Correlative EBIC-EBSD-APT Demonstrate Diverse Role of Grain Boundaries in $Cu(In,Ga)Se_2$ Solar Cells

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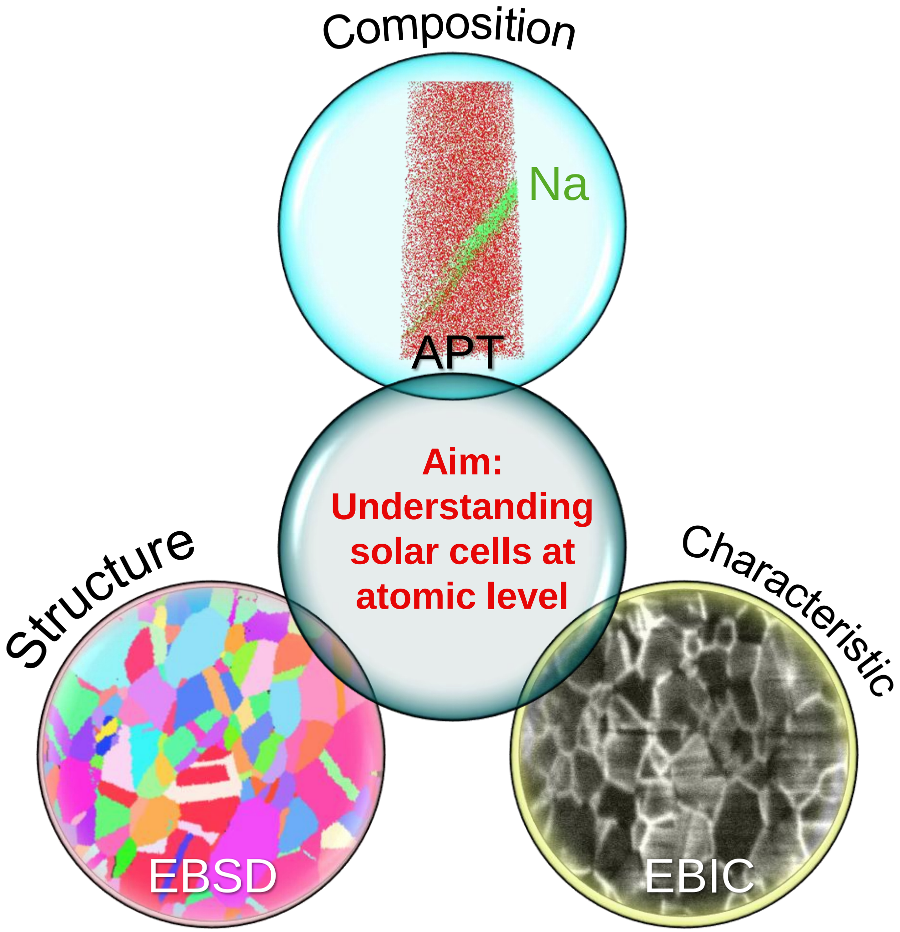

Atom Probe Group

I. Physikalisches Institut (IA) Physik neuer Materialien

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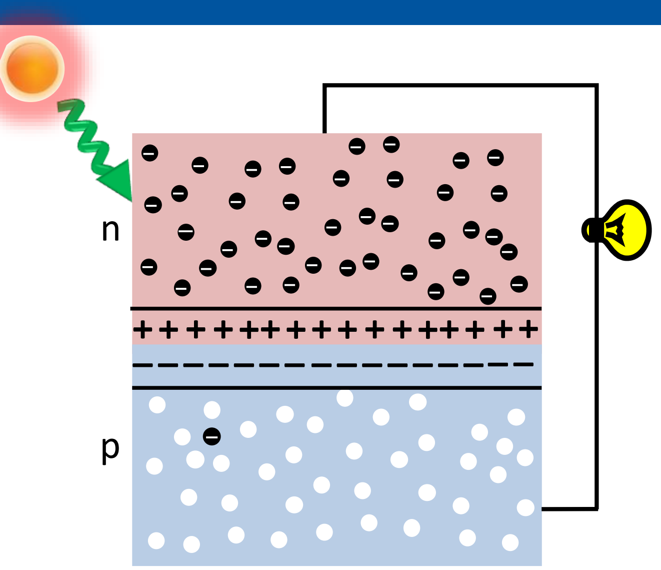
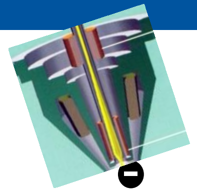
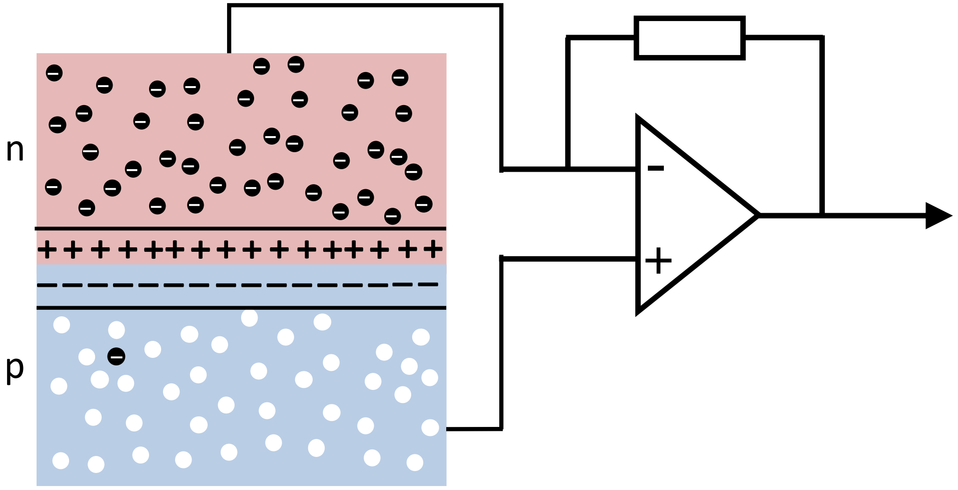
Electron Beam Induced Current (EBIC)



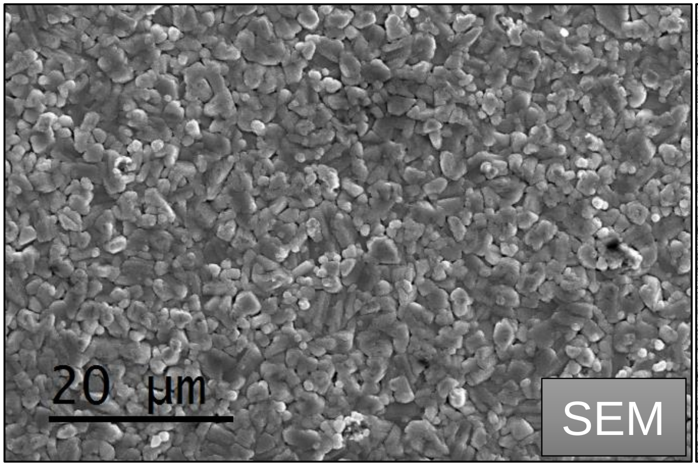


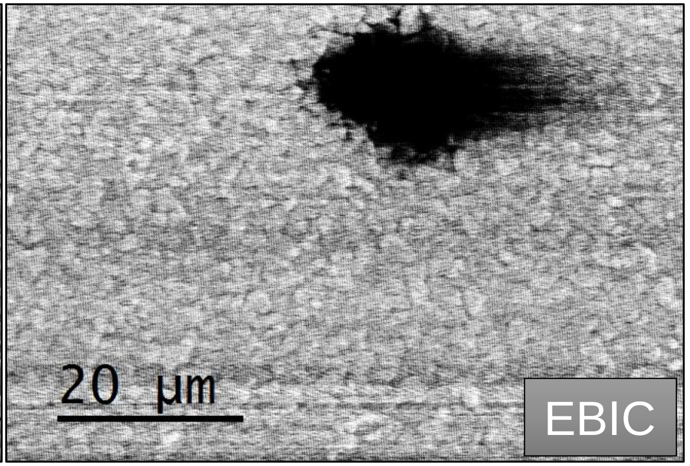


Current at x

Contrast $c(x) = \frac{I(x) - I_0}{I_0}$

$$I_0 = I(x \to \infty)$$

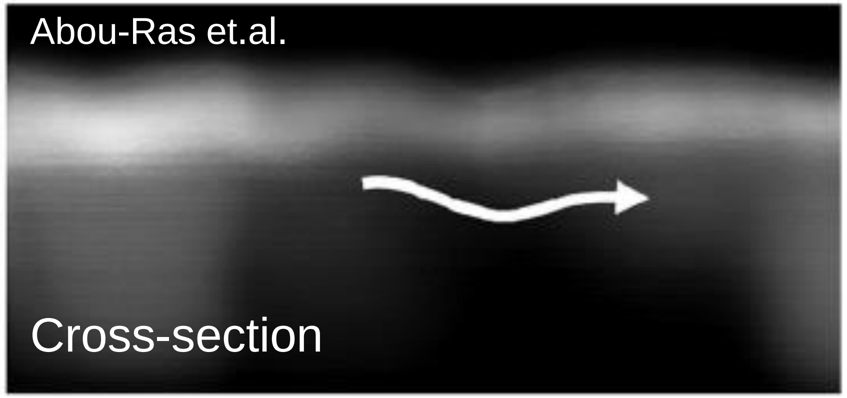


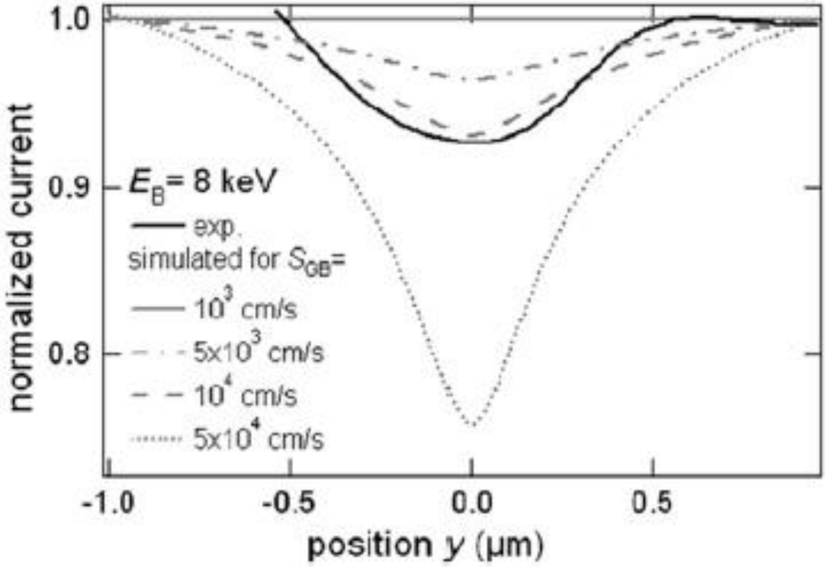


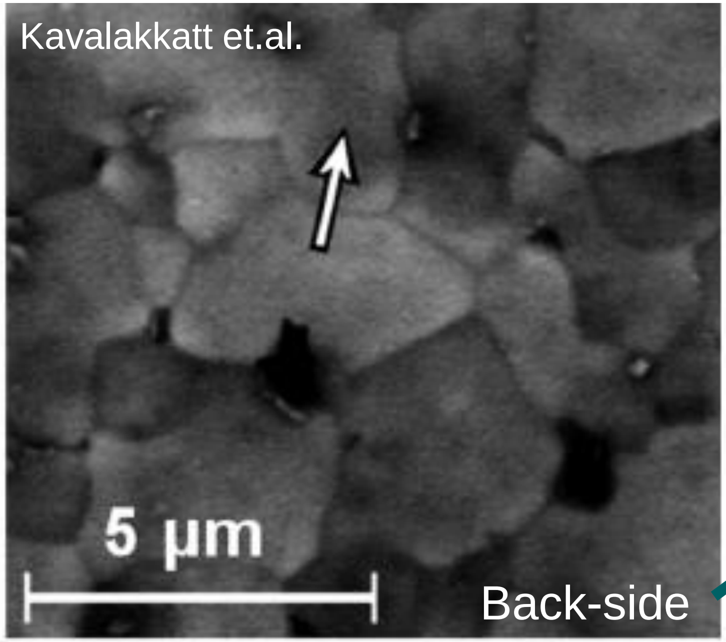
Bright: More current collection
Dark: Less current collection

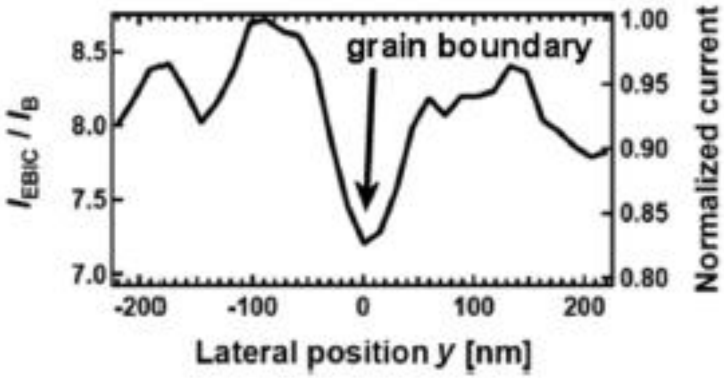
- Using electrons to generate e-h+ pair
- One electron can generate 0 to 1000 e-h+ pair
- e-h+ pairs are collected by an external circuit thus measuring the current

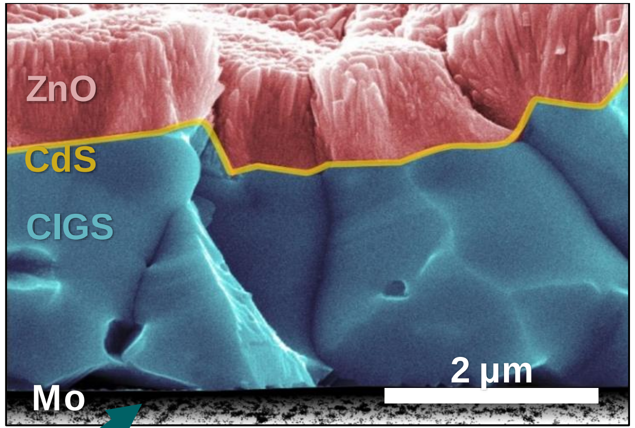
EBIC on CIGS: Previous studies







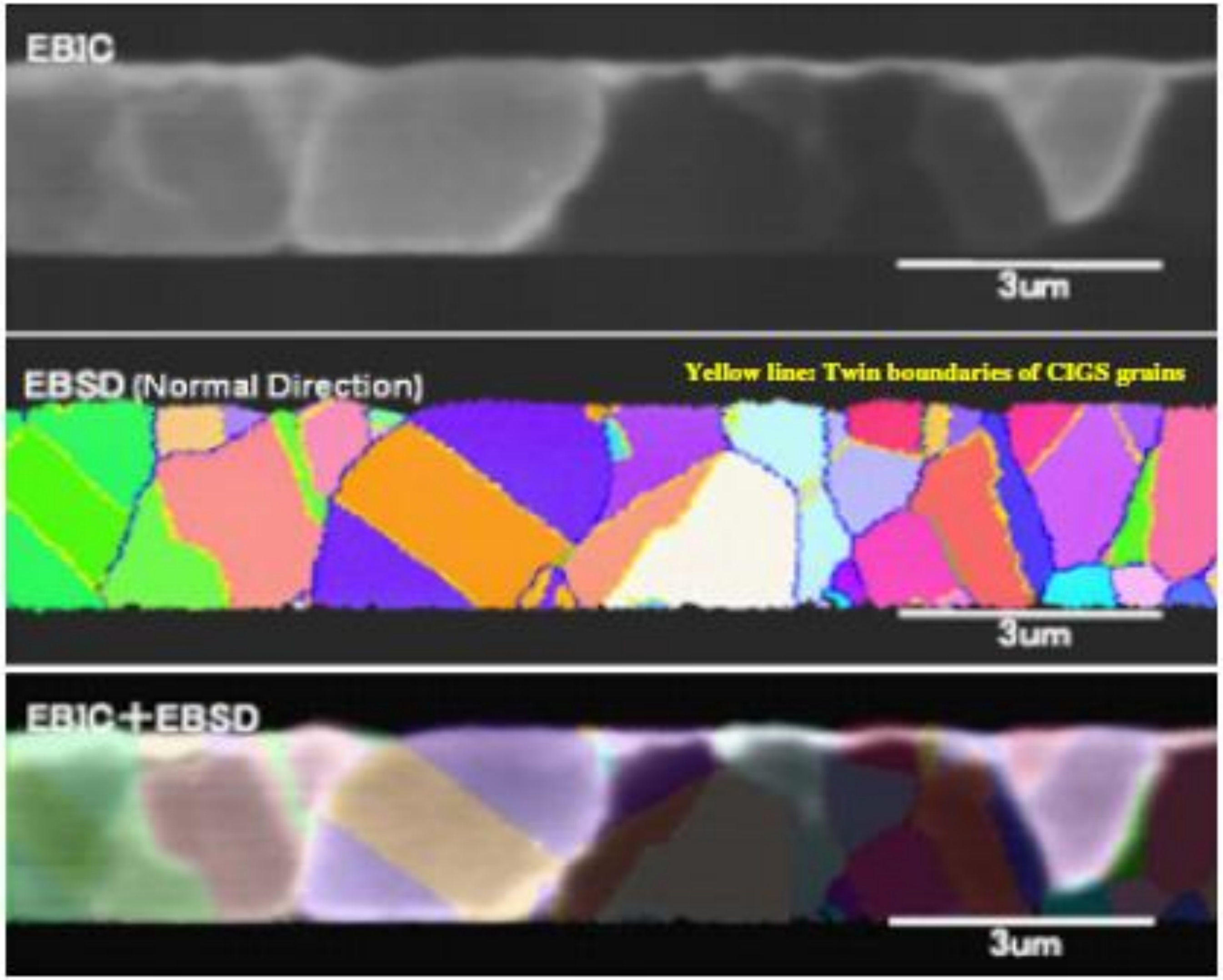




1) Does not explain high efficiency of CIGS in polycrystalline form
2) Back side of CIGS not crucial for solar cell efficiency
3) Only 1-2 GBs in cross section shown

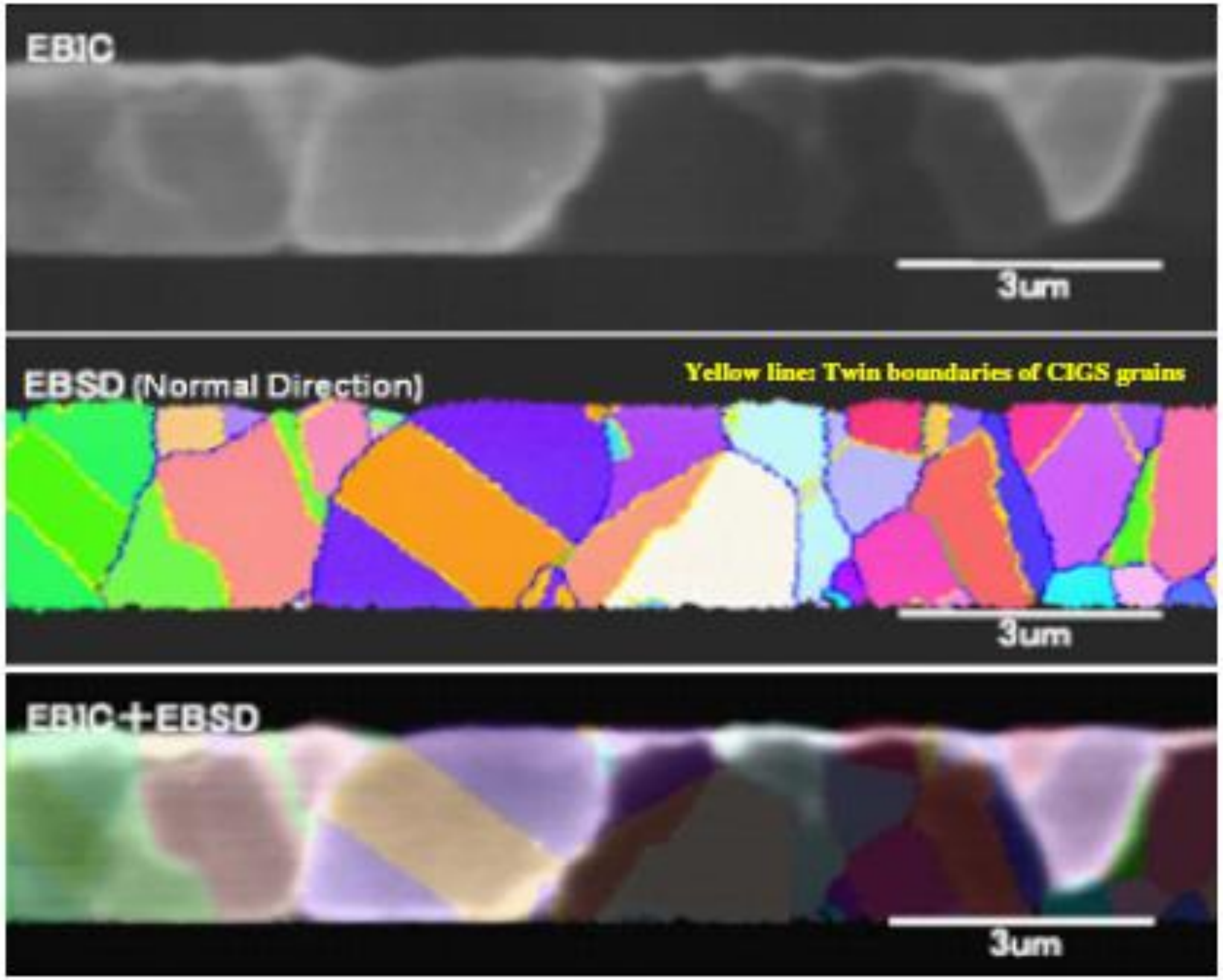
Abou-Ras, et.al Solar Energy Materials and Solar Cells, 95, no. 6 2011
Kavalakkatt et al *Journal of Applied Physics* 115, no. 1 14504, 2014

EBIC on CIGS: Previous studies



Only few GBs in cross section shown

EBIC on CIGS: Previous studies



Only few GBs in cross section shown

Motivation:

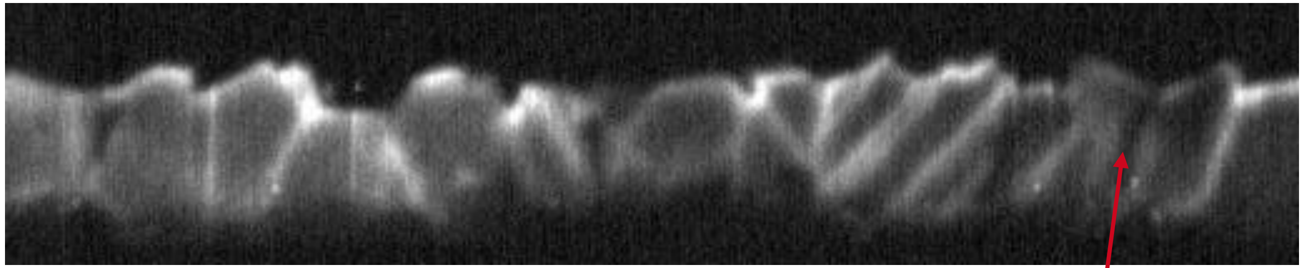
1) Investigate GBs in space charge and middle region

2) Does the GB composition influence the EBIC signal

Kawamura et al, Japanese Journal of Applied Physics 49 (2010) 062301

EBIC measurements on CIGS

Polished Cross-section



Bright means better generation/collection of carriers

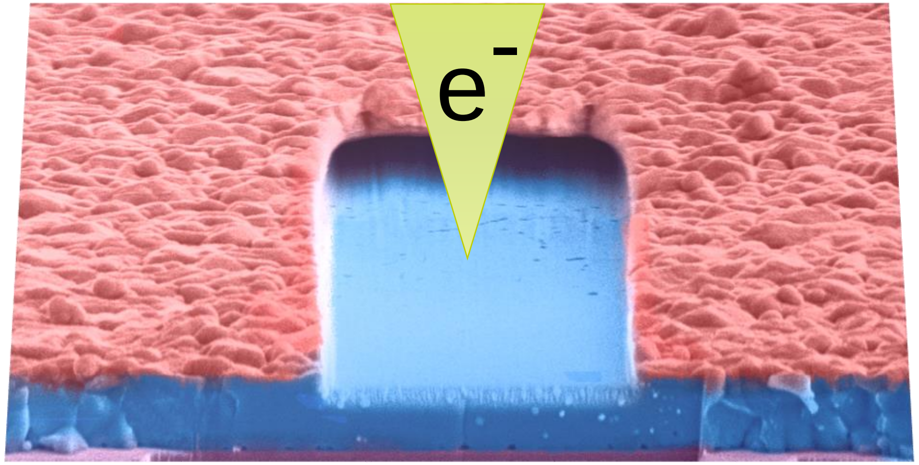
1 260

$$\eta = \frac{I_{EBIC}}{I_{SEM}}$$

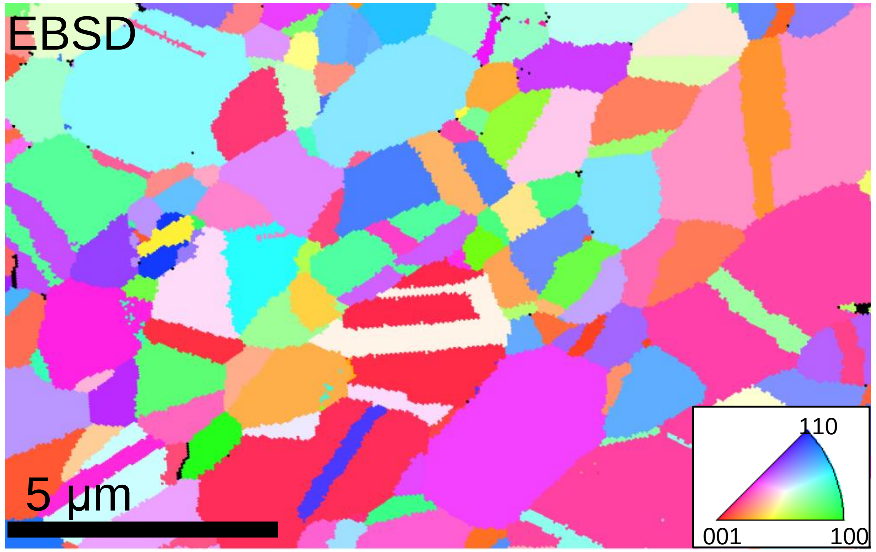
Benign

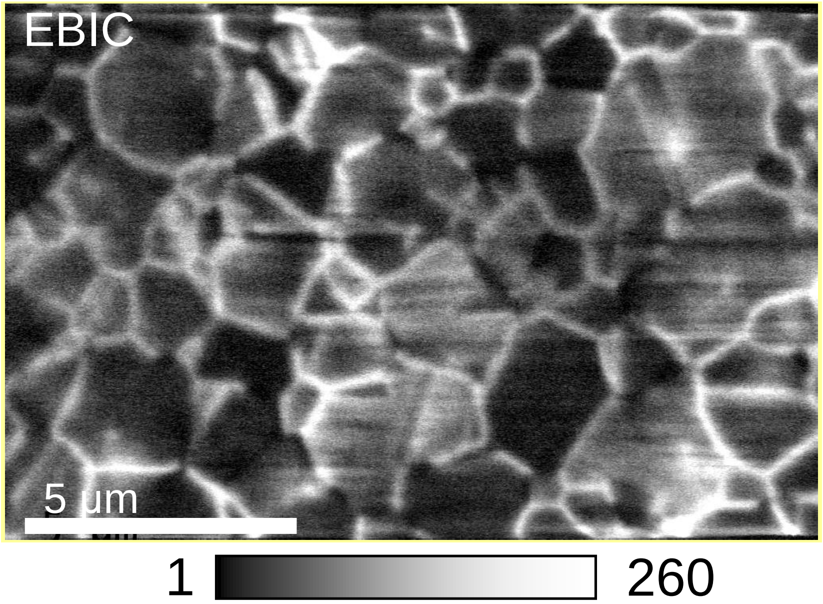
Detrimental

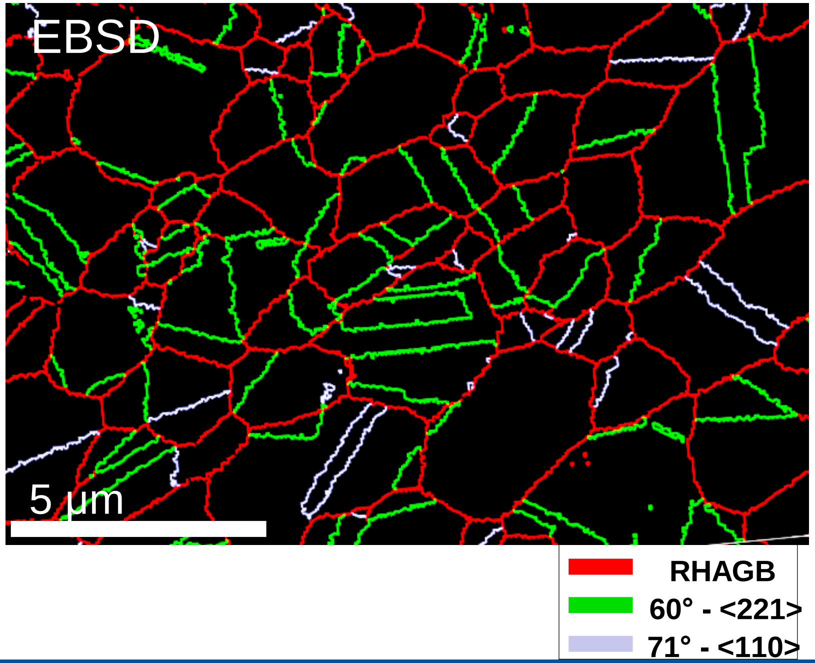
EBIC measurements on CIGS



Bright means better generation/collection of carriers

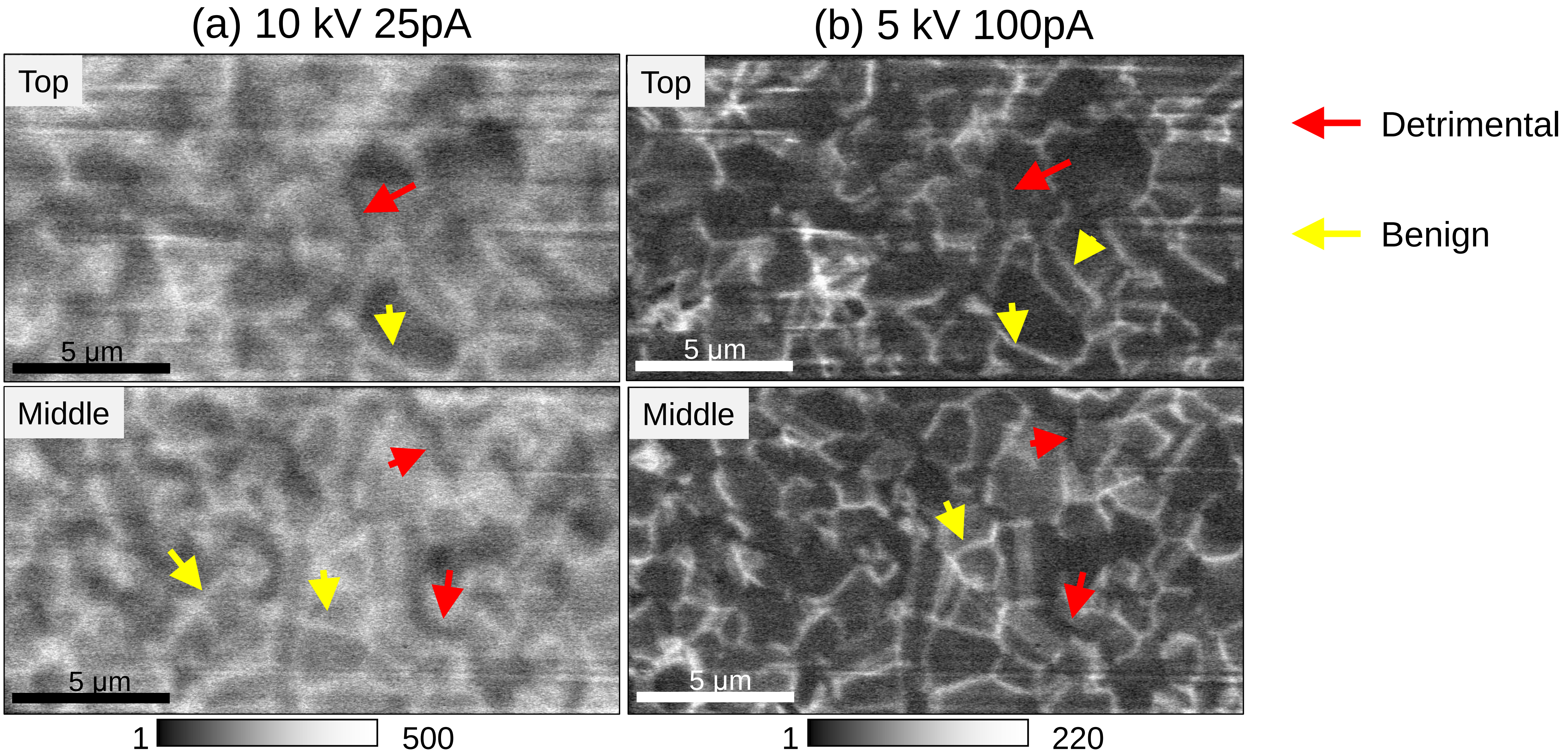






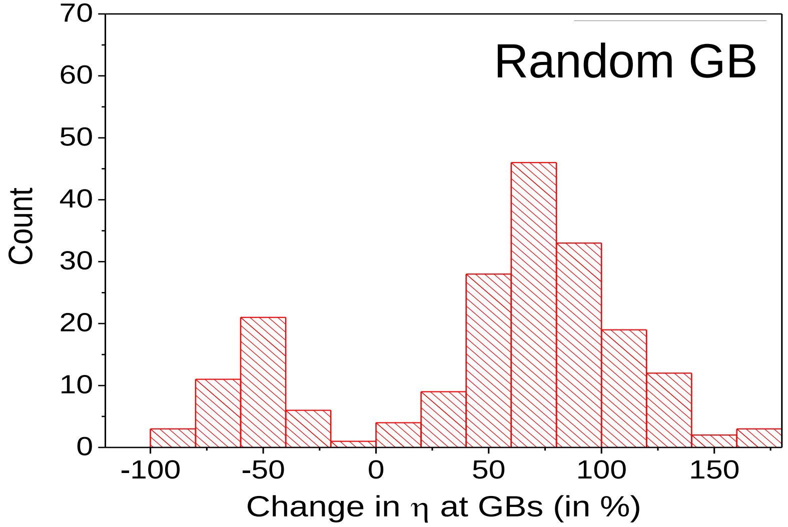
$$\eta = \frac{I_{EBIC}}{I_{SEM}}$$

Influence of injection conditions

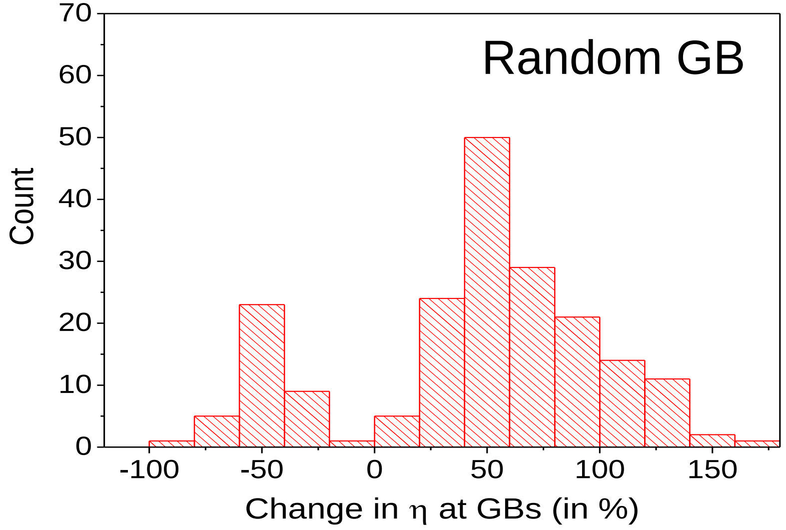


Statistics: change in EBIC current at Grain Boundaries

Space Charge Region



Middle region

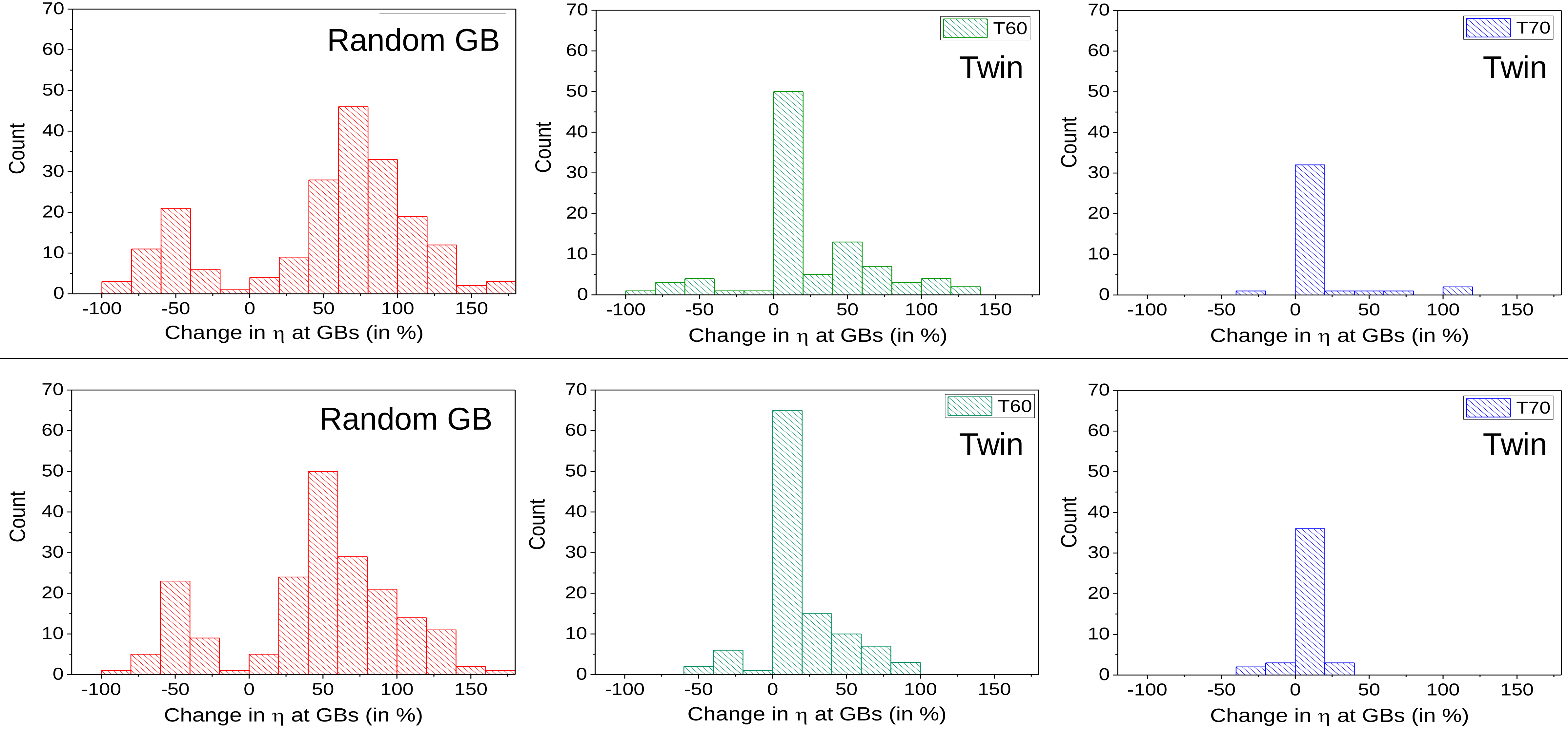


Raghuwanshi et al ACS Appl Mater Interfaces (2018) **10**:14759–14766.

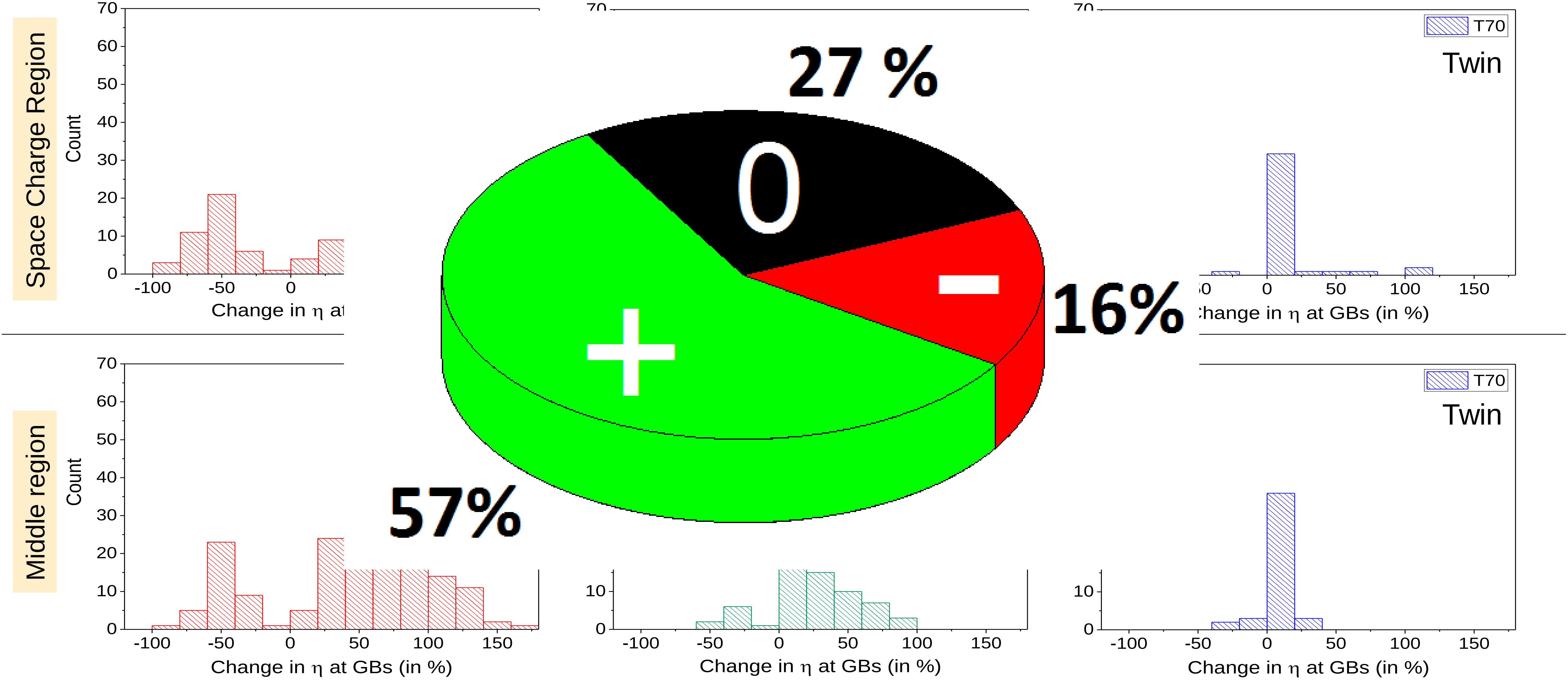
Statistics: change in EBIC current at Grain Boundaries

Space Charge Region

Middle region

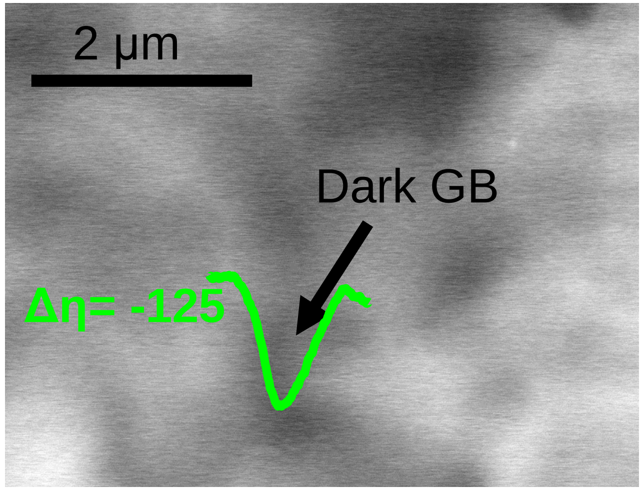


Statistics: change in EBIC current at Grain Boundaries



Raghuwanshi et al ACS Appl Mater Interfaces (2018) **10**:14759–14766.

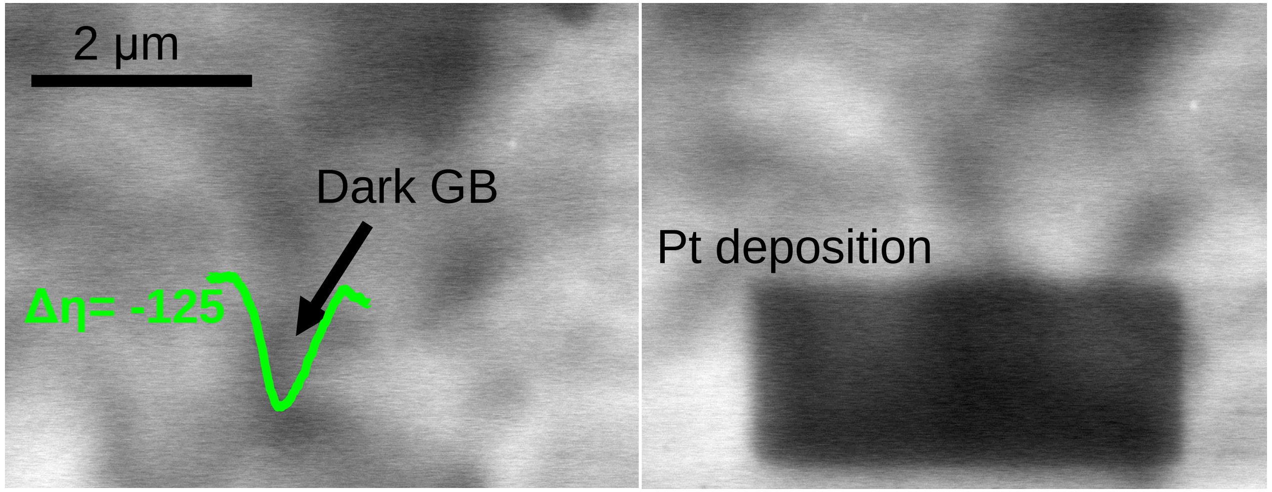
SEM/FIB/Micromanipulator/EBIC/EBSD/APT



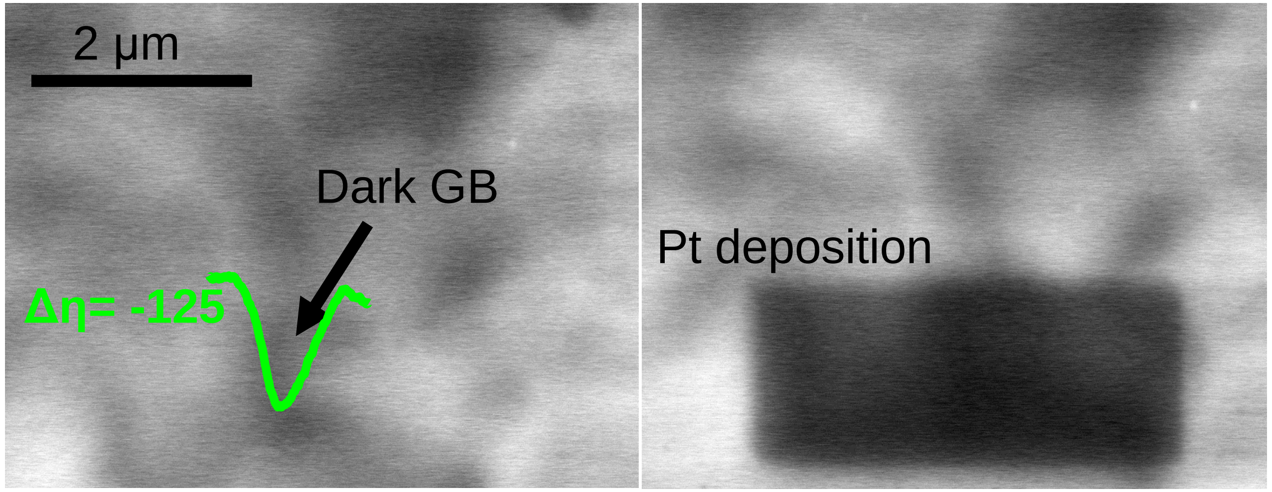
$$\boxed{\eta = \frac{I_{EBIC}}{I_{SEM}}}$$

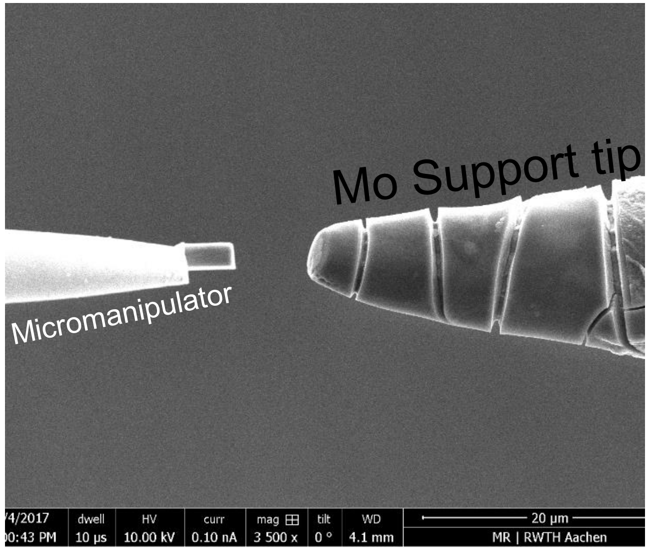
$$\boxed{\Delta\eta = \frac{\eta_{GB} - \eta_{Grain}}{\eta_{Grain}}}$$

SEM/FIB/Micromanipulator/EBIC/EBSD/APT

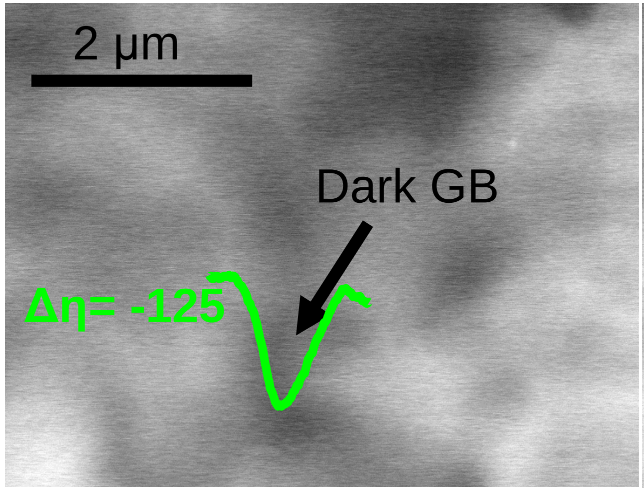


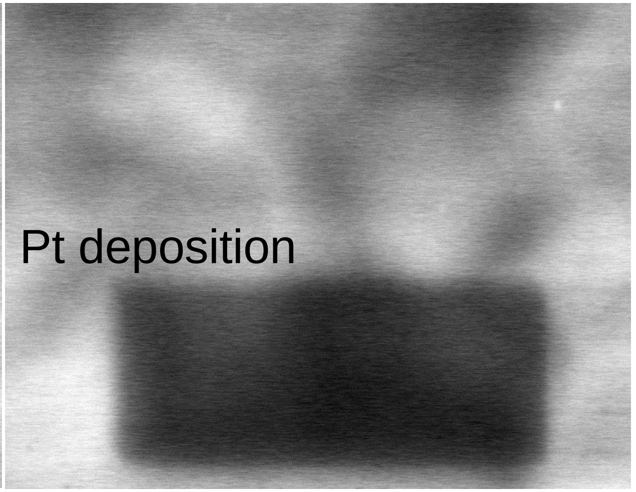
SEM/FIB/Micromanipulator/EBIC/EBSD/APT

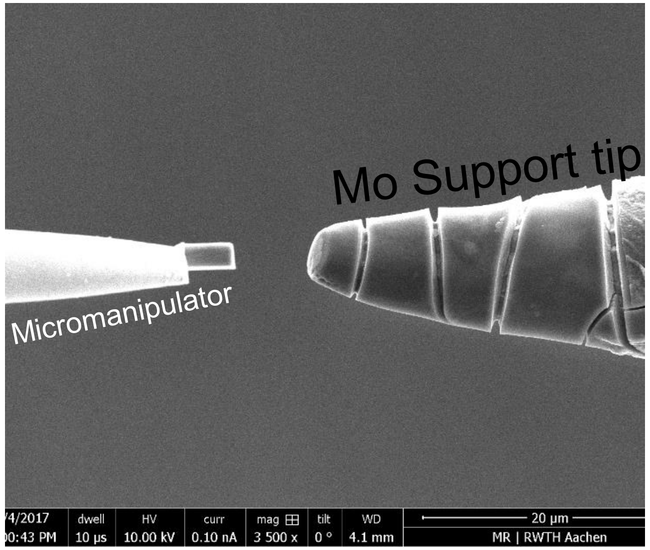


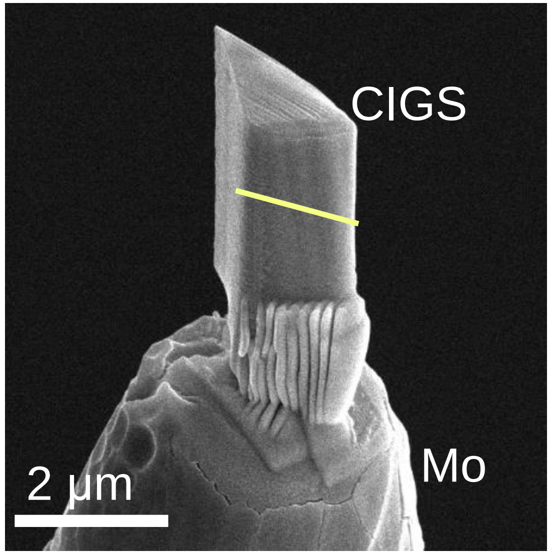


SEM/FIB/Micromanipulator/EBIC/EBSD/APT

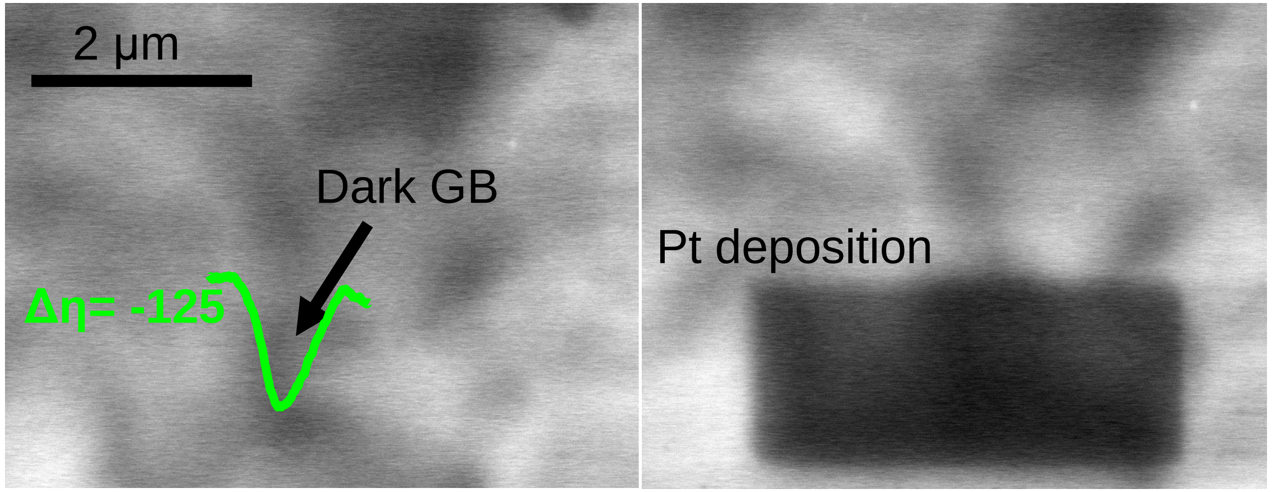


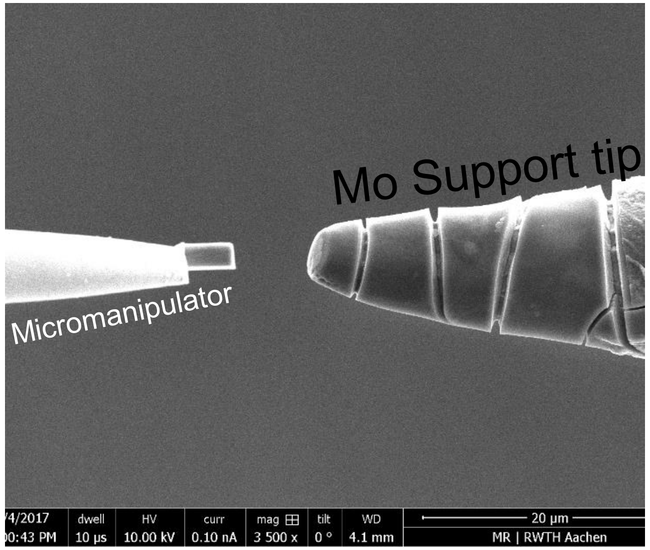


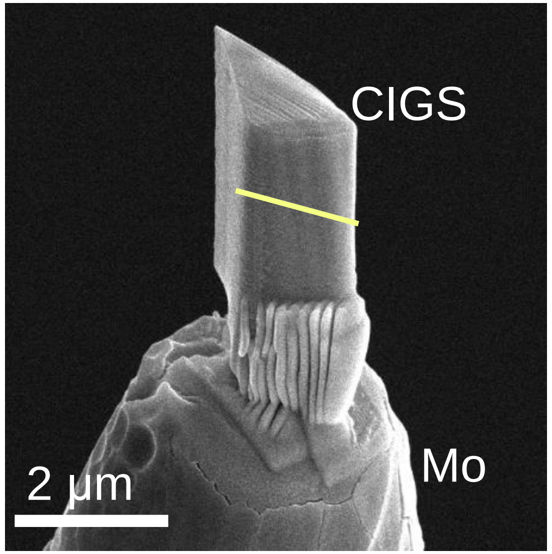




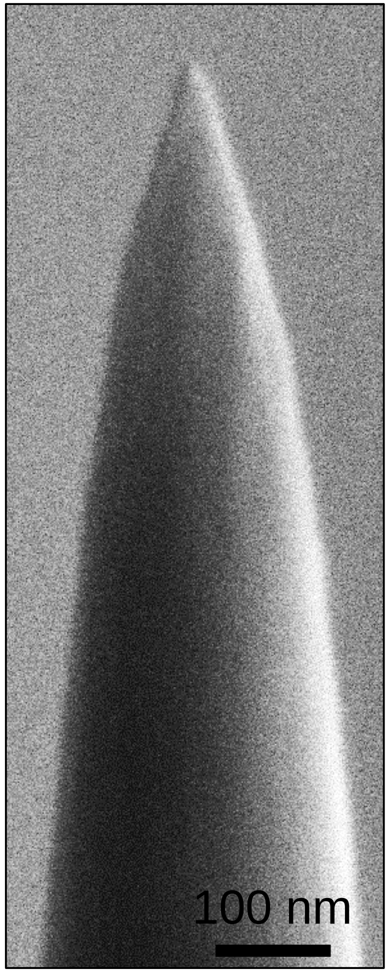
SEM/FIB/Micromanipulator/EBIC/EBSD/APT



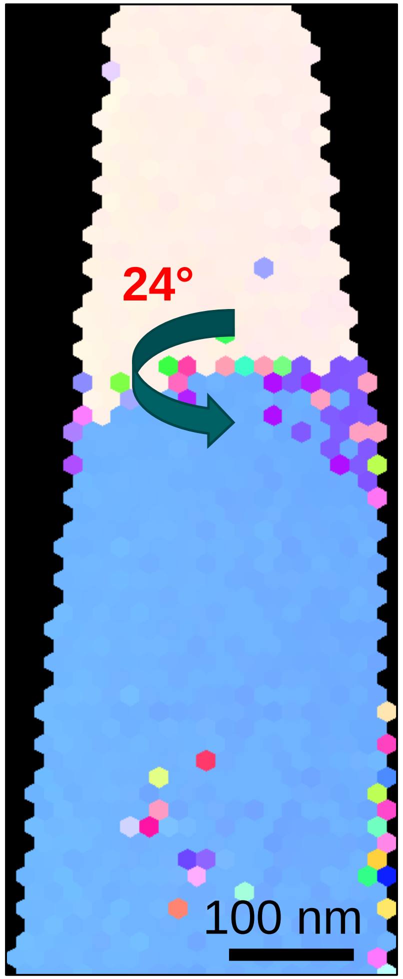




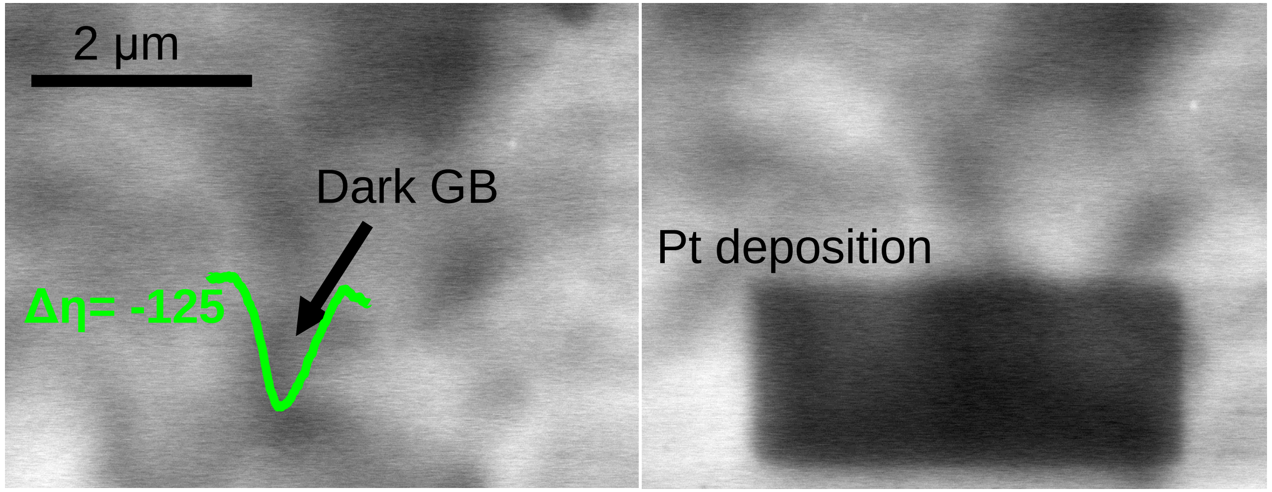
SEM

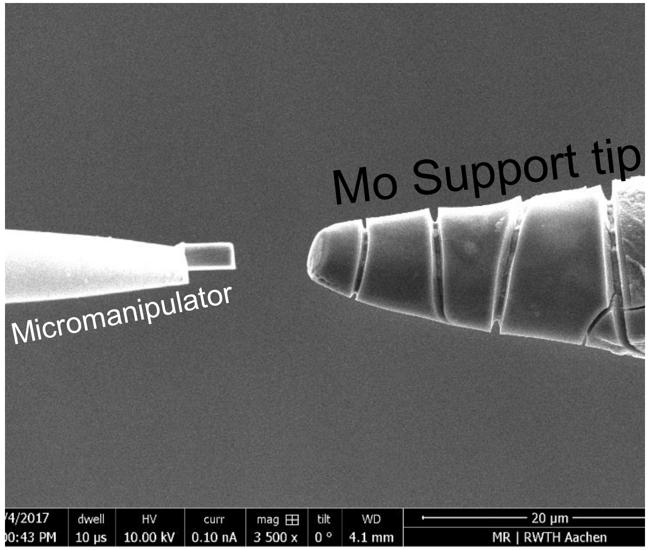


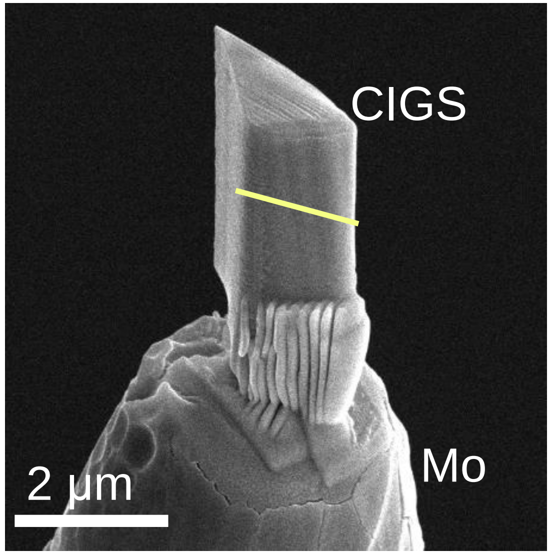
EBSD/TKD



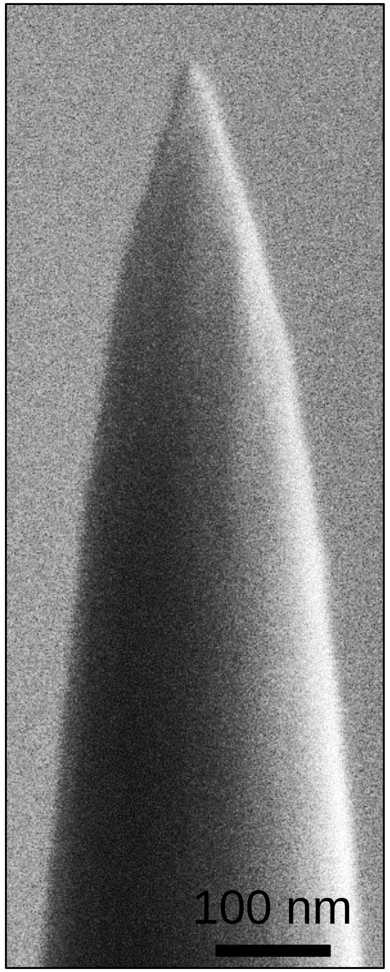
SEM/FIB/Micromanipulator/EBIC/EBSD/APT



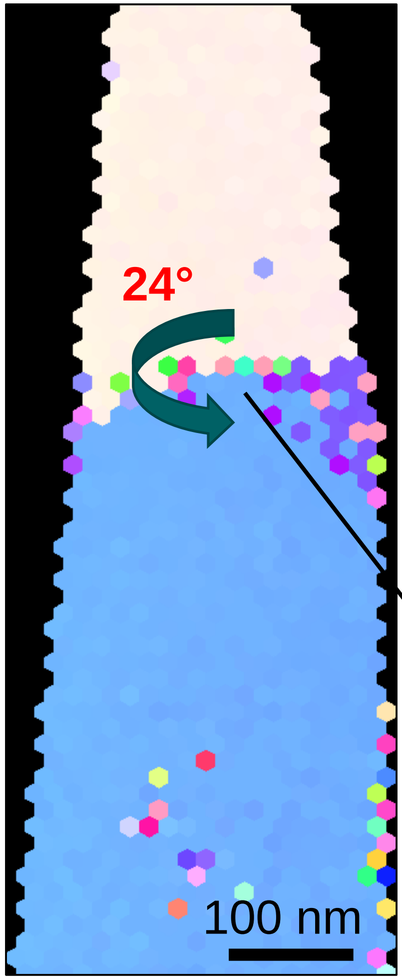




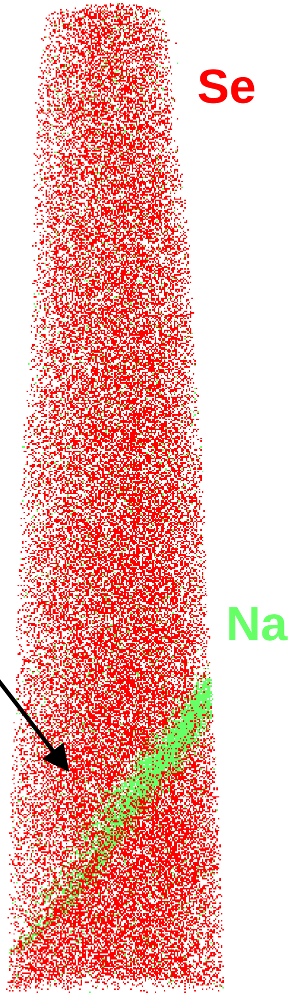
SEM



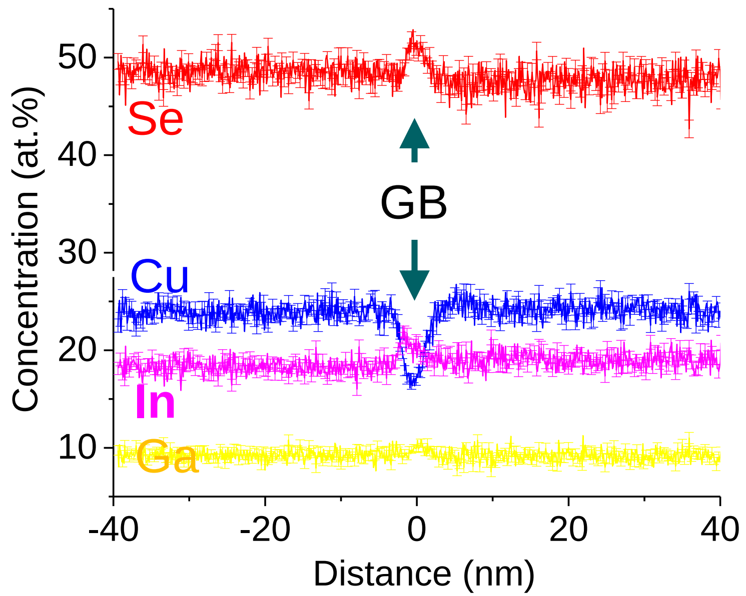
EBSD/TKD

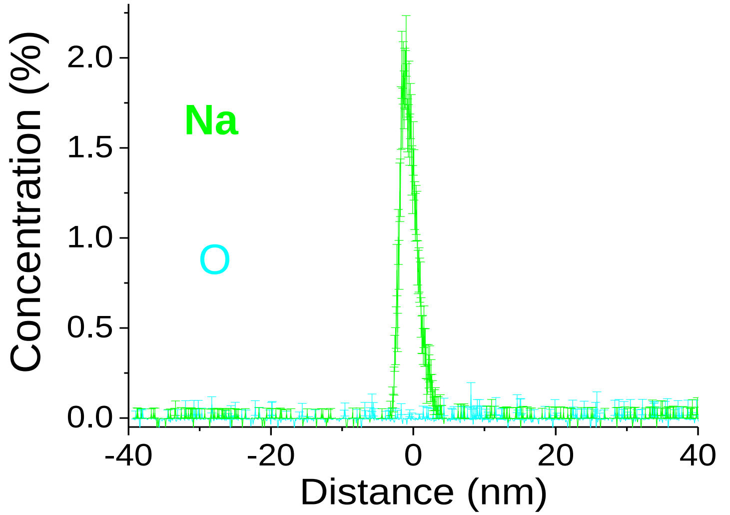


APT



Benign GB



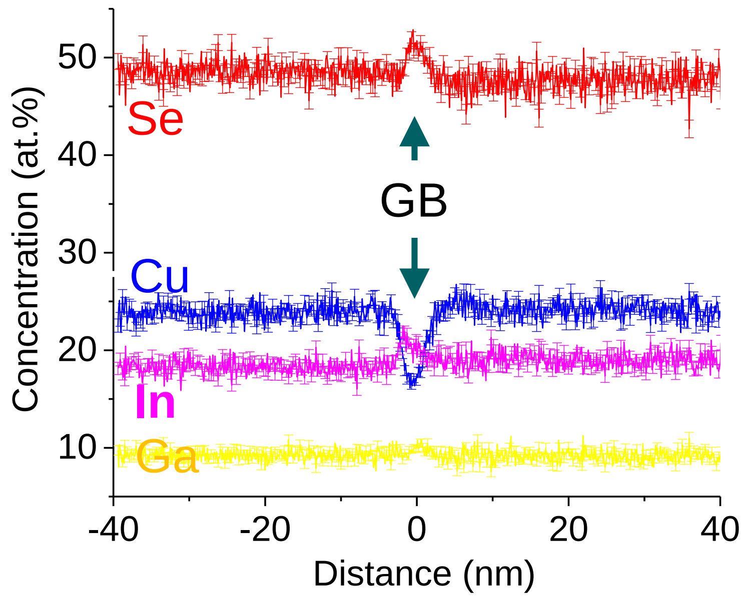


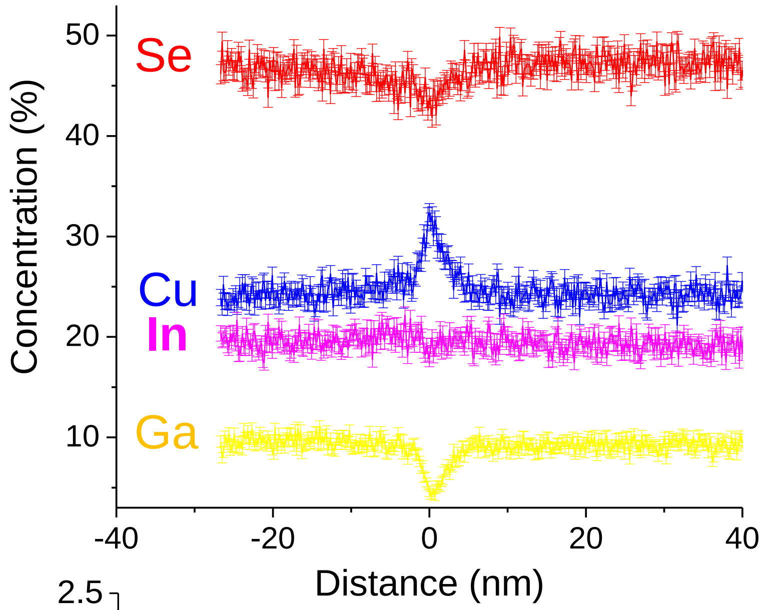
Similar grain boundary profile was obtained on high efficient (21.1% from ZSW) cells[1]

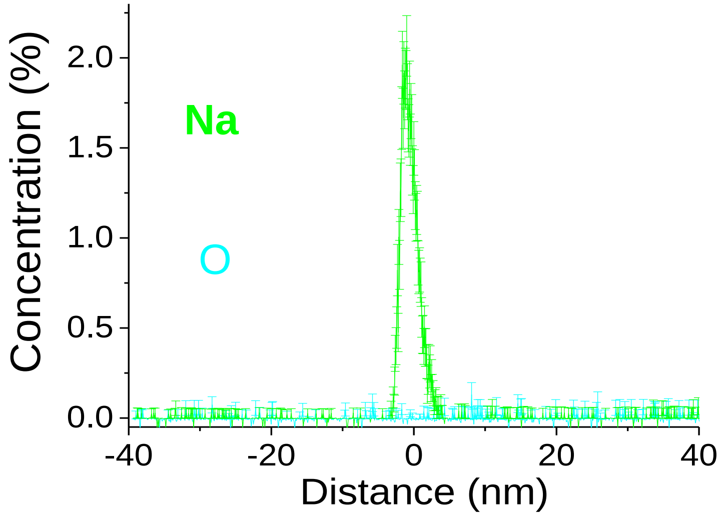
What happens at a dark GB?

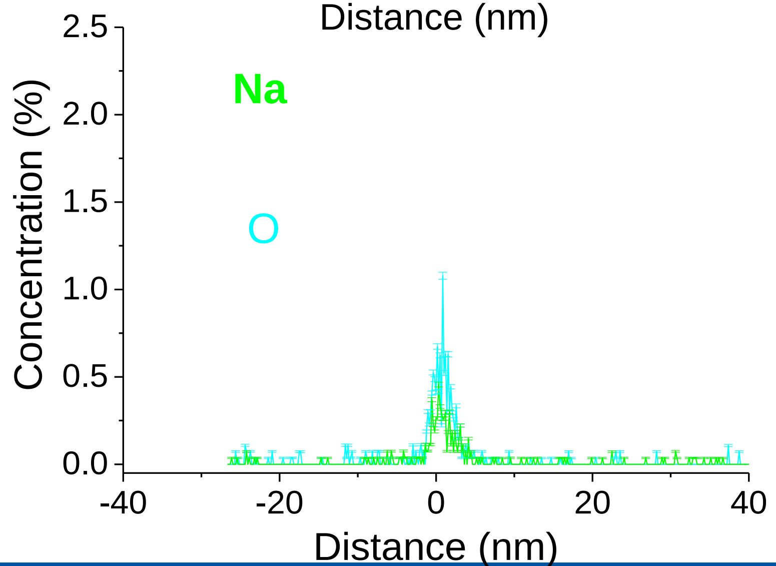
1) Raghuwanshi et.al. Nano Energy 10.1016/j.nanoen.2019.03.028

Benign GB   Detrimental GB



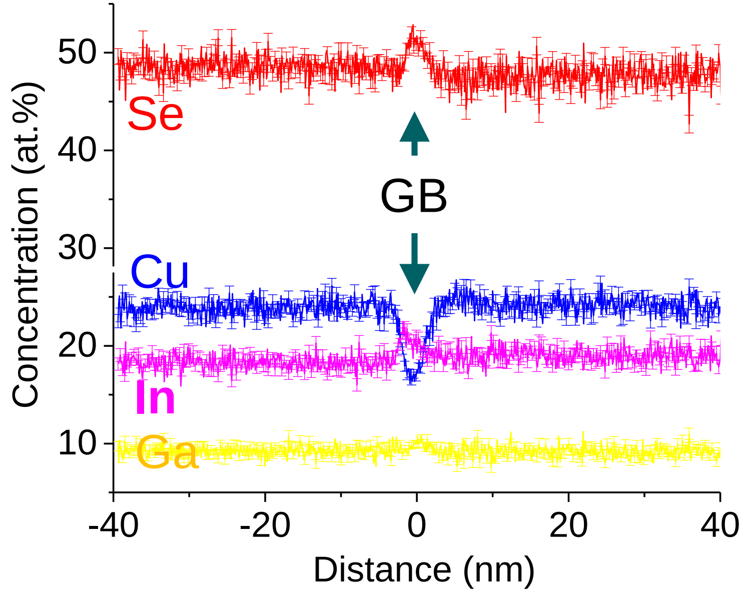


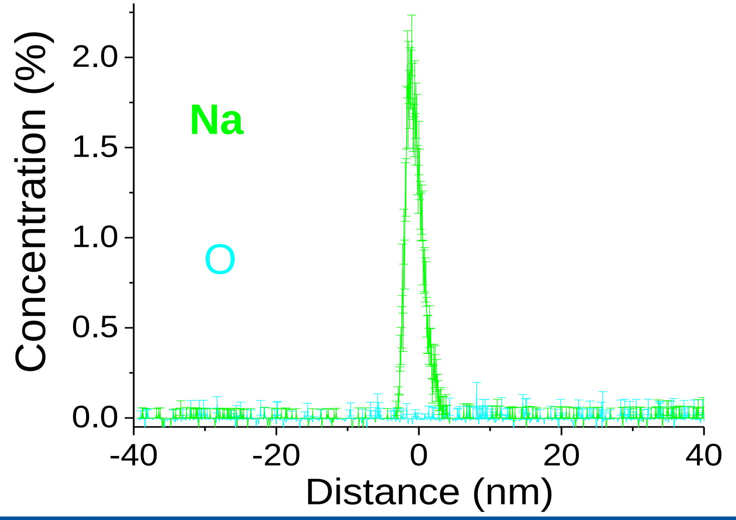




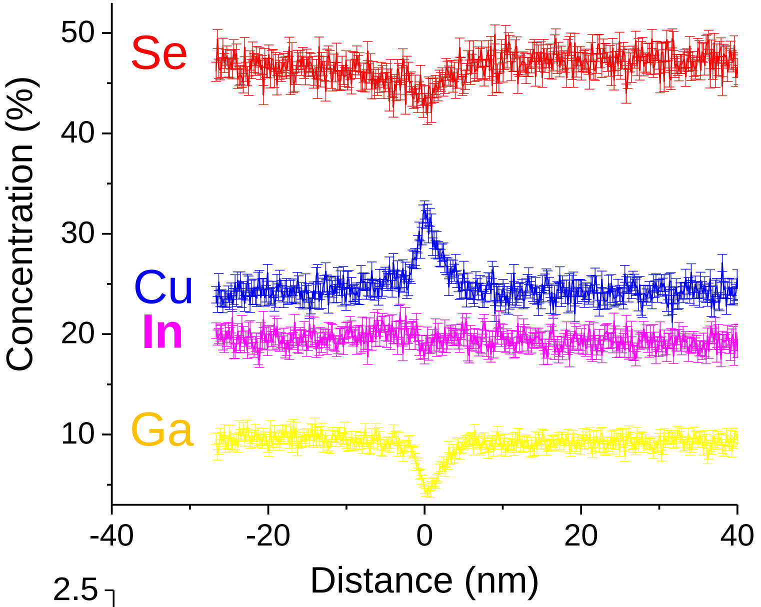
What happens at a neutral GB?

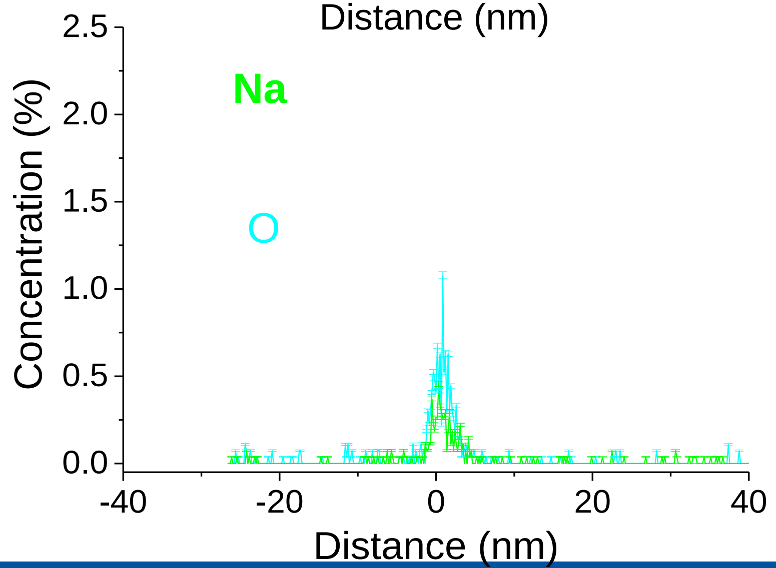
Benign GB



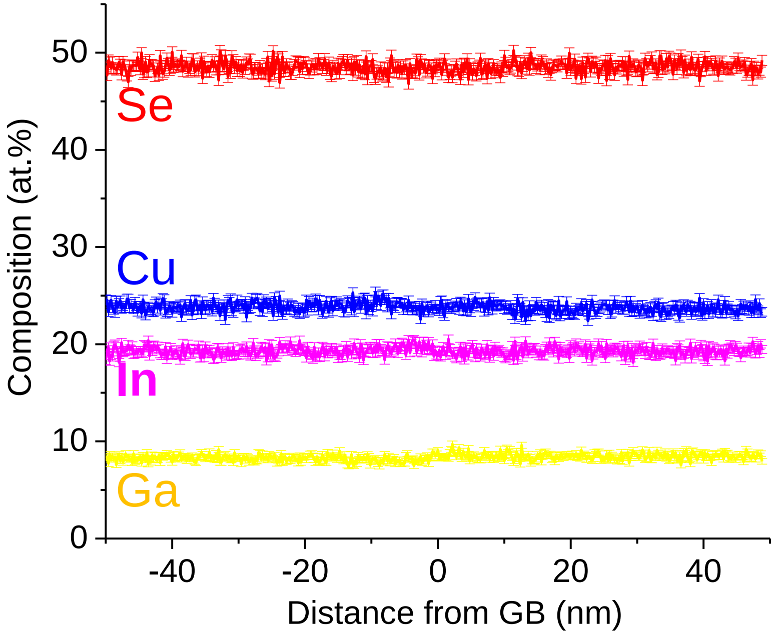


Detrimental GB





Neutral GB



No Change in concentration
No impurities

Statistics

	Change in EBIC Δη	GB angle	Na (at. %)	O (at. %)	Δ Cu (at. %)	Δ Se (at. %)	Δ In (at. %)	Δ Ga (at. %)
Neutral	0	60°(Σ3)	0	0	0	0	0	0
	0	60°(Σ3)	0	0	0	0	0	0
	0	60°(Σ3)	0	0	0	0	0	0
Benign								
Detrimental								

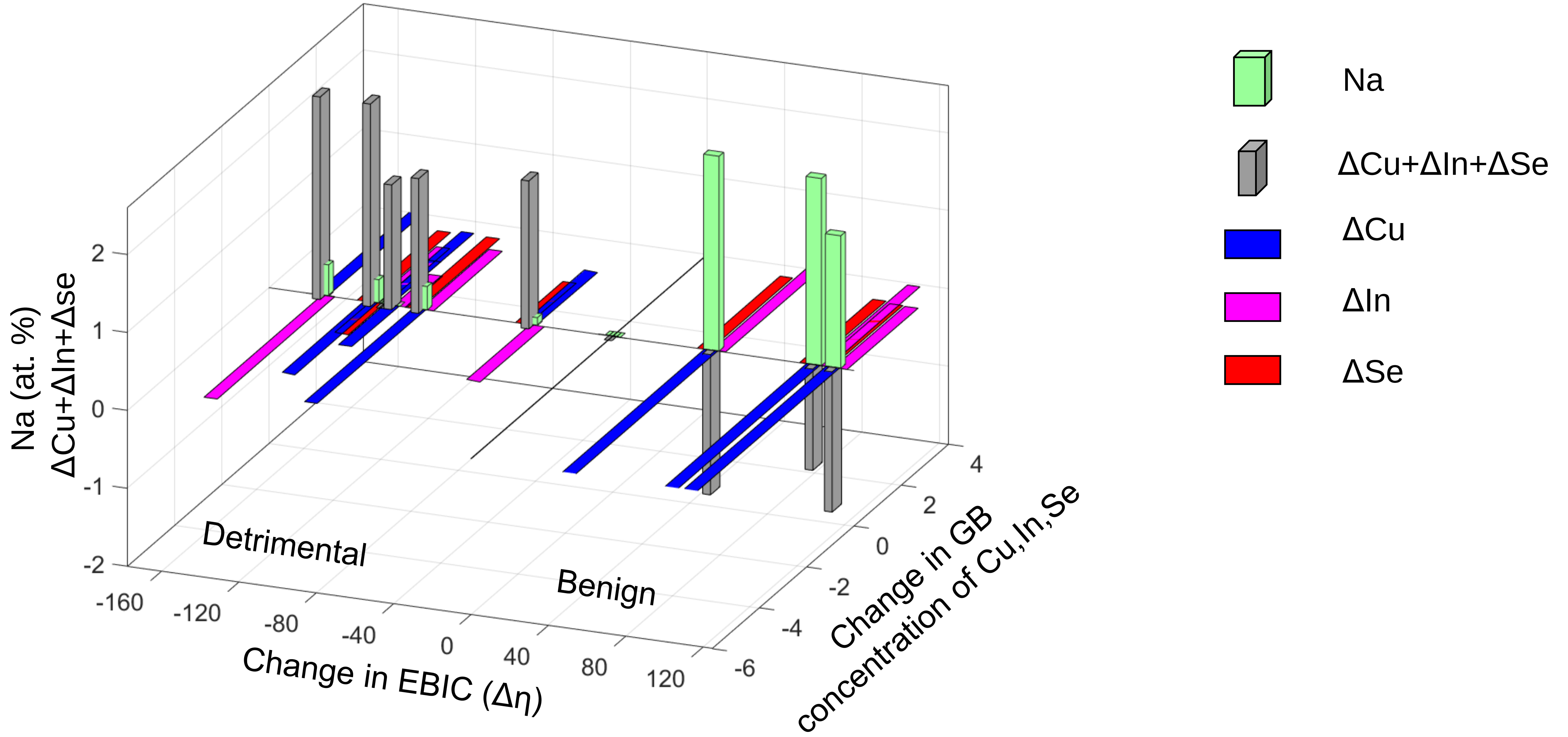
Statistics

	Change in EBIC Δη	GB angle	Na (at. %)	O (at. %)	Δ Cu (at. %)	Δ Se (at. %)	Δ In (at. %)	Δ Ga (at. %)
Neutral	0	60°(Σ3)	0	0	0	0	0	0
	0	60°(Σ3)	0	0	0	0	0	0
	0	60°(Σ3)	0	0	0	0	0	0
Benign	+104	81°	2	0	-8.0	+3.8	+2.9	0
	+114	46.5°	1.7	0	-7.8	+3.0	+3.0	0
	+51	21.8°	2.5	0	-9.3	+4	+3.5	0
Detrimental								

Statistics

	Change in EBIC Δη	GB angle	Na (at. %)	O (at. %)	Δ Cu (at. %)	Δ Se (at. %)	Δ In (at. %)	Δ Ga (at. %)
Neutral	0	60°(Σ3)	0	0	0	0	0	0
	0	60°(Σ3)	0	0	0	0	0	0
	0	60°(Σ3)	0	0	0	0	0	0
Benign	+104	81°	2	0	-8.0	+3.8	+2.9	0
	+114	46.5°	1.7	0	-7.8	+3.0	+3.0	0
	+51	21.8°	2.5	0	-9.3	+4	+3.5	0
Detrimental	-118	24°	0	0	+3.5	-2.0	-1.5	0
	-151	88°	0.4	0.6	+4.5	-1.7	0	-3.5
	-43	22.2°	0.1	0.3	+2.5	-1.3	+4.2	-5.4
	-114	44.3°	0	0.1	-2.0	+1.5	+2.1	-1.3
	-125	59°	0.3	0.4	-3.8	+3.4	+2.0	-1.5
	-100	32°	0.3	0.4	-4.6	+3.0	+2.5	-2.5

Overall trend in composition



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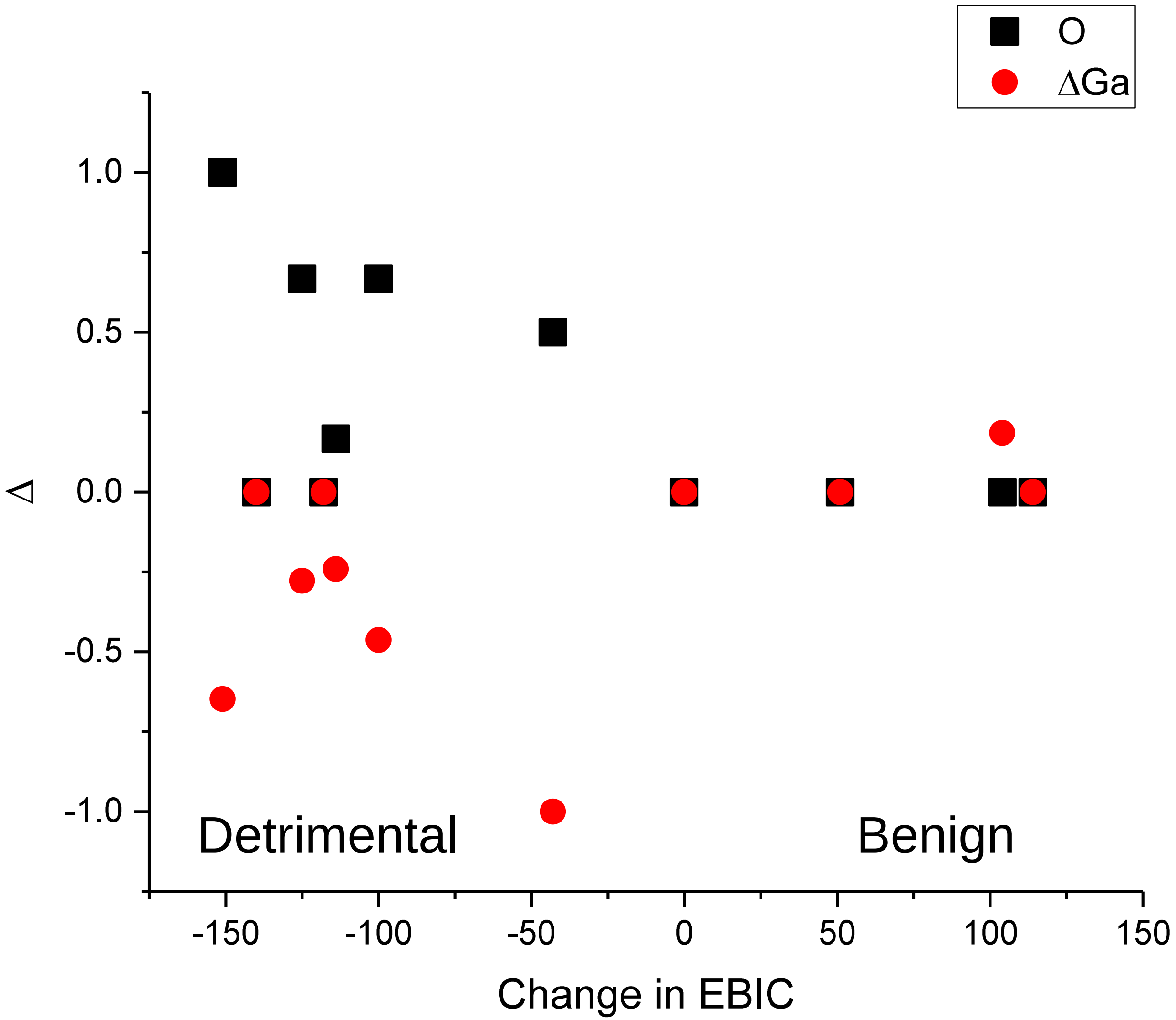
Accepted in Advanced Functional Materials

O and Ga at GB



- Clear correlation observed for change in EBIC with Ga and O at GB
- O was previously predicted to act like a passivating agent for GBs, [1] and have shown to be even beneficial for CIGS device in Cahen and Noufi model. [2]

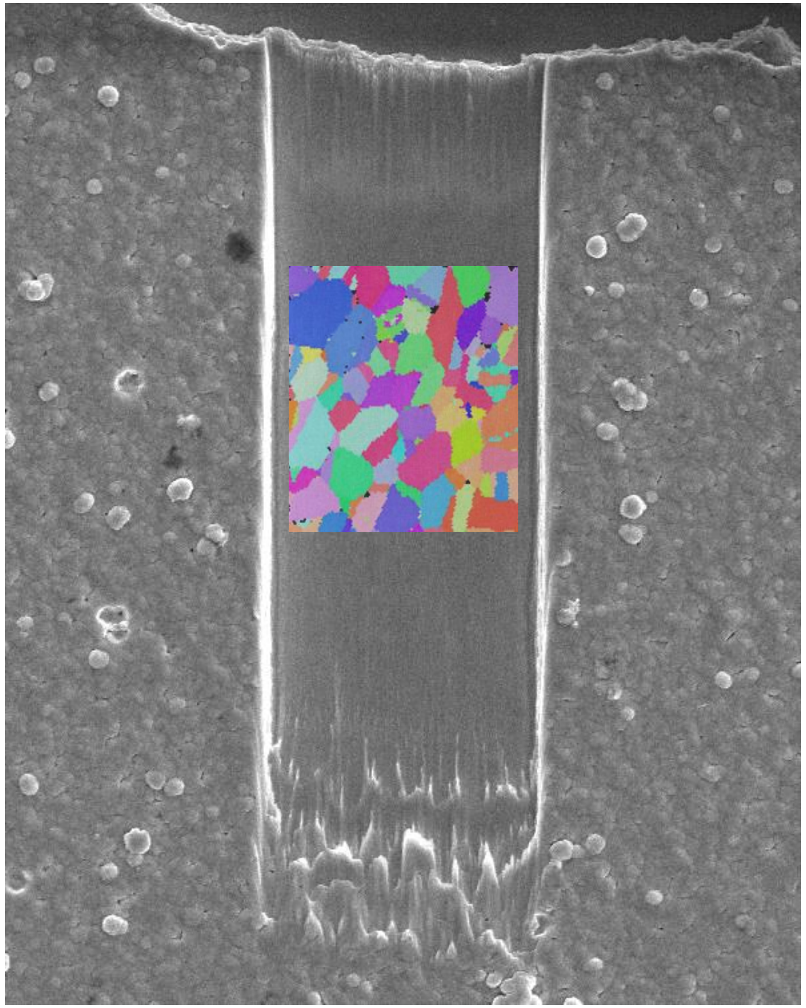
1) U. Rau, et al. *Appl. Phys. A* **2009**, *96*, 221.

2) R. Noufi, et al. *Solar Cells* **1986**, *16*, 479.

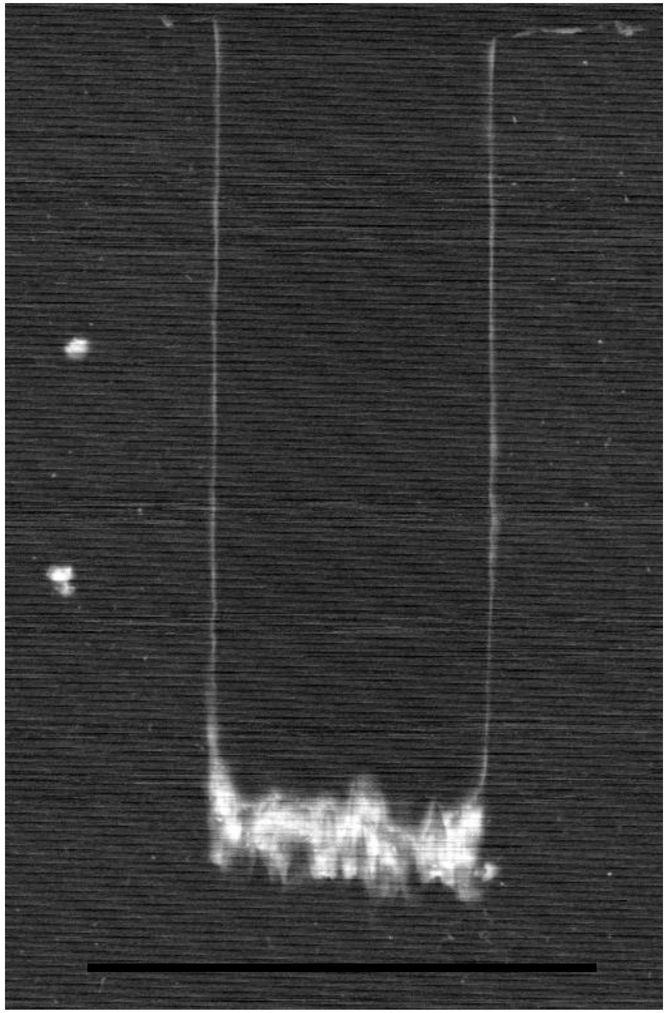
Cu rich CIGS

Surface

SEM

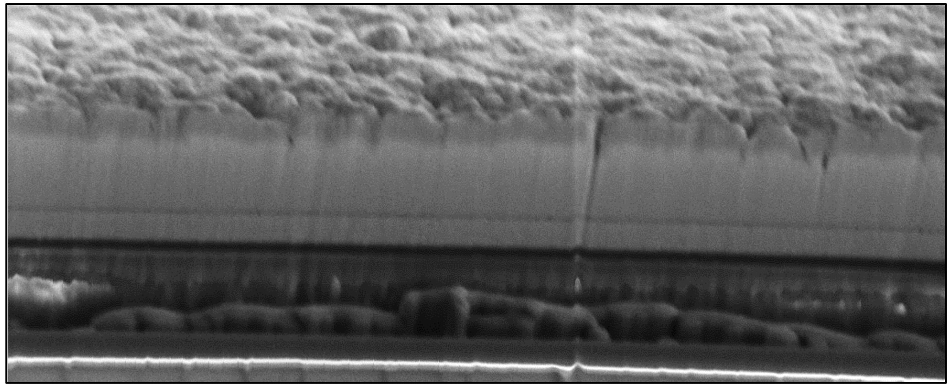


EBIC

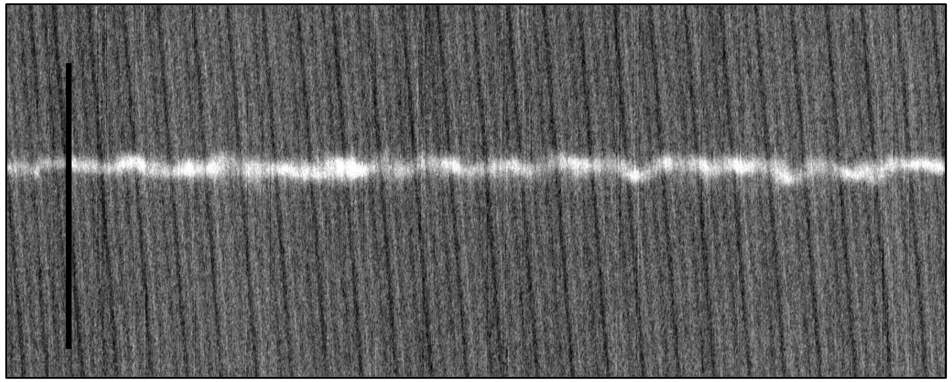


PN Junction

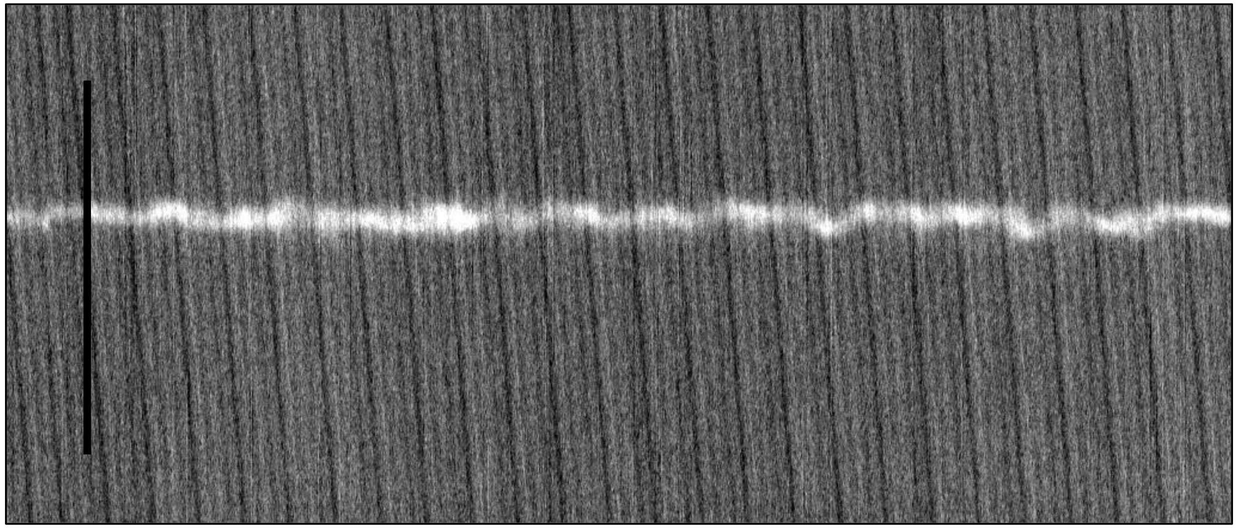
SEM

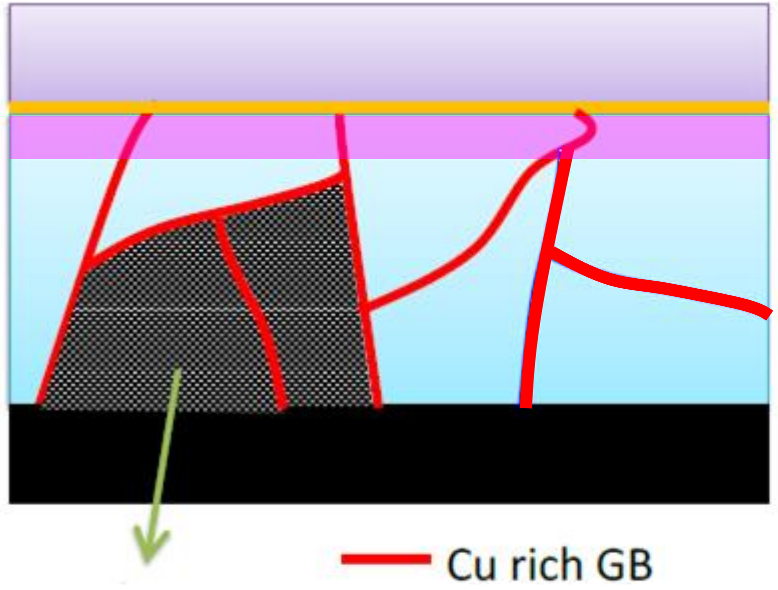


EBIC



Cu rich CIGS





$V_{Cu} < Cu_{In} < V_{In} < Cu_i < In_{Cu}$ (Cu rich; In rich; n type),

$V_{Cu} < Cu_{In} < In_{Cu} < Cu_i < V_{In}$ (Cu rich; In rich; p type),

$V_{Cu} < V_{In} < In_{Cu} < Cu_{In} < Cu_i$ (Cu poor; In rich; n type),

$V_{Cu} < In_{Cu} < V_{In} < Cu_{In} < Cu_i$ (Cu poor; In rich; p type),

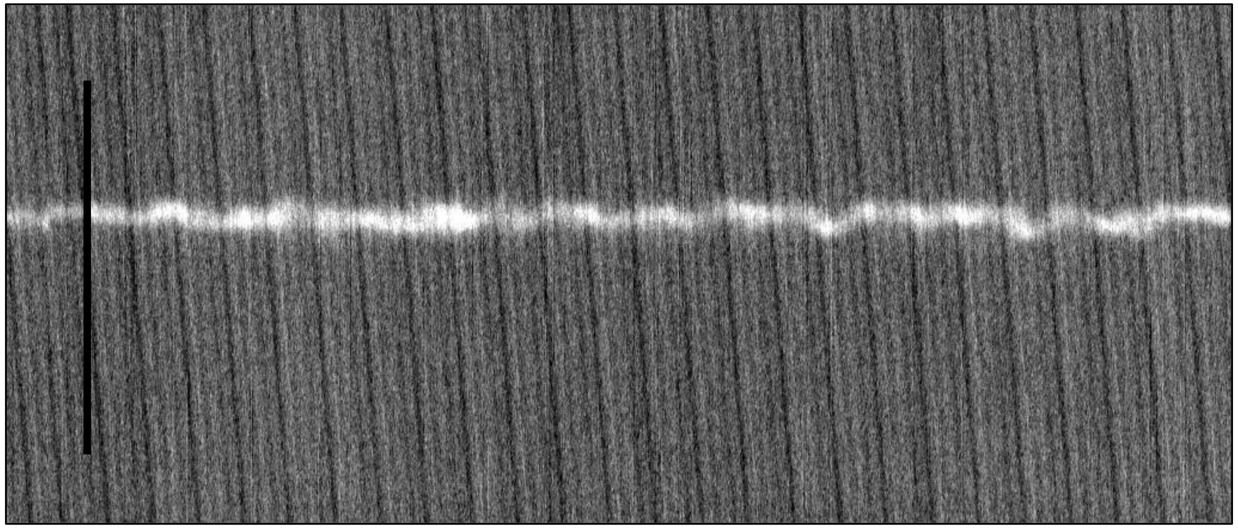
$Cu_{In} < V_{In} < V_{Cu} < Cu_i < In_{Cu}$ (Cu rich; In poor; n type),

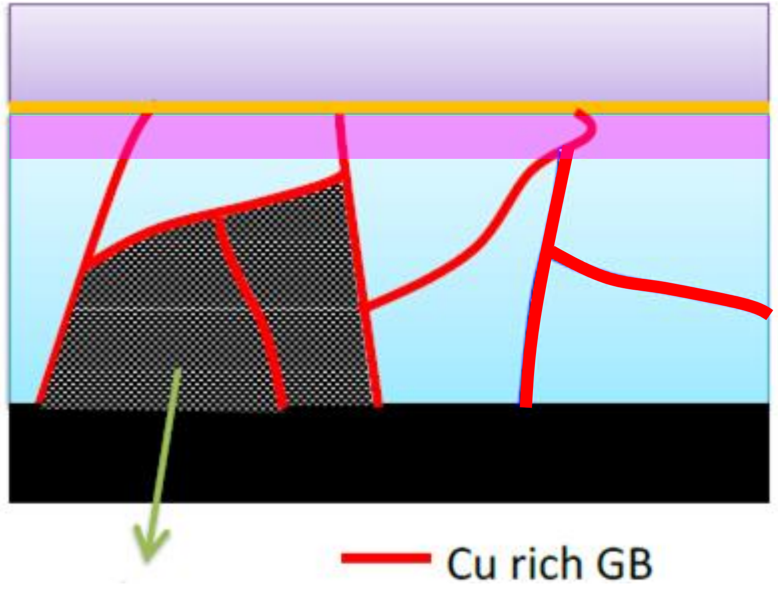
$Cu_{In} < V_{Cu} < V_{In} < Cu_i < In_{Cu}$ (Cu rich; In poor; p type),

Electron hole pairs are produced in grains but are actively recombined at GBs

Hence no signal from deeper grains

Cu rich CIGS





$V_{Cu}<Cu_{In}<V_{In}<Cu_i<In_{Cu}$ (Cu rich; In rich; n type),

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$Cu_{In}<V_{In}<V_{Cu}<Cu_i<In_{Cu}$ (Cu rich; In poor; n type),

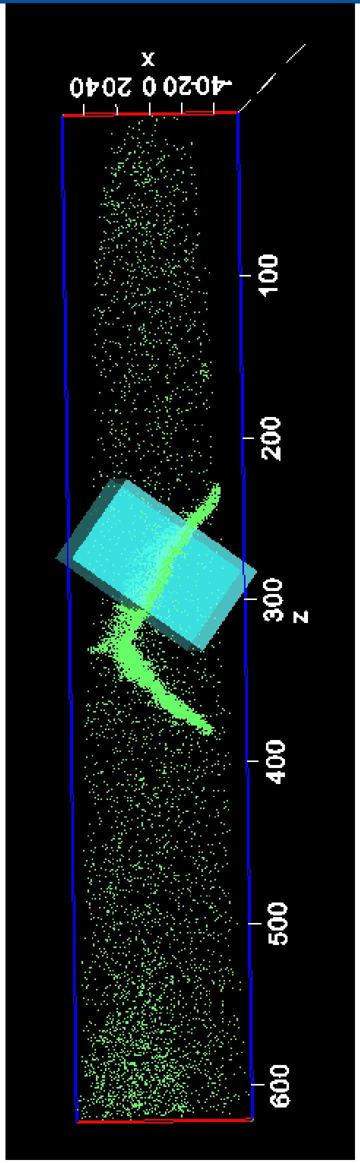
$Cu_{In}<V_{Cu}<V_{In}<Cu_i<In_{Cu}$ (Cu rich; In poor; p type),

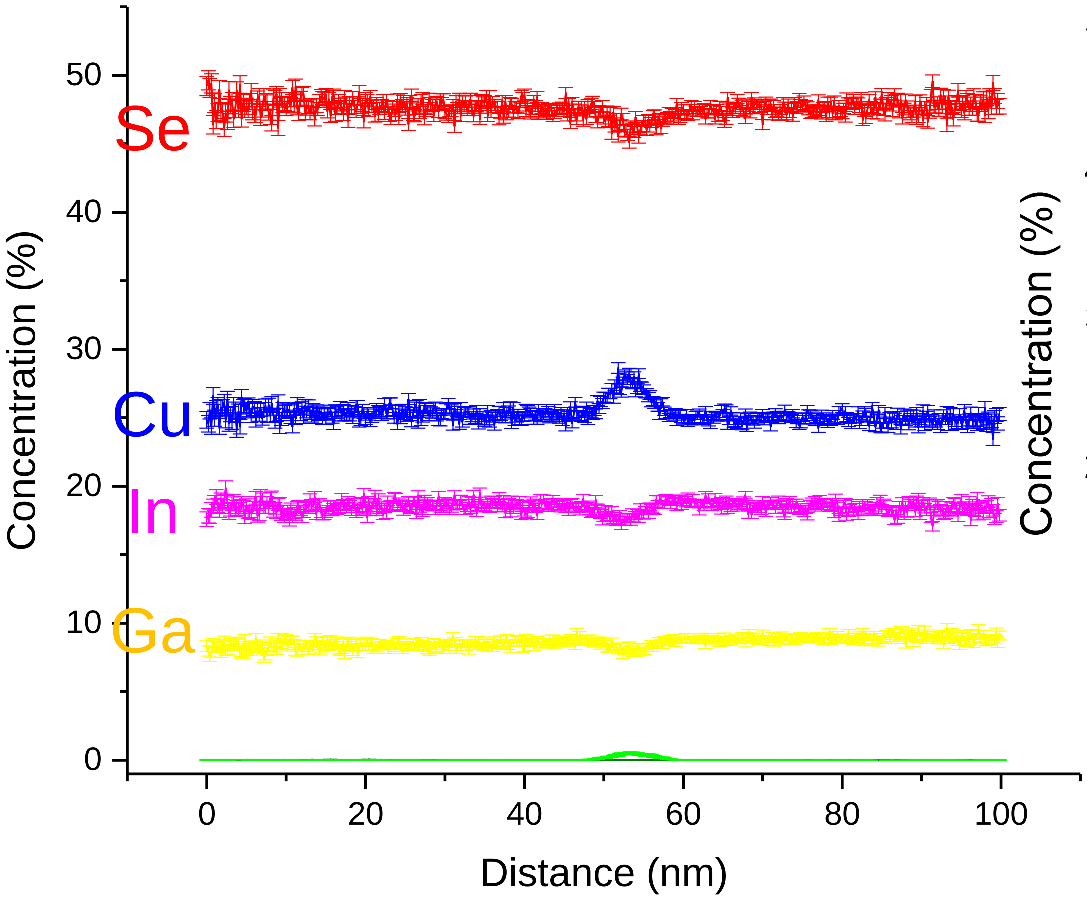
Electron hole pairs are produced in grains but are actively recombined at GBs

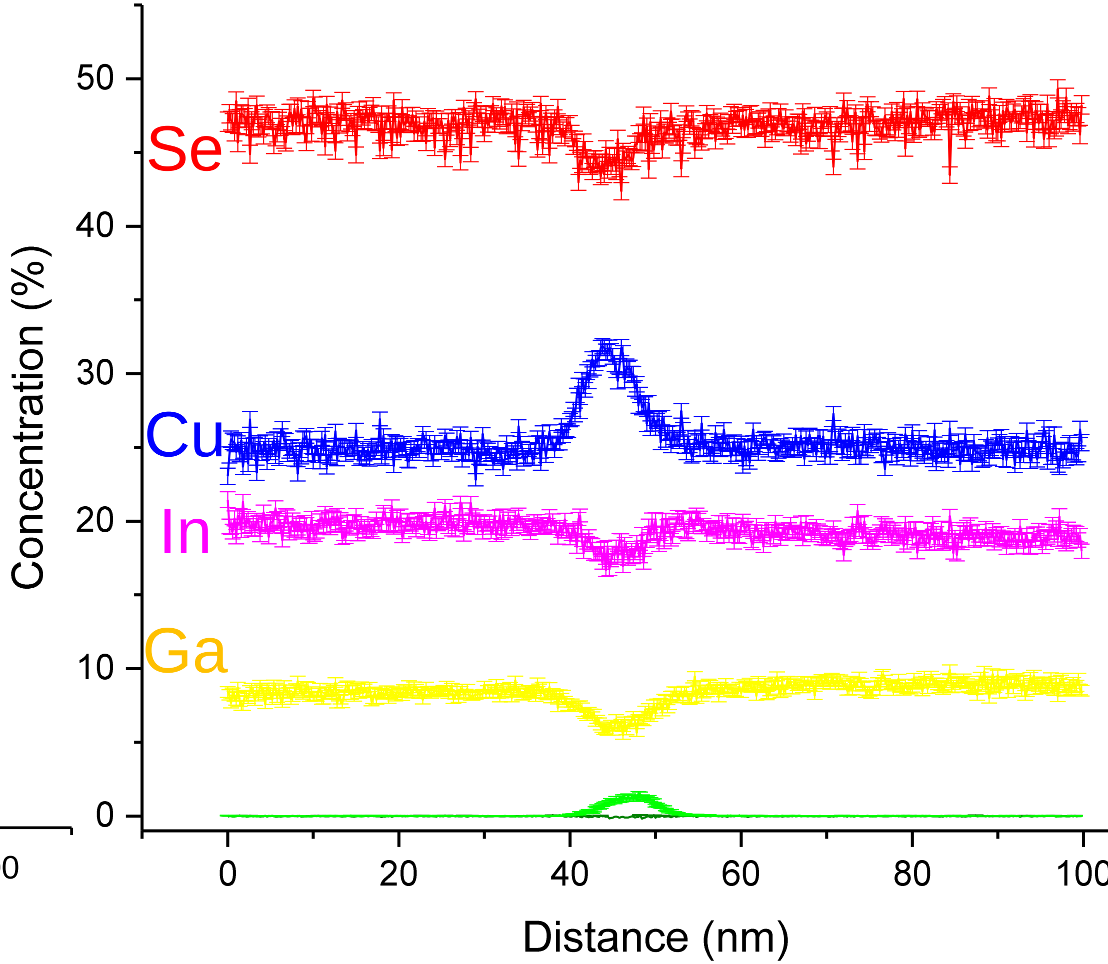
Hence no signal from deeper grains

What is the composition?

Cu rich CIGS GB composition







Conclusions

- Strong correlation between GB properties and its composition is found
- Trait of a benign GB: **Cu ooooor, In/Se rich, Na (1-3 at%), No O, Ga unchange**
- Trait of a detrimental GB: **Cu rich, Na (<1 at%), O, Ga depletion**
- Trait of a neutral GB: **Twin, no change in composition**
- No correlation between (random) GB **misorientation** and its composition/trait

Discussions

- Existence of Bright GBs: type inversion/band bending/hole barrier: better separation of electron hole pairs hence more current
- Most of the GBs are bright: explains why most publications report Cu depletion at GB, also consistent with theoretical expectations.
- Some GBs are dark: explains some publications reporting Cu enrichment
- Reality: All the types of GBs coexist with different compositions.
- Strongly depends on the deposition process/grain-composition.

Open Questions Future work

- All elements (CIGS,Na,O) at GB reflects change in its electrical properties, it is unknown whether impurities or the matrix elements play the most important role
- Why some twin boundaries are bright?
  - HRTEM investigations

Thank you for your attention

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