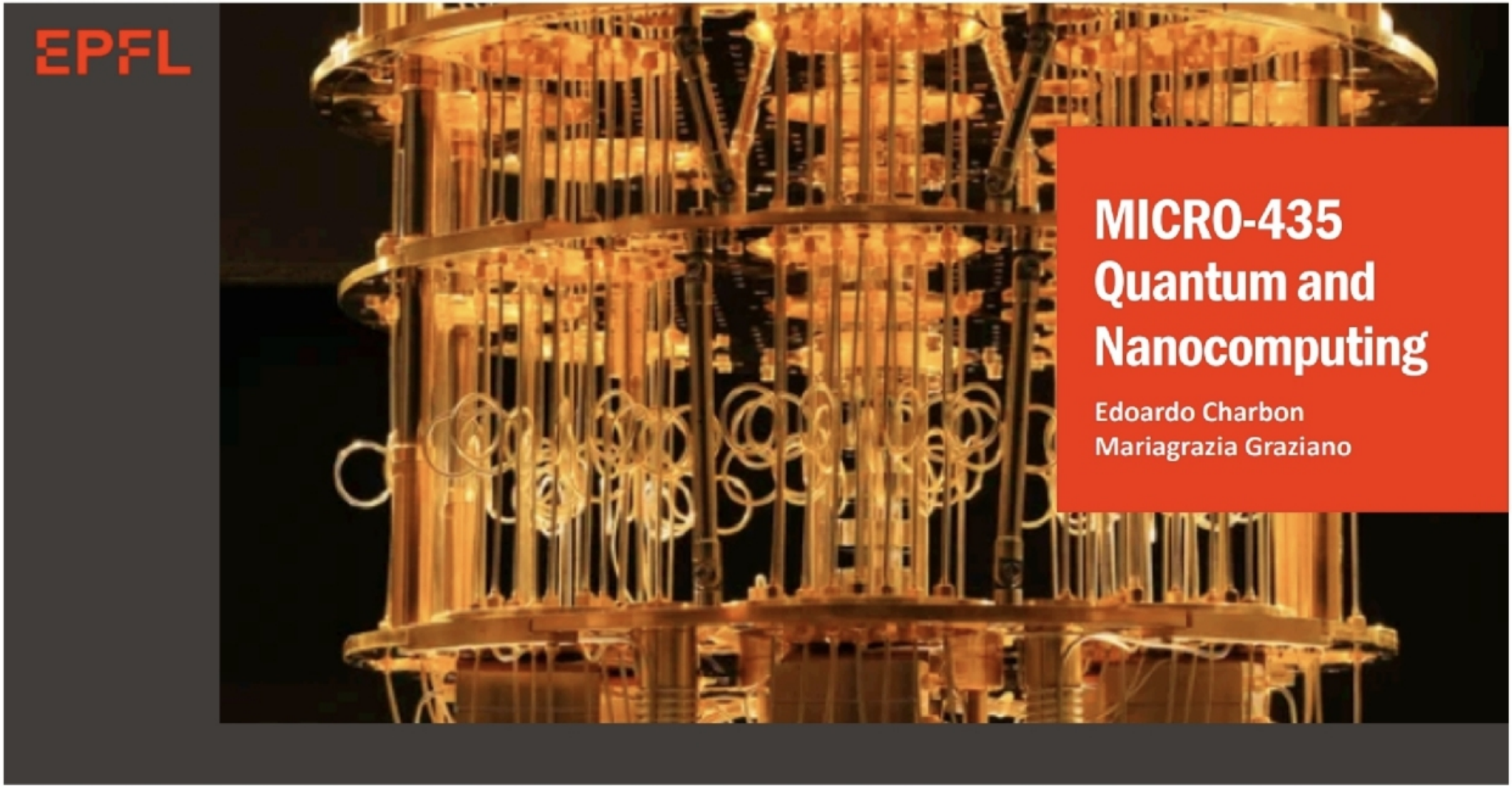


MOLECULAR TRANSISTOR FABRICATION

PART 1

M. GRAZIANO

4/11/25

MOLECULAR TRANSISTOR FABRICATION

OBJECTIVES

a) M.T. FABRICATION OVERVIEW

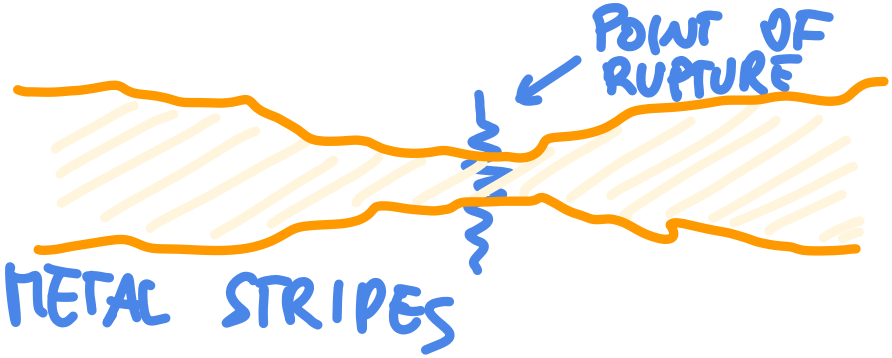
b) FIB BASED & EM INITIAL VIEW METHODS

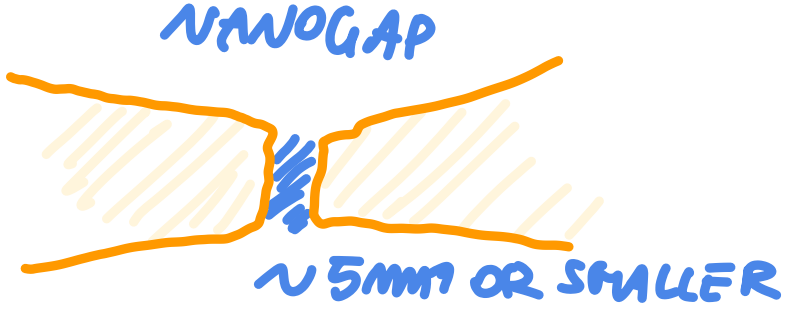
N.T. FABRICATION OVERVIEW

1) STRUCTURE PREPARATION FOR NANOGAP CREATION
   FROM MICRO TO NANO
   SUBSTRATE

2) CREATE NANOGAP
   - DIRECT
   - ELECTROMIGRATION (EM)
   - MECHANICAL STRESS
     - STRIP

3) FAVOUR MOLECULAR ATTACHMENT





FROM A REVIEW PAPER ON NANOGAP CREATION 10.1002/smll.2018 4177
SMALL, WHYLEY : Y.YANG ET. AL : "SUB-5nm Metal Nanogaps..."

Fabrication method		Key fabrication technique	Minimum gap size	Single/ large area	Controllability[a]	Reproducibility	Addressability	Cost	Application/ functionality[b]
Physical fabrication methods	Direct nanofabrication	FIB	1 nm	Single	M	M	M	H	■★
		TEM	Sub-nanometer	Single	M	M	H	H	■
		EBL	Sub-nanometer	Large area	H	H	M	M	■●★
		SPM	Sub-nanometer	Single	H	H	L	H	■●
	Controllable metal deposition	Metal deposition	3 nm	Large area	M	M	L	M	■◆●
		Nanosphere lithography	5 nm	Large area	M	M	L	L	■●
	Insertion of ultrathin layers	ALD	2 nm	Large area	M	M	L	M	●★
		2D material	1 nm	Large area	L	M	L	M	●★
	Breaking-/ cracking-defined	Electromigration	1 nm	Large area	M	L	H	M	■◆
		Mechanical	1 nm	Single	M	L	H	H	■
		Strain	3 nm	Large area	H	H	M	M	■●
Chemical fabrication methods	Nanoparticle self-assembly	Nanoparticle	Sub-nanometer	Large area	L	L	L	L	●
		Nanospacer	Sub-nanometer	Large area	H	H	L	L	●
	Covering ultrathin shell	Dielectric shell	Sub-nanometer	Large area	H	H	L	L	●
	Embedding interior nanogaps	Interior gap	1 nm	Large area	H	H	L	L	●
	Electrochemical	Electrochemical	1 nm	Large area	H	L	H	L	■

DIRECT NANOGAP CREATION

→ LITHOGRAPHY

- HIGH END OPTICAL LITHOGRAPHY

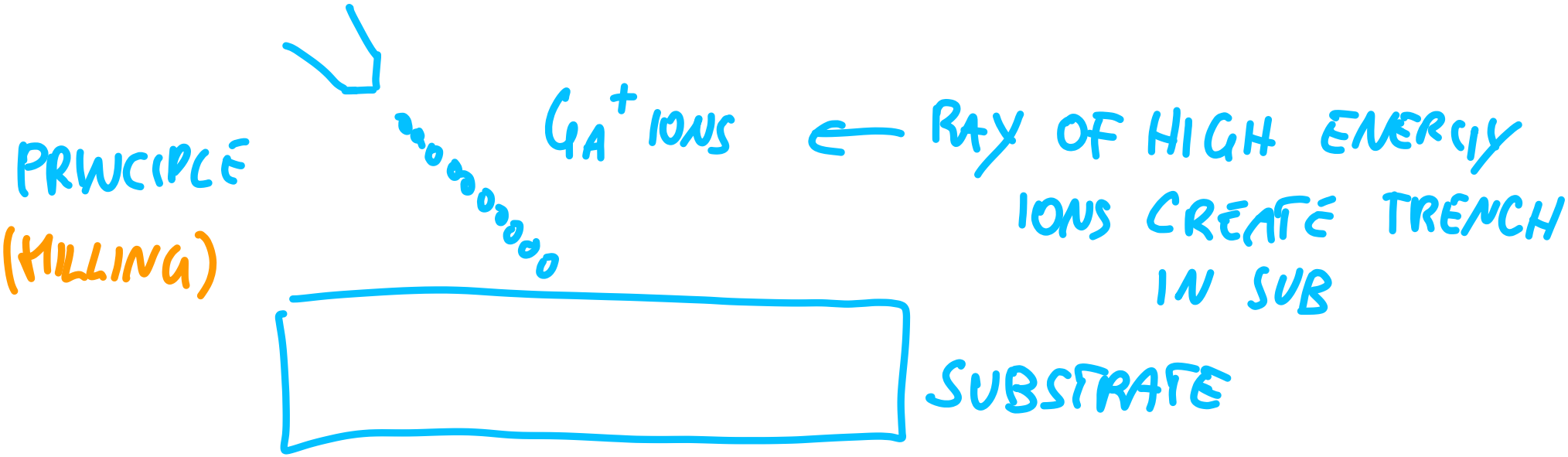
- ELECTRON BEAM LITHOGRAPHY (EBL) ~10 nm

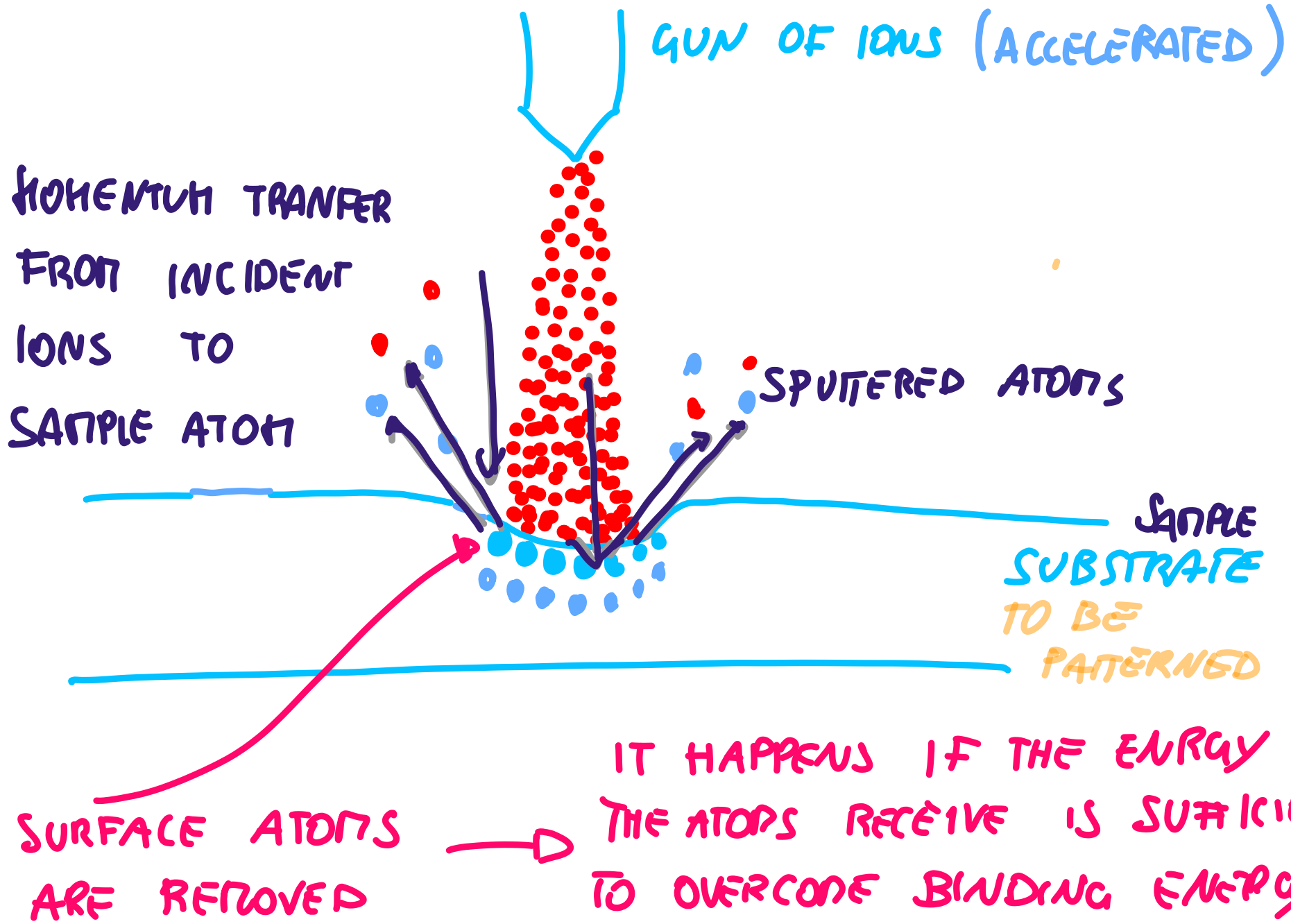
TYPICAL RESOLUTION ~ 20 nm

→ TREND DOWN TO 10 .... 7 nm

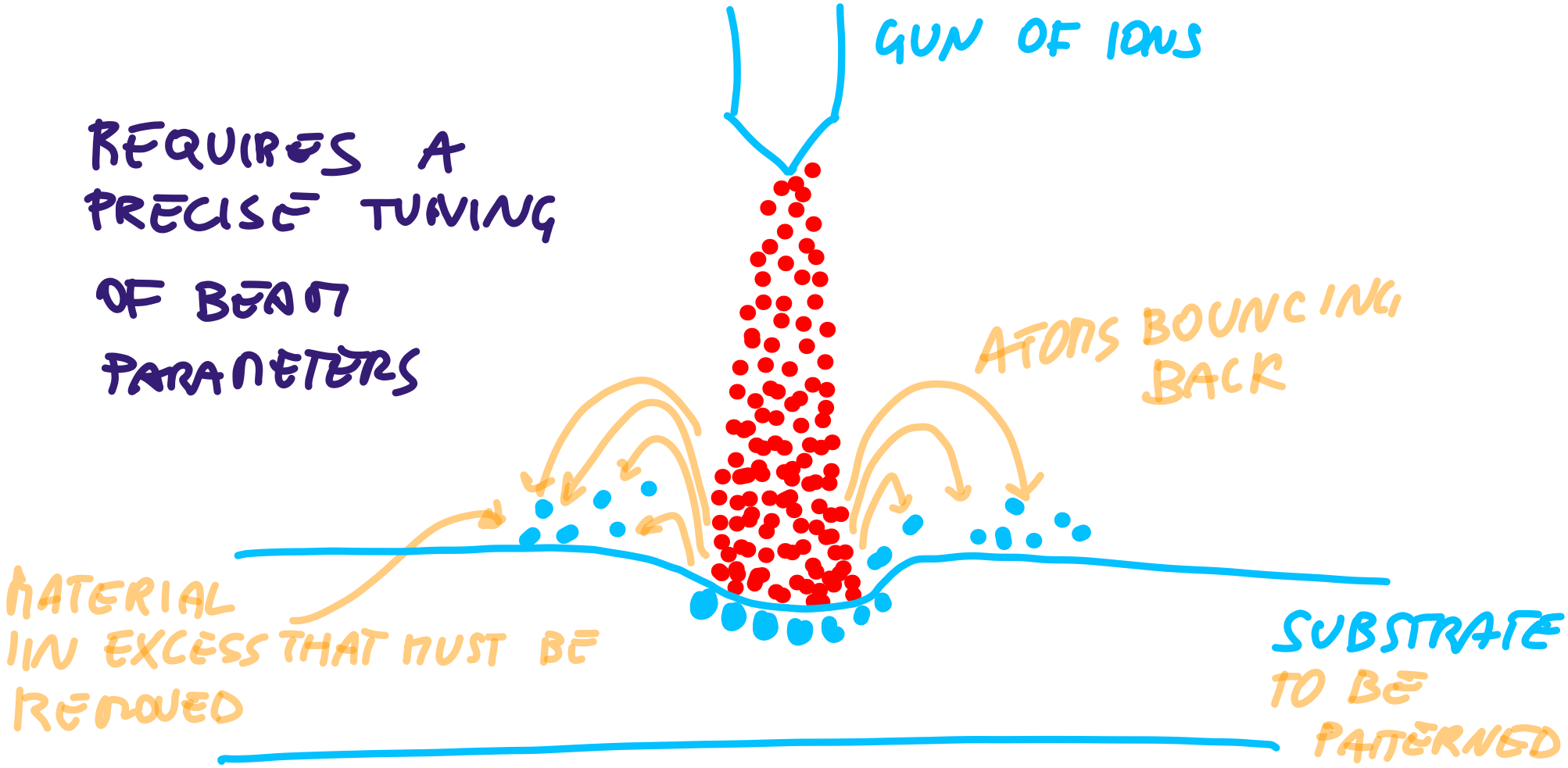
↑ TOO BIG !!

FOCUS ION BEAM (FIB) ~ 5nm




GUN OF IONS (ACCELERATED)
MOMENTUM TRANFER FROM INCIDENT IONS TO SAMPLE ATOM
SPUTTERED ATOMS
SAMPLE
SUBSTRATE TO BE PATTERNED
SURFACE ATOMS ARE REMOVED
IT HAPPENS IF THE ENRGY THE ATOMS RECEIVE IS SUFFICIENT TO OVERCOME BINDING ENERGY

REQUIRES A PRECISE TUNING OF BEAM PARAMETERS



BEAM LOOSES FOCUS (RESOLUTION) INCREASING THE DISTANCE OF THE GUN

GOTO

Youtube.com/watch?v=X8aw6k4bdhg

FOR A NICE TALK ON FIB IN GENERAL

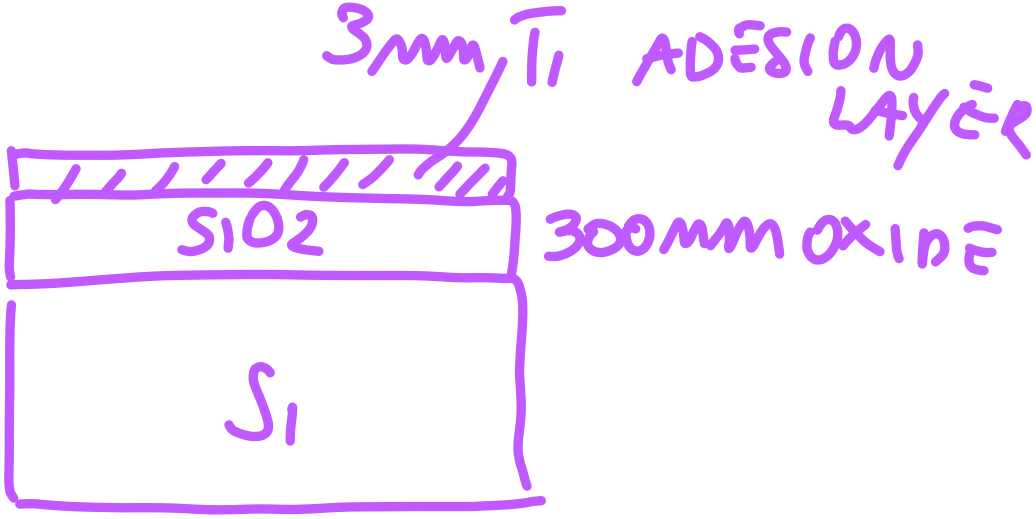
INTRODUCTION TO FOCUSED ION BEAM

FROM ILLINOIS MATERIALS RESEACH LABORATORY

H. ZHOU

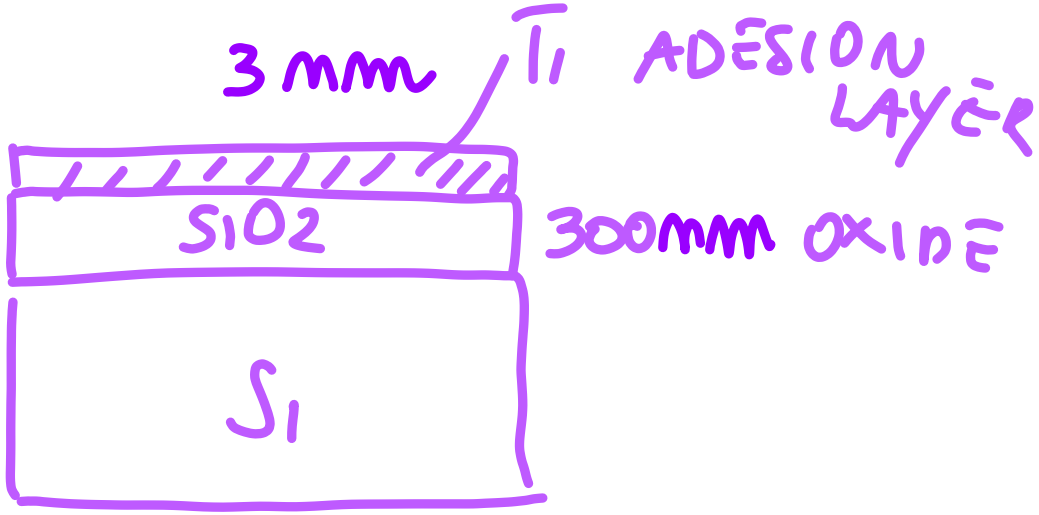
FIB FOR N.GAP

① SUBSTRATE ARRANGEMENT

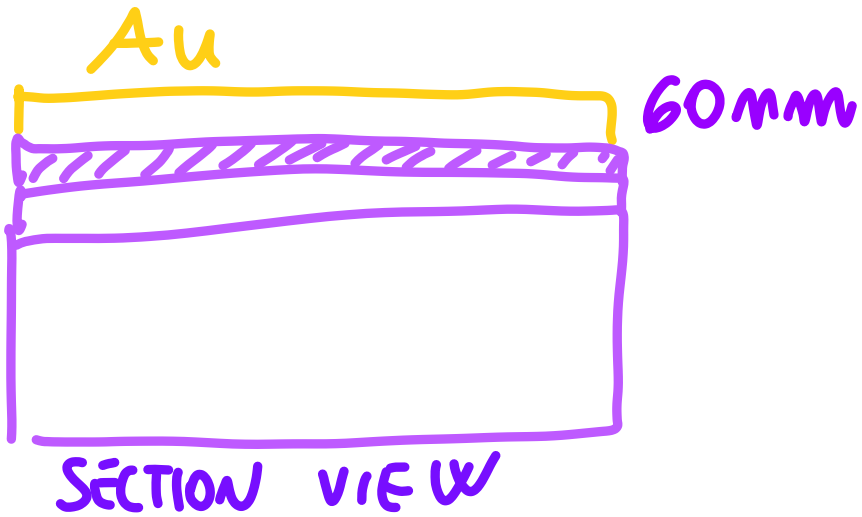


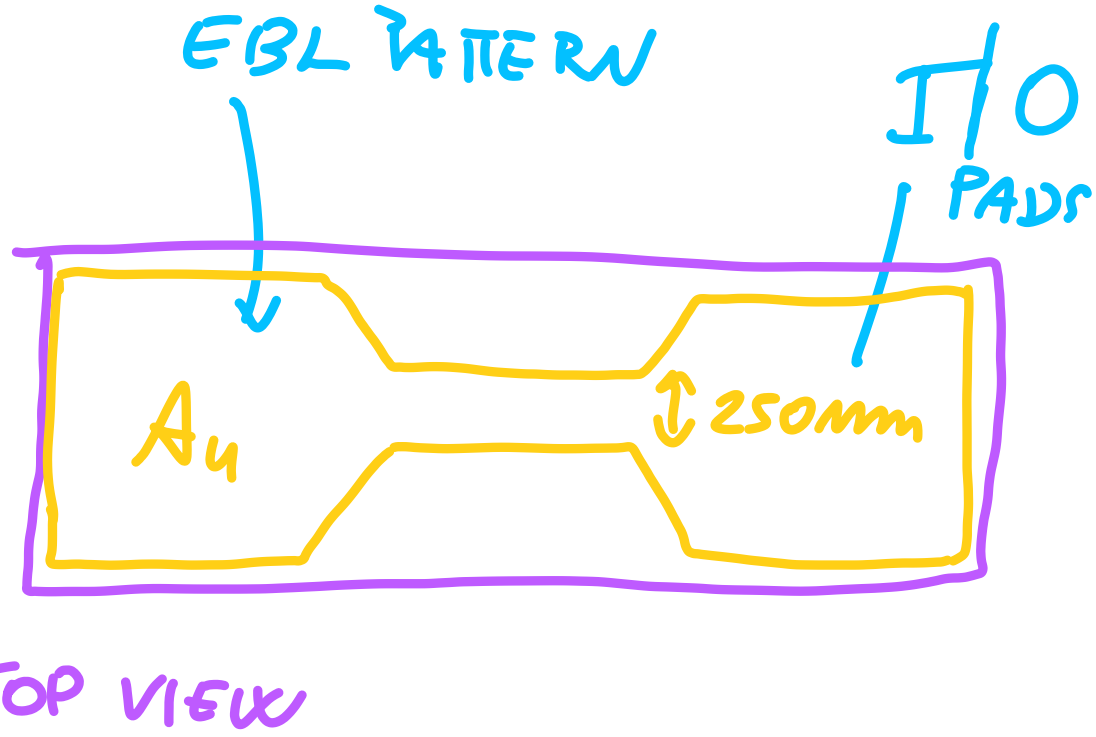
FIB FOR N.GAP

① SUBSTRATE ARRANGEMENT

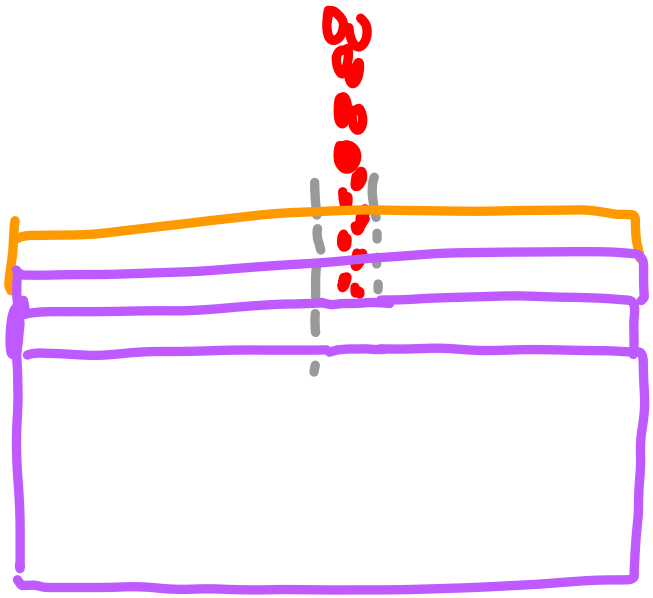


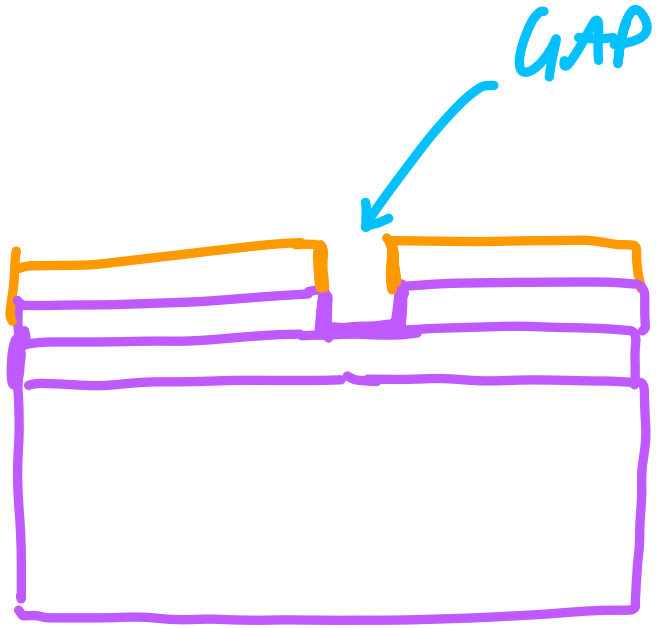
② NANOWIRE CREATION





③ ION BEAM IRRADIATION





IONS/cm

- FINE CONTROL IS NEEDED
- PROBLEMATIC FOR MASS PRODUCTION

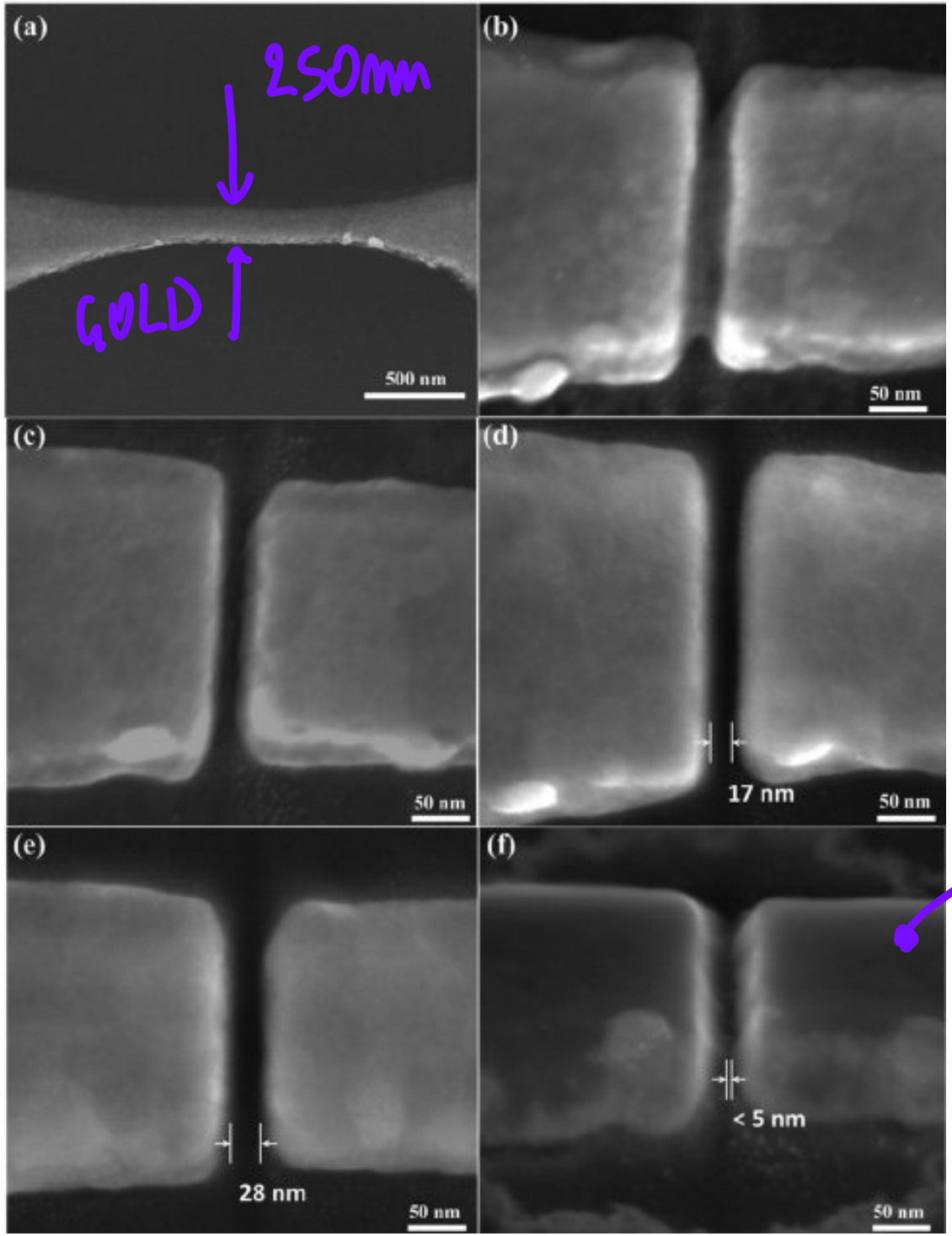
GAP DEPENDS ON ION DOSAGE

EX $4.6 \cdot 10^{10}$/cm NO GAP

$5 \cdot 10^{10}$/cm < 5mm GAP

$6.7 \cdot 10^{10}$/cm ~ 17mm GAP

$8.3 \cdot 10^{10}$/cm ~ 28mm GAP



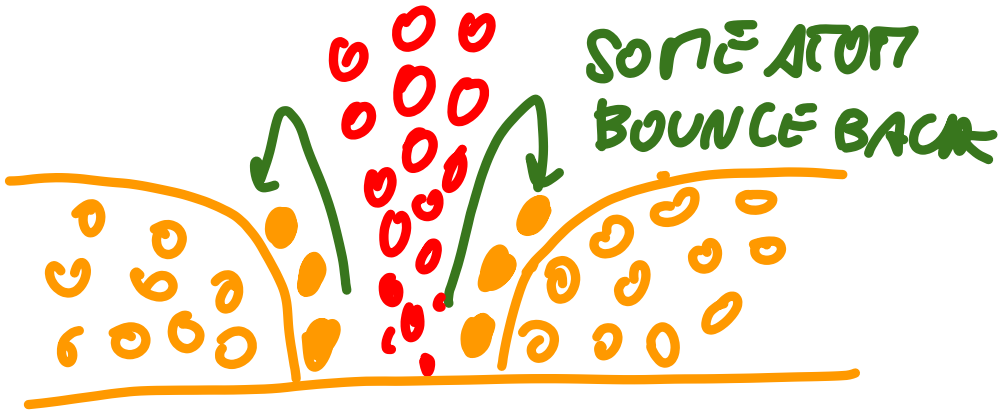
EXAMPLE 250 nm GOLD WIRE

SEM IMAGE AFTER FIB MILLING FOR DIFFERENT DOSAGES

$5 \cdot 10^{10}$ ions/cm

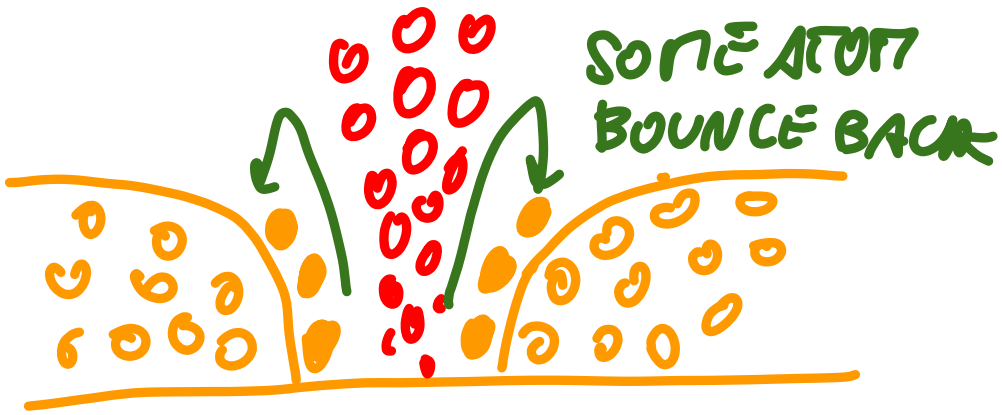
Hu Li, Klaus Leifer et al
AIP: 107. doi 10.1063/1.4930821

A FIB PROBLEM



PROBLEM TYPICALLY FOR EM.

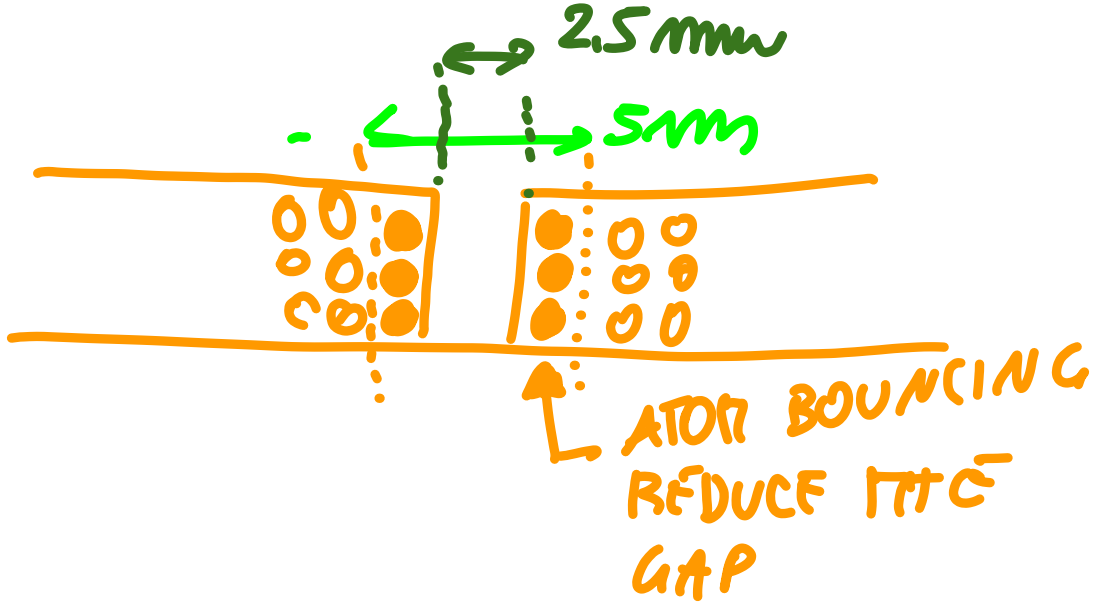
A FIB PROBLEM



PROBLEM TYPICALLY FOR EN.

EFFECTIVE GAP IS EXPLOITED

COULD BECOME A SOLUTION.



ELECTROMIGRATION (EM)

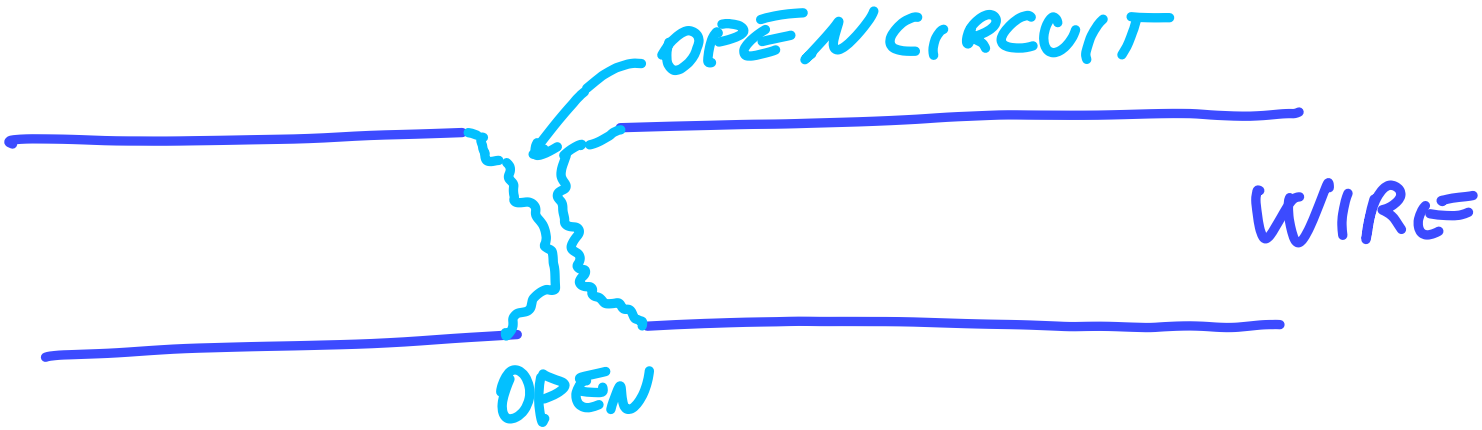
PART 1 - GENERAL DESCRIPTION

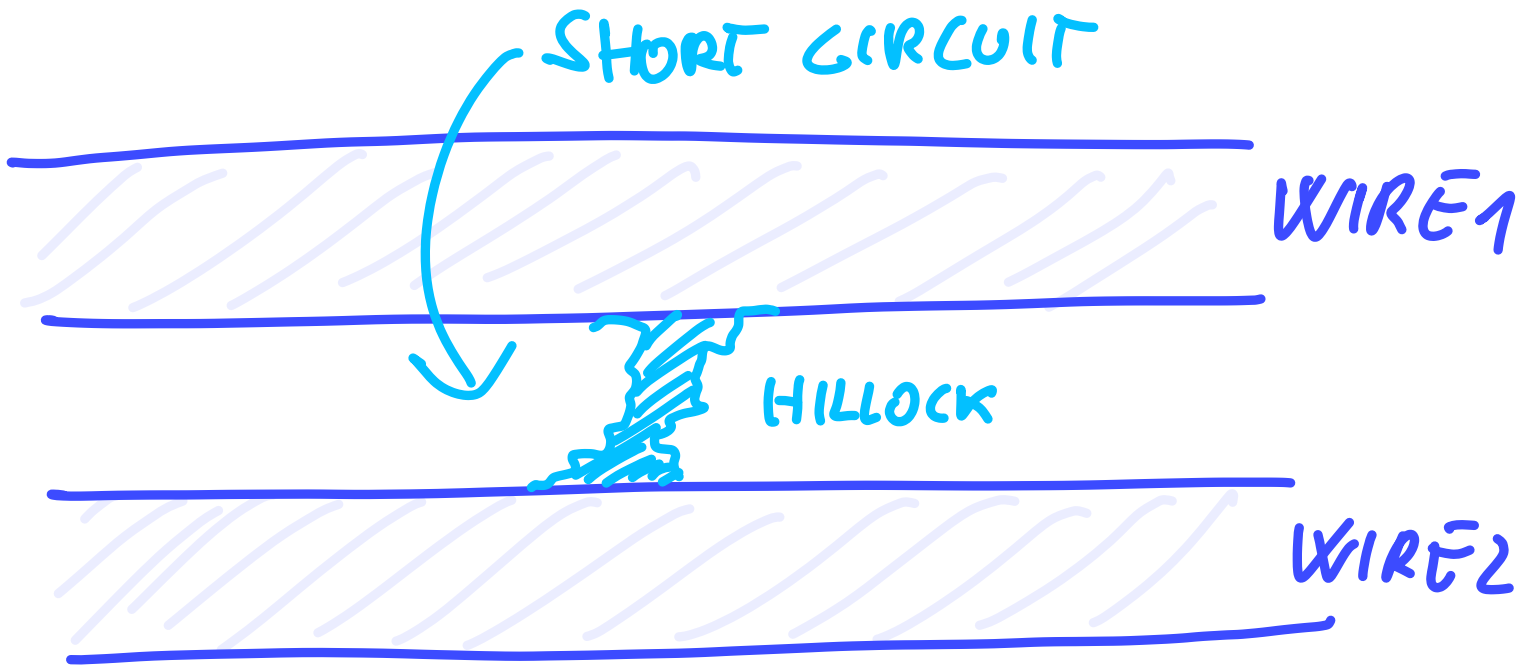
IF ELECTRONS IN A CONDUCTOR HAVE SUFFICIENT ENERGY

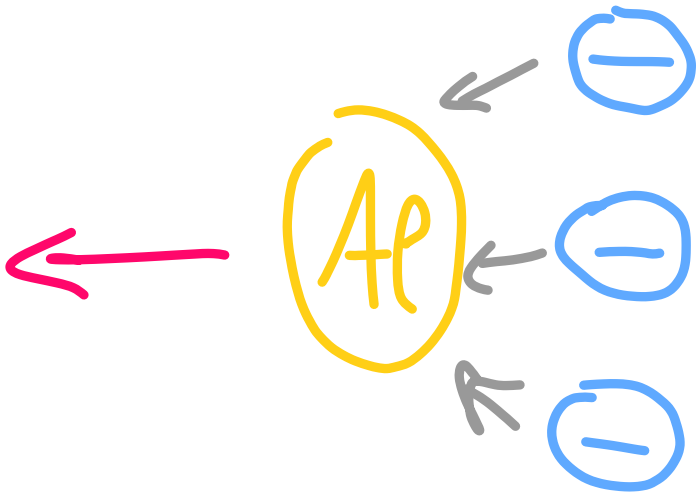
VOIDS OR HILLOKS COULD BE GENERATED

VOIDS → OPEN CIRCUIT

HILLOKS → SHORT CIRCUITS


OPEN CIRCUIT
WIRE
OPEN


SHORT CIRCUIT
WIRE1
HILLOCK
WIRE2



FLOW OF ELECTRONS

THE ELECTRIC WIND MOVES ELECTRONS THAT TRANSFER QUANTITY OF MOTIONS TO ATOMS

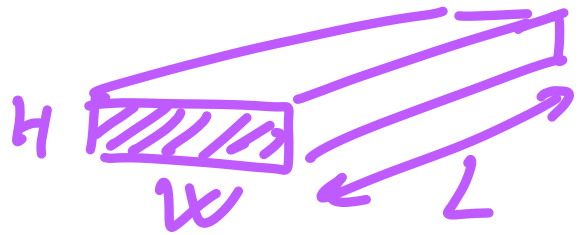
IF THIS HAPPENS CONTINUATIVELY THE METAL ATOM COULD MOVE AND LEAVE SPACE TO ANOTER ATOM TO MOVE....

⟶ AVALANCHE

VIDEO sd.mp4
@ 50" – 60"

EM MORE PROBABLE IF

- MANY ELECTRONS ARE PRESENT (METAL, POLY
- HIGH CURRENT DENSITY $J = \frac{I}{W \cdot H}$
- ATOMS ARE FREE TO MOVE



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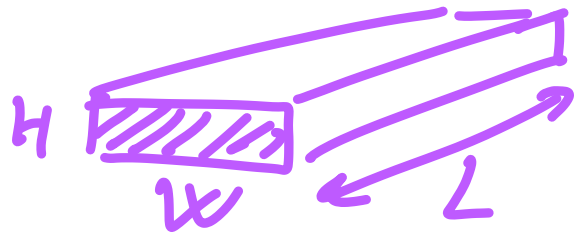
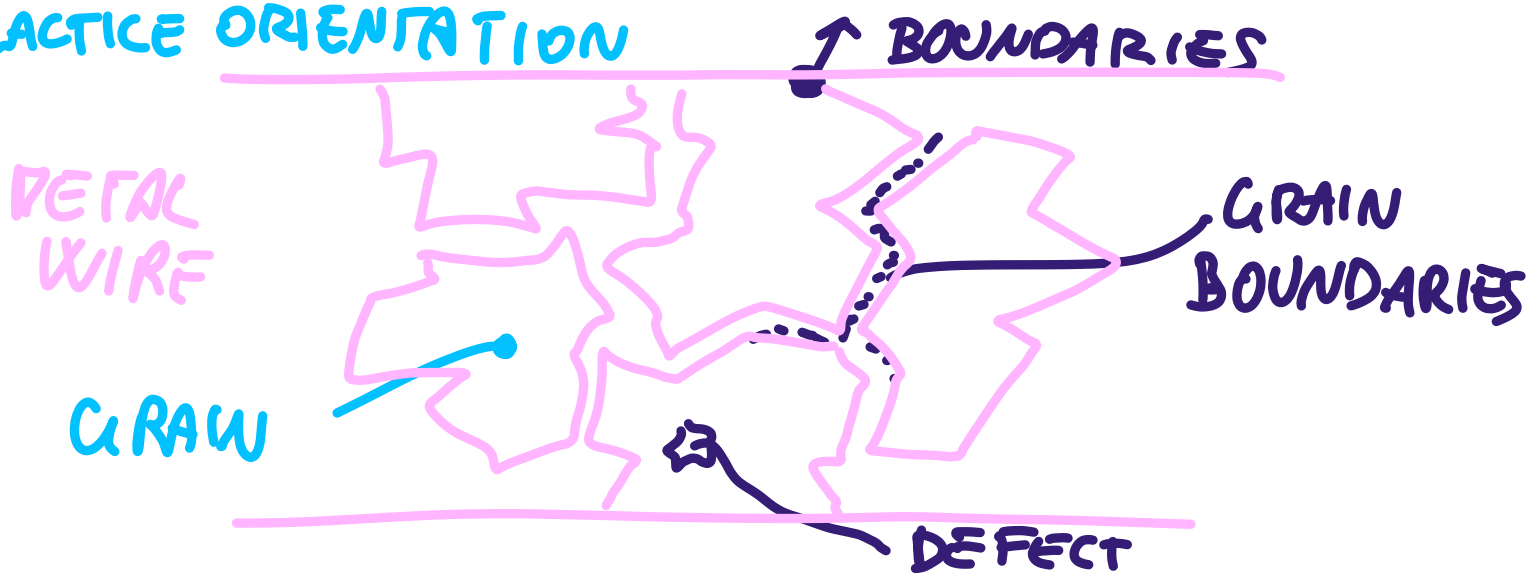


- BOUNDARIES
- DEFECT
- GRAIN BOUNDARIES

DIFFERENT GRAINS HAVE DIFFERENT LACTICE ORIENTATION



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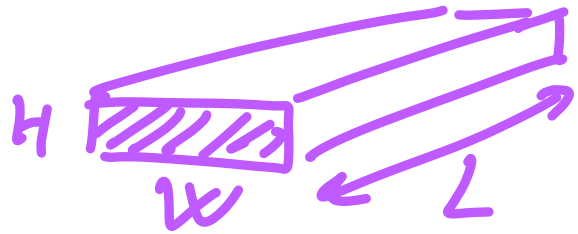

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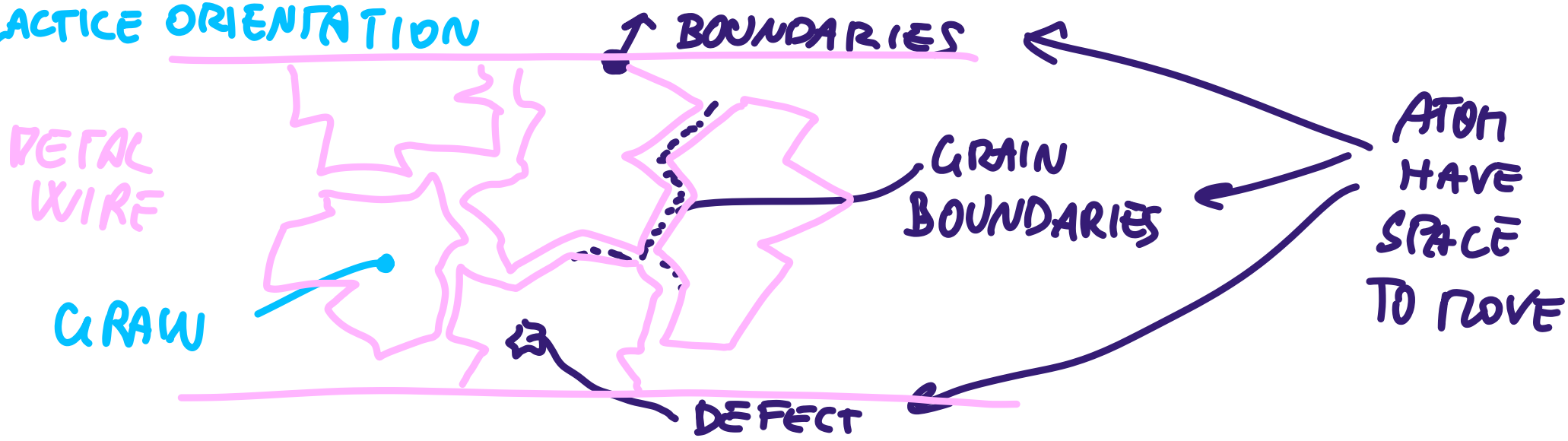


CRISTALLIZATION

- FIB FOR N.G.
- E.M. PART 1 : GENERAL VIEW

MOLECULAR TRANSISTOR FABRICATION

OBJECTIVES

a) GENERAL EXPLANATION FOR EM

b) EXPLOITING EM FOR NG A FIRST VIEW

c) PREORGANIZED STRUCTURE

LET'S SEE A COUPLE OF EXAMPLES

(VIDEOS)

EMPIRICALLY DESCRIBED BY BLACK'S LAW

$$M.T.F. \propto \left(\frac{1}{J^2}\right) \cdot e^{\frac{Q}{k \cdot Tm}}$$

MEAN TIME TO FAILURE

J^2 ← CURRENT DENSITY

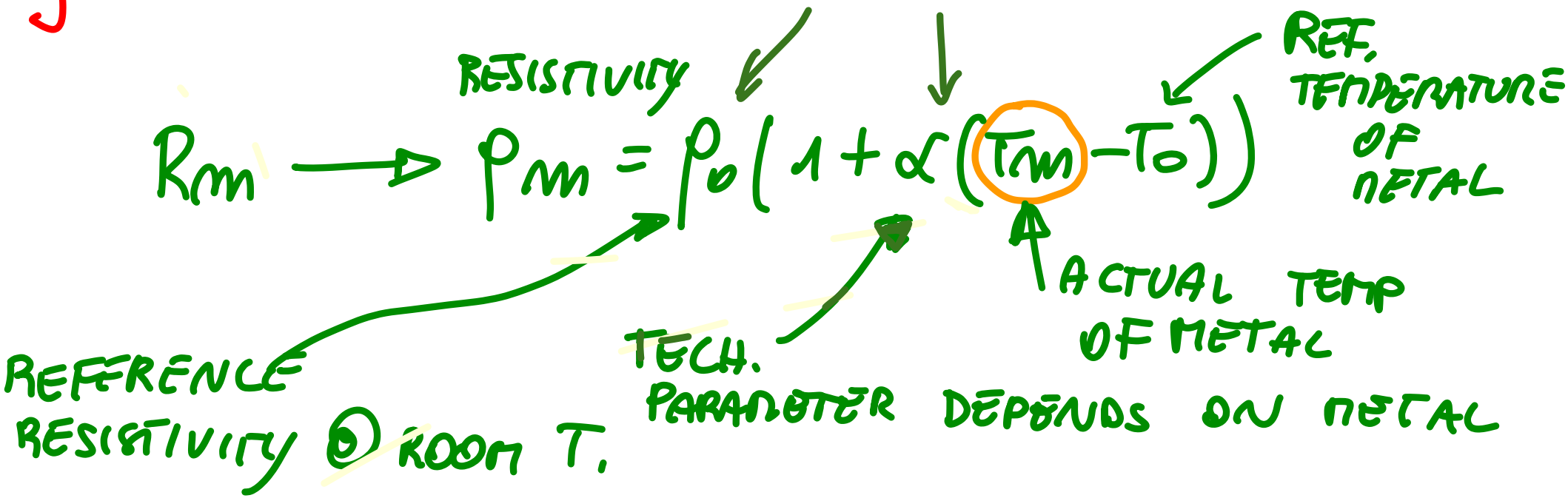
$\frac{Q}{k \cdot Tm}$ ← EXP DEPENDENCY!

k Boltzmann's constant

Q activation energy

Tm actual temperature of metal

JOULE EFFECT



JOULE EFFECT

$$R_m \longrightarrow \rho_m = \rho_0 \left(1 + \alpha \left(T_m - T_0\right)\right)$$

RESISTIVITY

REF. TEMPERATURE OF METAL

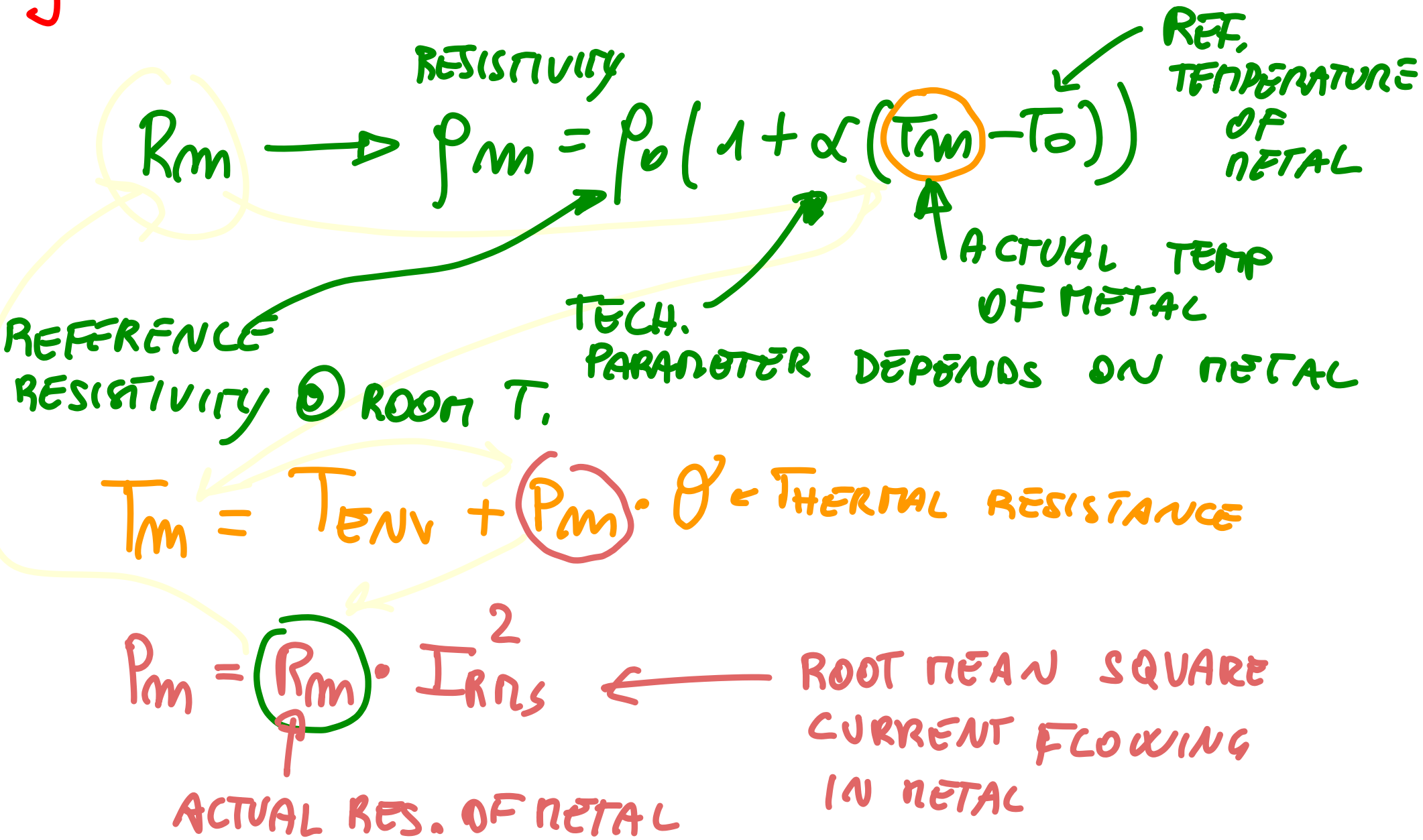
ACTUAL TEMP OF METAL

TECH. PARAMETER DEPENDS ON METAL

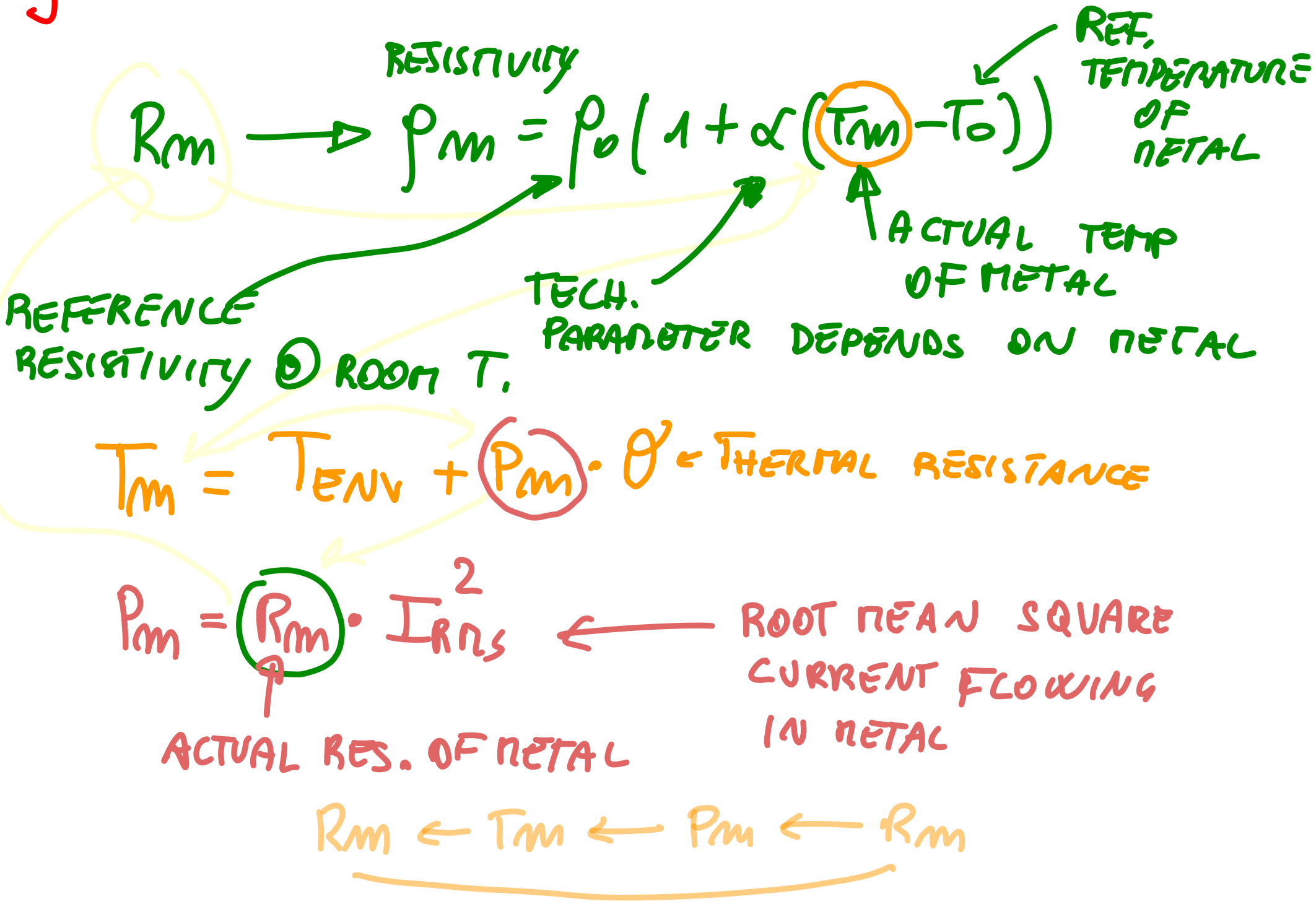
REFERENCE RESISTIVITY @ ROOM T.

$$T_m = T_{ENV} + P_m \cdot \theta \quad \theta = \text{THERMAL RESISTANCE}$$

JOULE EFFECT



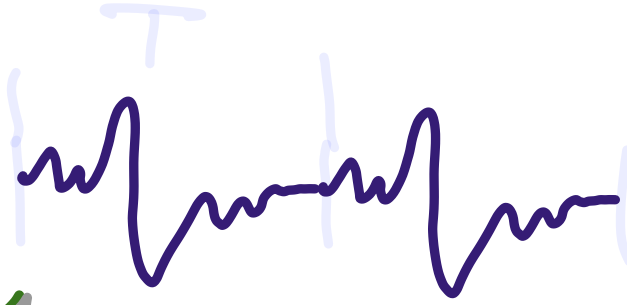
JOULE EFFECT



$$I_{RMS} = \sqrt{\frac{1}{T}\int_0^T I^2(t)\,dt}$$

$f = \frac{1}{T}$ EXAMPLE OF PERIODIC SIGNAL

$$I_{RMS} = \sqrt{\frac{1}{T}\int_0^T I^2(t)\,dt}$$



$$f = \frac{1}{T}$$

EXAMPLE OF PERIODIC SIGNAL

THERMAL RESISTANCE

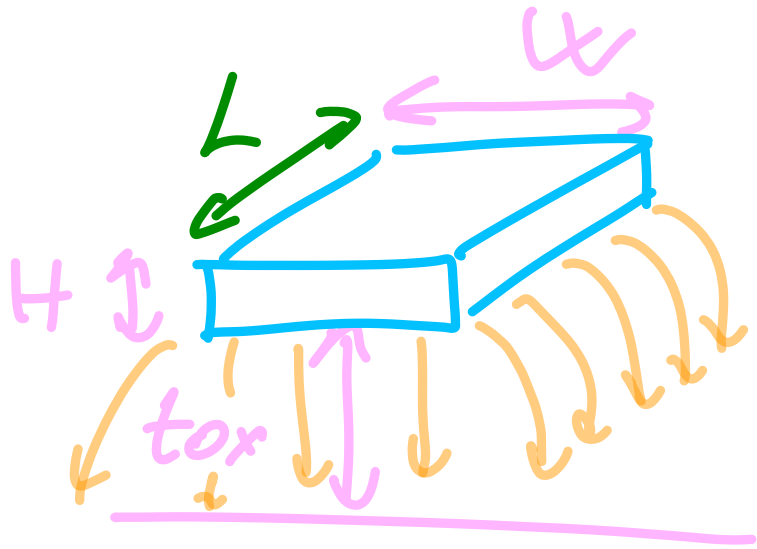
$$\theta = \frac{t_{ox}}{k_{ox} \cdot L(W + \varphi t_{ox})}$$

THERMAL CONDUCTIVITY

BOTTOM DISSIPATION

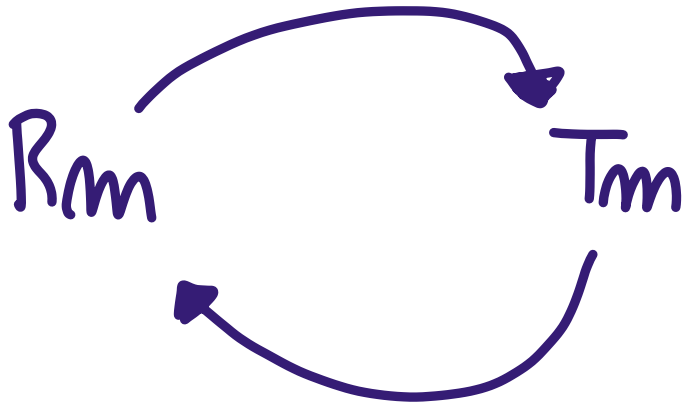
LATERAL DISSIPATION

DUE TO SIDES OF THE WIRES

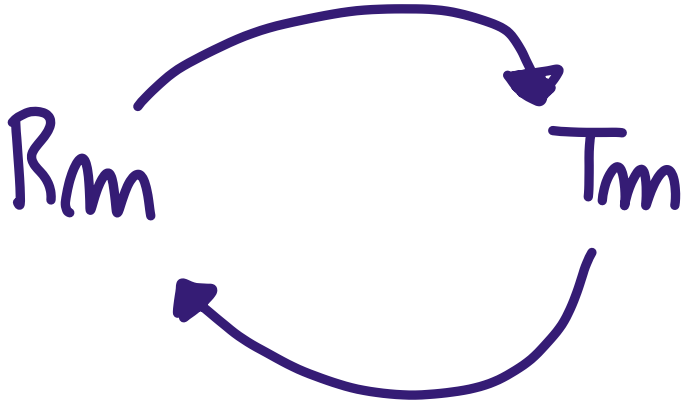


SUB HEAT SINK

JOULE EFFECT



JOULE EFFECT



THERMAL RUNAWAY IN THE METAL

CAUSES THE CREATED BREAK POINT

TO BE UNCONTROLLED → ATOMS GROUP AND MOVE WHERE THEY WANT ☹

CRISTALLIZATION

a) BLOCK'S LAW FOR E.M. EMPIRICAL DESCRIPTION

b) JOULE HEATING & THERMAL RUNAWAY

MOLECULAR TRANSISTOR FABRICATION

OBJECTIVES

a) EXPLOITING EM FOR NG

b) PREORGANIZED STRUCTURE

c) FEEDBACK CONTROLLED EM. - FCE

d) MOLECULE DEPOSITION

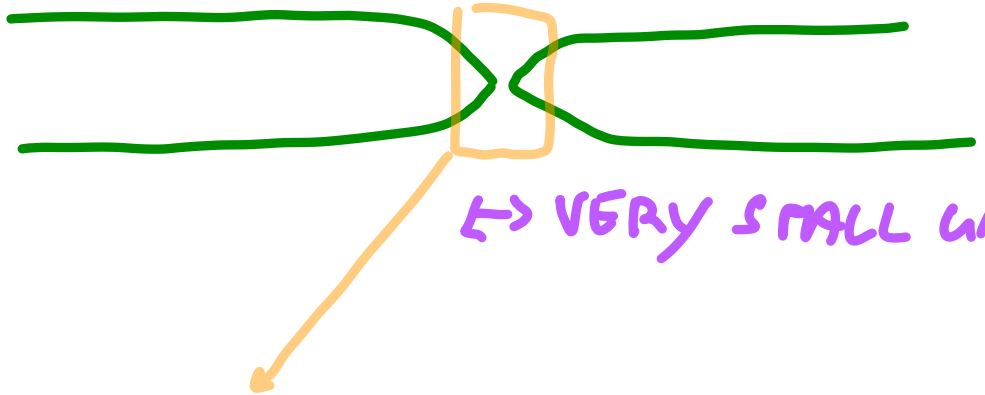
NEXT:

HOW CAN WE EXPLOIT ELECTROMIGRATION FOR N.G. AVOIDING THERMAL RUNAWAY?

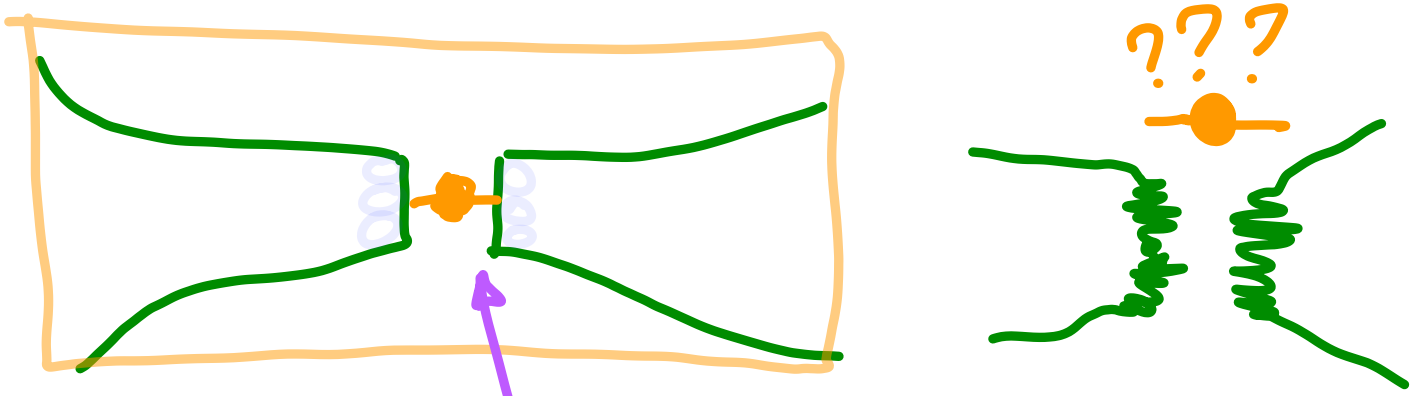
EM IN CASE OF NANOGAP : USE EM AS AN ADVANTAGE

2 REQUIREMENTS FOR FINAL GAP

a)



b)



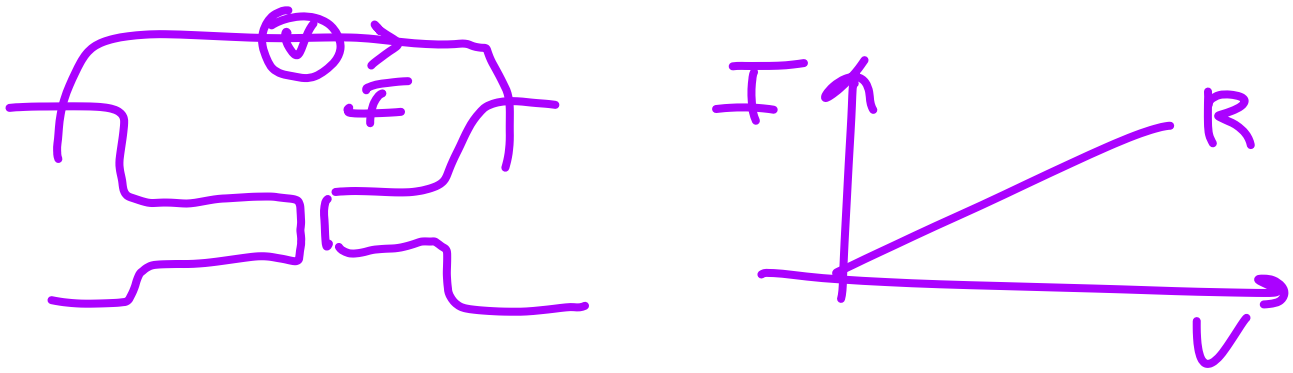
HOW GAPS ARE DETECTED

of $W_{GAP} < 10\,mm$

↳ INSPECTION → STM

→ AFM

↳ MEASURE RESISTANCE



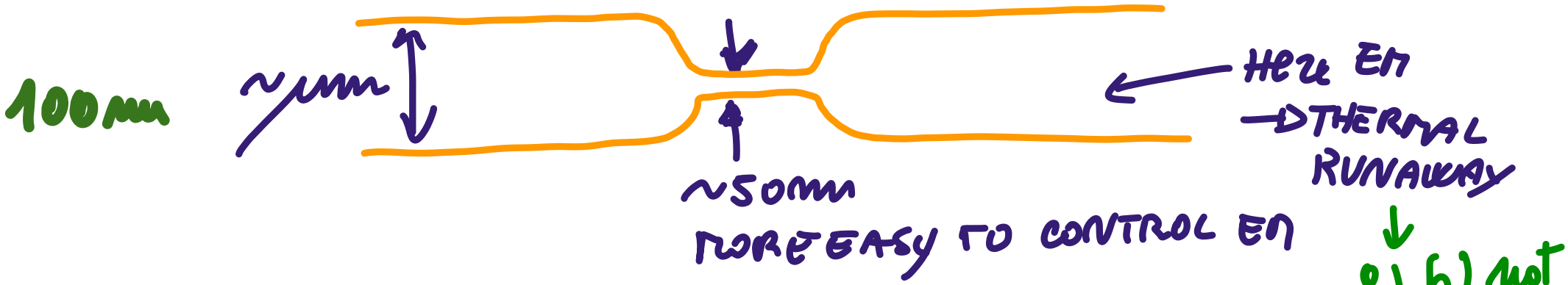
$R \sim 10^2 \div 10^4\,\Omega$: CONDUCTIVE BEHAVIOR ↓ NO GAP

$R \sim 10^{14}\,\Omega$: ELECTRODES ISOLATED : GAP WIDE!

$R \sim 10^4 \div 10^{14}\,\Omega$: CONDUCTION THROUGH TUNNEL : $W_{GAP} \sim 3\,mm$

EM FOR NANOGAP IN MOLECULAR ELECTRONIC

① • PREORGANIZATION OF NGAP STRUCTURE



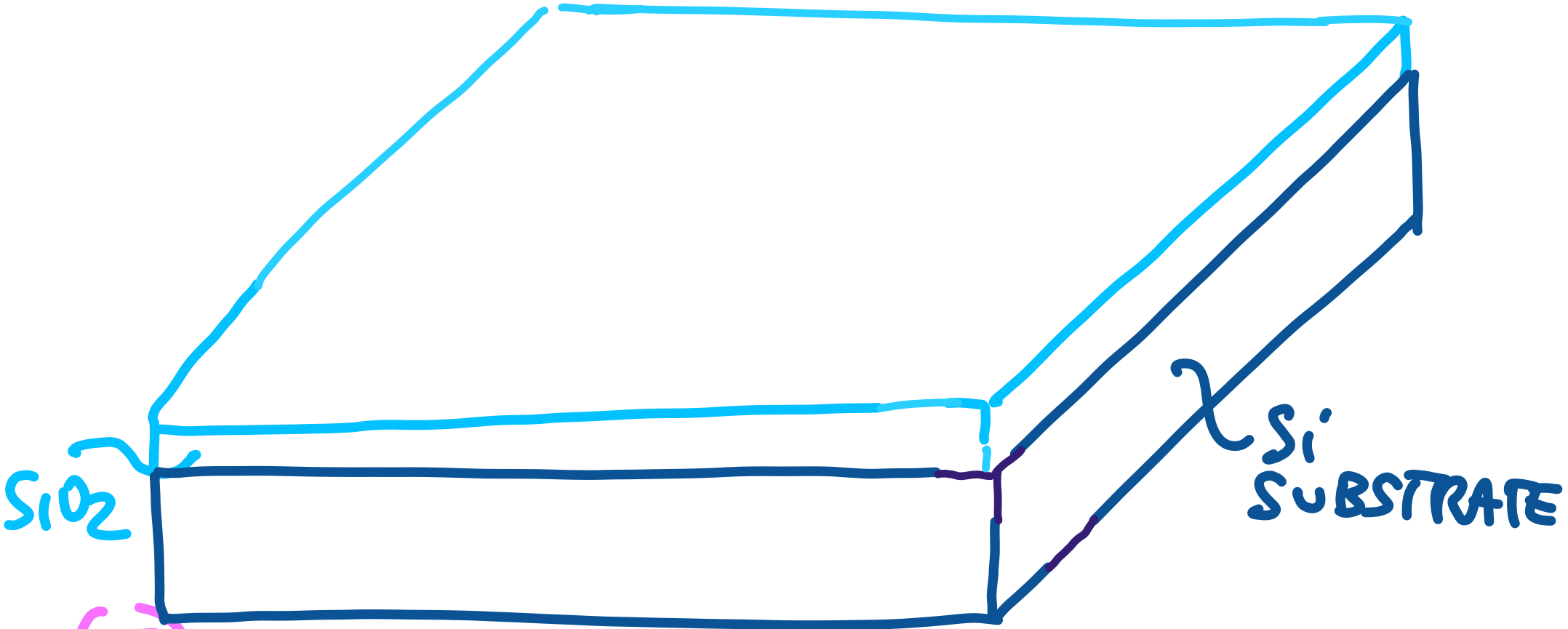
② APPLY FCE

FEEDBACK CONTROLLED EM

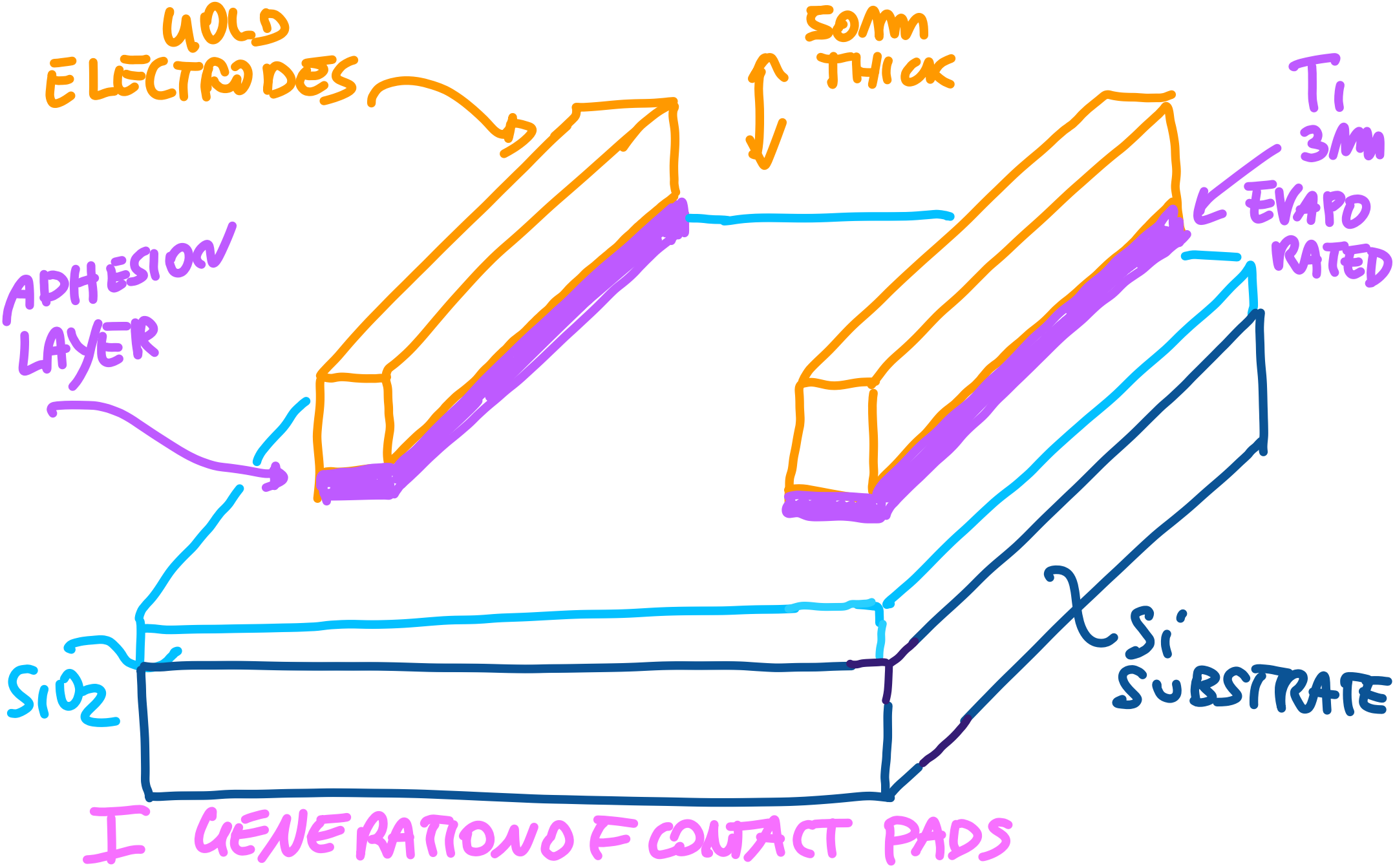
→ CURRENT IS APPLIED IN SUCCESSIVE STEPS, IN EACH STEP LIMITING I TO THE MINIMUM TO CAUSE WIRE CONSUMING WITHOUT T.R.

① • PREORGANIZATION OF NGAP STRUCTURE

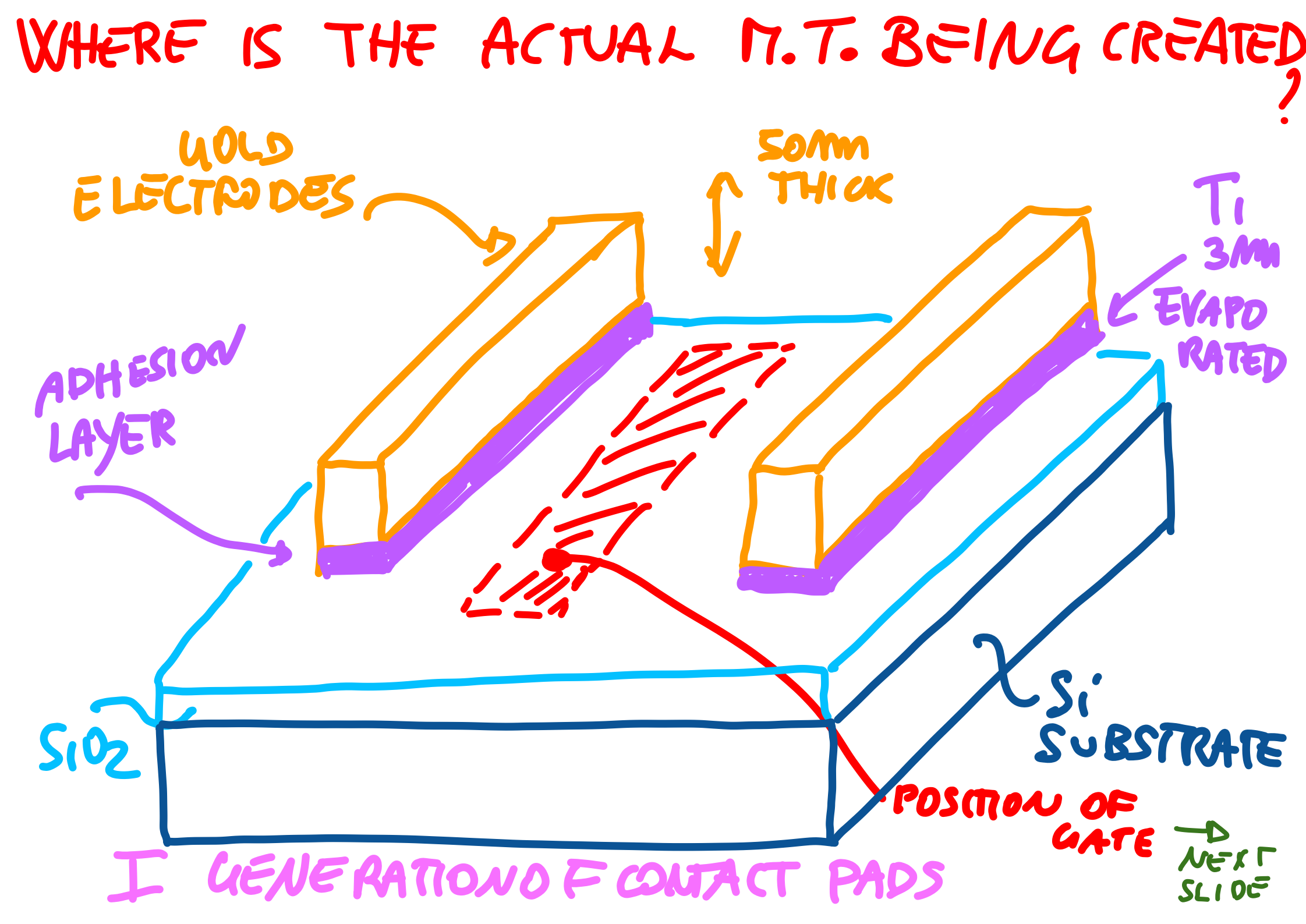
① EXAMPLE OF A PREORGANIZATION STRUCTURE

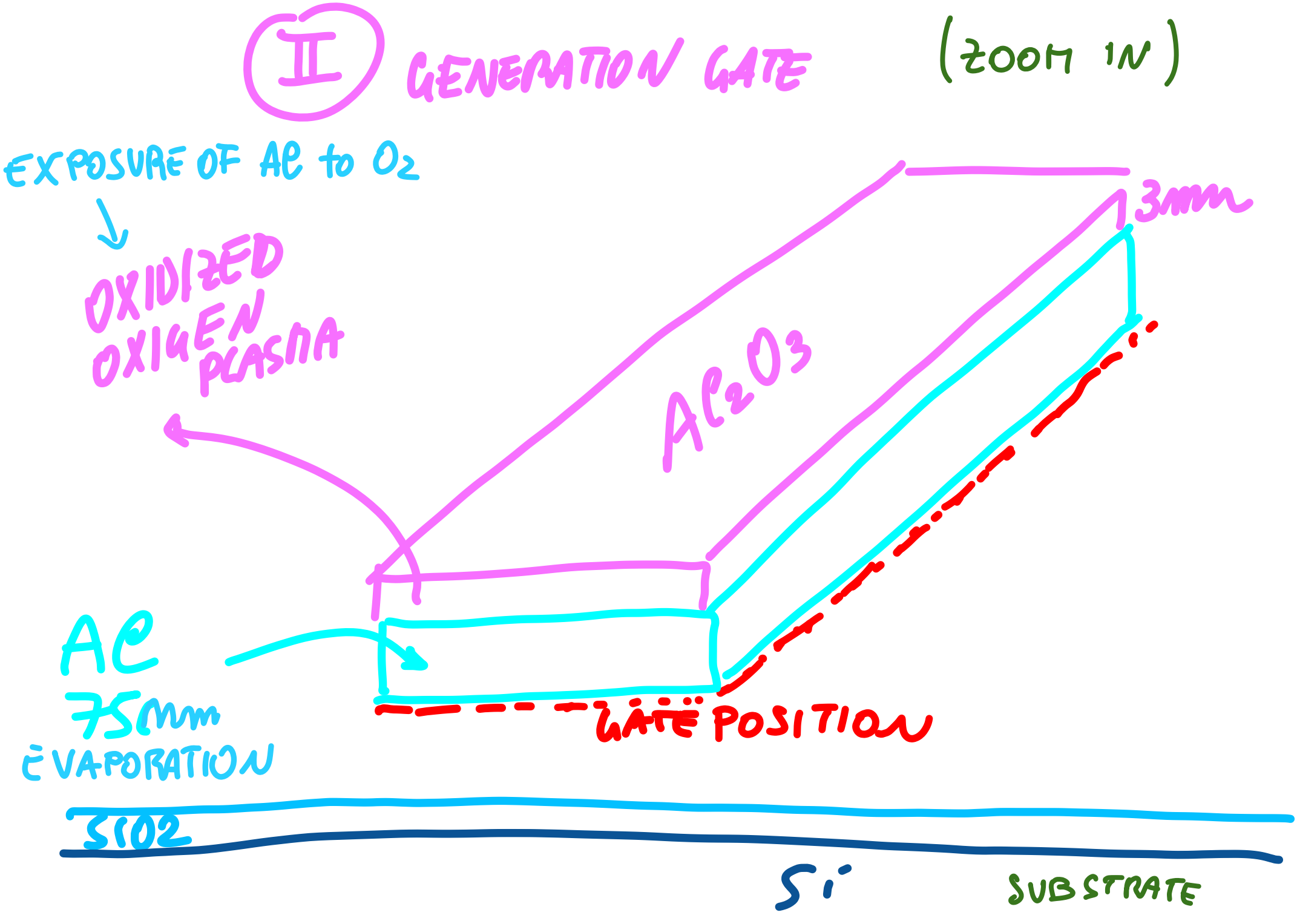


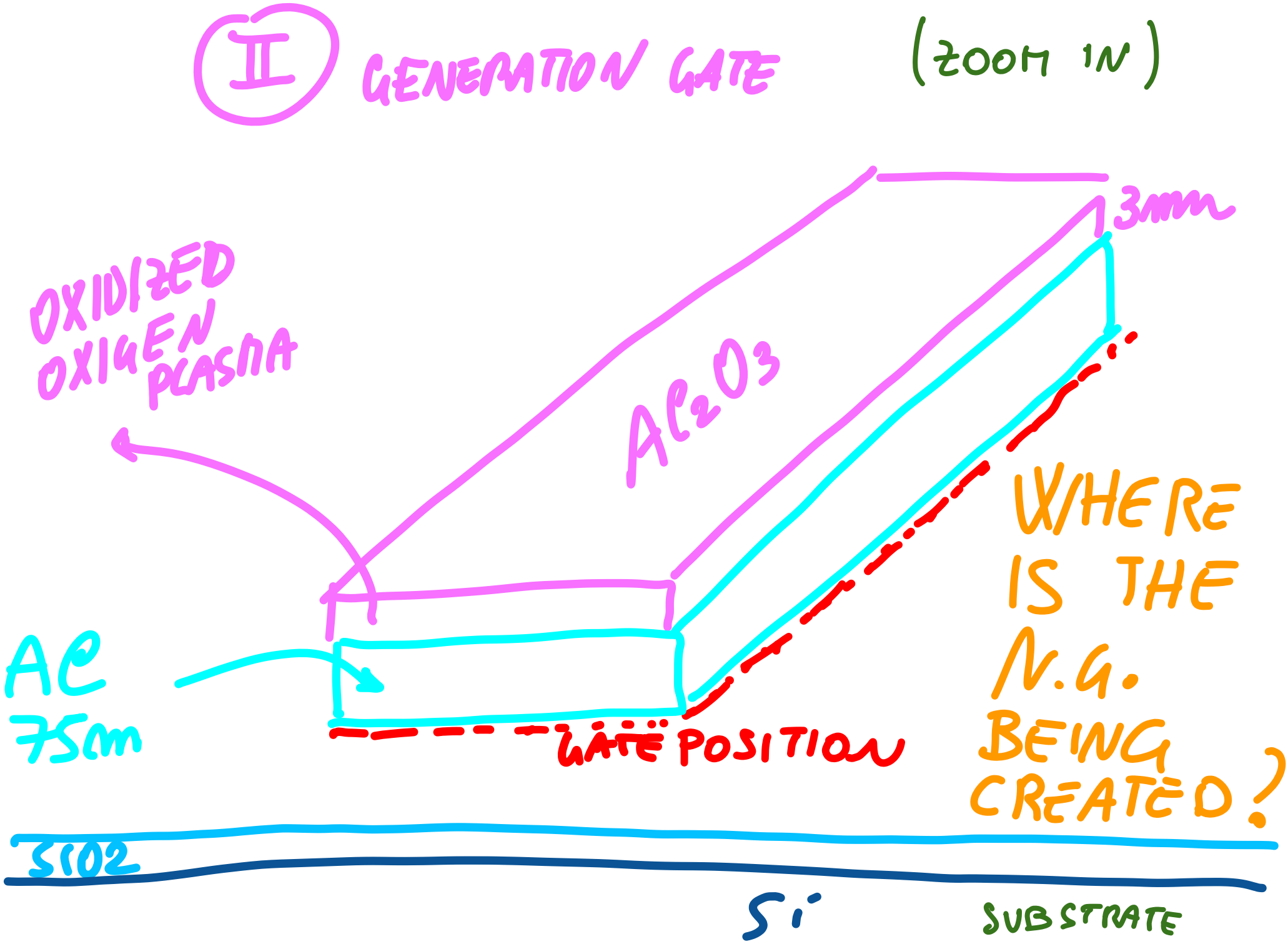
(I) GENERATION OF CONTACT PADS : SUBSTRATE


GOLD
ELECTRODES
50nm
THICK
Ti
3nm
EVAPO
RATED
ADHESION
LAYER
SiO2
Si
SUBSTRATE
I GENERATION OF CONTACT PADS

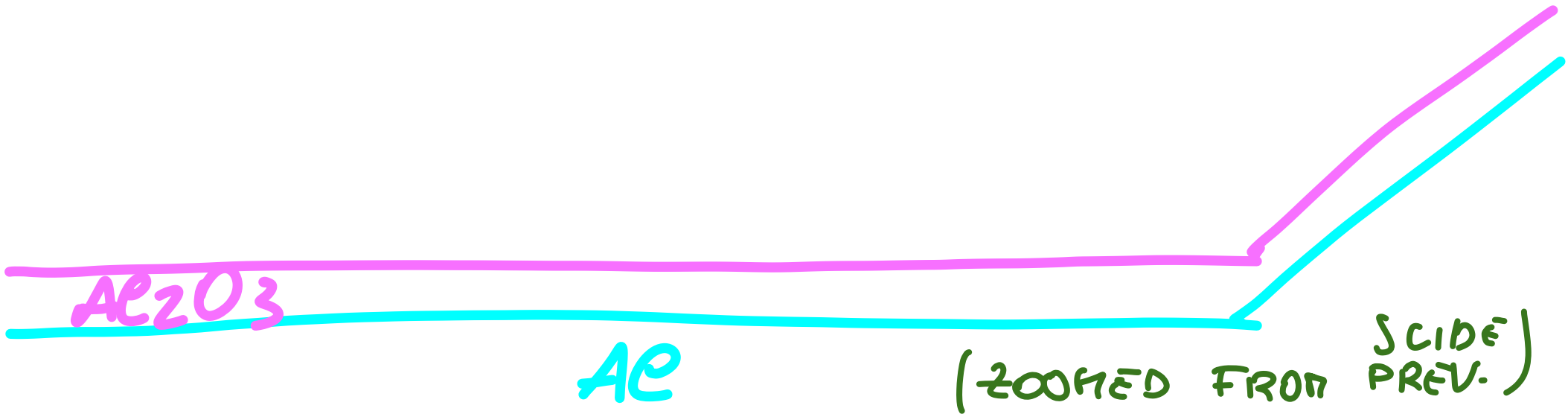
WHERE IS THE ACTUAL M.T. BEING CREATED?



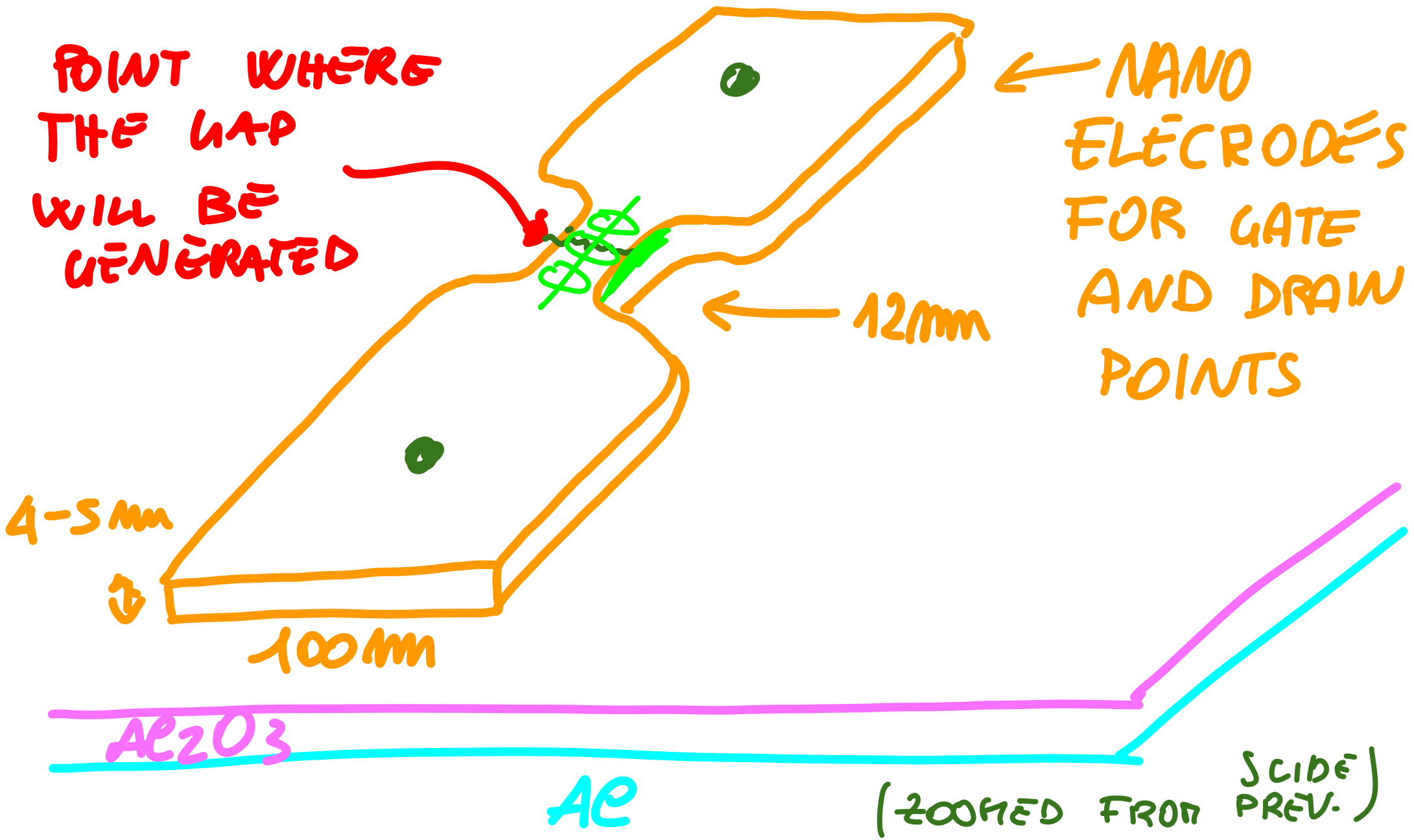

II
GENERATION GATE
(ZOOM IN)
EXPOSURE OF Al to O_2
OXIDIZED OXIGEN PLASMA
3mm
Al_2O_3
Al
75nm
EVAPORATION
GATE POSITION
SiO2
Si
SUBSTRATE


II
GENERATION GATE
(ZOOM IN)
3mm
OXIDIZED
OXIGEN
PLASMA
Al_2O_3
AL
75nm
GATE POSITION
WHERE
IS THE
N.G.
BEING
CREATED?
SiO2
Si
SUBSTRATE

III ELECTRODE FOR NANOGAP GENERATION

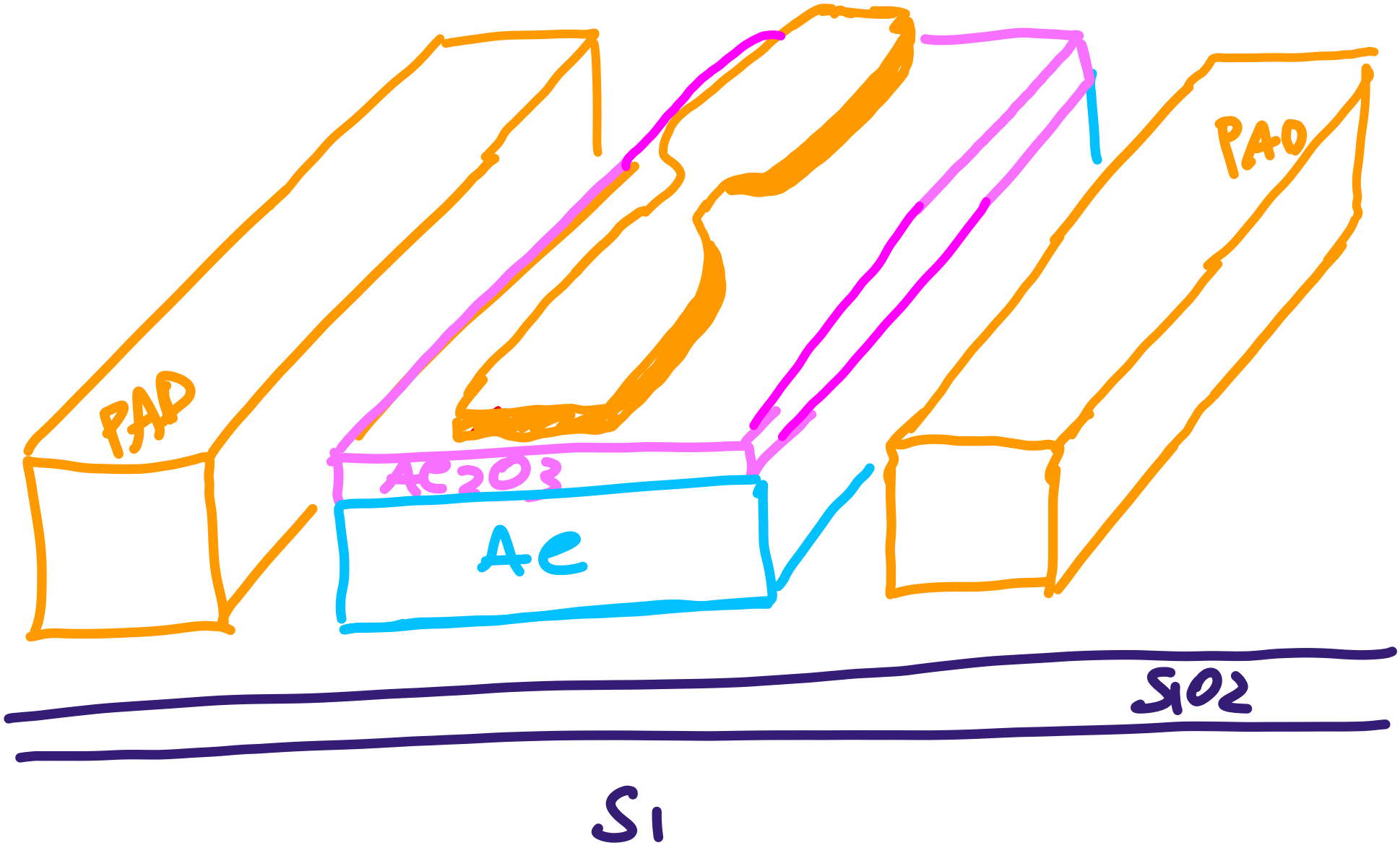


III ELECTRODE FOR NANOGAP GENERATION

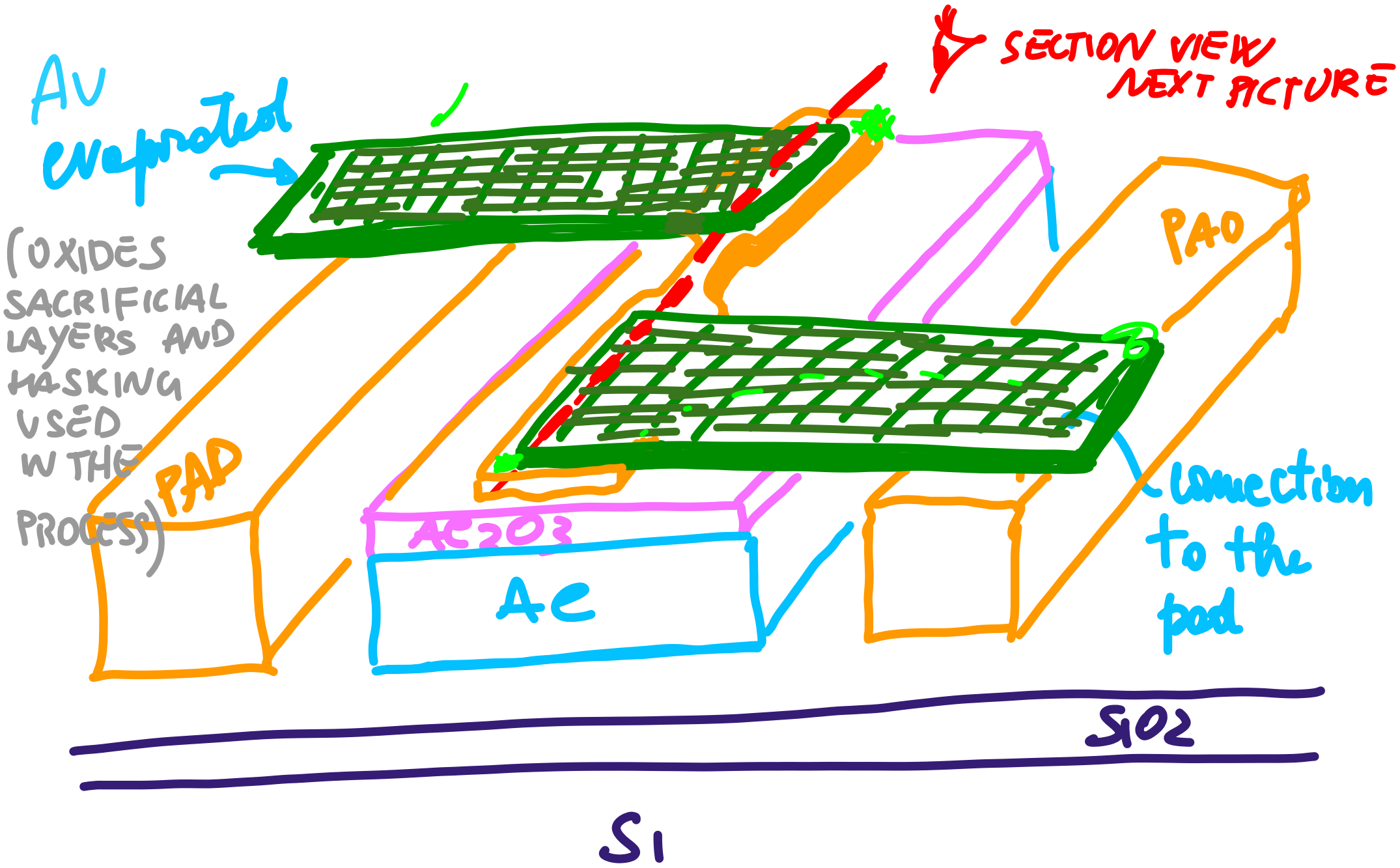


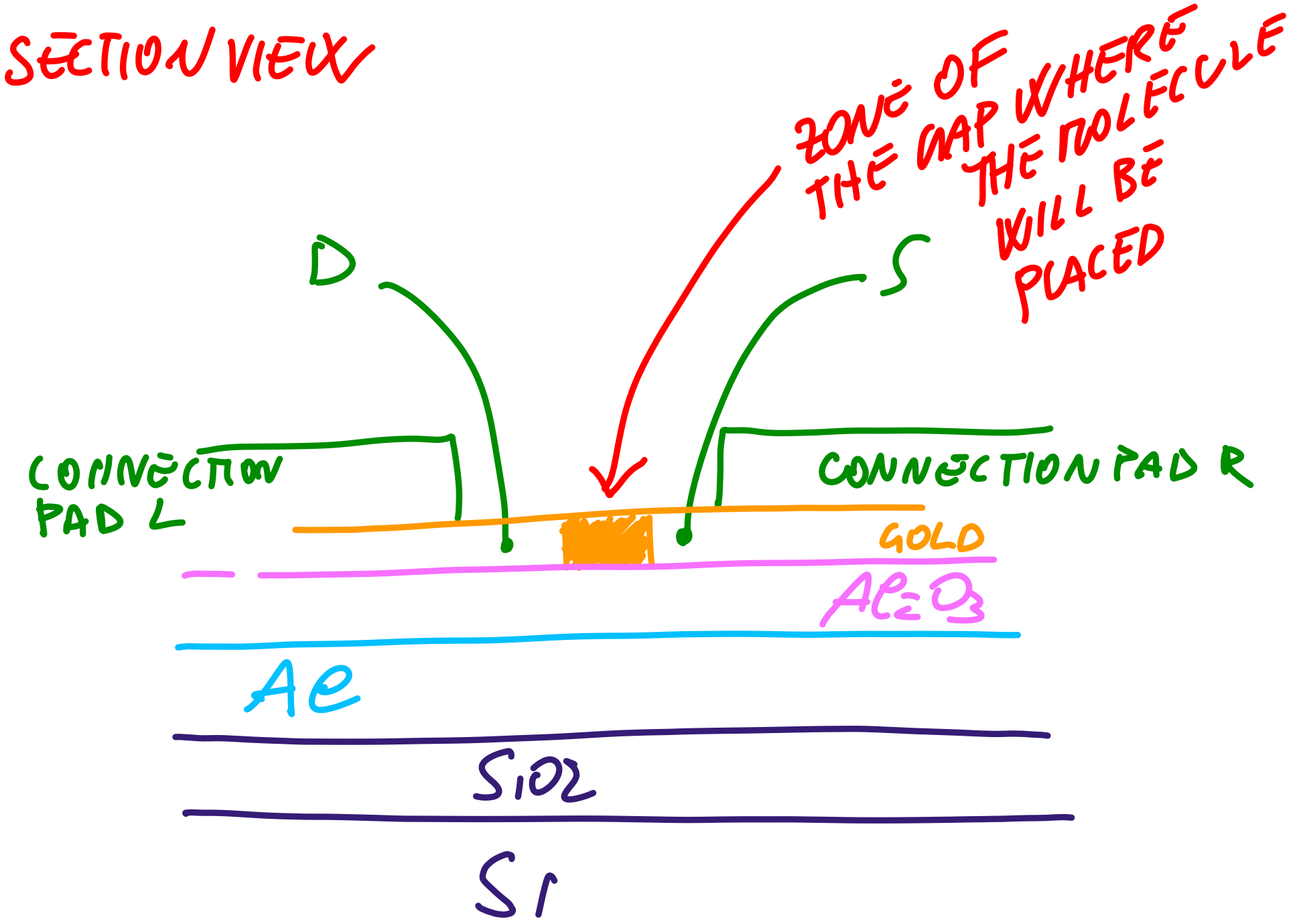
IV CONNECTION TO ELECTRODES

ZOOM OUT

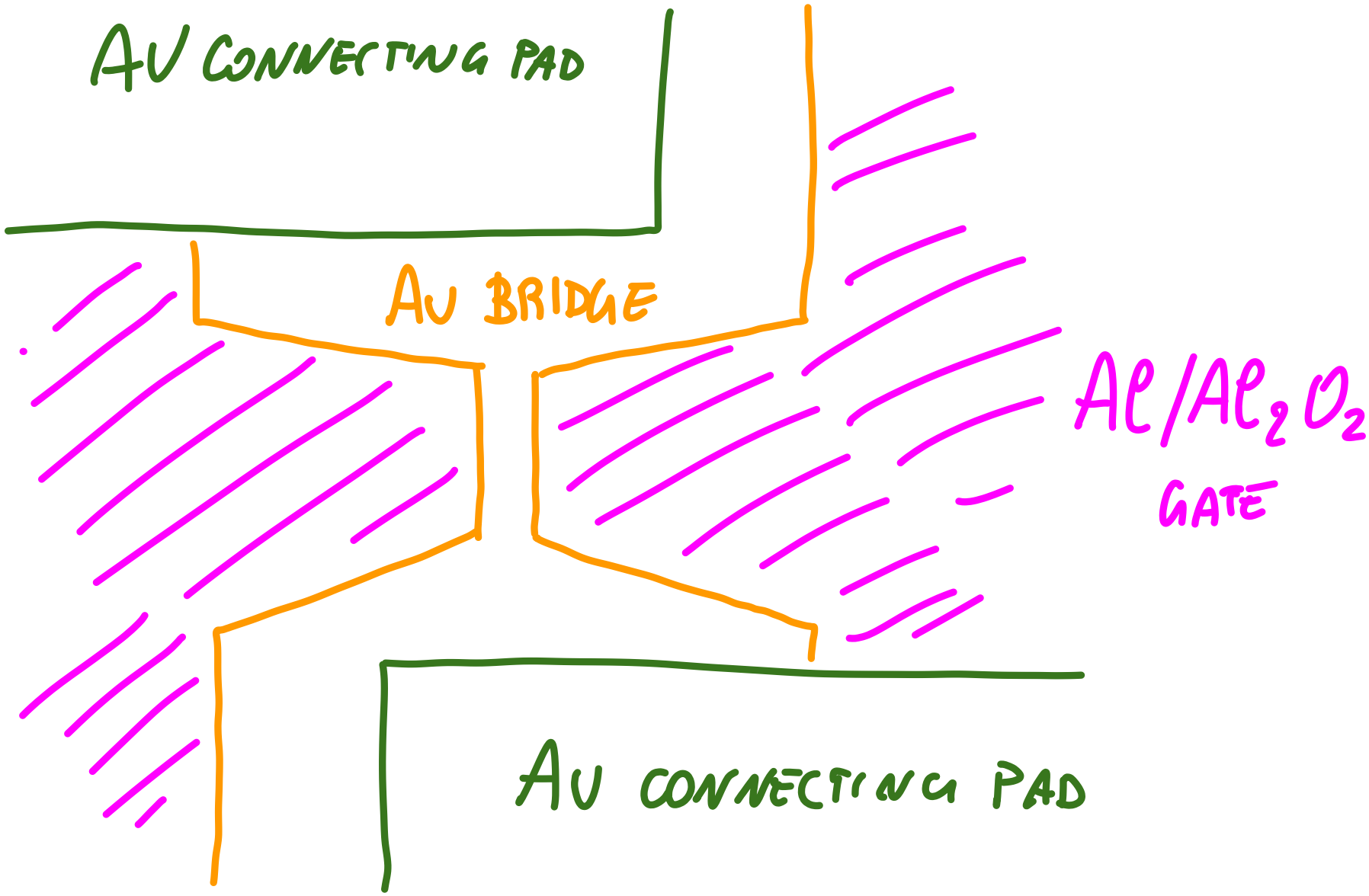


IV CONNECTION TO ELECTRODES

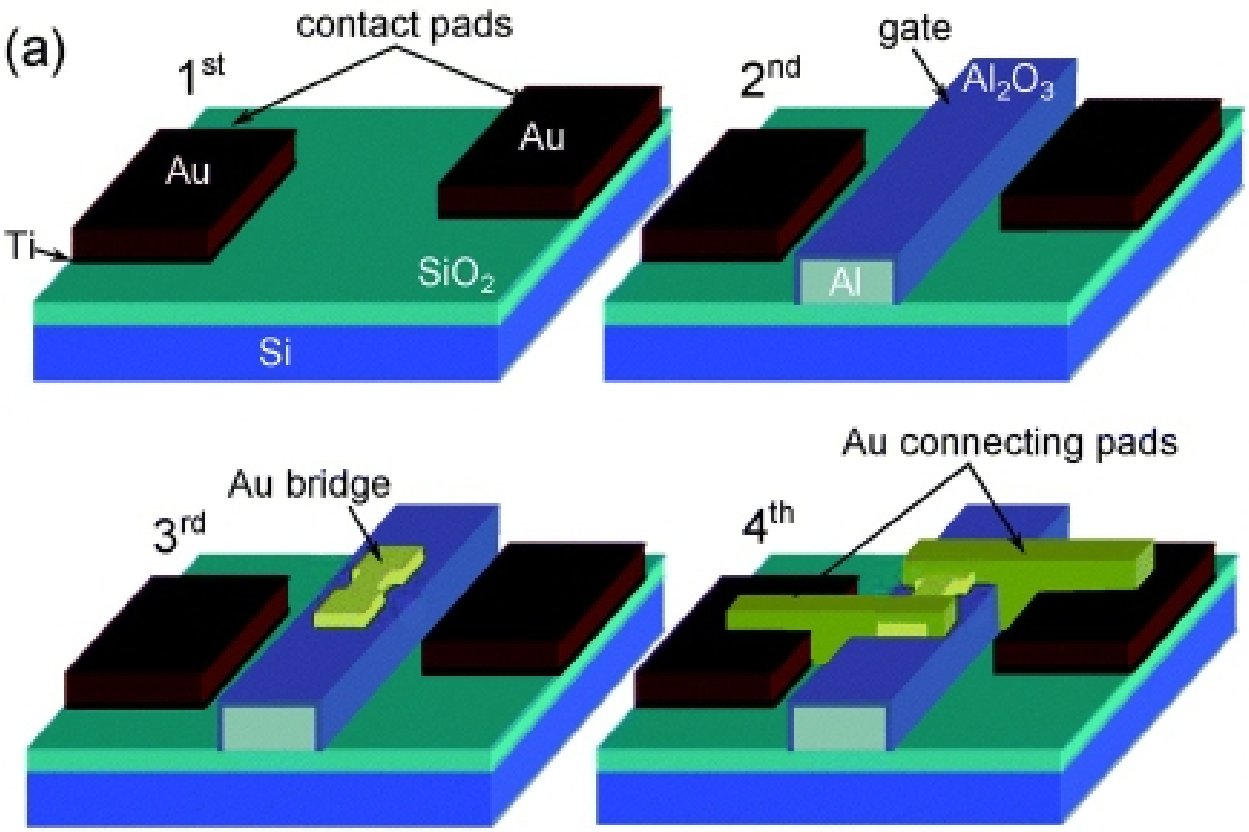


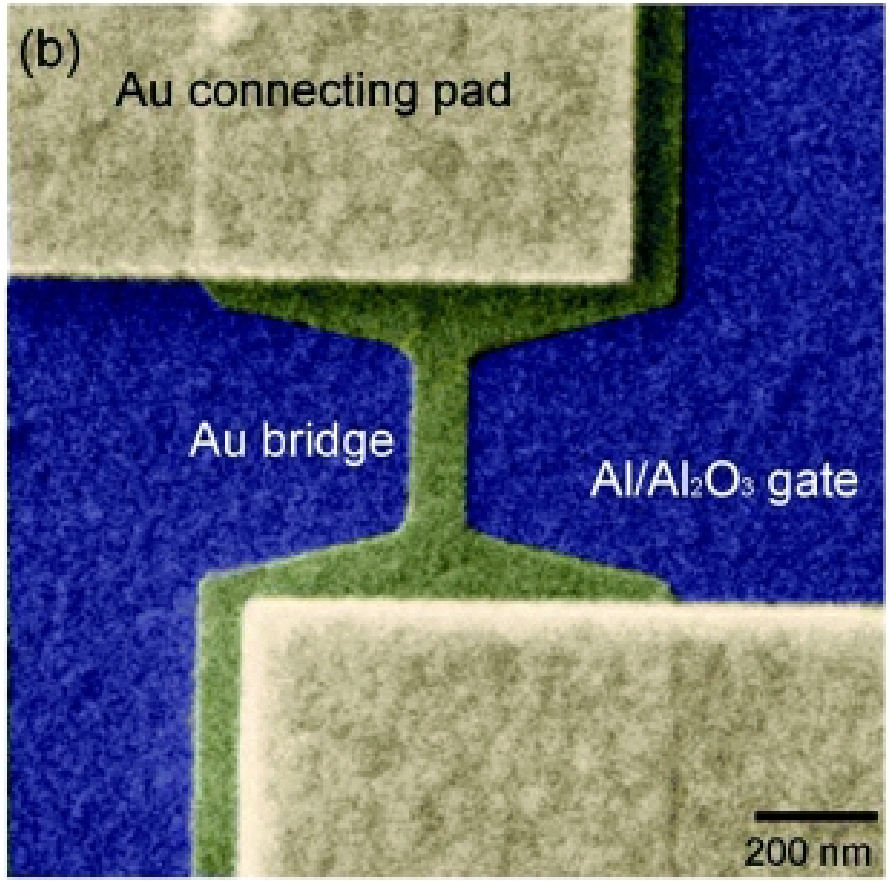

SECTION VIEW
ZONE OF THE GAP WHERE THE MOLECULE WILL BE PLACED
D
S
CONNECTION PAD L
CONNECTION PAD R
GOLD
Al2O3
Ae
SiO2
Si

TOP VIEW (ZOOM IN N.G. ZONE)



THE FABRICATED EXAMPLE [*]



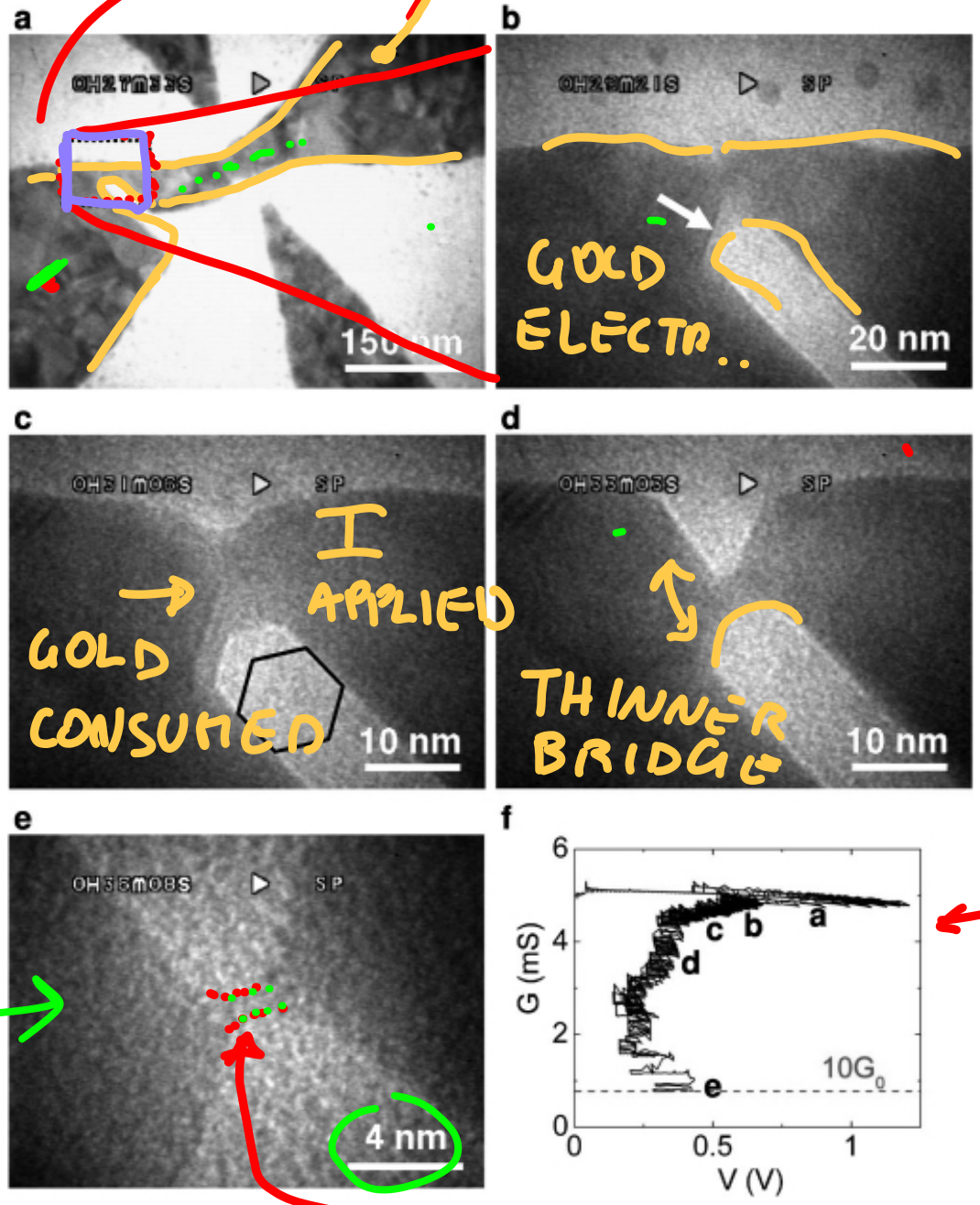


DELFT GROUP

[*] FROM: "SINGLE MOLECULE TRANSISTOR", CHEM. SOC. REV. 2015, 44, 902-919

(2) APPLY FCE

FEEDBACK CONTROLLED EM



TEM VIEW OF A FCE PROGRESSIVE APPLICATION

VIDEO

CONDUCTANCE REDUCES AT EACH STEP

FEW GOLD ATOMS BEFORE BREAKING

NEXT:

DETAILS ON HOW IT WORKS AND PHYSICAL MODELING

HOW EM HAPPENS IN NGAPS

2 REQUIREMENTS

1) $\int$ ↗ BIG ENOUGH → must reach J_{min} (SEE THEORY PART)

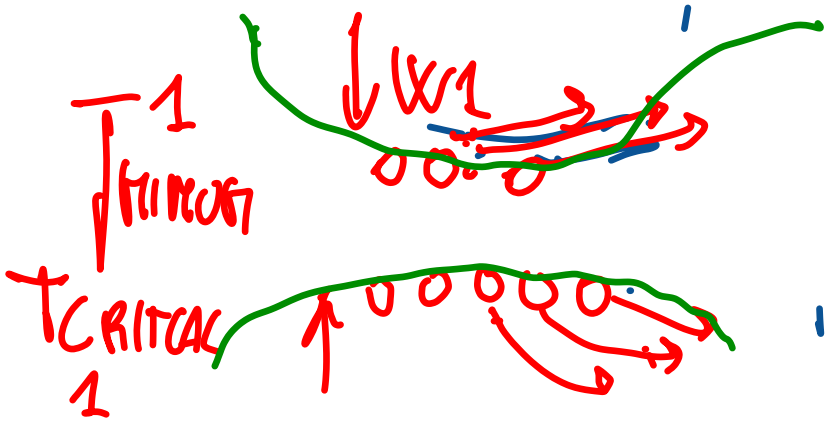
2) ATOMIC MOBILITY MUST RISE ← ALLOWED ↗ T

T → must reach T_{CRIT} SUFFICIENT TEMP. IS NEEDED TO START MIGRATION

$\int$ MUST BE: BIG ENOUGH TO START EM
SMALL ENOUGH TO AVOID RUNAWAY

if J_{MIN}, T_{CRIT} ⟹ the process starts

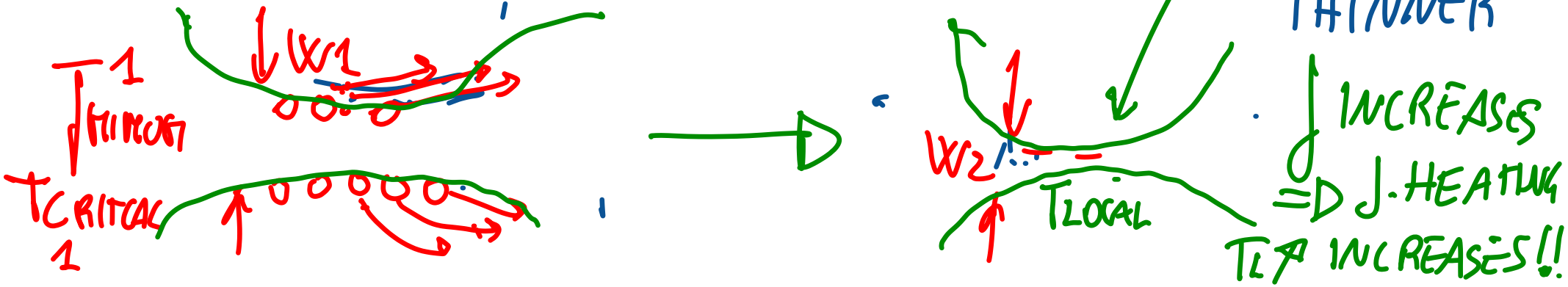
METAL IONS START TO MOVE



W_1

if j_{HIGH}, T_{CRIT} ⇒ the process starts

METAL IONS START TO MOVE



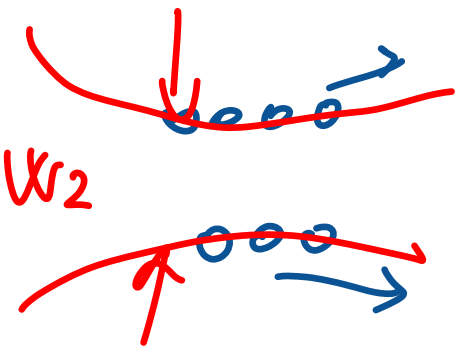
W_1

R_1

W_2

R_2

THE PROCESS IS STOPPED AND STARTED AGAIN IN W_2 CONDITIONS

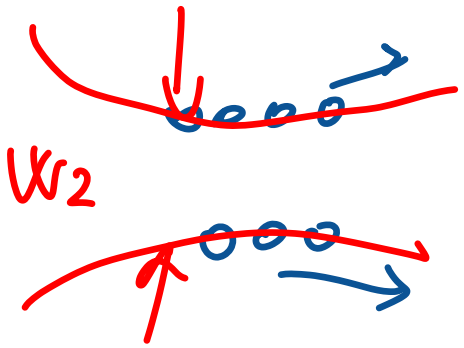


J^2_{TRIN}

$J^2_{CRIT.}$

I CHANGED so that J^2_{TRIN} is reached.

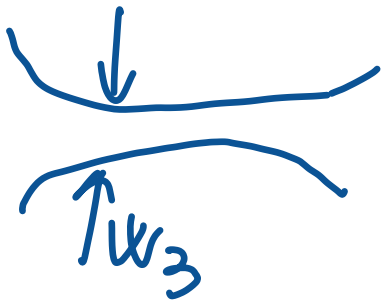
THE PROCESS IS STOPPED AND STARTED AGAIN IN W_2 CONDITIONS



J^2_{MIN}

$J^2_{CRIT.}$

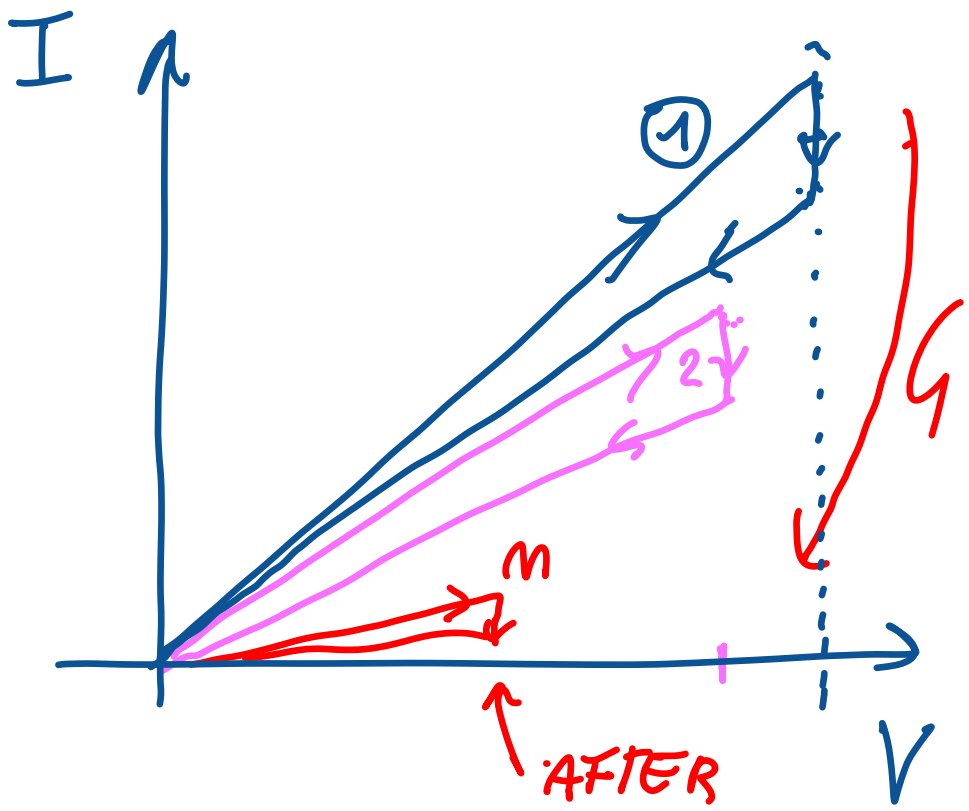
I CHANGED SO THAT J^2_{MIN} IS REACHED



R_3

W_3 IS SMALLER AND AGAIN I MUST BE STOPPED TO AVOID THERMAL RUNAWAY

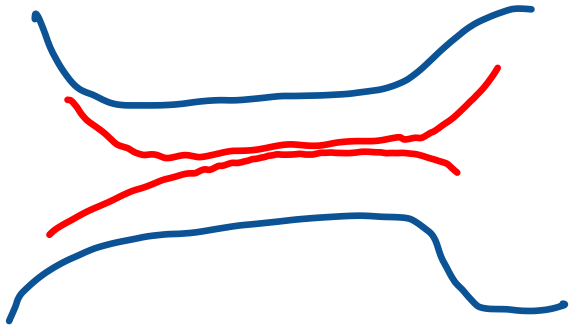
⋮



① J_{MAX}^{1}

② J_{MIN}^{2}

FEEDBACK CONTROLLED ELECTRO-MIGRATION



RESISTANCE IS MEASURED AT EACH STEP

→ R ↗ ~ 3KΩ
G ↘ very smooth

} AFTER THIS THE GAP WILL FORM IF I IS APPLIED, BUT .....

SEE LATER

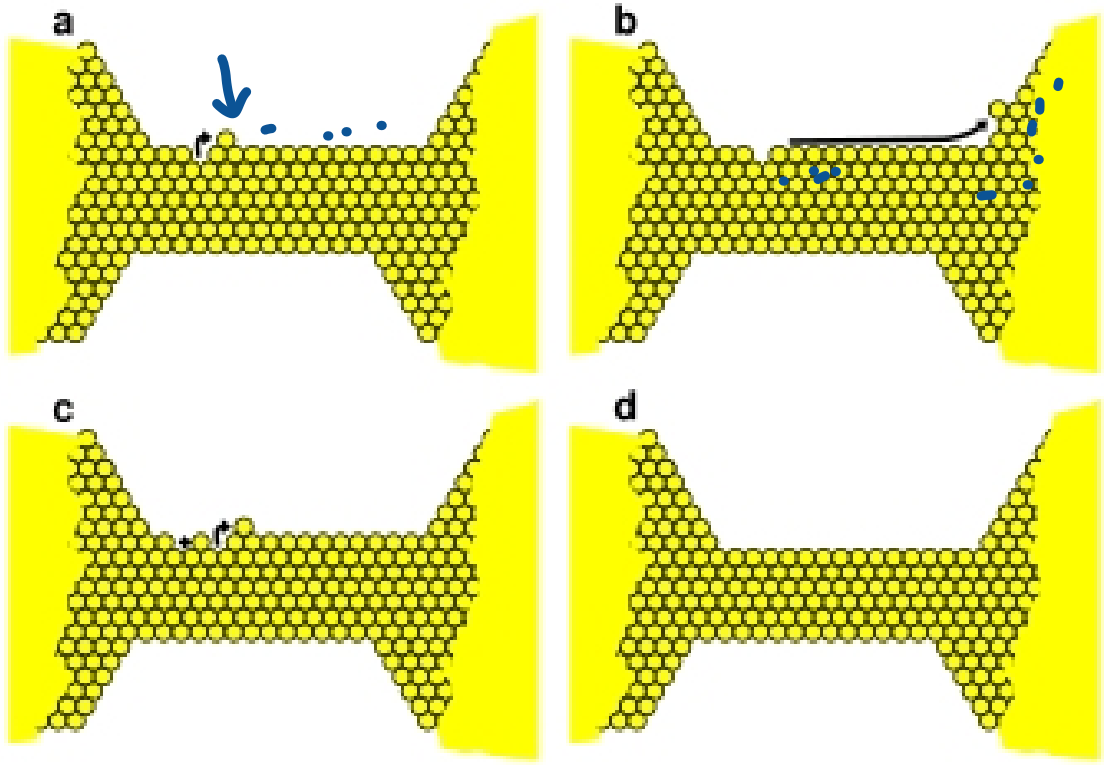


FIG. 2 (color online). Unzipping model of evolution of a nanogap during FCE. (a) Starting with the initial wire, an edge atom is thermally excited. (b) This atom is easily transported away by the applied current along the high-mobility ⟨110⟩ directions. (c) The edge vacancy allows adjacent atoms to easily electromigrate and jump to the edge due to their reduced number of nearest neighbors. (d) The edge is thus unstable once the unzipping of a layer begins.

EM HAPPENS @SURFACE ONLY IN THIS CONDITIONS

FROM PRL 100, 056805 (2008) - Real-Time TEM Imaging of the Formation of Crystalline Nanoscale Gaps

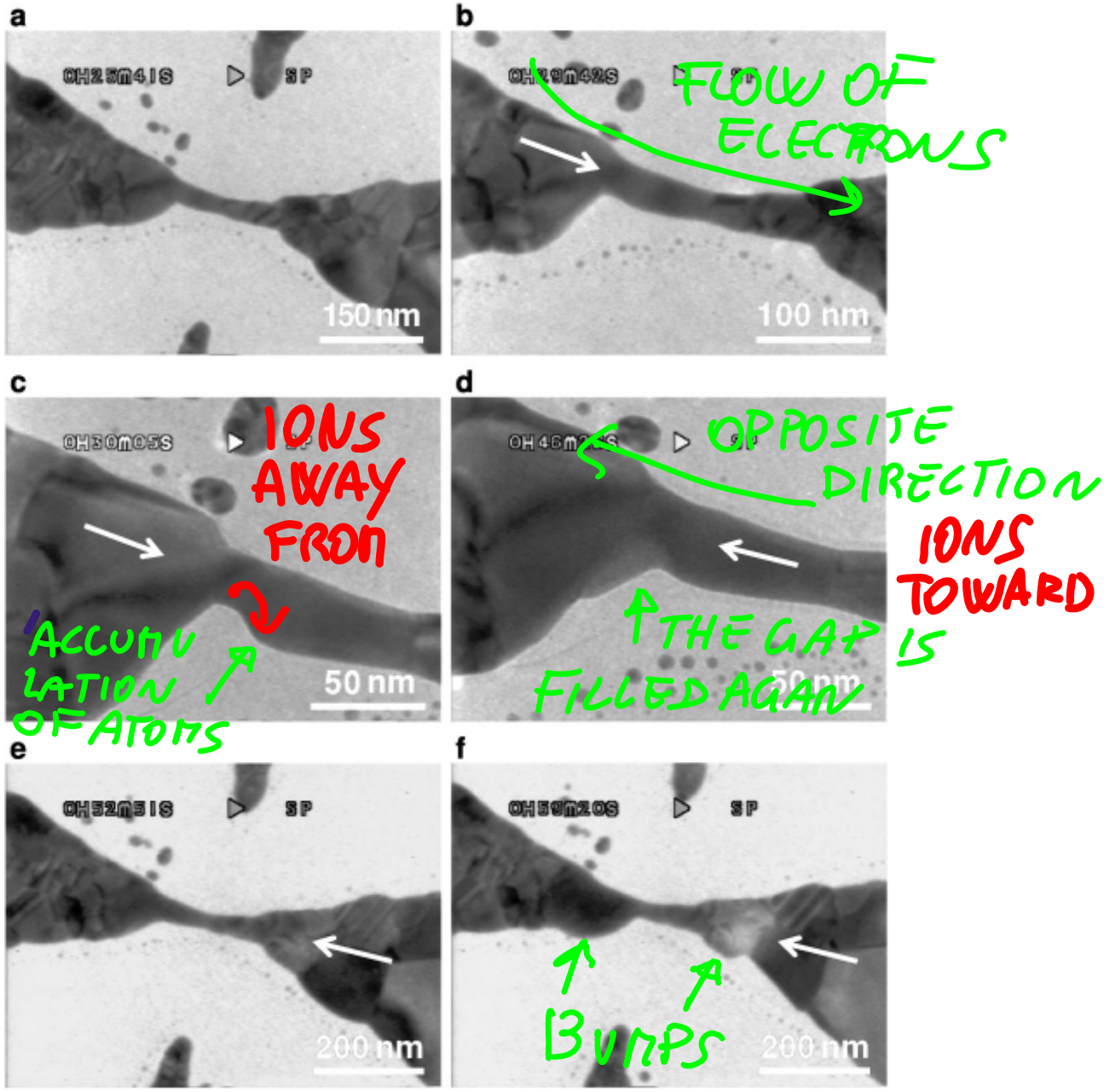
EM IN THE CORRECT CONDITIONS IS

REVERSIBLE

CURRENT APPLIED IN OPPOSITE DIRECTIONS MOVES IONS

→ FROM THE BRIDGE

→ TO THE BRIDGE



WHAT'S NEXT? A MOLECULE MUST BE TRAPPED IN THE GAP! HOW?

(1) PUT STRUCTURE IN SOLUTION WITH MOLECULES
BEFORE THE FINAL NG STEP
TO AVOID OTHER IMPURITIES
FILL THE GAP → VERY IMPORTANT!

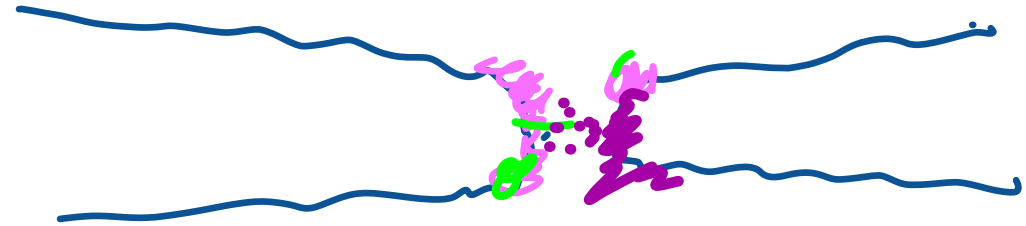
(2) TWO POSSIBLE CHOICES

2.1 • INSERT GAP STRUCTURE IN SOLUTION
• APPLY LAST I CYCLE → CREATE GAP
• WAIT FOR CONNECTION OF MOLECULE TO GAP SIDES

$R \to \infty$
NO MORE CURRENT!

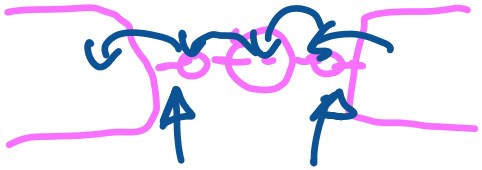
CHOICE 1 HAS PROBLEMS!

① APPLY I



METAL IONS AROUND THE GAP

→ CREATE



CREATE DURING CHARGE INJECTION

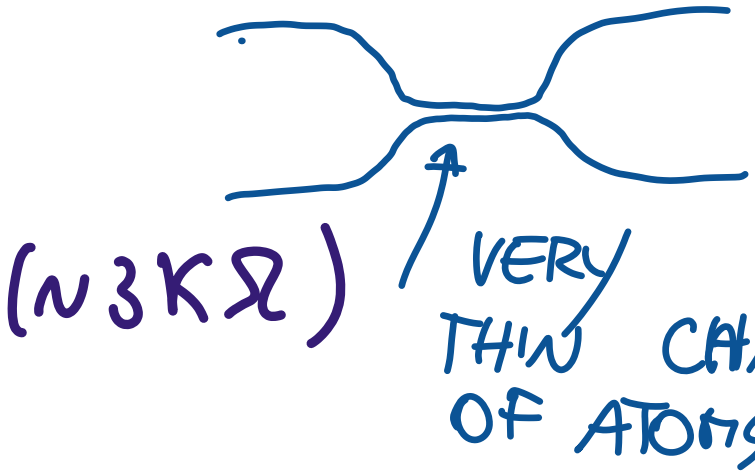
EVEN IF J IS SMALL, IONS CAN ACCUMULATE IN UNFAVOURABLE POSITIONS ALONG CAPSIDES → BAD CONNECTION OF MOLECULES!

② if THE MOL. IS PRESENT DURING FINAL I APPLICATION

↳ → HIGH TEMP → CHANGE MOLECULE CONDUCTANCE

ALTERNATIVE SOLUTION

2.2 EXPLOIT NATURAL



→ PUT IN SOLUTION

@ CONTROLLED T

↓

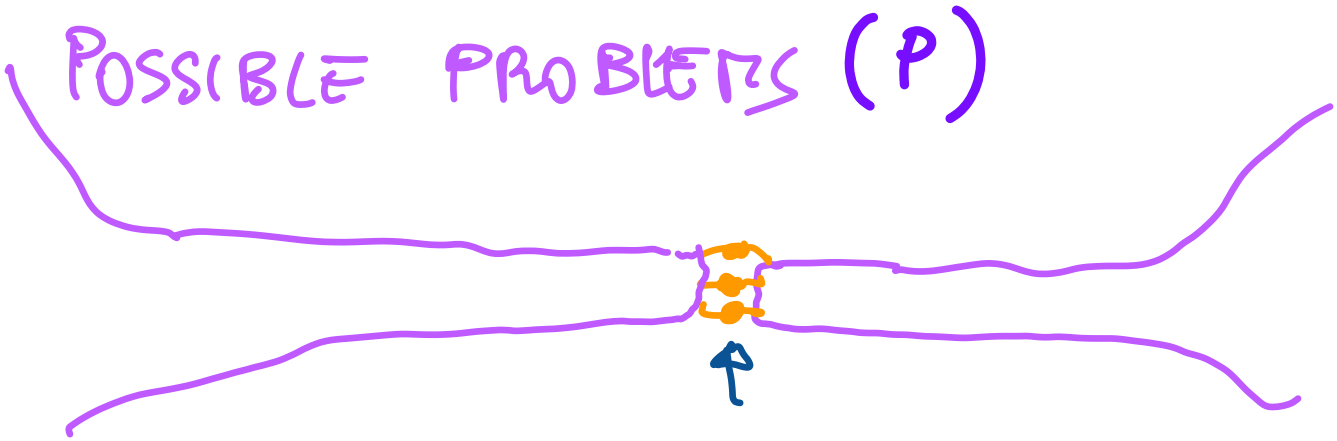
AFTER SOME TIME THE GAP CREATED NATURALLY

EX. 1 HOUR @ 100 KELVIN

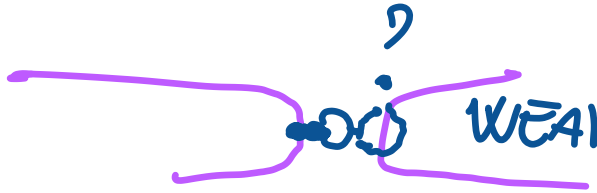
☺ NO BUMPS OF METAL

☺ NO DAMAGE OF MOLECULE

EVEN IN CASE 2.2 SOME PROBLEMS COULD ARISE



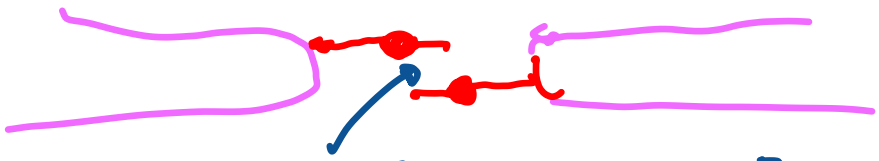
P_1 MORE THAN 1 POL



P_2

OR MISSING CONNECTION (DANGLING SIDE)

P_3



TUNNELING BW 2 UNCONNECTED POL.

CRISTALLIZATION

1) STRUCTURE CREATION

2) FCE HOW TO

3) MOLECULE DEPOSITION

NEXT: PHYSICAL MODELING