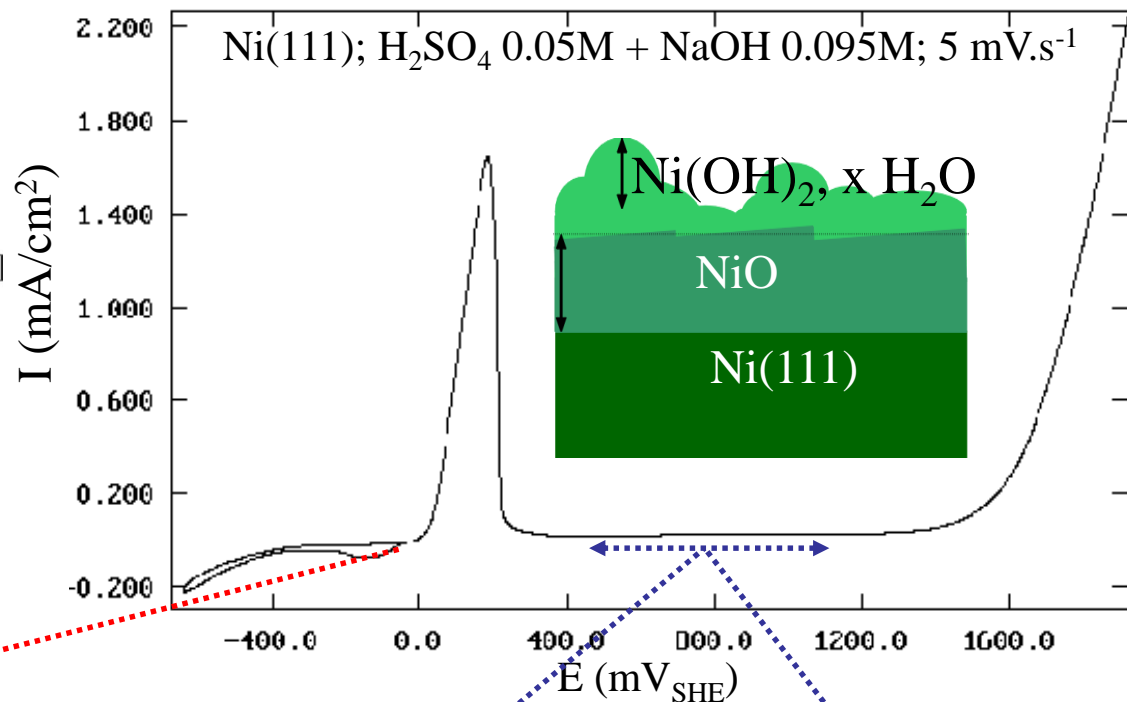
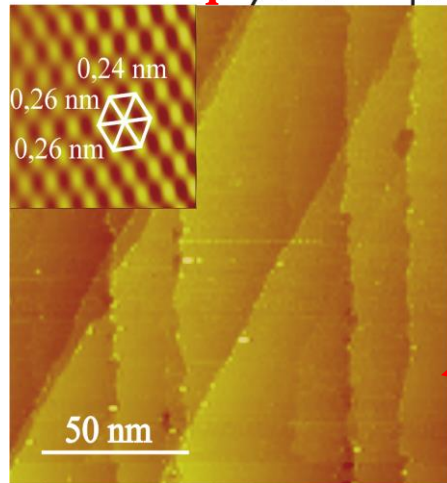
~7 monocouches de $\text{Cu}_2\text{O}(111)$ sur $\text{Cu}(111)$



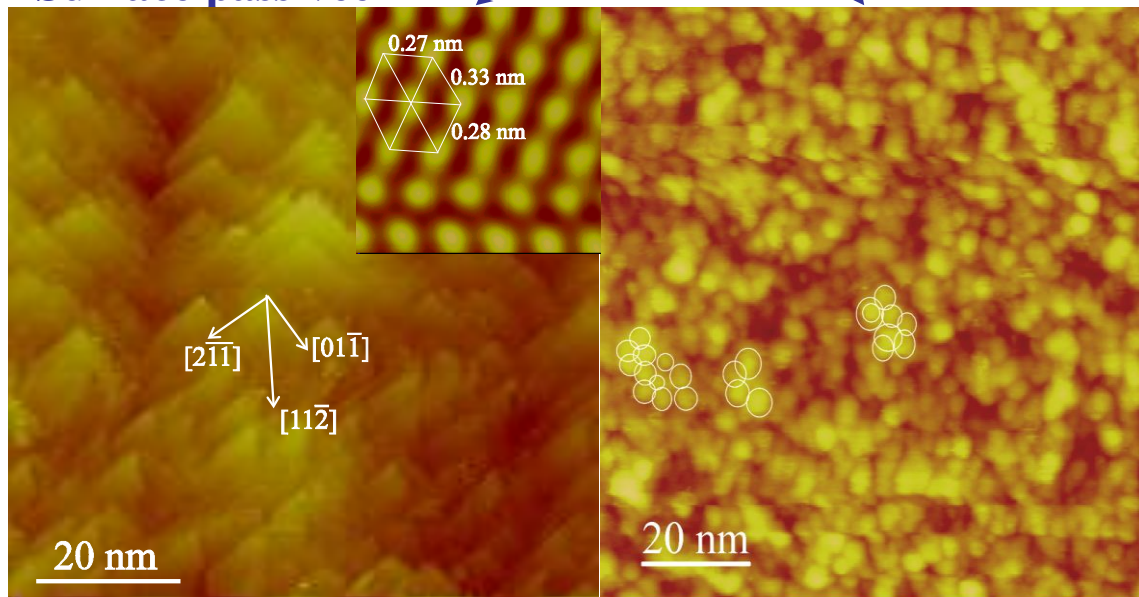
- largeur des terrasses : 2.7nm
- hauteur des marches : 0.25~0.3nm
 \Rightarrow marches de $\text{Cu}_2\text{O}(111)$ (0.246 nm dans le volume)
- réseau hexagonale de paramètre $0.3 \pm 0.03 \text{ nm}$ \Rightarrow sous-réseau Cu dans $\text{Cu}_2\text{O}(111)$
- épitaxie inclinée ($\sim 5^\circ$)
- hydroxylation superficielle

Passivation du Ni

Surface métallique $[\bar{1}01]$



Surface passivée



Structure interne

Structure externe

⇒ XPS : bicouche oxyde/hydroxyde

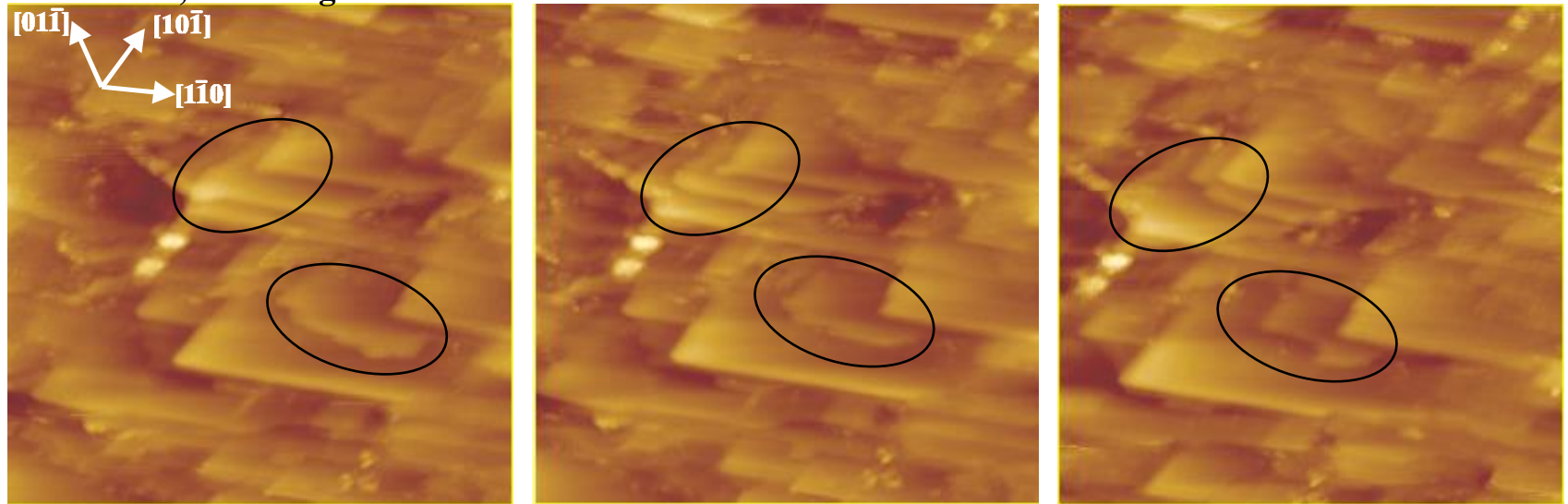
⇒ EC-STM : structure externe granulaire et amorphe, attribuée à Ni sous forme hydroxyde

⇒ EC-STM : structure interne cristalline attribuée à NiO(111)-(1x1), épitaxie inclinée entre les réseaux de l'oxyde et du métal (confirmée par SXS)

Dissolution de la surface passivée

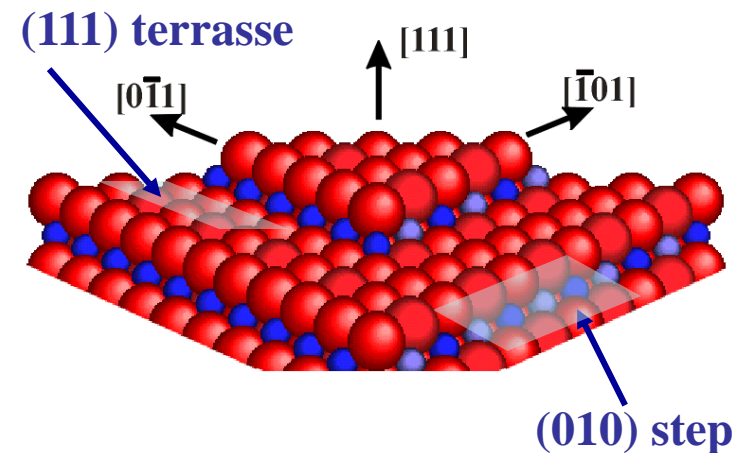
Ni(111) dans H₂SO₄ (pH 3) ; Séquence EC-STM @ +0.85 V/SHE (E_{pit} - 0.05 V)

75 x 75 nm ; 63 s/image



- dissolution localisée aux bords de marches => mécanisme 2D de rétraction des terrasses
- Bords de marches orientés suivant les directions compactes de l'oxyde se dissolvent moins rapidement

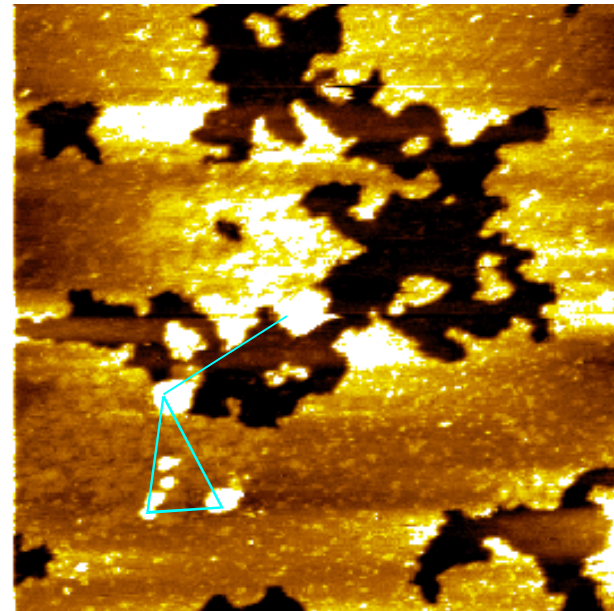
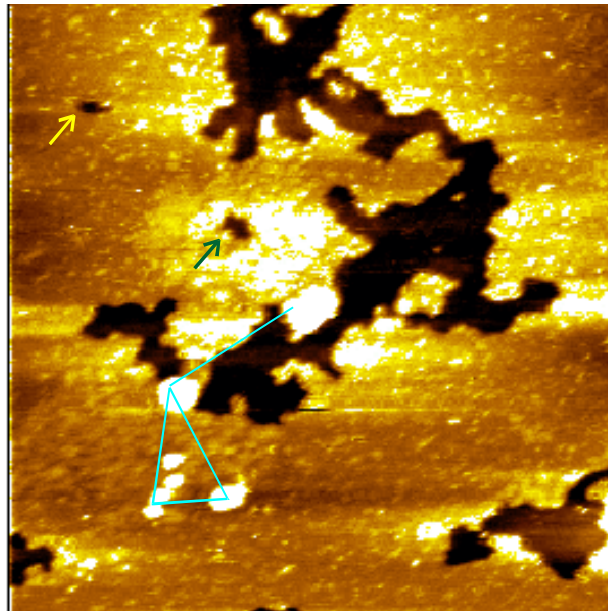
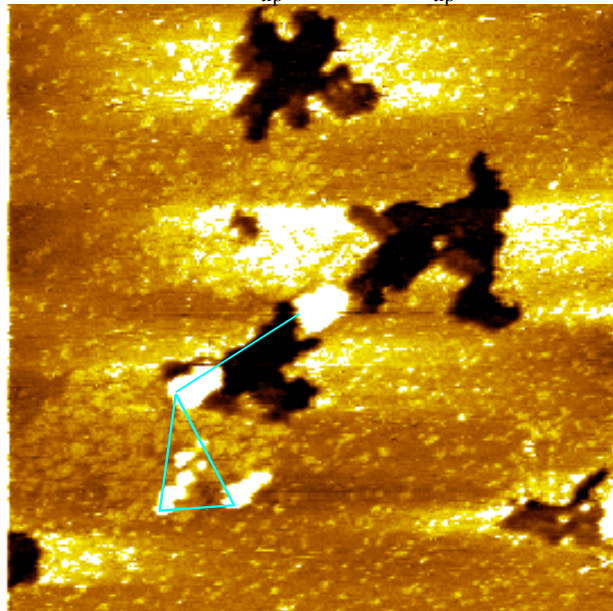
⇒ le mécanisme de dissolution est gouverné par la structure de l'oxyde. Il tend à stabiliser une surface terminée par des contre-marches orientées selon les directions les plus stables de l'oxyde (NiO{100})



Structure sensitive 2D dissolution

Ag(111) / 0.1M NaOH(aq) - EC-STM sequence @ E = 0.15 V (116 s/image)

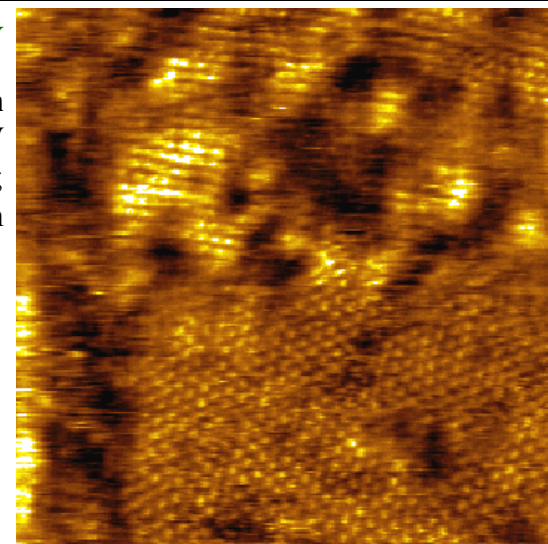
100 x 100 nm ; $E_{\text{tip}} = -0.35$ V ; $I_{\text{tip}} = 1.5$ nA ; $\Delta z = 0.45$ nm



- Dissolution nucleates and propagates in non-ordered areas of 2D hydroxide/oxide layer.
 - Dissolution is blocked in ordered 2D areas and by 3D grains (oxide nuclei).
- => Morphology of the corroding surface is governed by the structure of the passivating layer**

E = -0.05 V

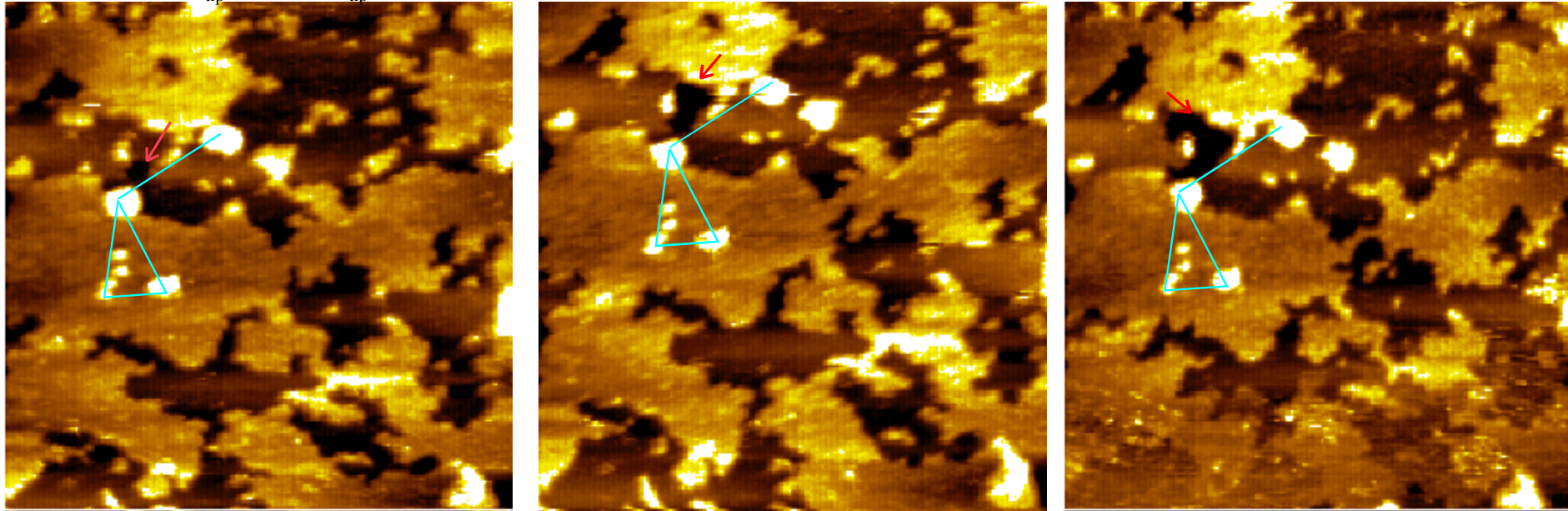
10 x 10 nm
 $E_{\text{tip}} = -0.45$ V
 $I_{\text{tip}} = 1.9$ nA ;
 $\Delta z = 0.12$ nm



Initiation of 3D dissolution

Ag(111) / 0.1M NaOH(aq) - EC-STM sequence @ E = 0.15 V (58 s/image)

150 x 150 nm ; $E_{\text{tip}} = -0.35$ V ; $I_{\text{tip}} = 1.5$ nA ; $\Delta z = 0.6$ nm



- Dissolution of the second layer also nucleates and propagates in non-ordered areas of 2D hydroxide/oxide layer newly formed
 - Dissolution is blocked by the ordered 2D areas of the first layer and by the 3D grains.
- => A similar structure sensitive dissolution mechanism induces the layer-by-layer propagation of the 3D nanopits.**

Microscopie EC-STM

Dispositif EC-STM

Préparation pointes STM et surfaces métalliques

Couches d'oxydes à l'interface solution aqueuse/surface métallique

Adsorption d'ions hydroxydes

Structure de couches passives 3D

Réactivité de surfaces passivées

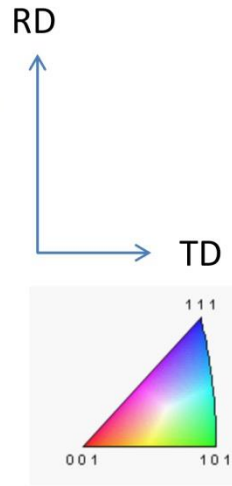
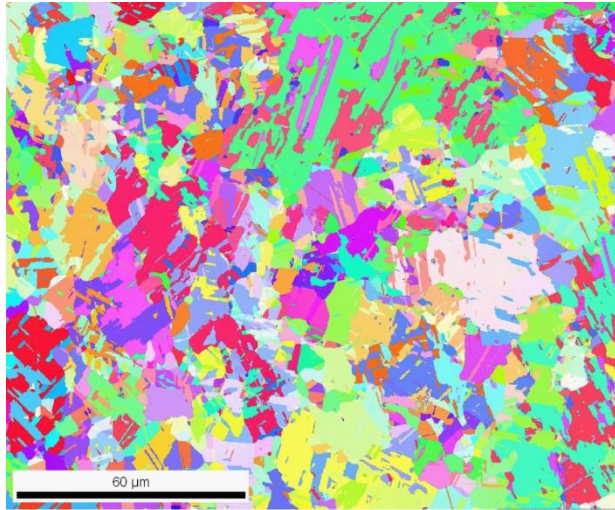
Relation microstructure/réactivité locale

Dissolution locale des joints de grains

Caractérisation des joints de grains par couplage EC-STM/EBSD

Microcrystalline sample

EBSD IPF map



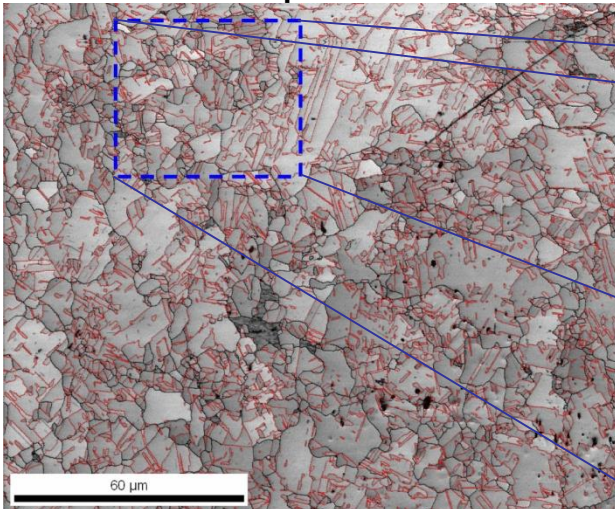
Material:

- Electrolytic tough pitch (ETP-) Cu
- 6N purity
- Cryogenic rolling to final reduction of 90%
- Post annealing 2 min at 200°C

EBSD grain analysis:

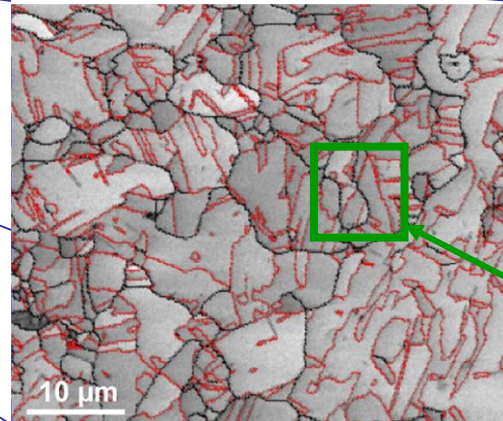
- Grain size: 0.1 to 37 μm (1.4 μm in average)
- Random texture

EBSD IQ map



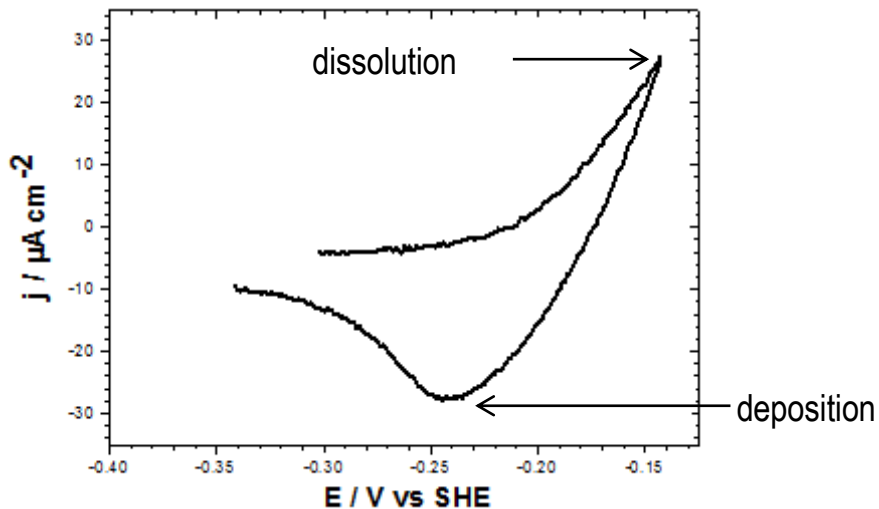
EBSD grain boundary analysis:

- $\Sigma 3$: 66%
- Random or other Σ 's: 34%



STM field of view
(10 x 10 μm²)

ECSTM protocol

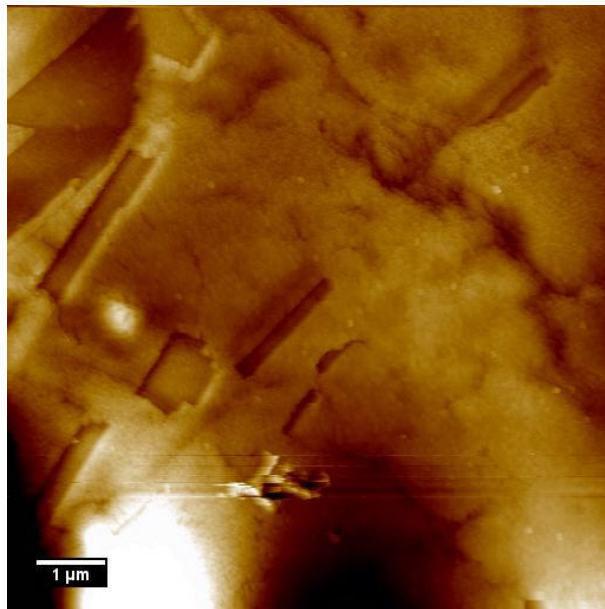


1 mM HCl(aq); ECSTM cell; 0.02 V/s

- In situ cathodic pre-treatment in order to reduce native oxide
- STM identification of a zone of interest
- Application of dissolution cycles (up to 6)
- STM imaging of surface alteration after cycling

ECSTM analysis at GBs

Initial metallic state

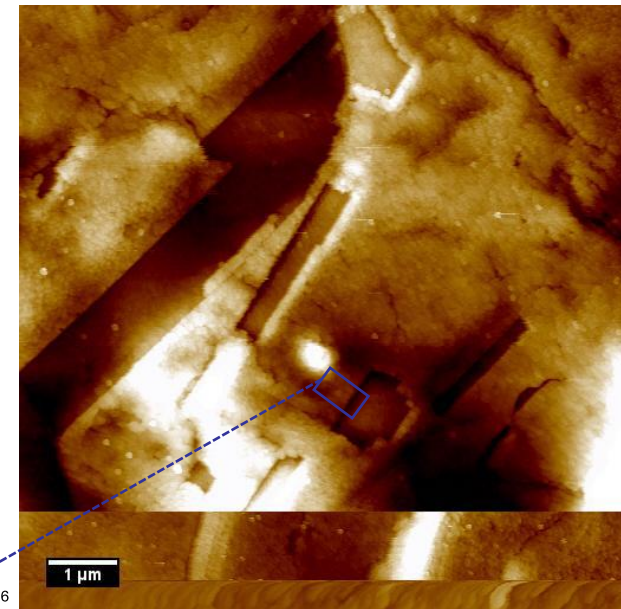


$\Delta Z = 18 \text{ nm}$, $E_{Cu} = -0.75 \text{ V}$, $E_{tip} = -0.6 \text{ V}$,
 $I_{tip} = 2 \text{ nA}$

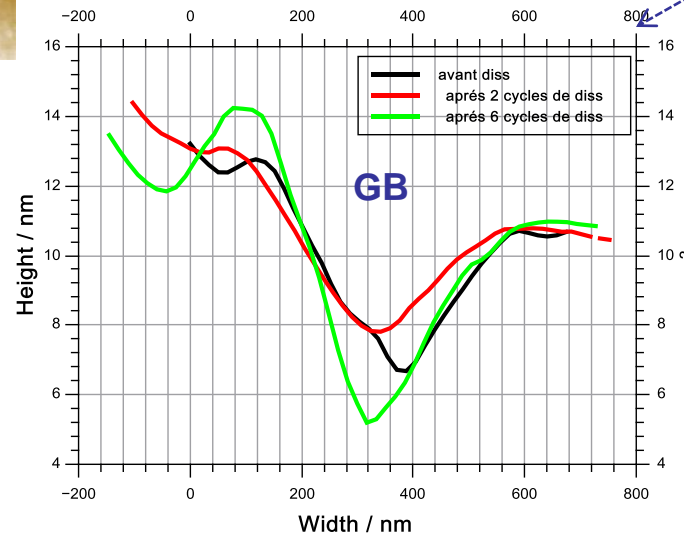
Dissolution charge density /
equivalent thickness:

(2): $84.8 \mu\text{C} \cdot \text{cm}^{-2} / \delta = 0.10 \text{ nm}$
(6): $275.6 \mu\text{C} \cdot \text{cm}^{-2} / \delta = 0.34 \text{ nm}$

Metallic state after 2 dissolution cycles

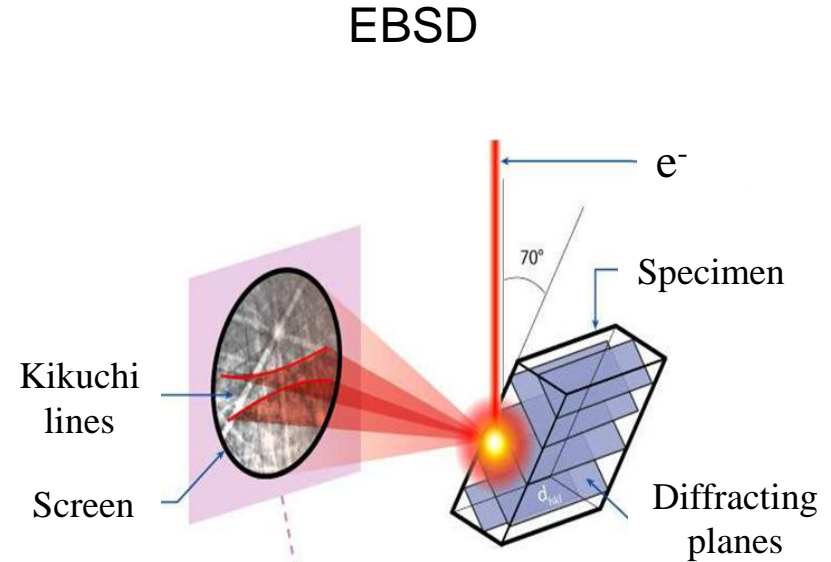
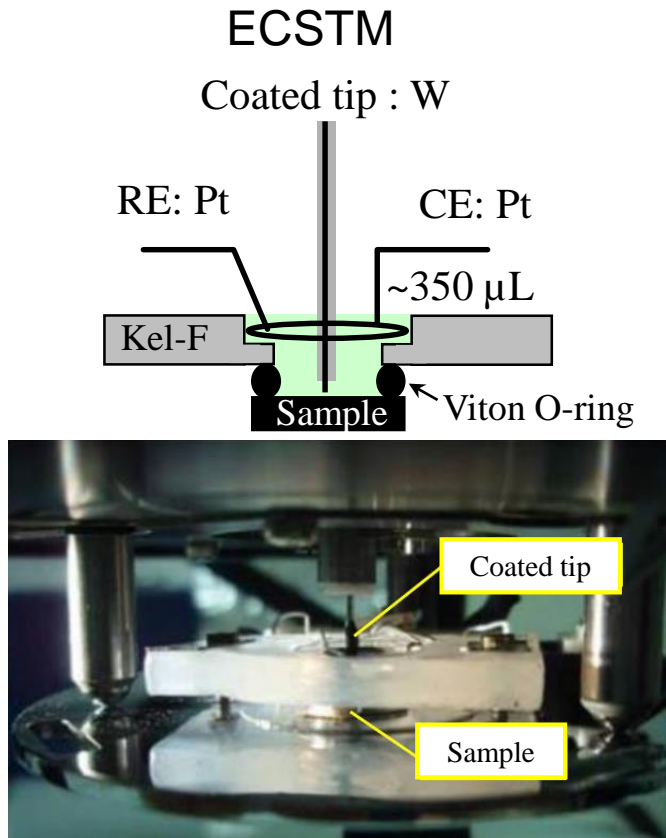


$\Delta Z = 24 \text{ nm}$, $E_{Cu} = -0.75 \text{ V}$, $E_{tip} = -0.6 \text{ V}$,
 $I_{tip} = 2 \text{ nA}$



- Grains and GBs localized
- Local topography measured after 2 and 6 (+4) dissolution cycles
- GB depth and its variation measured from height profiles

Coupling ECSTM with EBSD



Roadblock:

No optical access in ECSTM setup

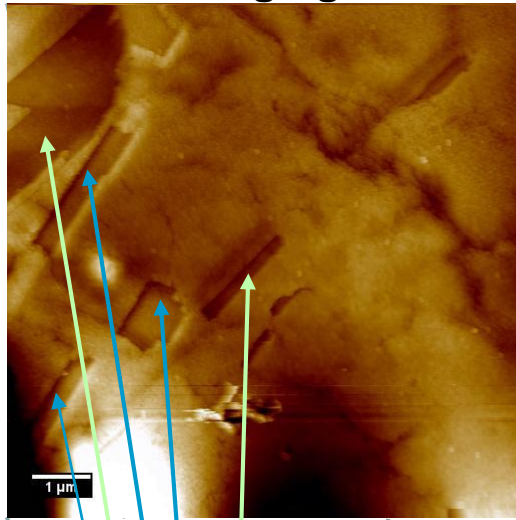
- EBSD → ECSTM ❌
- ECSTM → EBSD ✅

Lifter:

Use of STM tip to indent the sample surface and marked the area pre-analyzed by ECSTM for EBSD repositioning

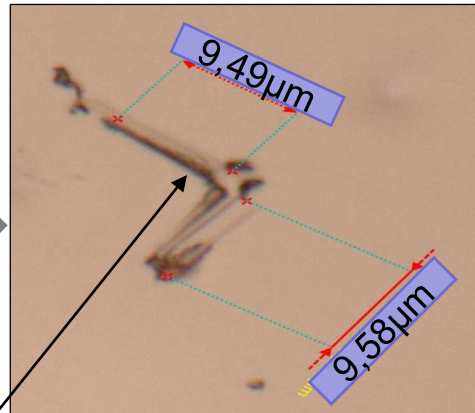
ECSTM / EBSD coupling protocol

1. ECSTM imaging + indentation

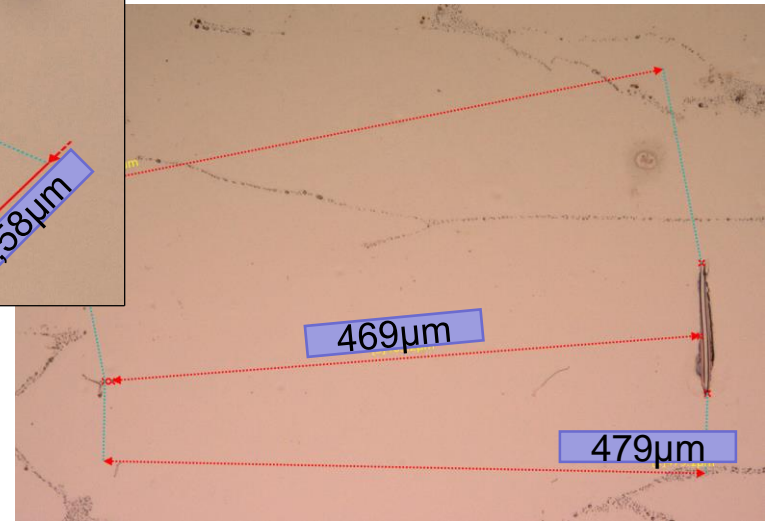


Stepper motor
+
scanner

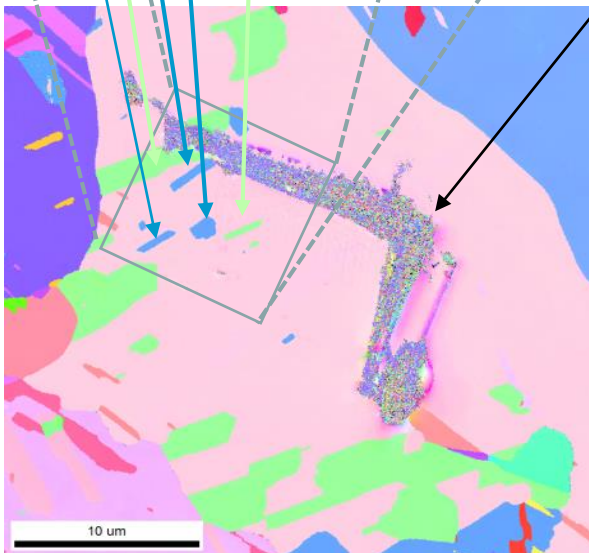
Transfer



2. Optical imaging after indentation and marking with STM tip



Transfer to EBSD



3. EBSD imaging (IPF map)

- Localization of grains and GBs by ECSTM
=> local corrosion-induced behavior
- Indentation and marking with STM tip
- Re-localization by EBSD
=> microstructure of same local area

- Cellule EC-STM à 4 électrodes contrôlée par un bipotentiostat
- Nettoyage rigoureux de la cellule (contamination...)
- Préparation adéquate des pointes et surfaces (rugosité...)
- Caractérisation préalable du comportement électrochimique de l'interface
- Transfert de matière limité
- Caractérisation locale généralement réalisée après altération
- Suivi dynamique en temps réel possible si altérations lentes
- Couplage avec d'autres méthodes d'analyse locale possible par repositionnement