The Harvey M. Krueger Family Center
for Nanoscience and Nanotechnology

האוניברסיטה העברית בירושלים
THE HEBREW UNIVERSITY OF JERUSALEM

Identification of Dislocation Structure in Cu Electrodes

Inna Popov

**The Center for Nanoscience and Nanotechnology,
the Hebrew University of Jerusalem**

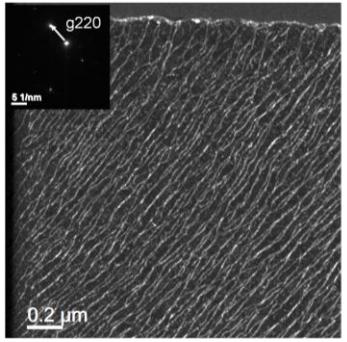
@The Hebrew University of Jerusalem: Ayelet Yashar, Yinon Ashkenazy,
Eli Engelberg, Sagy Lachman, *Itay Nachshon, Gad Raanan

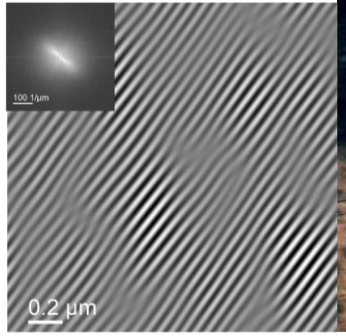
@CERN: Iaroslava Profatilova, Jan Paszkiewicz, Enrique Rodriguez Castro,

Walter Wuensch

PAZY
EXCELLING IN SCIENCE

Outline





Breakdowns were suggested to nucleate due to dislocations “stampedes”.

The experimental way to tune this suggestion is MICROSCOPY.

- A brief review of the experimental data confirming the presence of mobility dislocations in soft and hard Cu electrodes

- A detailed microscopic identification of specific dislocation structures.

  Relation between the structures, grain boundaries (GBs) and surface terracing observed in a soft Cu.

(based on the TEM orientation identification and identification of dislocation lines direction from the electron channeling images in FIB/SEM + in situ observation of the dislocation movement)

- Relation between the GBs and dislocation structures observed in a soft Cu (unloaded and severely compressed metal below the cathode crater) and hard Cu.
  - Demonstrating universal sessile/mobile dislocation array in Cu electrodes

- Conclusions
  - Dislocations arrays – so what?
  - Can we identify distinct conditioning effect?

- <u>A brief review of the experimental data confirming the presence of mobility dislocations in soft and hard Cu electrodes</u>

- A detailed microscopic identification of specific dislocation structures.

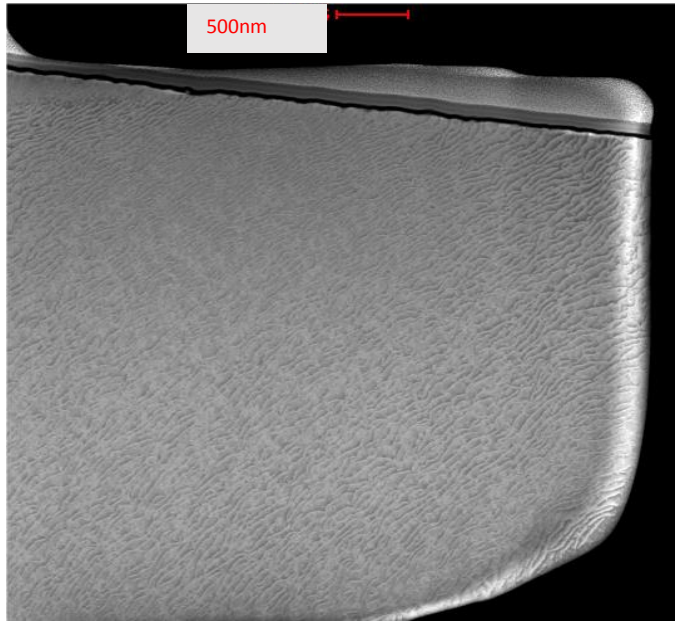
  Relation between the structures, grain boundaries (GBs) and surface terracing observed in a soft Cu.

(based on the TEM orientation identification and identification of dislocation lines direction from the electron channeling images in FIB/SEM + in situ observation of the dislocation movement)

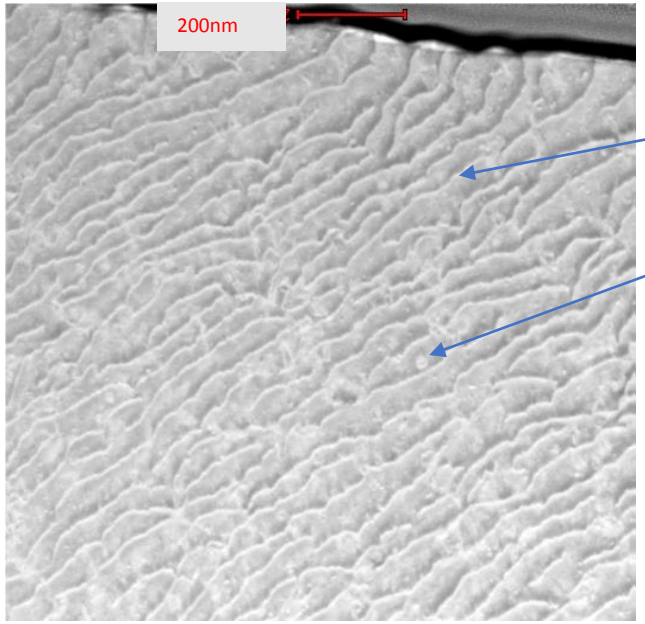
- Relation between the GBs and dislocation structures observed in a soft Cu (unloaded and severely compressed metal below the cathode crater) and hard Cu.
  - Demonstrating universal sessile/mobile dislocation array in Cu electrodes

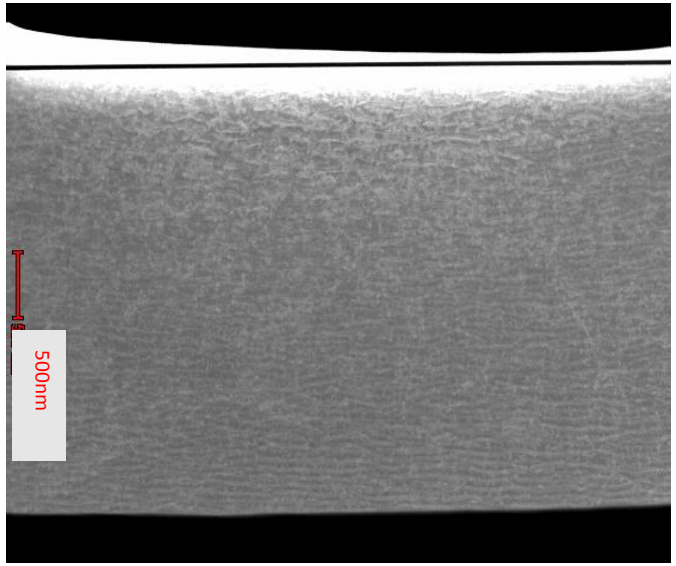
- Conclusions
  - Dislocations arrays – so what?
  - Can we identify distinct conditioning effect?

A specific dislocation pattern observed in a cross sectional TEM lamella extracted from a soft Cu with FIB

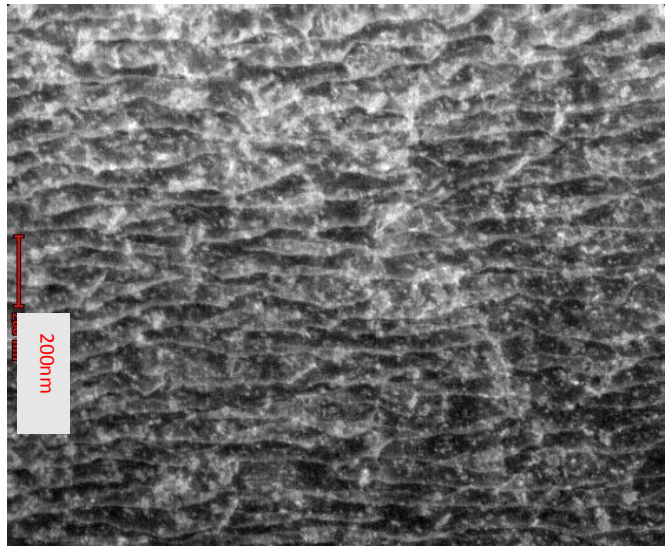


The RF sample#23 :
DF STEM images acquired at a reference site





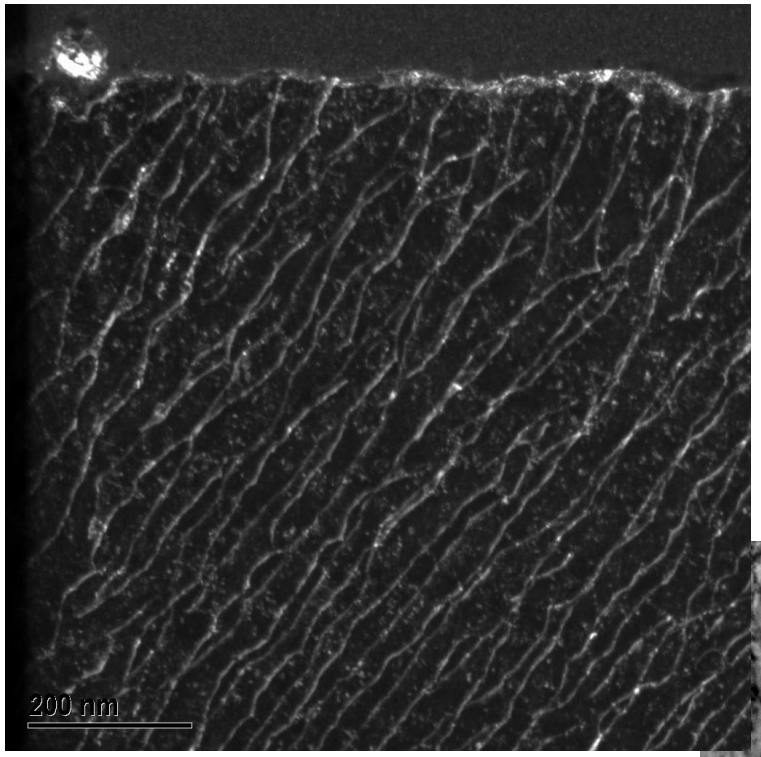
A small DC sample # 4 :



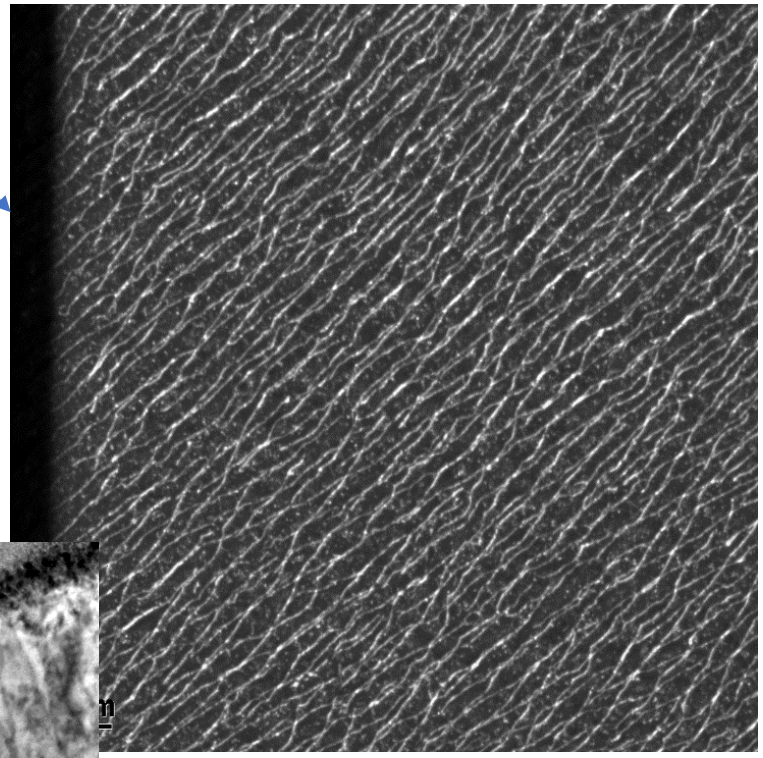
DF STEM

DF TEM

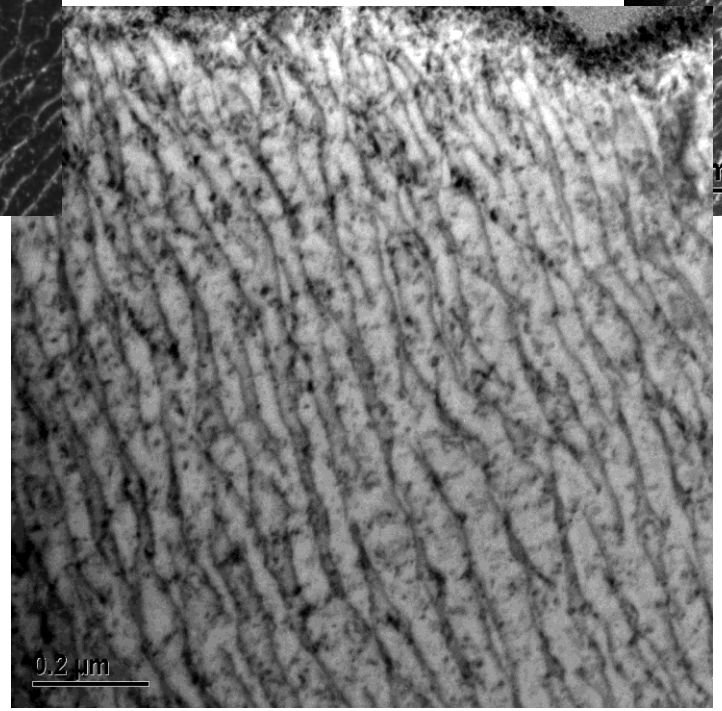
Cross sectional samples (soft Cu):



At the surface

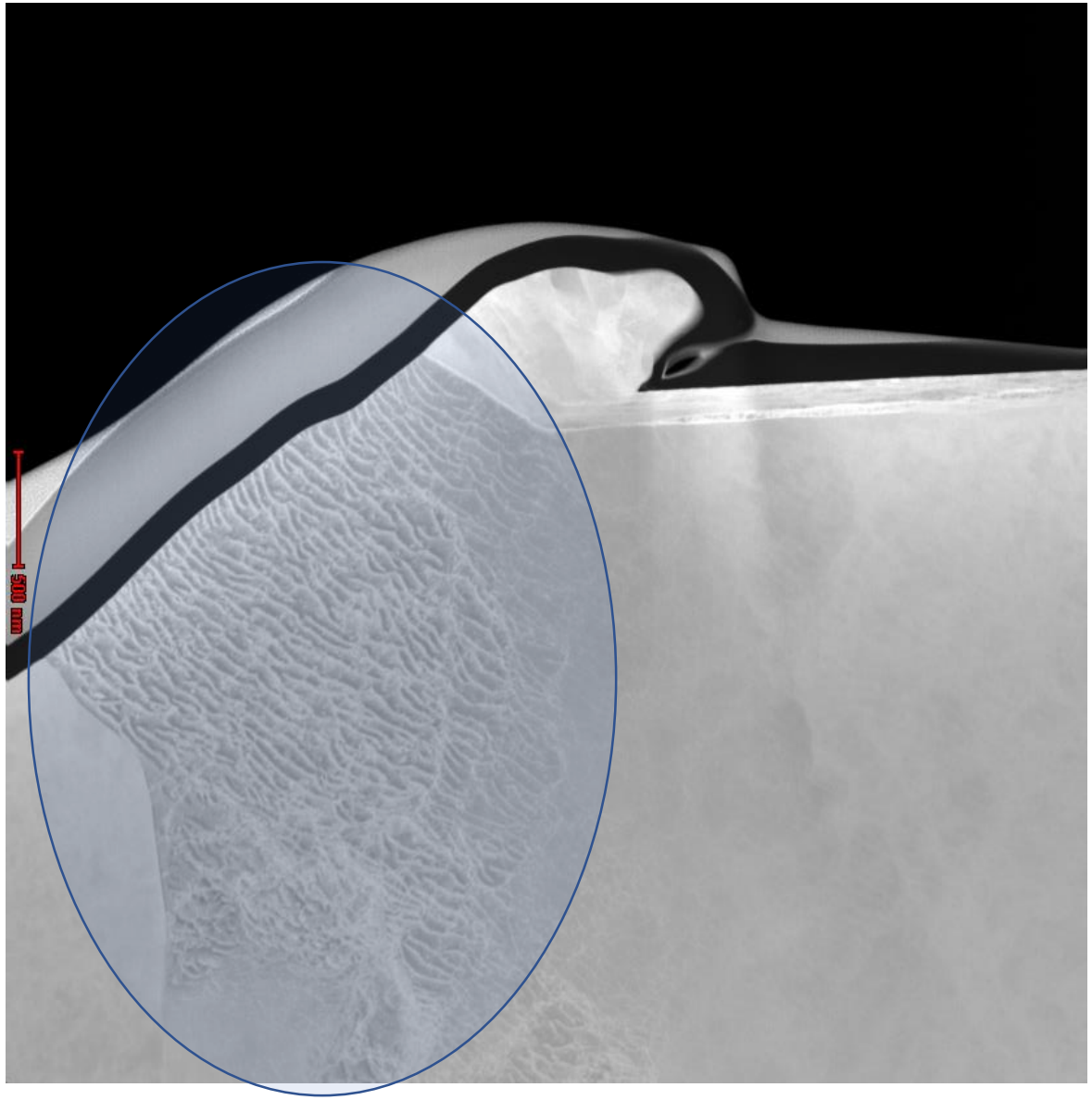


1 µm below the surface

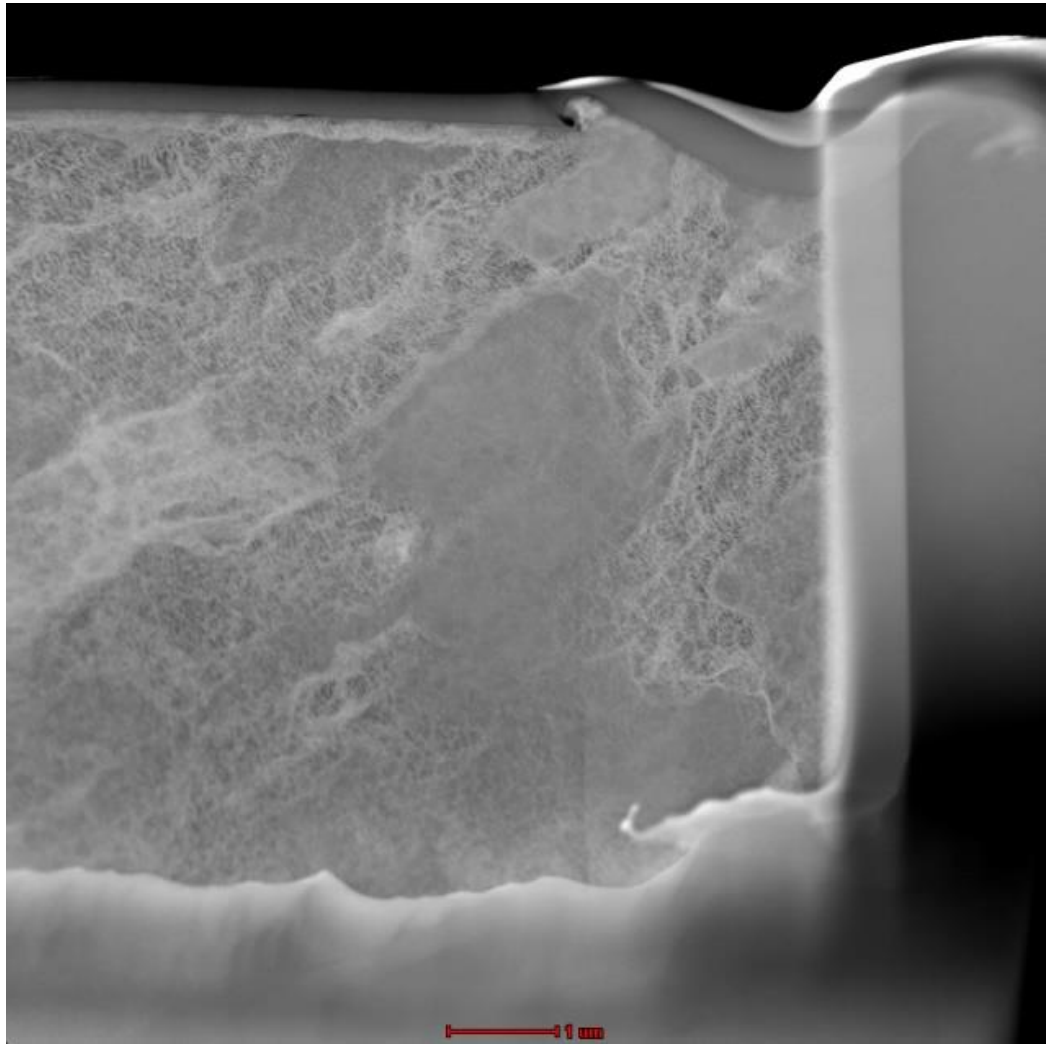


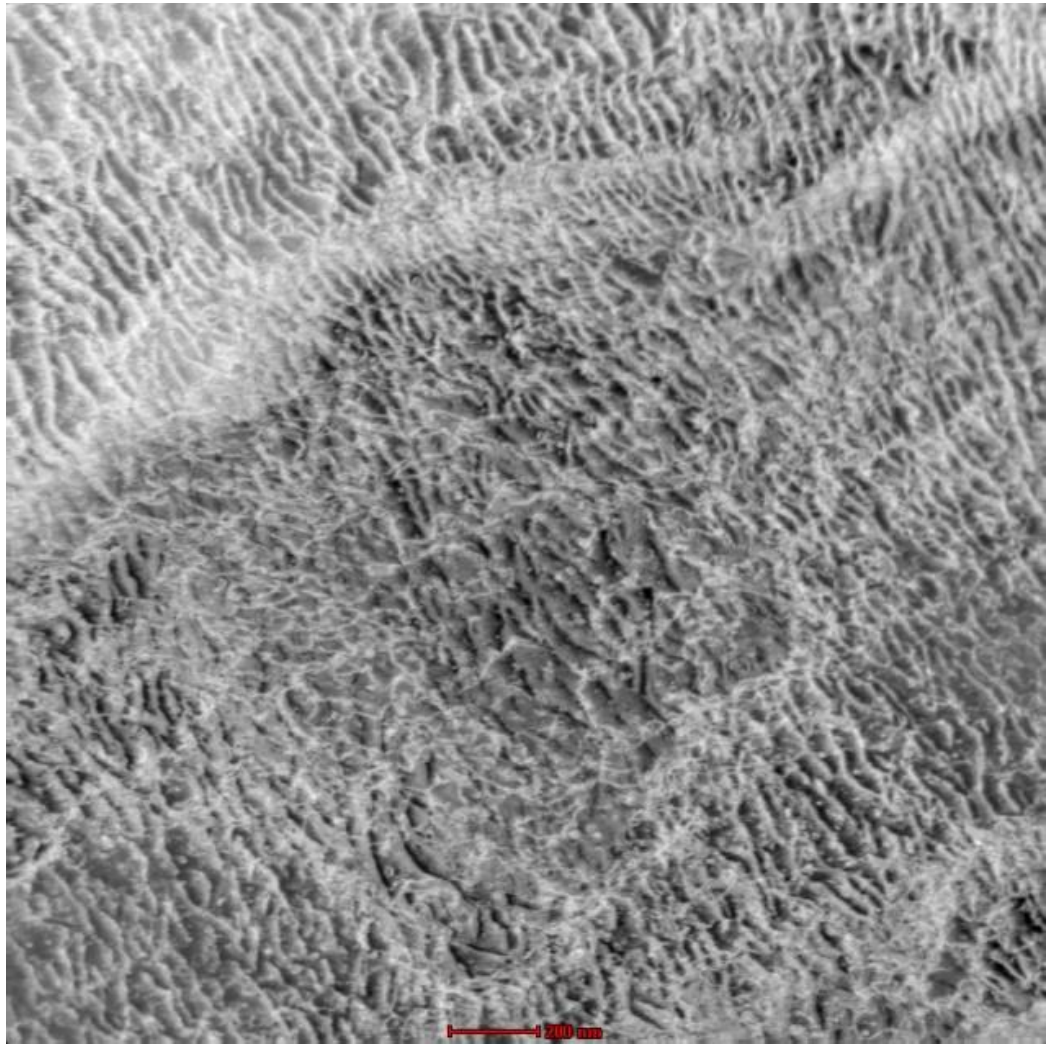
Top-view lamella (soft Cu)

Soft Cu, below 5 µm – size crater, DF STEM :

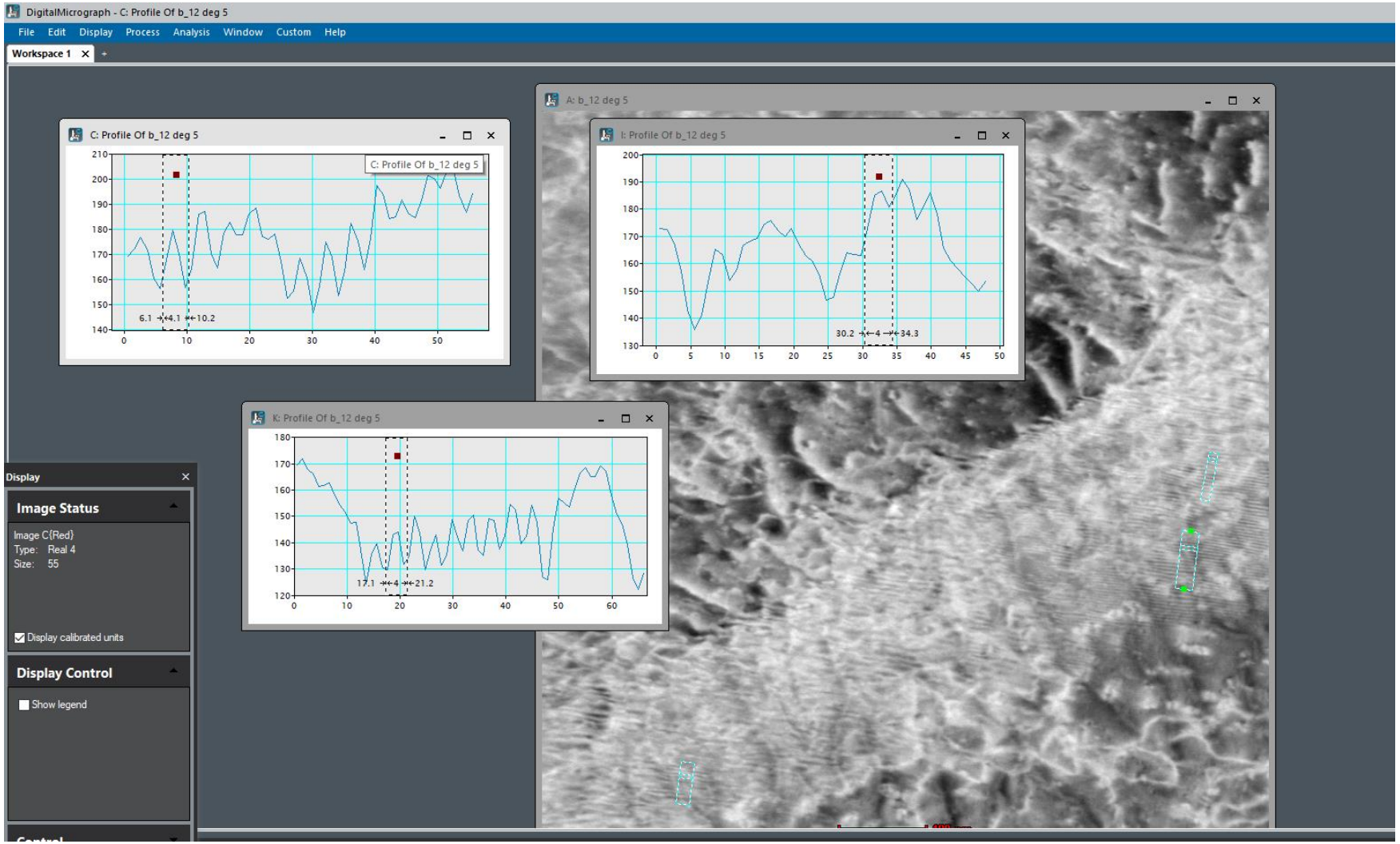


Soft Cu, DF STEM of a plastically deformed zone below 5 µm – size crater :

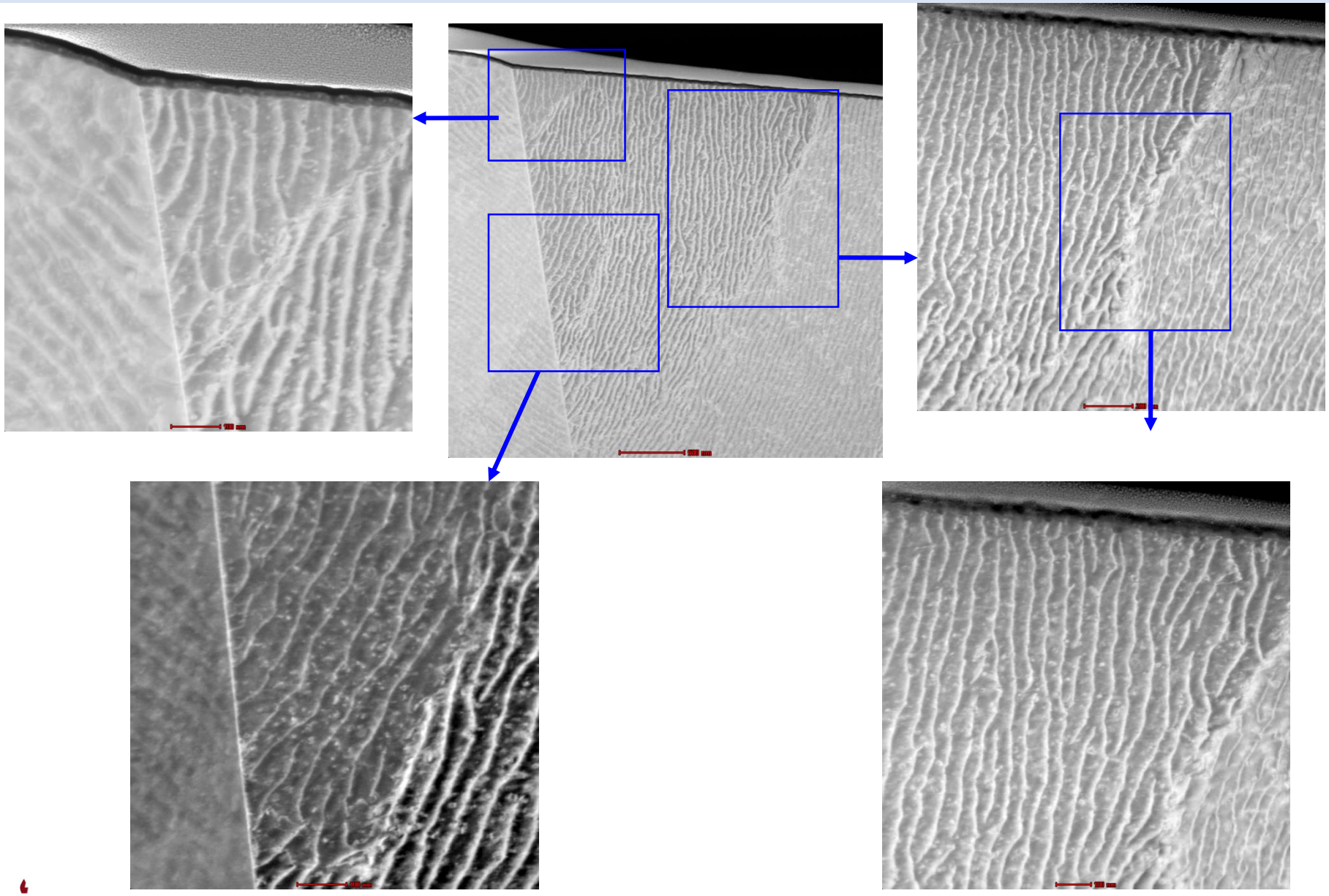




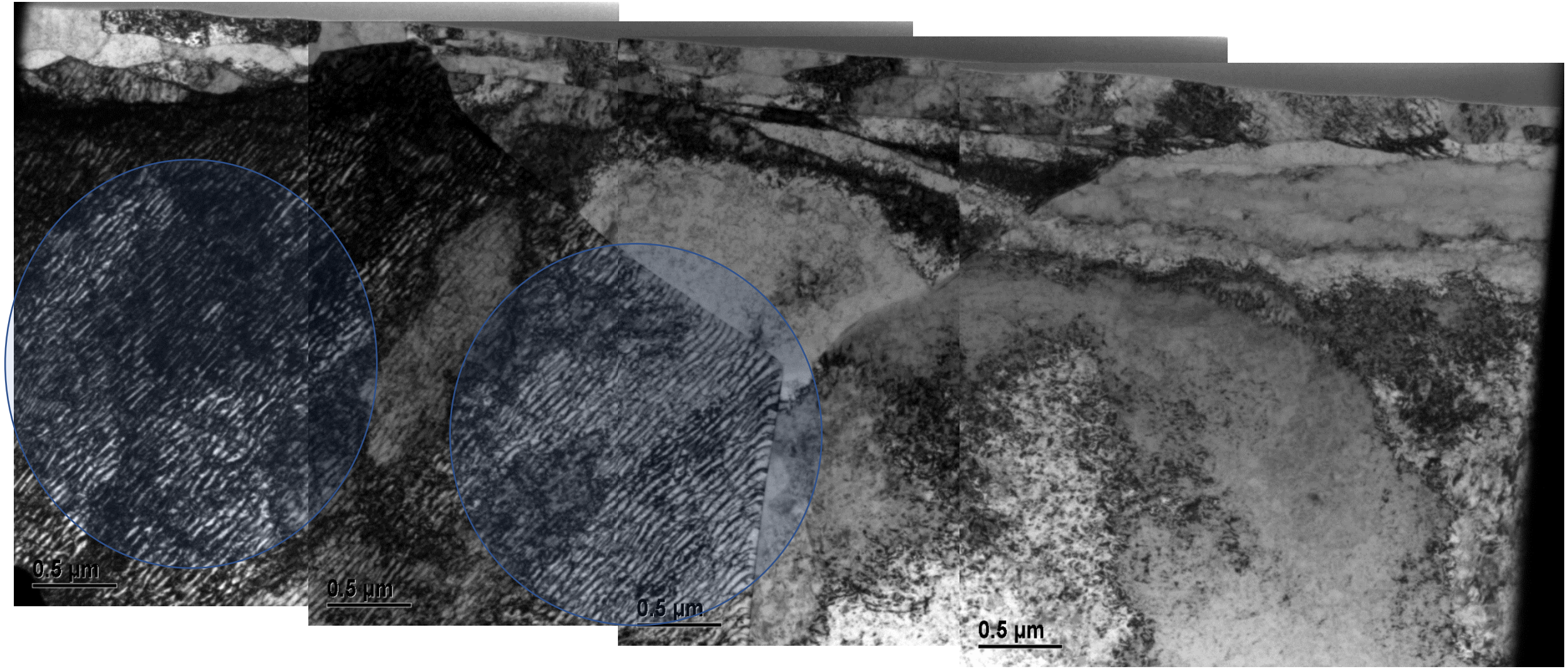
High angle/Σ GB produced due to compression in the deformation zone below the crater , dislocation space separation 4-5 nm



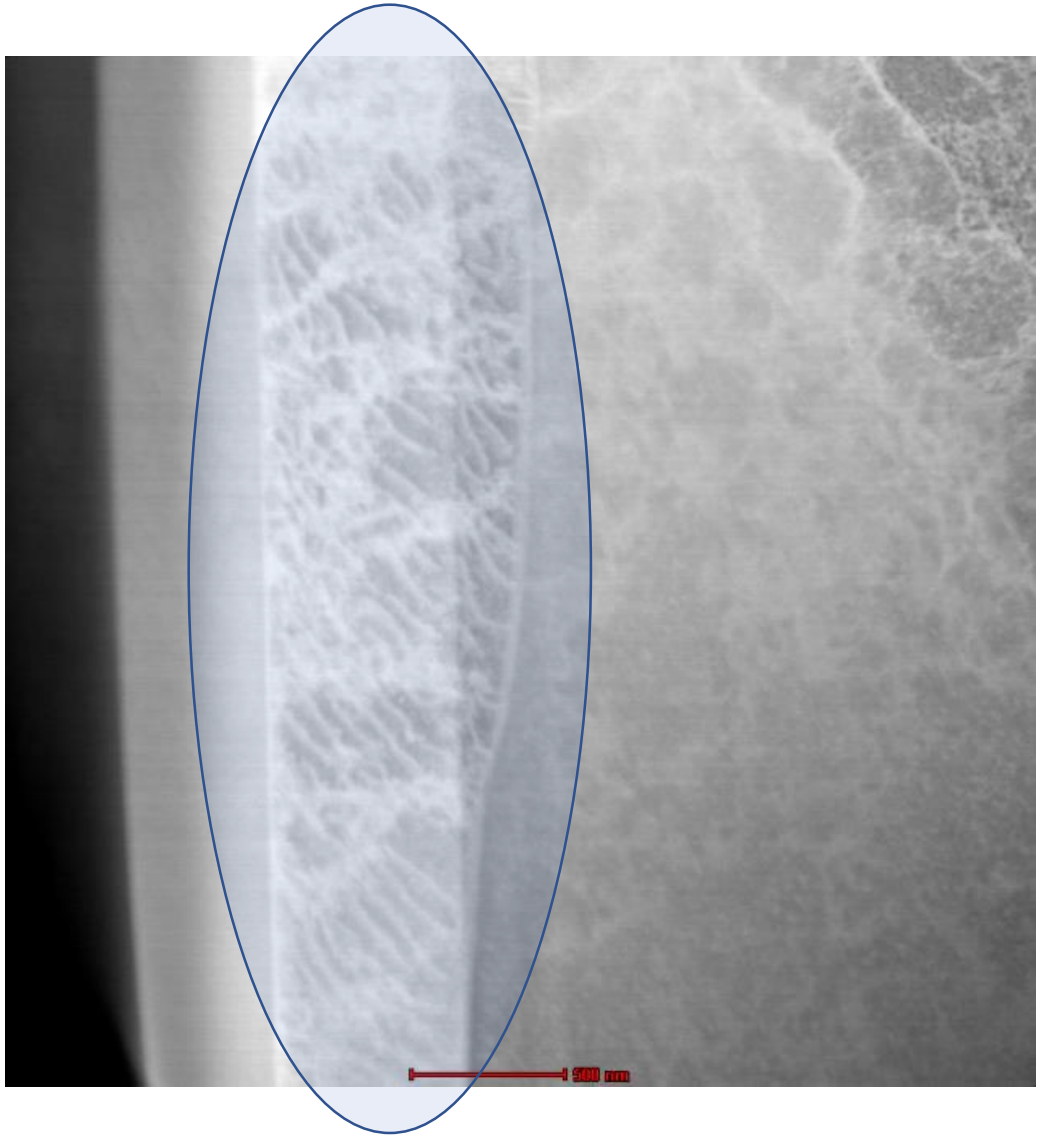
65% fatigue tested soft Cu (STEM)

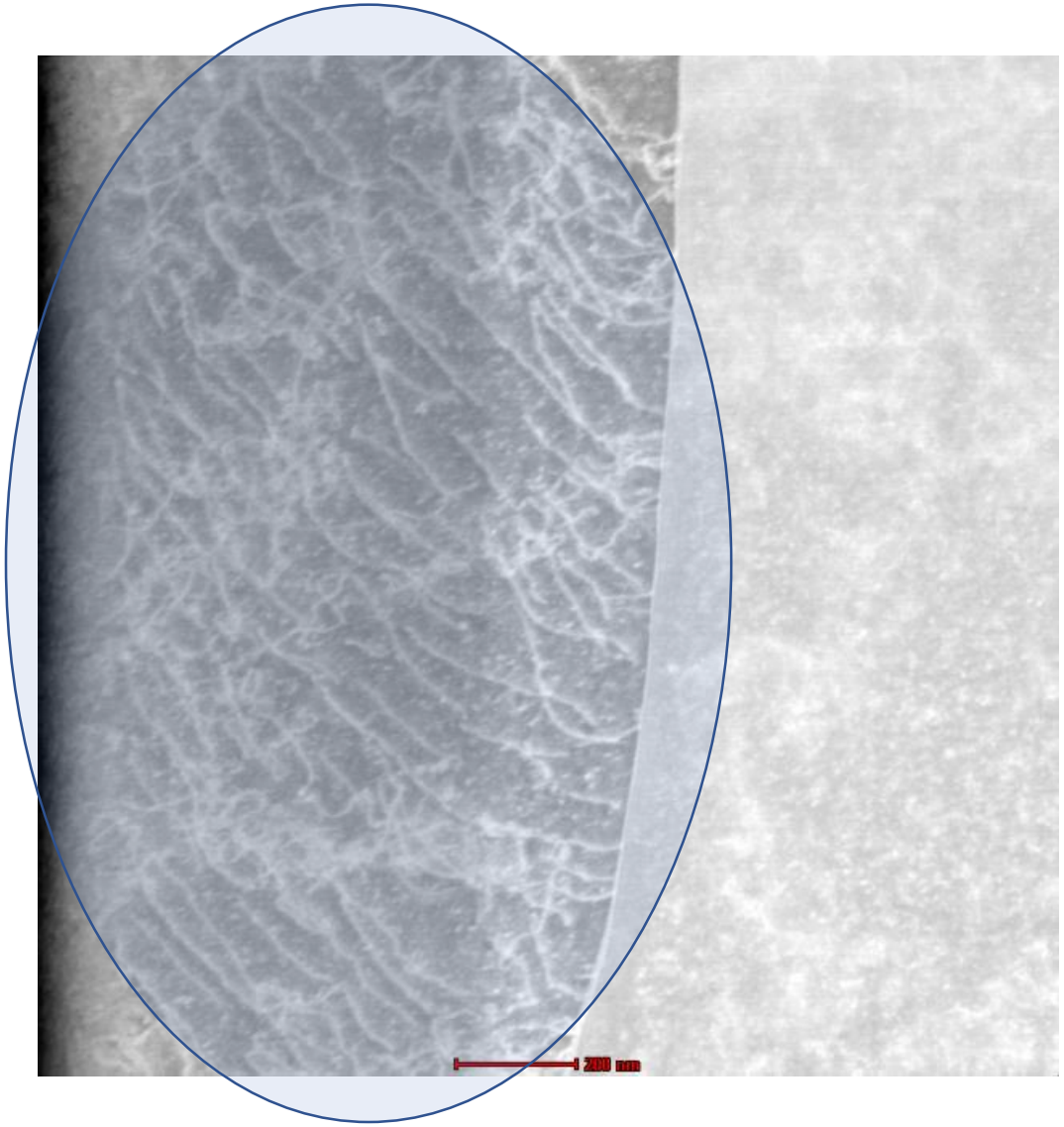


TEM BF on FIB cross sectioned sample of a hard Cu :



DF STEM of a hard Ag (fcc lattice as Cu) (scratch tested, a cross sectional FIB lamella was extracted from the edge of a scratch)





In the published data:

L. Meshi et al. / Acta Materialia 59 (2011) 342–348

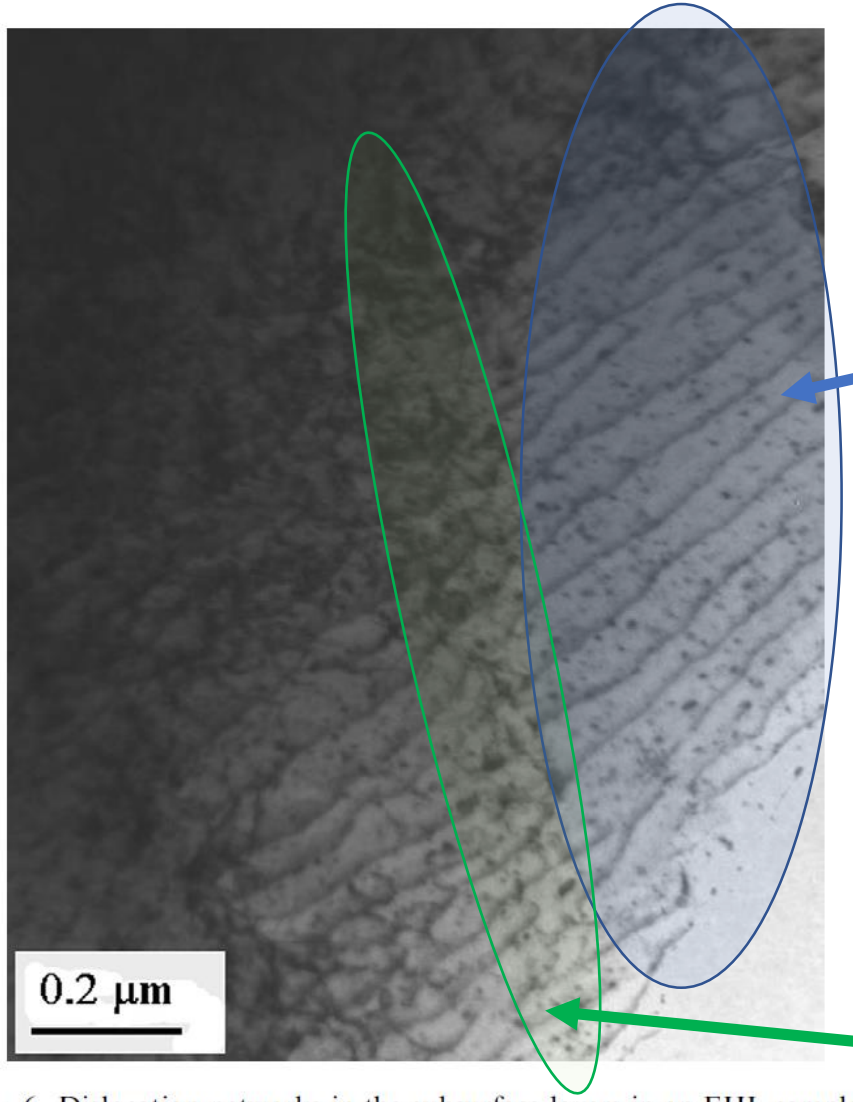
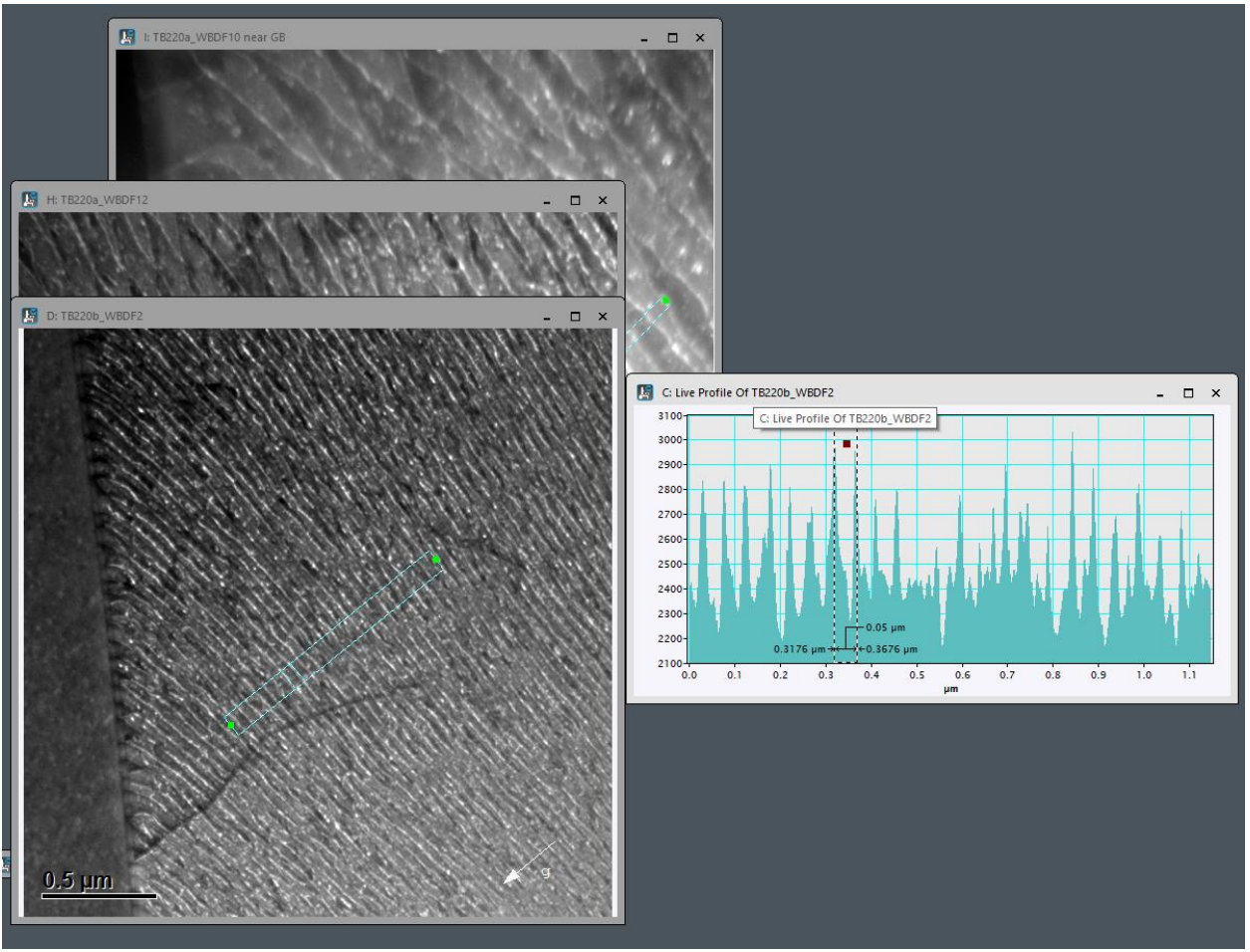


Fig. 6. Dislocation networks in the subsurface layers in an EHL sample. (The depth increases from right to left.)

The pattern was observed in the hard Cu subjected to tribological tests. TEM cross sections were prepared by mechanical polishing followed by Ar milling

the EHL area) but the most important observation is that the individual dislocations had only one type of Burgers vectors: $\bar{b} = \frac{a}{2}[0\,1\,\bar{1}]$. We propose here that the other types were involved in the creation of the dislocation networks (walls), which are seen in this specimen.

Quantificaiton of the pattern:



The typical distance between the dislocation lines composing the pattern is 25 – 65 nm with the highest frequency at 50 nm.

The dislocation density is ~ 2-3 x10^{14} m^{-2} .

The values are the same for all the structural states

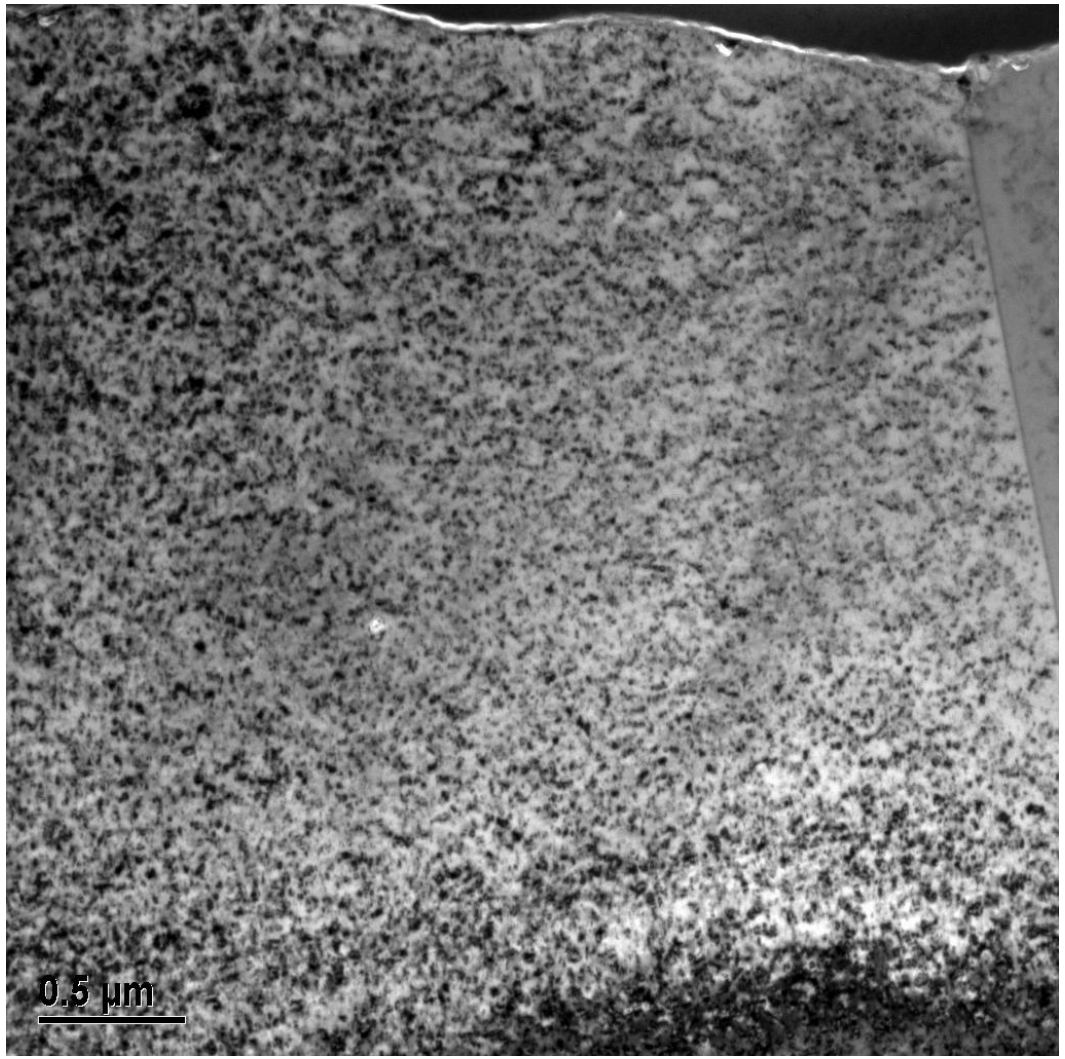
(the intact reference, close or farer from the BD site, below the BD site)

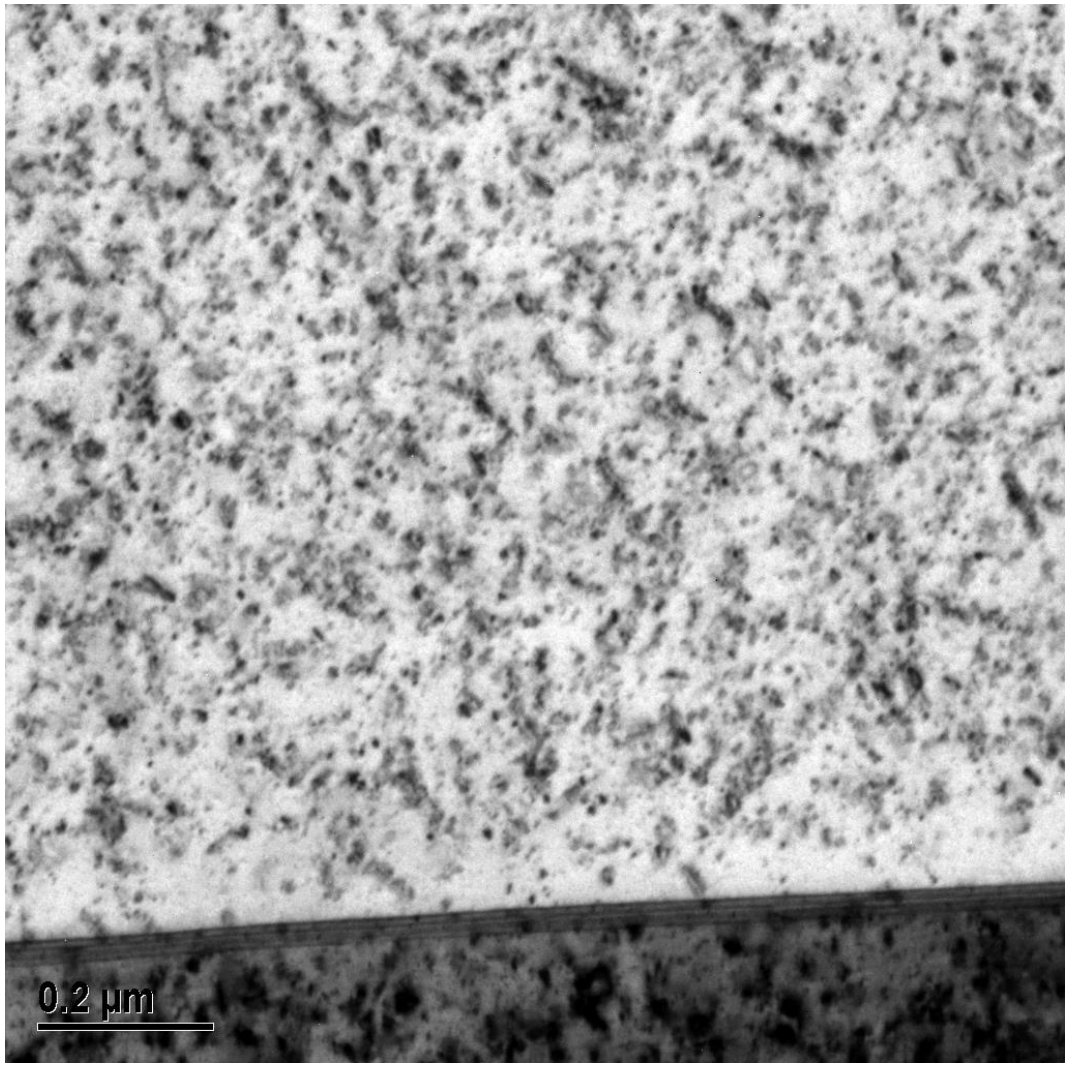
and do not depend on which direction the lamella was extracted (cross section or top view).

The dislocation density is a order of magnitude higher than the recently reported value for hard Cu (x10^{13} m^{-2}).

Y. Miyajima et al. / Materials Characterization 104 (2015) 101–106

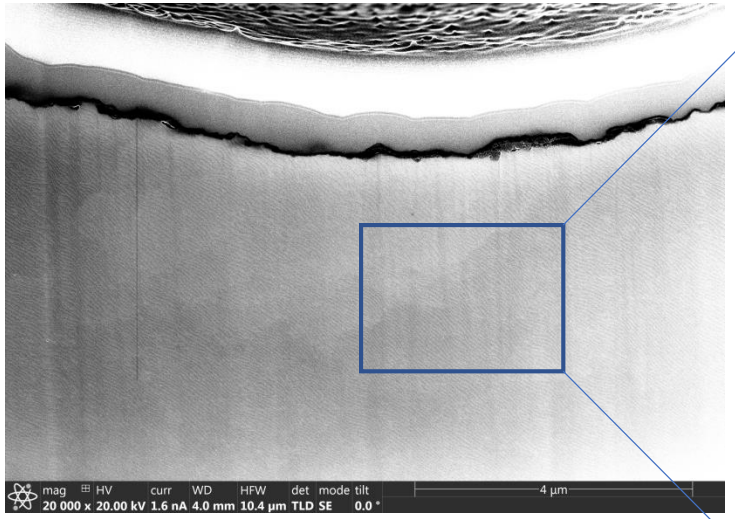
Less frequently observed dislocation structures are composed of dots only :

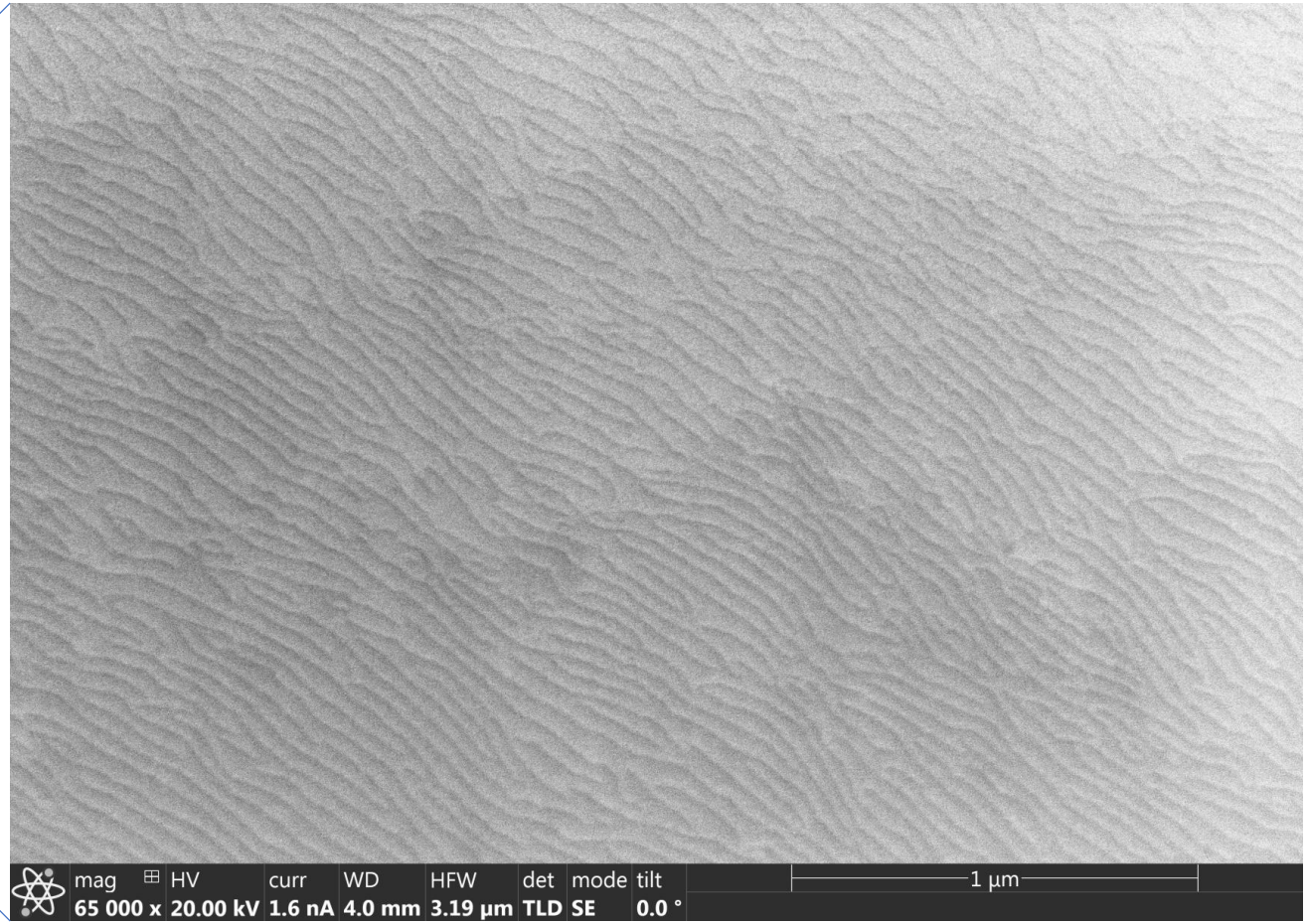




Top-view lamella

We observe this dislocation pattern not only in TEM samples, but also in SEM due to the contrast provided by the electron channeling (ECC imaging)





FIB cross section below the 10 µm wide crater; crab-cavity sample;
For Cu at TBs 111 – 200- 220 – 311 and 331 (I used) the signal comes from 60-150 nm below the surface (= typical thickness of TEM lamella)

The specific patterns were observed :

- in TEM samples extracted from :

- Soft, Hard and fatigue tested Cu samples obtained from CERN
- In the intact regions and plastically deformed zones below BD craters
- In a wear tested hard Cu (HIT);
- In a scratch tested hard Ag sample (HIT)
- In the published data

- in the TEM samples prepared by different techniques:

- in the samples prepared with Ga-ion FIB
- in the samples prepared by manual polishing followed by Ar-milling

- in the grains of sufficiently different sizes :

- in huge fully relaxed grains of CERN soft Cu annealed at pre-melting temperature;
- in small grains (less than 500 nm) deformed plastically to different extent of deformation

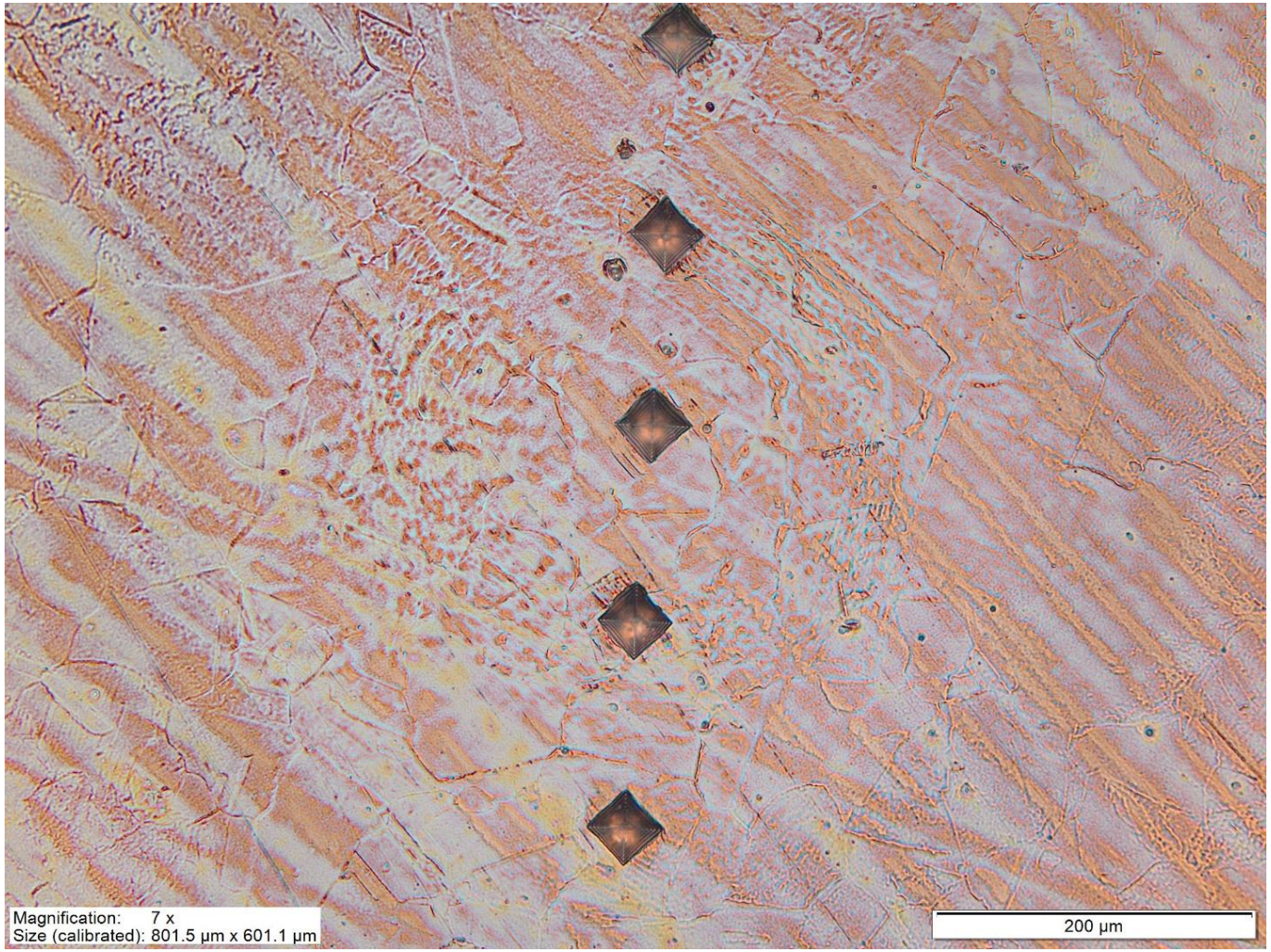
- SEM images containing the electron channeling contrast (ECC)

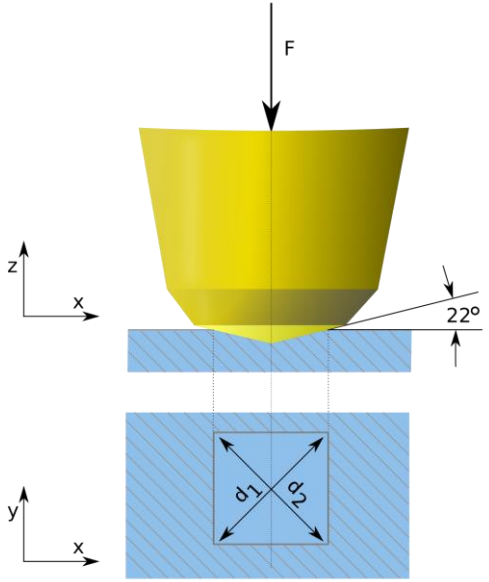
Q1. How mobile the observed system(s) are?

Q2. Which dislocations compose the observed system(s)?

Q2. How many such systems present simultaneously in a single grain/crystal?

We measured Vickers microhardness in a soft and a hard Cu samples





A hard Cu , anode 0185-02, 20 gf, 10 s

The values of microhardness of Cu electrodes

Magnification X100, a load of 20grf, loading time 10s

Sample	Measurement locations		Average Hardness Vickers (HV)	Standard deviation
Soft Cu reference	Three measurement each one in a different grain. Each measurement was consisted of 5 tests.		46.36	0.99
			48.12	0.38
			46.77	1.00
Hard Cu reference 03	One measurement that was consisted of 10 tests.		116.04	3.64
Soft Cu FGS cathode number 16 (engraved), 62mm diameter, conditioned	On a BD crater in the center of the sample	Each measurement was consisted of 5 tests.	76.46	7.07
	On a BD crater in the edge of the sample		78.8	6.9
	On a clean region in-between BD craters – in the center of the sample		48.57	1.47
	On a clean region in-between BD craters – in the edge of the sample		46.3	1.10
Hard Cu FGS cathode 007-06 0186-06, 40mm diameter, conditioned	On a BD crater in the center of the sample	Each measurement was consisted of 5 tests.	97.29	6.33
	On a BD crater in the edge of the sample		93.19	3.26
	On a clean region in-between BD craters – in the center of the sample		107.74	3.48
	On a clean region in-between BD craters – in the edge of the sample		109.54	3.27
Fatigue tested sample	Three measurement each one in a different grain. Each measurement was consisted of 5 tests.		84.75	1.20
			84.61	1.98
			77.50	2.03

- In the absolute numbers, both soft and hard Cu are extremely soft@plastic, the yield strength of hard Cu anode in the previous slide is ~60 MPa = a plastic flow starts almost immediately = a very little stress must be applied to overcome the resistance to dislocation motion = the presenting dislocations are easy moving, not sessile.
- A soft Cu becomes a bit stronger after BD = mechanical strengthening dominates
- A hard Cu becomes a bit softer after BD = heat release dominates

Q1. How mobile the observed system(s) are?

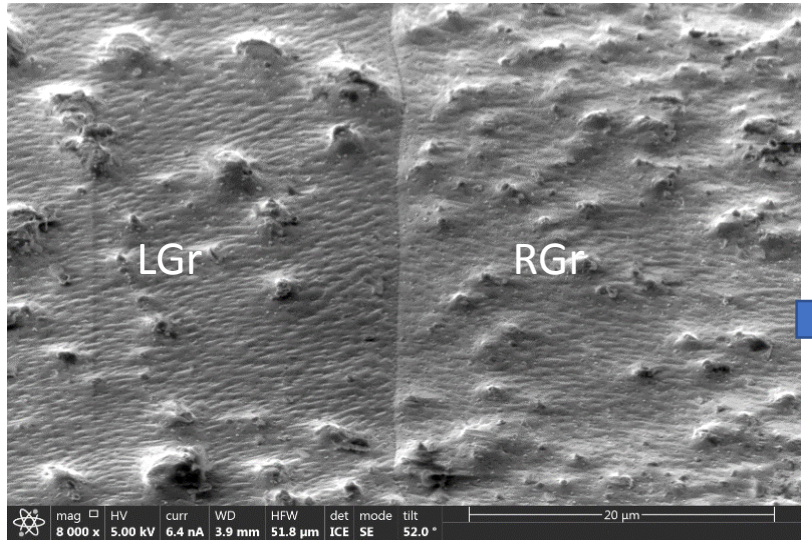
The dislocations are extremely mobile

Q2. Which dislocations compose the observed system(s)?

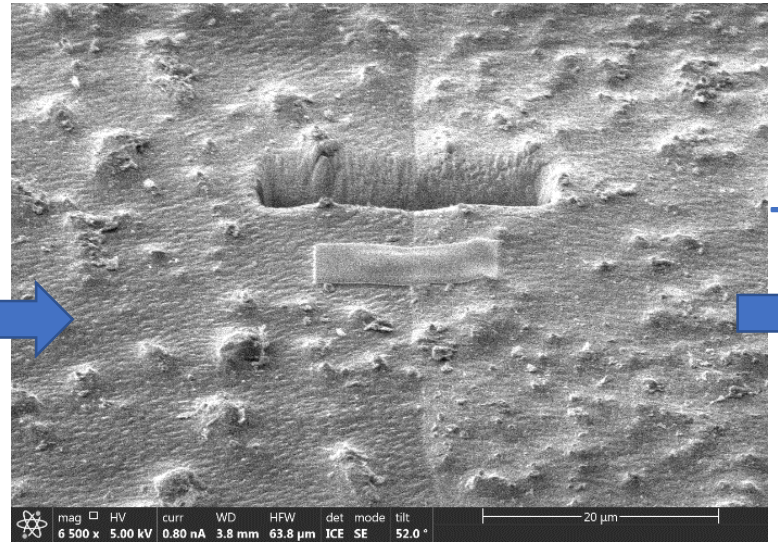
Q2. How many such systems present simultaneously in a single grain/crystal?

1. ECCI gives information about very large volumes, but cannot be directly interpreted without complimentary diffraction technique (EBSD in SEM or TEM). Due to instrumental limitations we used TEM.

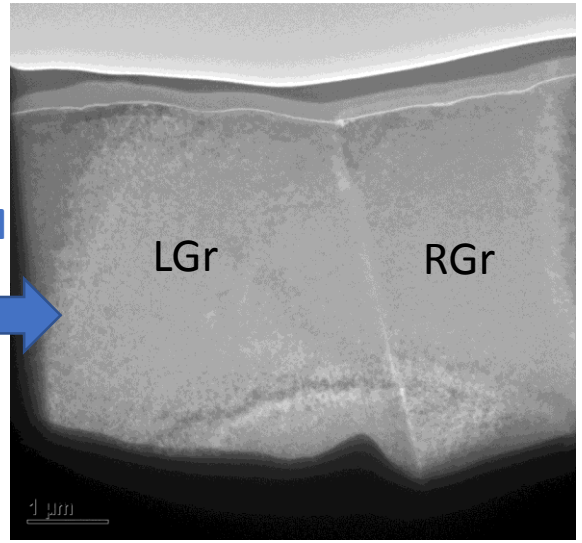
2. We extracted a cross sectional lamella across the occasional GB in soft Cu sample (#50) and identified found of two neighboring grains



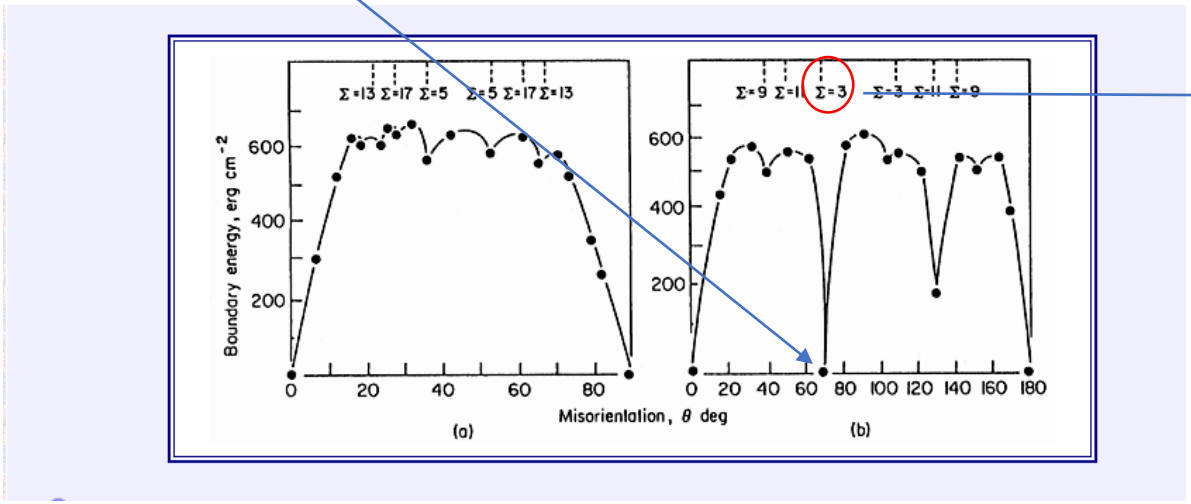
FIB



TEM

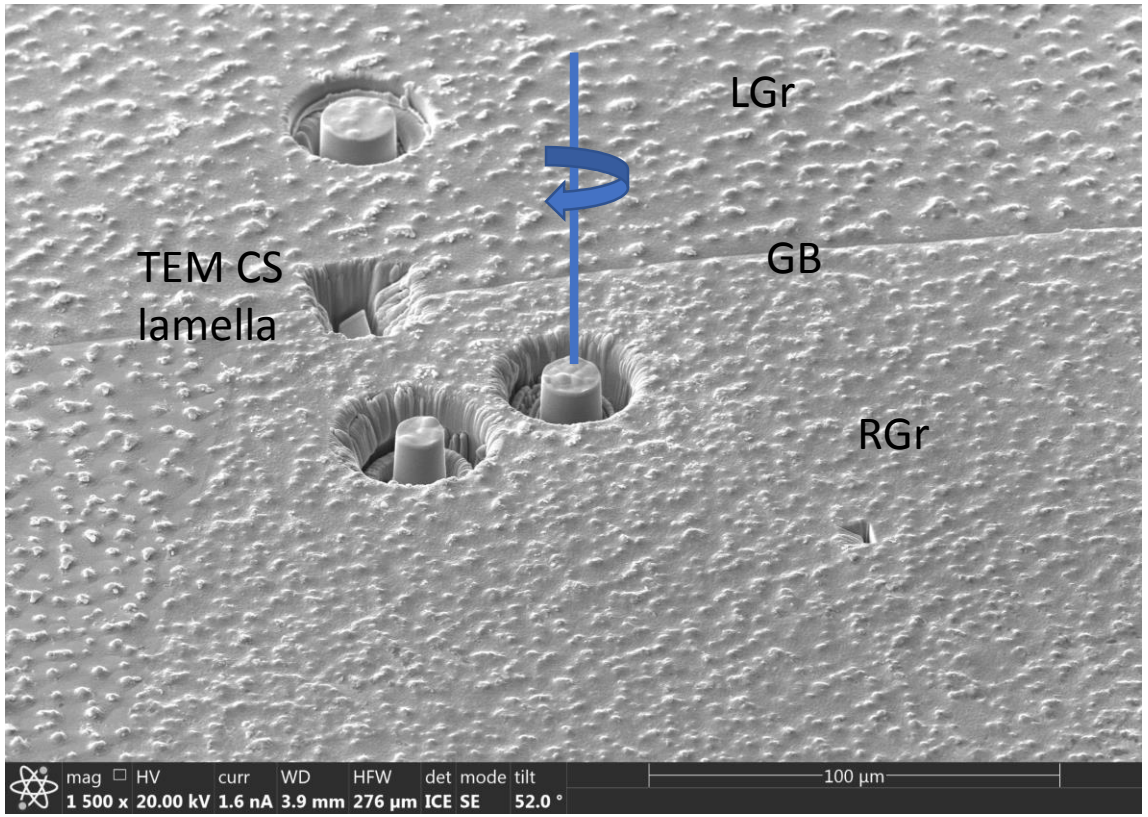


LGr is oriented along [-130]
RGr is oriented along [-215]
The misorientation angle θ = 73.22 deg



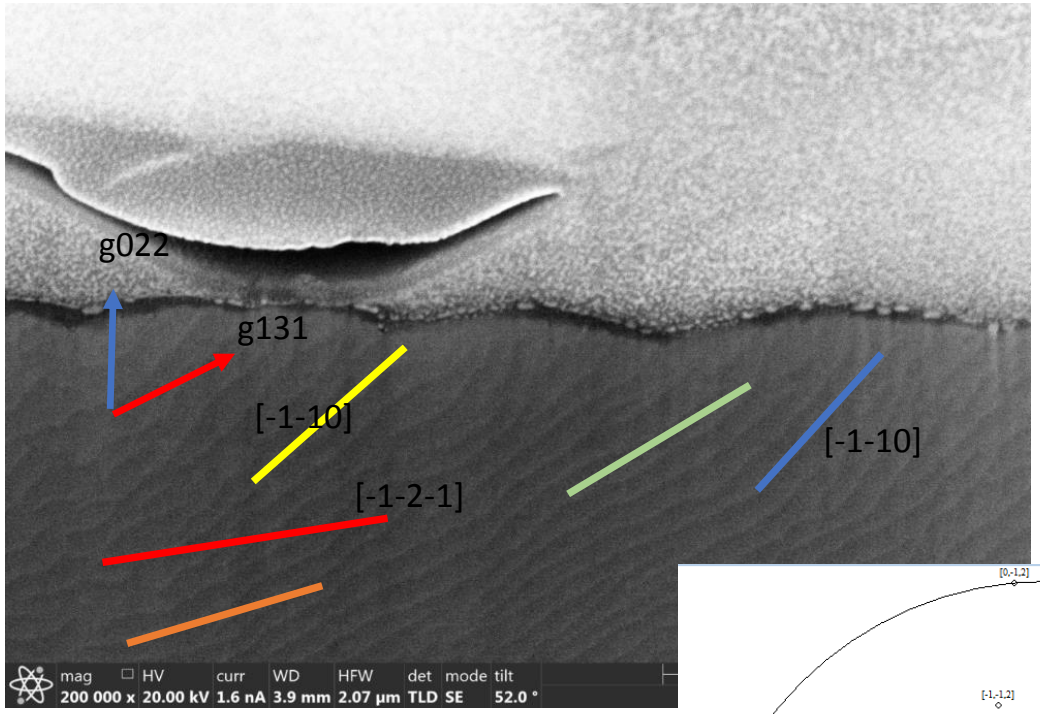
Σ3 type GB (twin-type GB) of the lowest energy

https://www.tf.uni-kiel.de/matwis/amat/def_en/index.html

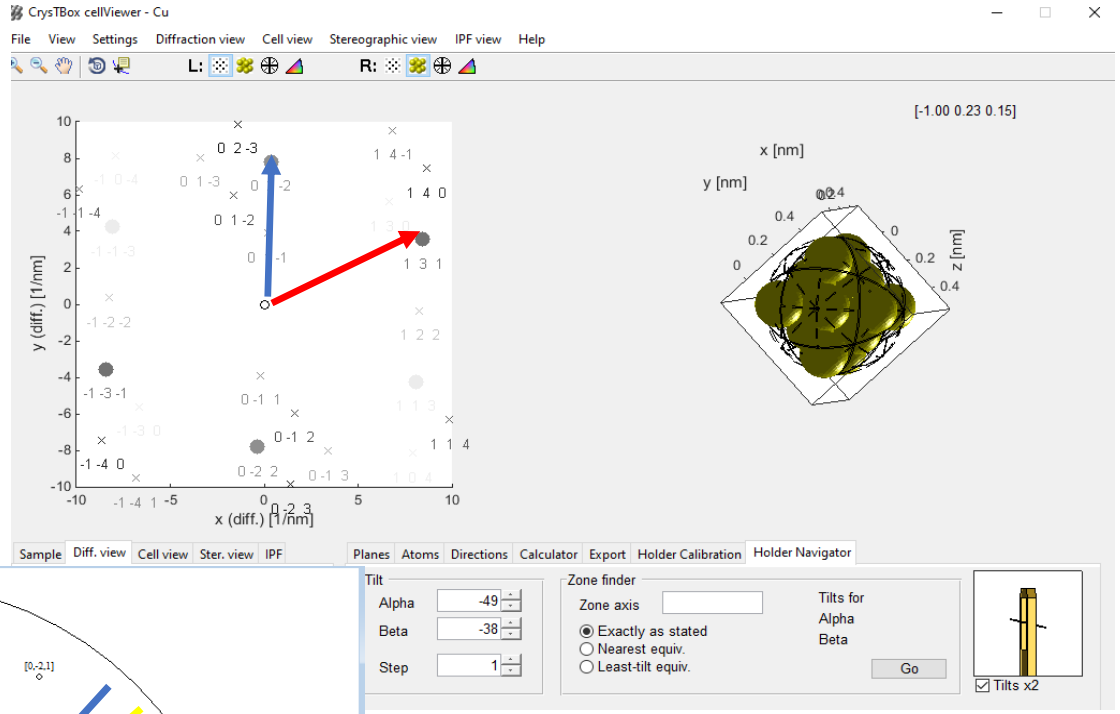


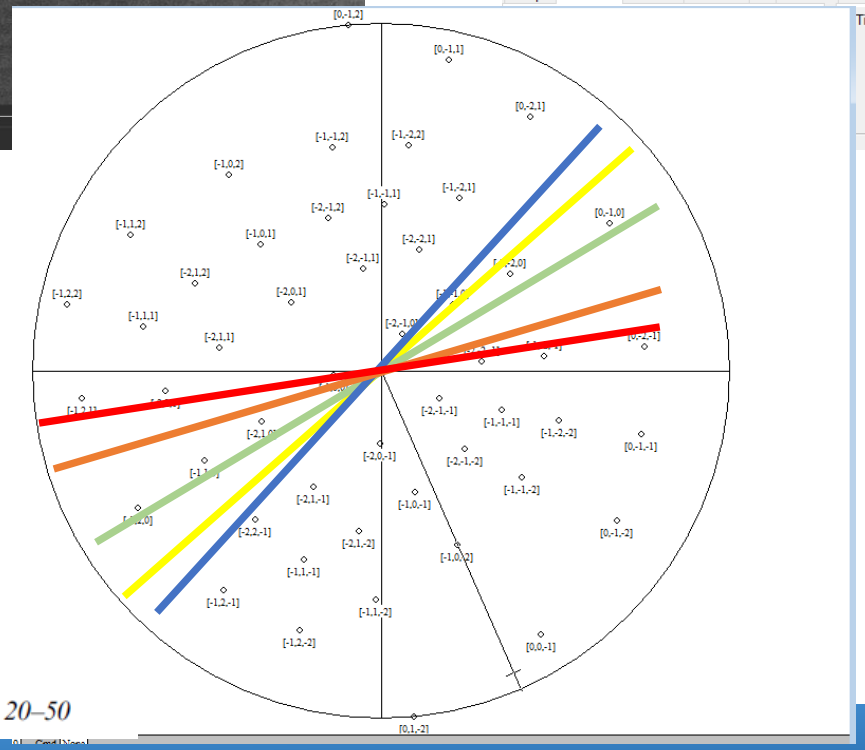
1. We milled round columns at both sides of a GB : in LGr and RGr.
2. We acquired ECCIs at the column walls while rotating a FIB stage (360 deg = full circle) and recording ECCIs at all those locations where the dislocation pattern was visible (at constant tilt angle = 52 deg)
3. For each “position of visibility” we identified the grain orientation by simulation of FIB stage movement in TEM holder (we overlaid navigation systems of FIB and TEM).
4. From the grain orientation we found the diffraction conditions, i.e. which g-vectors were excited or which atomic planed were strongly diffracting when dislocation pattern was visible in ECCI.
5. Based on this data we identified the indexes of dislocation lines in ECCIs (we built a stereographic projection, superimposed on it the traces of the dislocation lines visible in ECCIs)
6. The rest was to refine the type of the observed dislocation via calculation of dislocation contrast “$g \cdot b$” for the alternative dislocation types (perfect or Shockley partial) for the known g- vector and possible Burgers vector b .

ECCI image of a column wall in LGr



Orientation of the crystal at this "visibility position





stg rot = -35.4; A=-49.4; B= -38

TBs=**022, 131,**

Dislocation lines: [-1-10]; [-1-2-1]

S. Zaefferer, N.-N. Elhami / Acta Materialia 75 (2014) 20–50

In fcc structure the basic slip direction is along <110> , therefore mobile perfect dislocations in fcc have Burgers vector b = ½ <110>.
An additional type of mobile dislocation in fcc are Shockley partial. They have much smaller value of Burgers vector b= 1/6 <112> and are energetically favorable (in general case of plastic deformation).
For perfect lattice dislocations with b = ½ <110> the dislocation lines have directions :
<110> in pure screw case and <112> in pure edge case.

For Shockley partial with b= 1/6 <112> the dislocation lines are:
<112> in pure screw case and <110> in pure edge case.

S. Zaefferer, N.-N. Elhami / Acta Materialia 75 (2014) 20–50

RGr = 4 cases of dislocation visibility:

#1 U = [112] or [-110] ; perfect edge with b=[1-10] or perfect screw b= [-110]
#2 U = [-2-1-1] perfect edge b=[011]
#3 U = [-1-1-2] or [1-21] Shockley partial screw b = [-1-1-2] or [1-21]
#4 U = [-11-2] equally possible perfect edge b=[110] and Shockley partial screw b=[-11-2]

LGr = 11 cases of visibility; non-equivalent - 8, 1 pair of mirrored

#1 U =[-1-10] equally possible perfect screw b=[-1-10] and Shockley partial edge b=[1-12]
#2 U =[112] perfect edge b=[1-10]
#3 U=[-101] equally possible perfect screw [-101] and Shockley partial edge b=[121]
#4 U=[-211]; perfect edge b=[01-1]
#5 U=[-211]; perfect edge b=[01-1]
#6 U = [011] Shockley partial edge b=[21-1]; U= [112] equally possible perfect edge b=[1-10] and Shockey screw b =[112]
#7 U = [011] Shockley partial edge b=[21-1]; for U=[211] perfect edge b=[01-1]
#8 U =[-1-10] equally possible perfect screw b=[-1-10] and Shockley partial edge b=[1-12]

Q2. Which dislocations compose the observed system(s)?
RGr – perfect edge and Shockley partial screw ; LGr - perfect edge and Shockley partial edge and
Q2. How many such systems present simultaneously in a single grain/crystal? -
LGr - perfect edge b=[01-1] - a single dislocation system ?

Attribution of the dislocations: are they lattice dislocations or GB dislocations of domain boundaries?

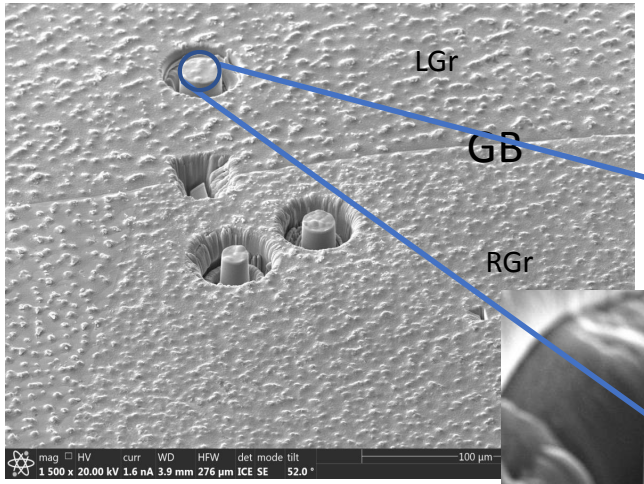
We analyzed soft Cu, the grains are ~500 µm = a high probability for domain boundaries to present

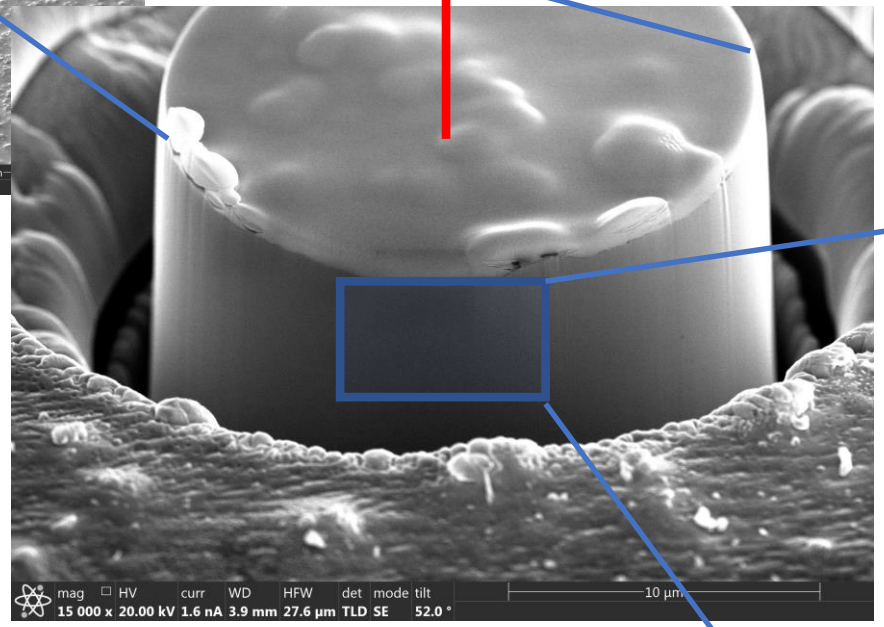
Σ	Generation	*b* from DSC-lattice
1	"Small-angle GB"	a/2 <110>, possibly split into partials
3	Twin	a/6 <112>, a/3 <111>
5	37° around <100>	a/10 <130>
9	39,9° around <110>	1/18<114>, 1/9<122>, 1/18<127>,
19	26,5° around <110>	a/38 <116>, a/19<133>, a/19 <10,9,3>
41	12,7° around <100>	a/82<41,5,4>, a/82<910>, ...

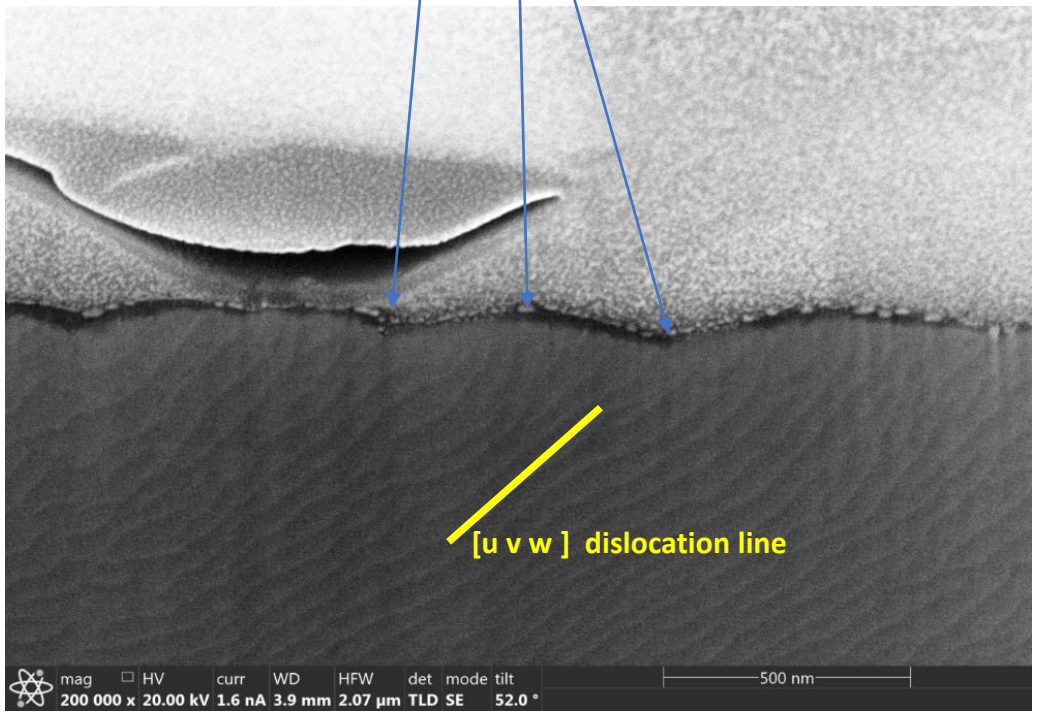
immobile

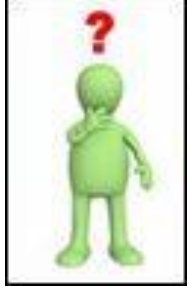
https://www.tf.uni-kiel.de/matwis/amat/def_en/index.html

The dislocations and the terraces



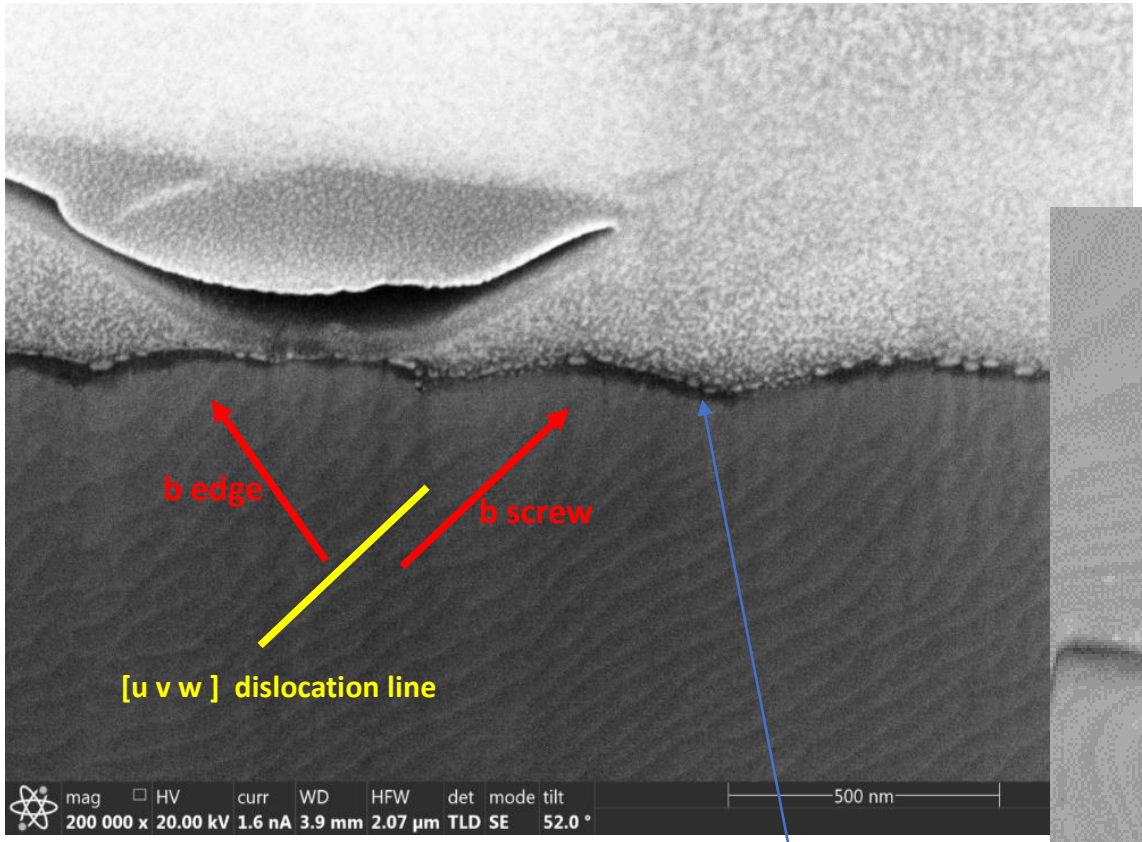


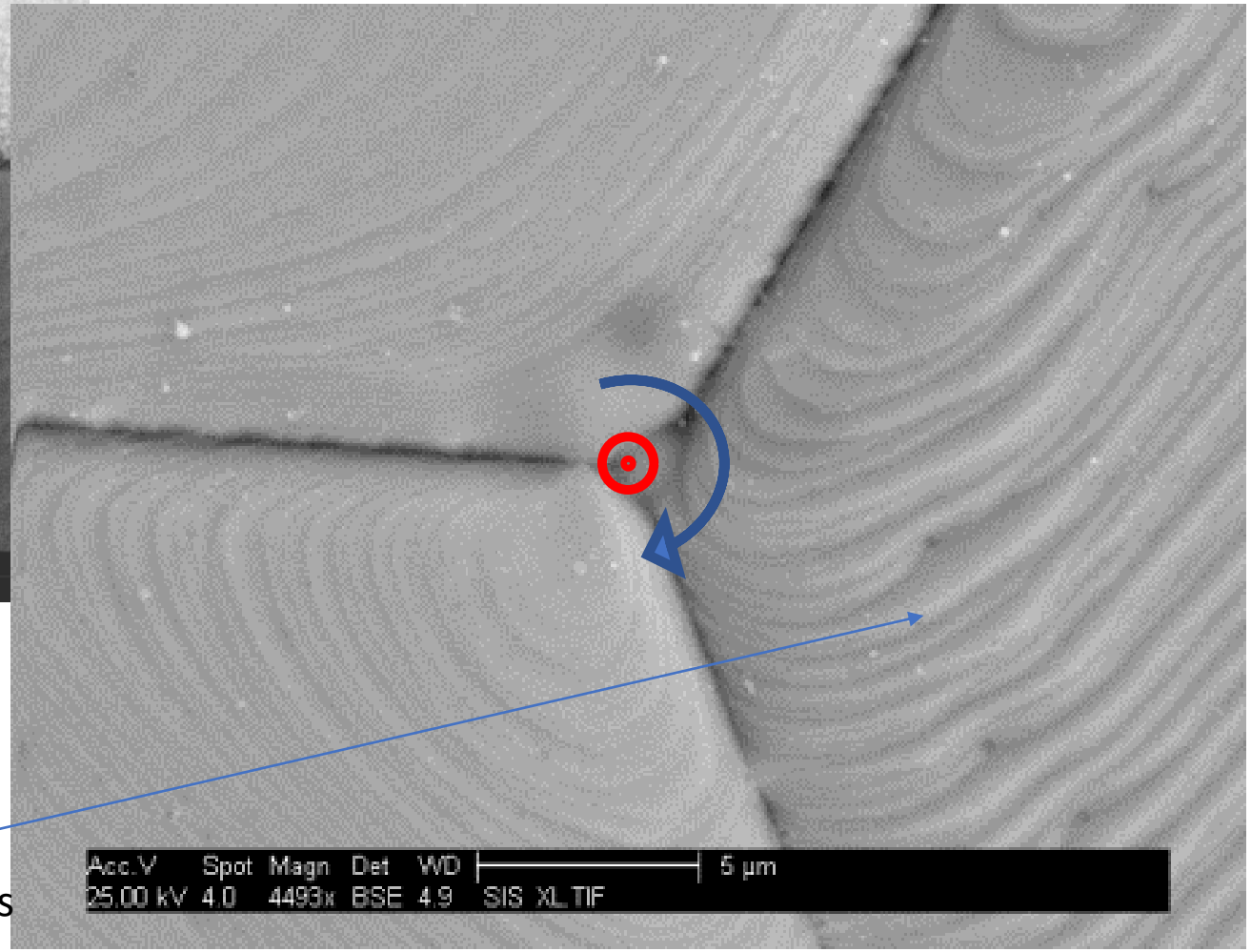




The images are taken at 52 deg tilt

The dislocations and the terraces; b indicates the direction of shift = dislocation movement to the surface

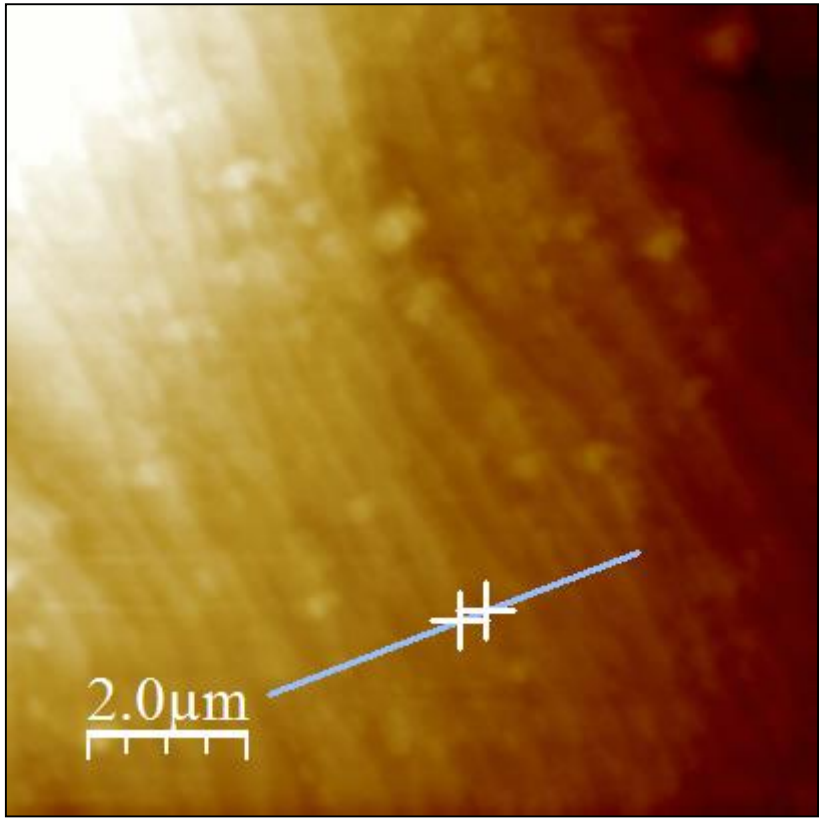




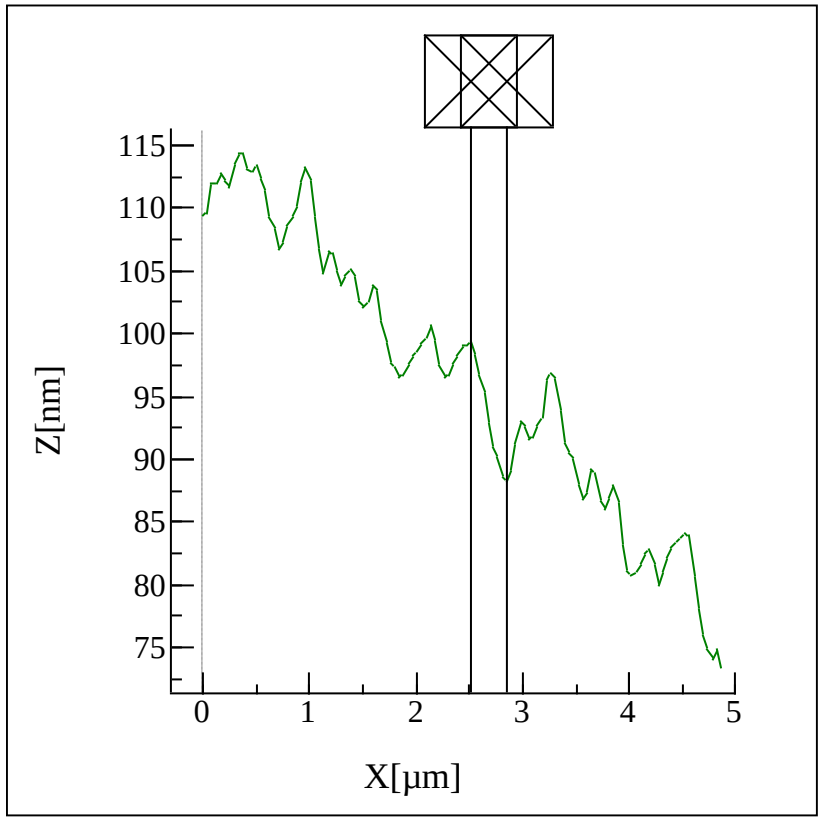
The large surface terraces = movement of dislocations towards the surface + heating at pre-melting temperature

the terraced sample surface is observed at 0 deg tilt

AFM: Line Scan of the Topographic Image



dZ=11 nm

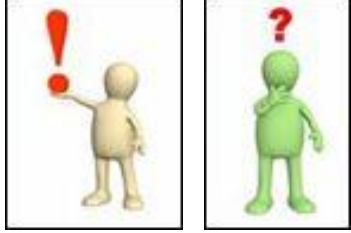


The unit shift provided by a single perfect dislocation with b=1/2 <110> is 0.5x2.556 = 1.278 A
11 nm = 110 A = ~ 100 dislocations should relax to the surface to produce 11 nm high terrace;
in the case of b=1/6 <112> = 0.246 A (110 A means ~ 450 dislocations left the surface to produce the 11 nm height terrace)

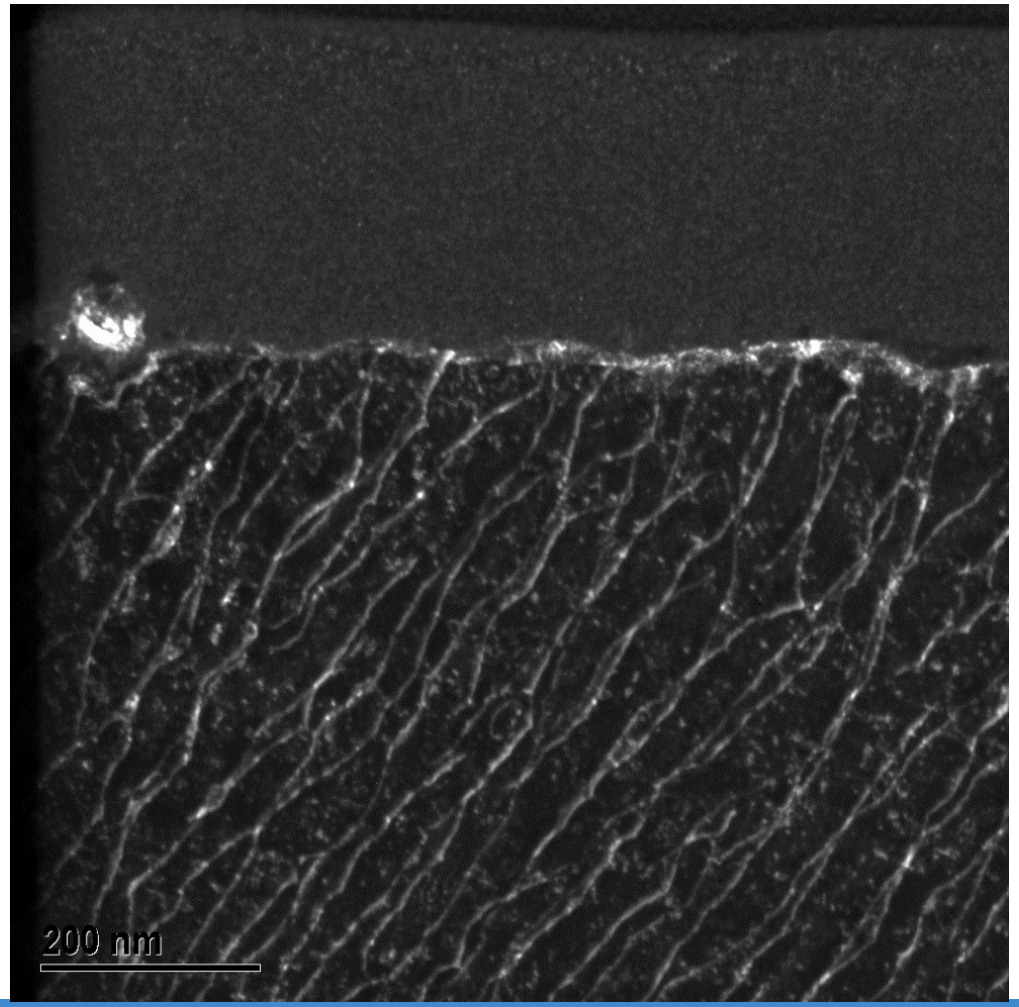
But, we didn't observe the depletion below the surface !

Is there an unlimited source of dislocations ?

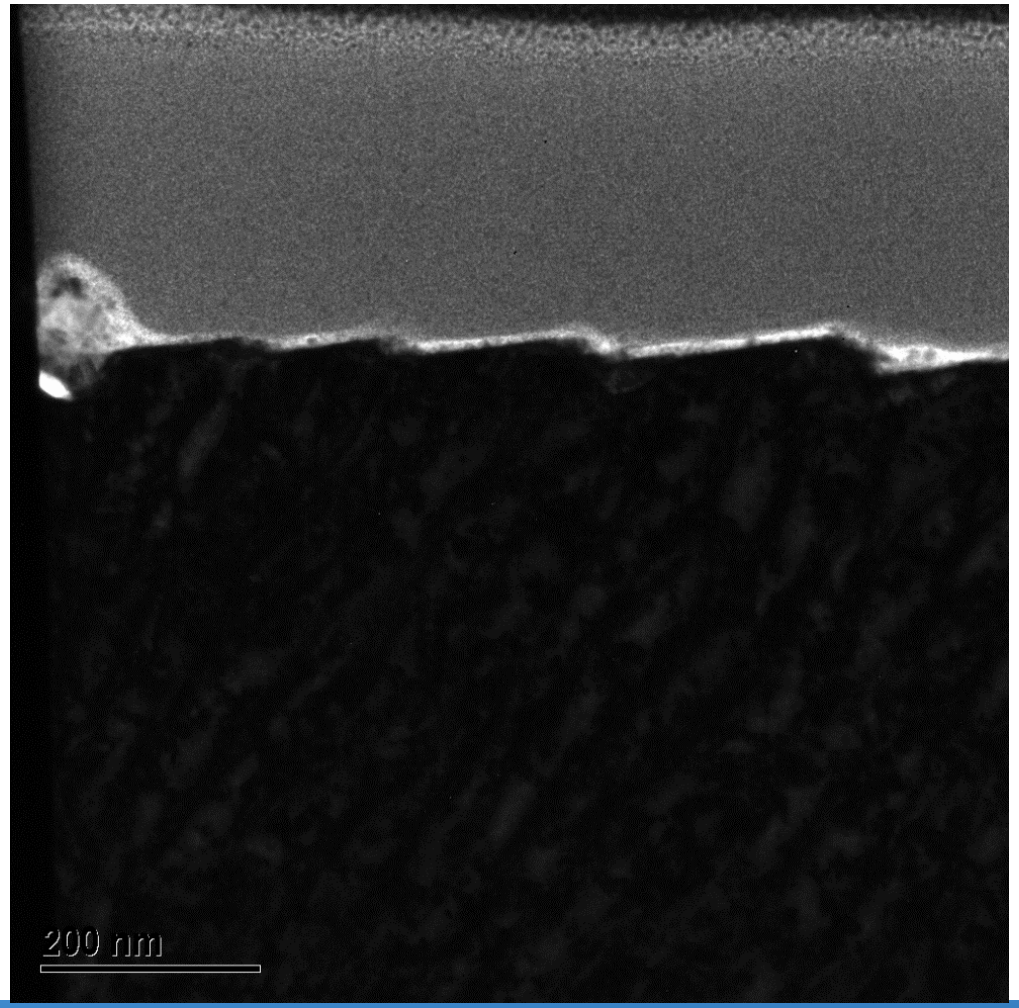
Surface terracing observed in TEM,
no depletion (dislocation – free zone) below the surface



TB WBDF for dislocation visibility

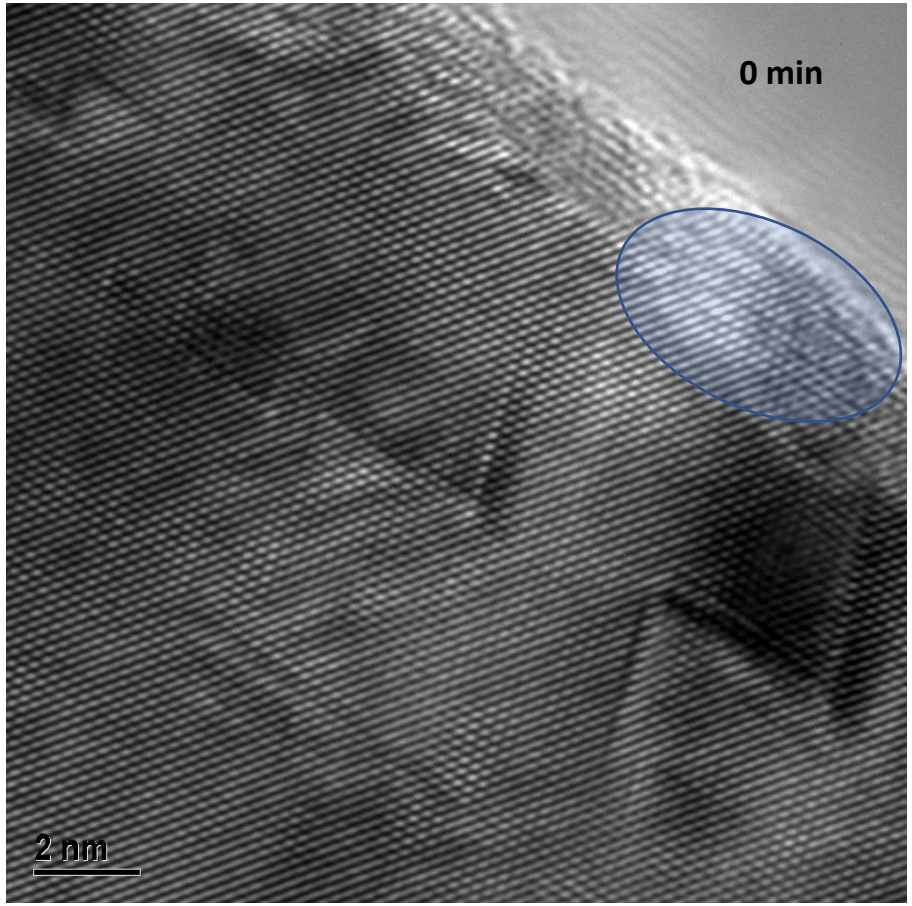


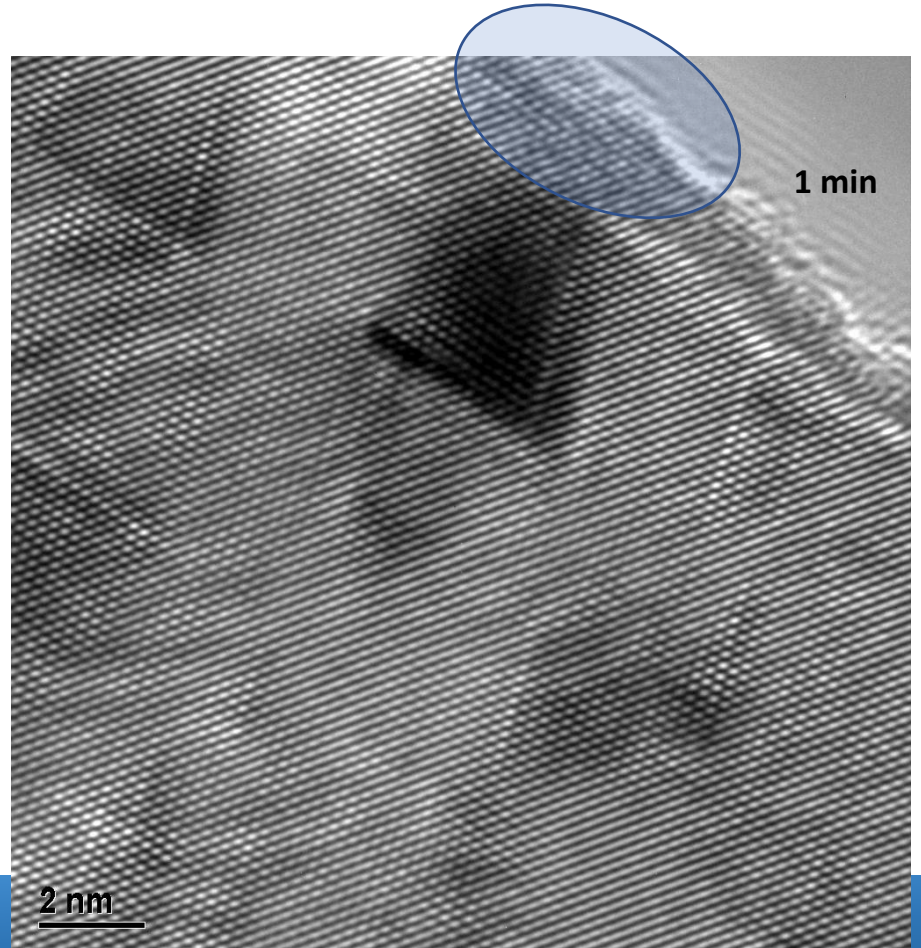
ZA BF for precise terraces' shape and size



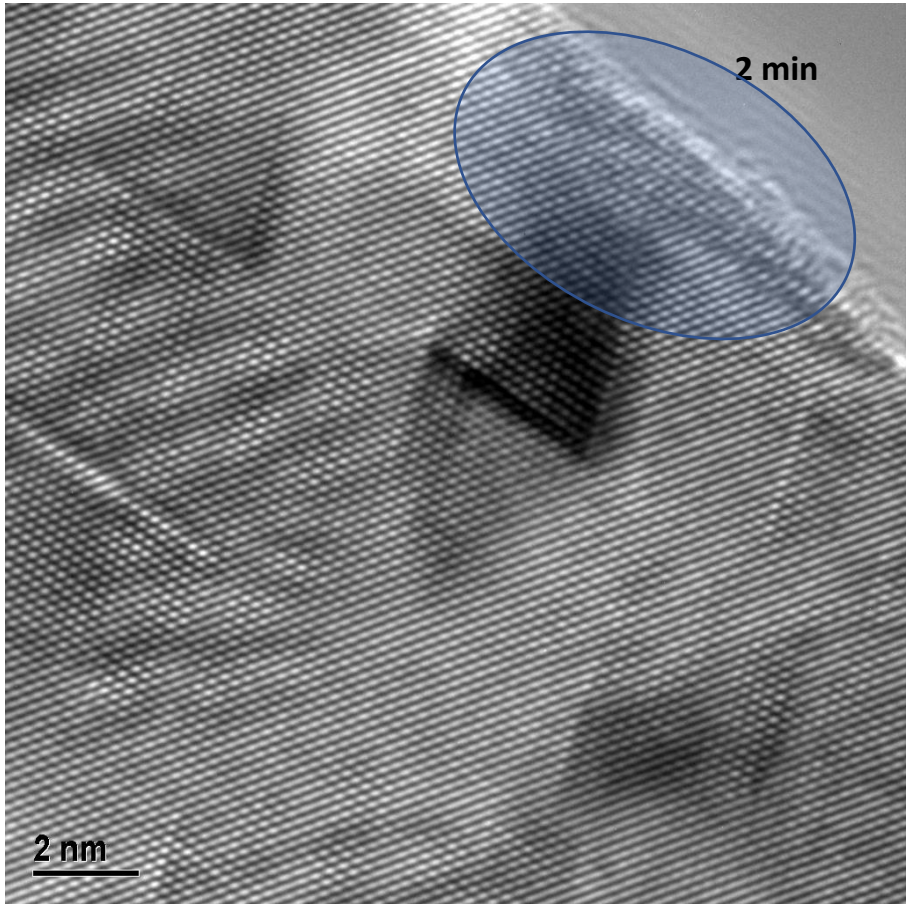
Is there an unlimited source of dislocations ?

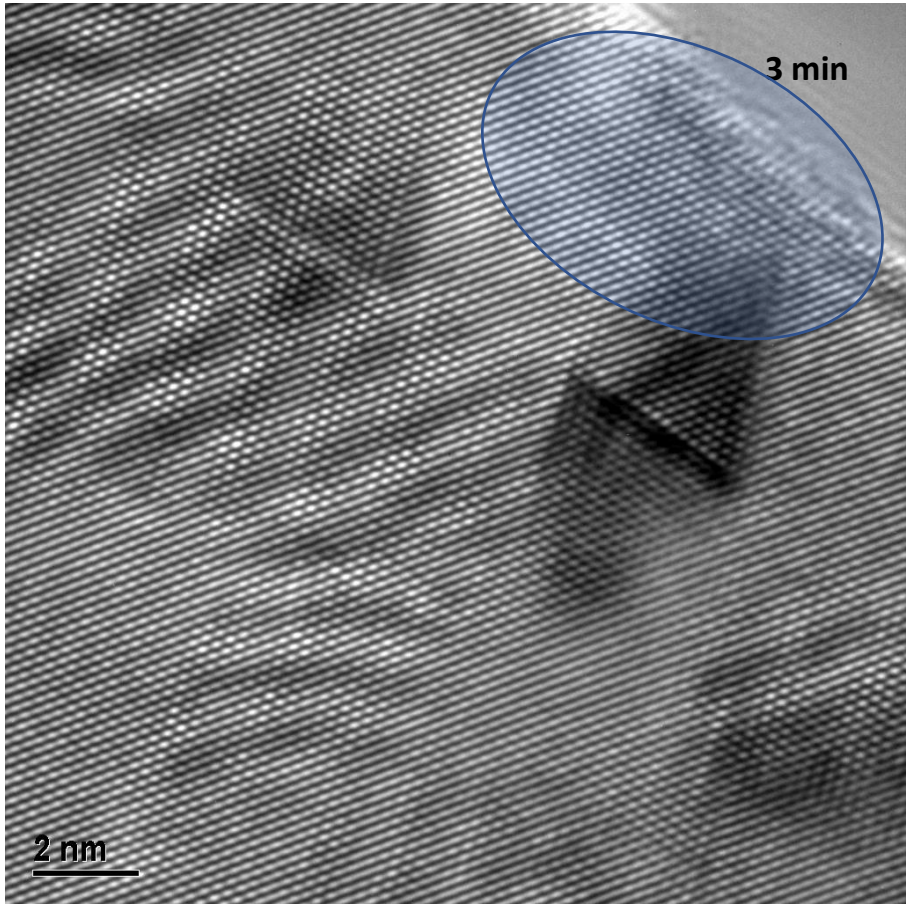
In situ observation : defects relax at free surface



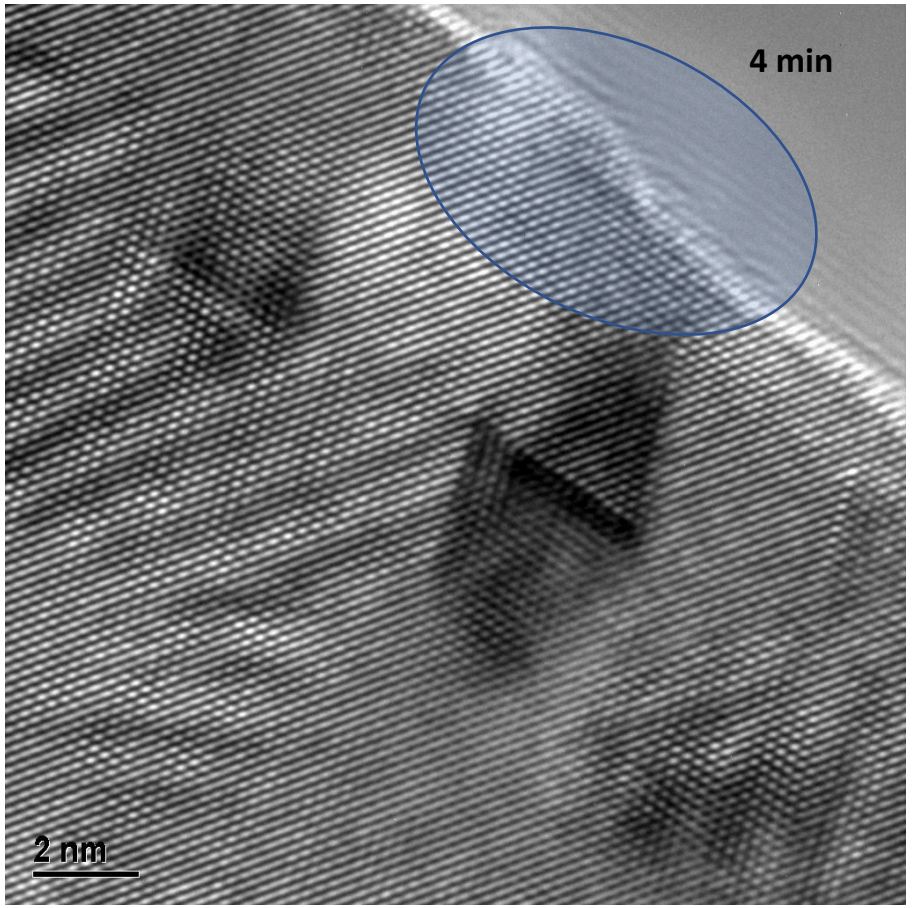


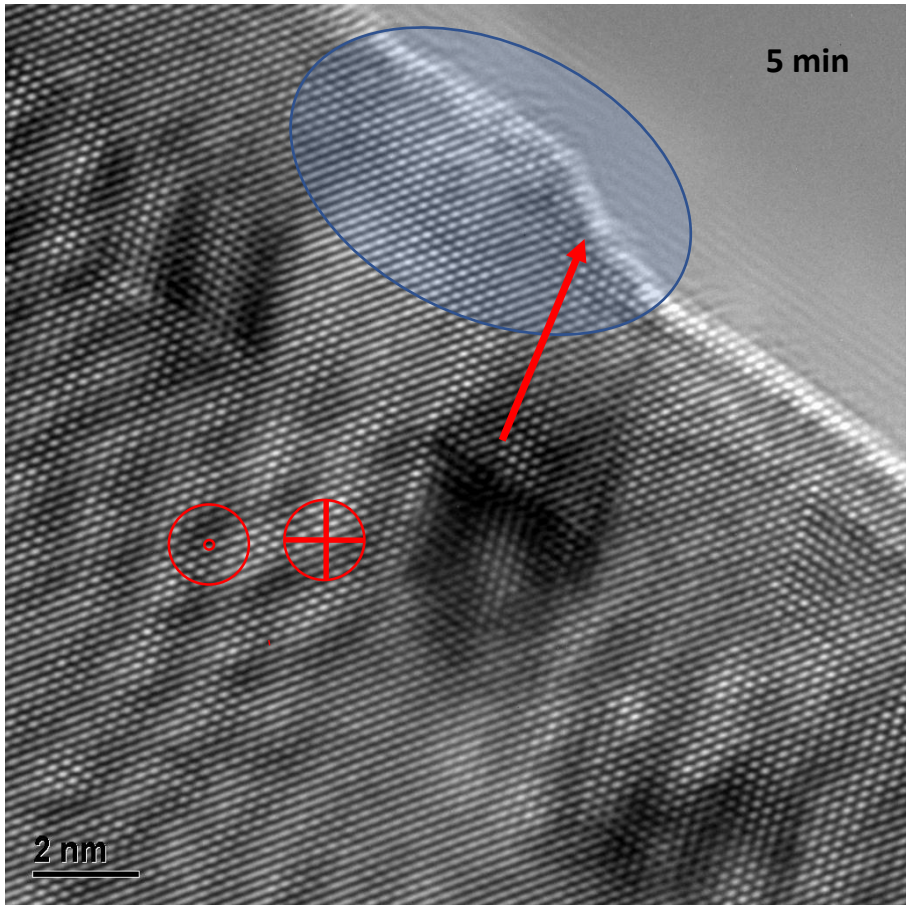
In situ observation : defects relax at free surface





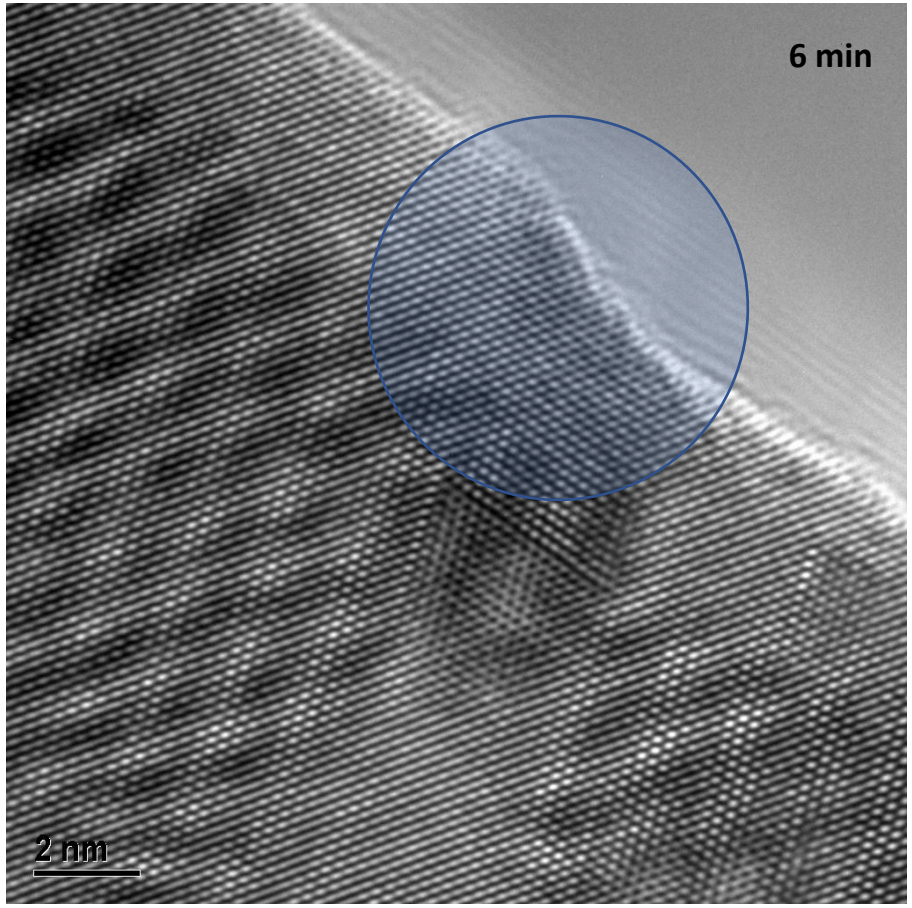
In situ observation : defects relax at free surface

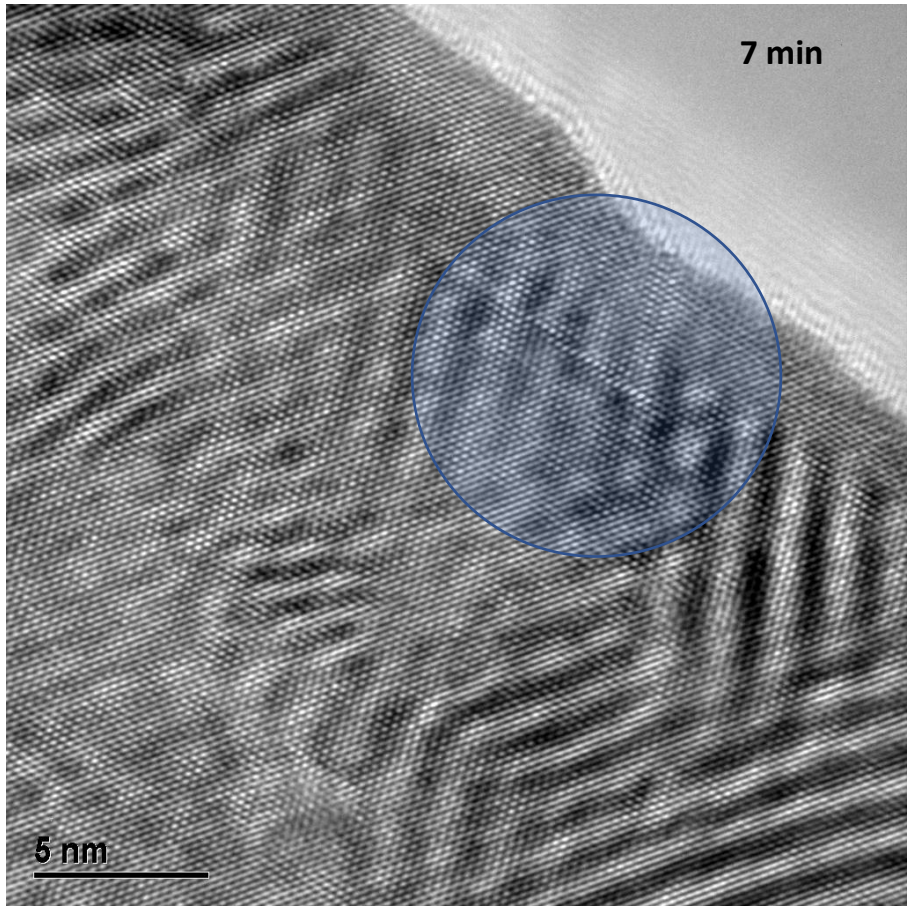




The dislocations relax towards the surfaces in the directions labeled in red (**aside, up and down**)

In situ observation : defects relax at free surface





Conclusion/Suggestion/Question :

Soft Cu has a well ordered self organized dislocation structure (density … and space separation …)
the structure of this array seems insensitive to the high voltage tests

Similar structure is observed in other structural states of Cu and Ag , where the structure appears on the largest “single crystal” length scale (+ published data by others).

The self organized system is related to the polyhedral shape of a crystal, other dislocation systems, grain boundaries (GBs) and surface terracing .

The universality of the observed structure and the fact it is agnostic to the high filed history and conditioning process leads to the proposition that it is not related to the conditioning process.
And that conditioning is the process of removal of other possible sources of breakdown.