ALD

Kye Okabe

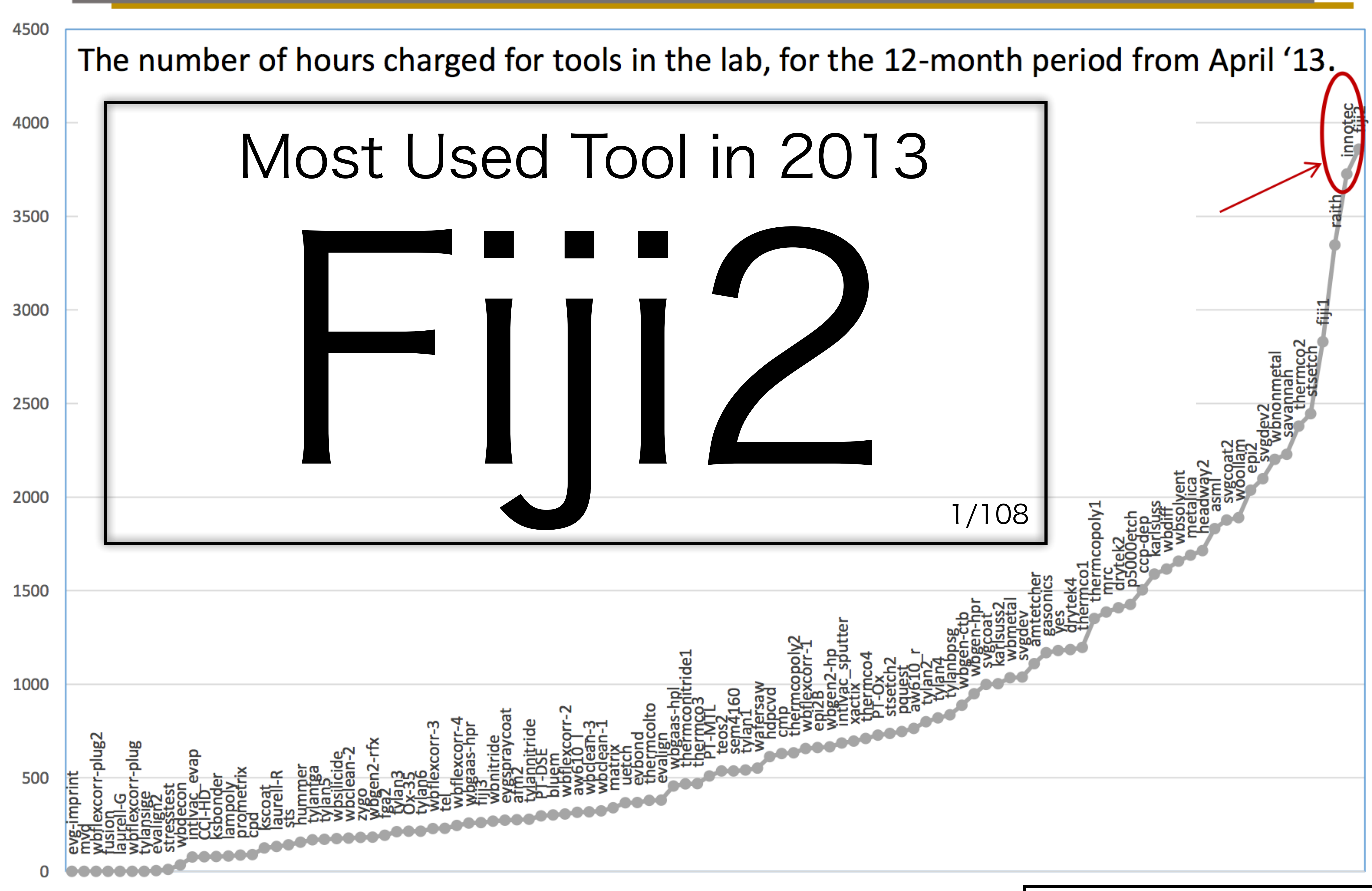
TiN

- Introduction
- Methodology
- Results
- Discussion
- Future Direction

Why ALD TiN?

- Diffusion barrier for contacts
- Useful for electrodes for RRAM
- Easy to etch
- Hard & dense
- Relatively low resistivity
- Biocompatible (FDA approved)

no documentation of ρ standards
vague claims of degraded properties



Slide from Mary's "State of the Lab" talk

Interests

P. Wong Group

Dionne Group

S. Wong Group

Nishi Group

Interests

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Dionne Group

S. Wong Group

Nishi Group

It draws money!

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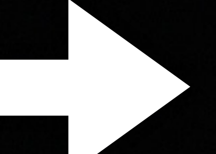
Fabricate



Measure

No organics & metals
Good surface chemistry

RCA Clean

reproducible
environment

100 cycle
seasoning

bake surface
moisture

pre run bake
1~2 hours

vary these
parameters

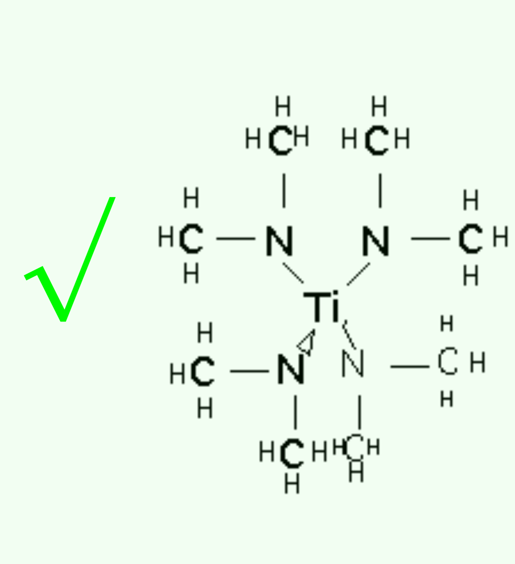
run recipe

prevent oxidation
as much as poss.

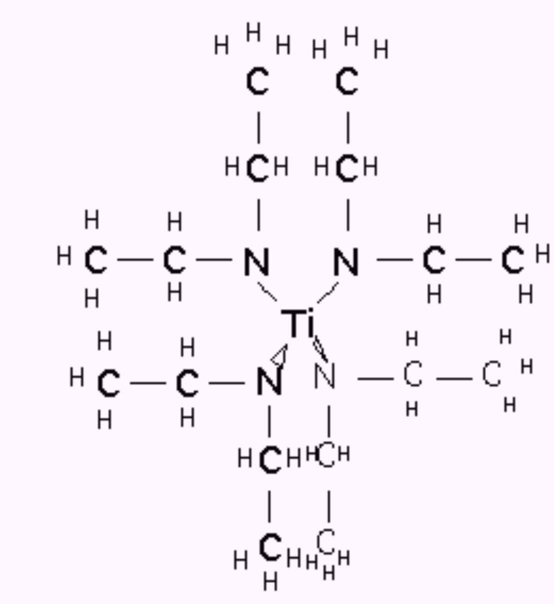
post vacuum
cool > 1 hour

- sheet resistance
- composition

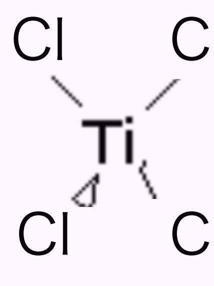
precursor select



tetrakis-(dimethylamido)titanium
aka···TDMA-Ti



tetrakis-(diethylamido)titanium
aka···TDEA-Ti



Cl

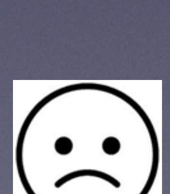
titanium tetrachloride

was default precursor at SNF

low temp capable < 300℃

more volatile than TDEA-Ti

low temp capable



C contamination → lowers resistivity

C contamination → lowers resistivity

Cl contamination → lowers resistivity

Requires high temp > 600℃

analytics select

Shared Analytical Tools at SNC/SNL

(solid box), (dashed box) … bottleneck of the tool

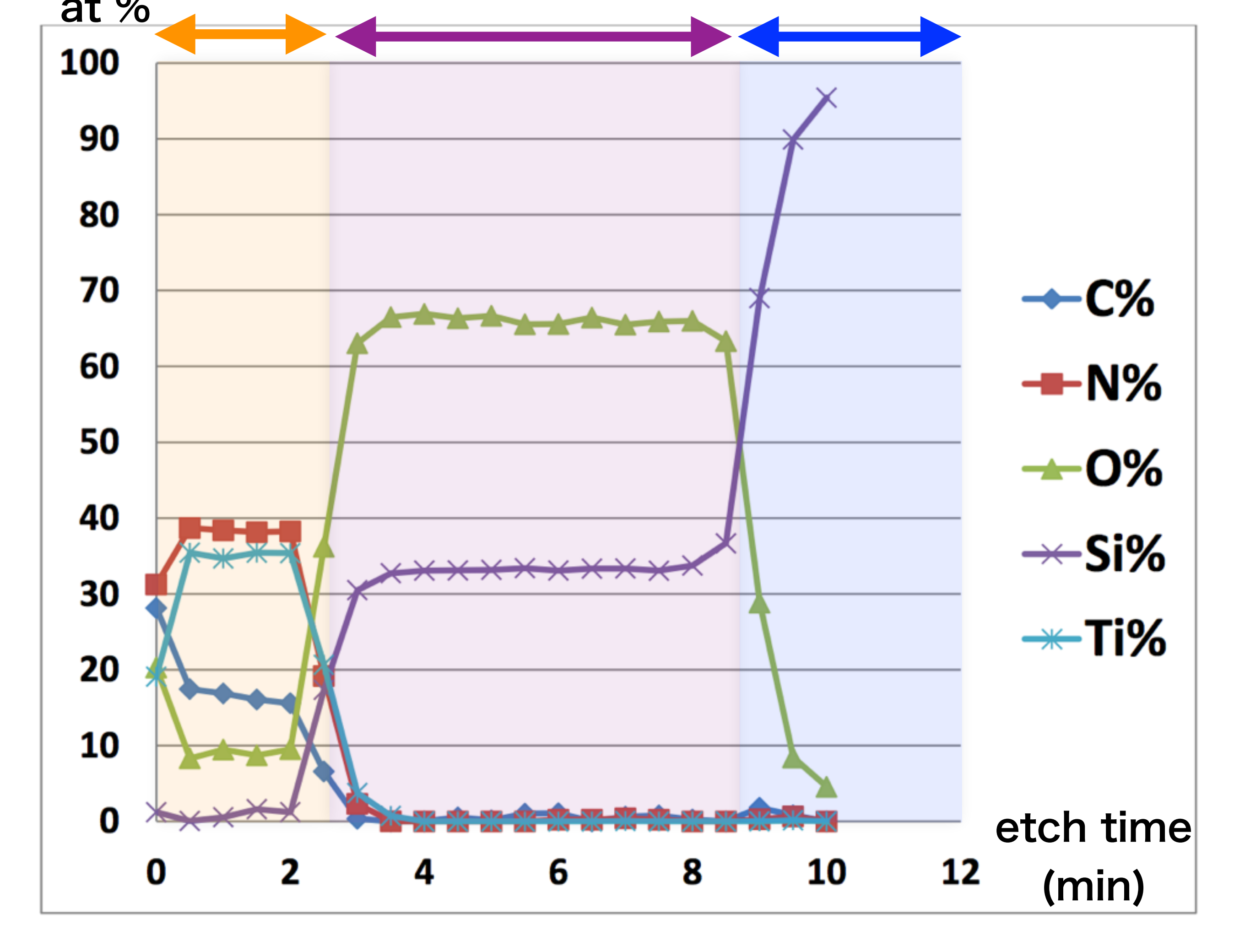
	Signal in	Signal out	Lateral resolution	Depth resolution	Volume analyzed (x nm * z nm)	Minimum detectability (%)	Accuracy (%)	Specimen prep. (difficult/easy)	Characteristic of analyzed species (eg. E_K-E_L)
EPMA-WDS	electron	Photon (x-ray)	1 – 10 μm	1 μm	1 μm * 1 μm – 10 μm * 1 μm	0.1%	0.1-1%	easy	E_K-E_L
SEM-EDS	electron	Photon (x-ray)	0.5 – 1 μm	100 nm – 1 μm	500 nm * 100 nm – 1 μm * 1 μm	1%	1-5%	easy	E_K-E_L
TEM-EDS	electron	Photon (x-ray)	1 nm	10-100nm	1 nm * 10 nm – 1 nm * 100 nm	0.1-1%	1%	difficult	E_K-E_L
STEM-EELS	electron	electron	0.2 nm	10 – 100 nm	0.2 nm * 10 nm – 0.2 nm * 100 nm	1-5%	1%	difficult	E_o-E_i
SAM	electron	electron	10 nm	1 – 5 nm	10 nm * 1 nm – 10 nm * 5 nm	1%	1-10%	easy	E_K-E_L- E_L
XPS	photon (x-ray)	electron	10 μm	0.5 – 5 nm	10 μm * 0.5 nm – 10 μm * 5 nm	1%	1%	easy	hv-E_i
SIMS	ion	ion	Nano-SIMS 50 nm	5 nm	50 nm * 5 nm	100 ppb	w/o standards ± 1000%, with standards ±1-10%	easy	m / q
~~**APFIM**~~		~~ion~~	~~0.3 nm~~	~~0.2 nm~~	~~0.3 nm * 0.2 nm~~	~~1-5%~~		~~difficult~~	~~m / q~~

XPS was the best fit for our needs

THE ISSUE = O&C contamination = LOW ρ

R = 700~800 [Ω/□]

ρ ≒ 1960~2240 [μΩcm]

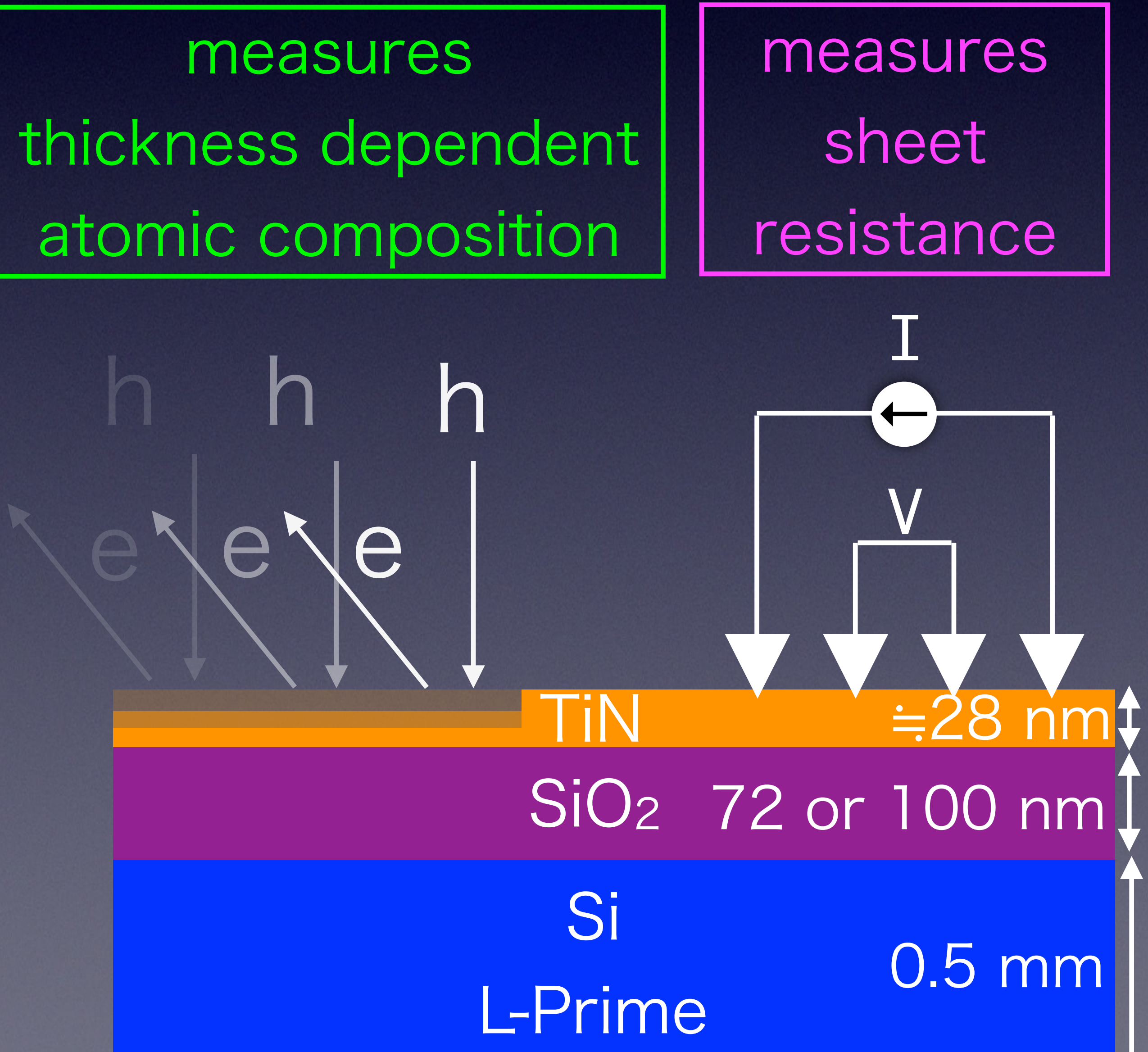


XPS PHI

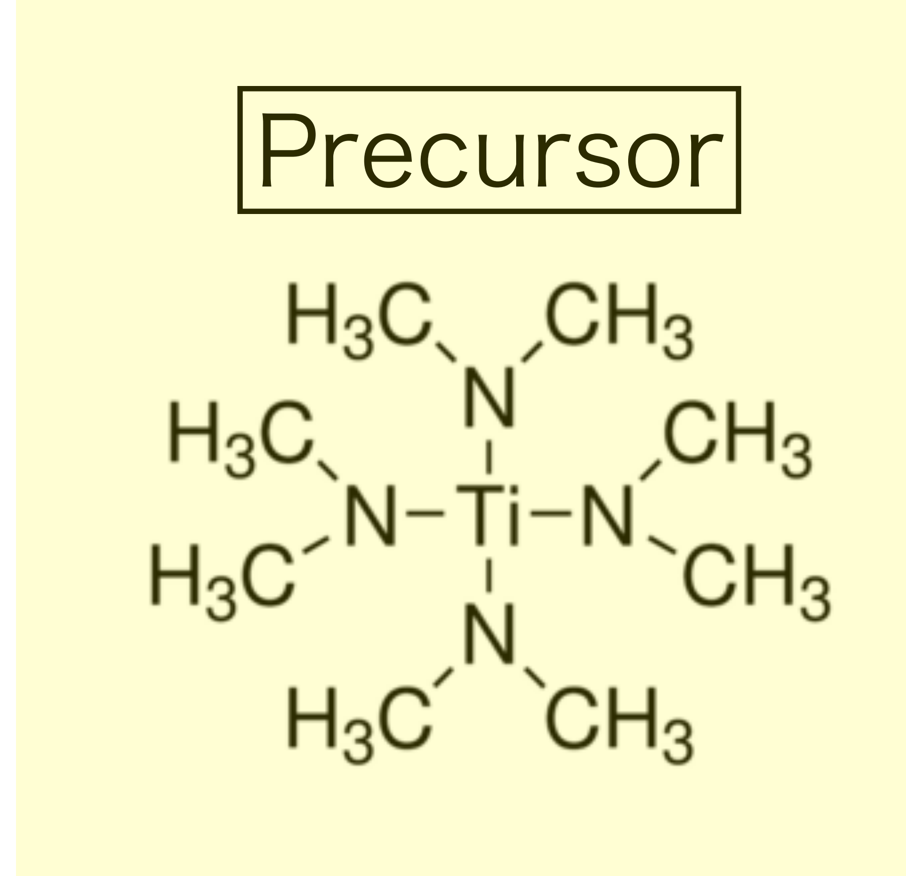
measures thickness dependent atomic composition

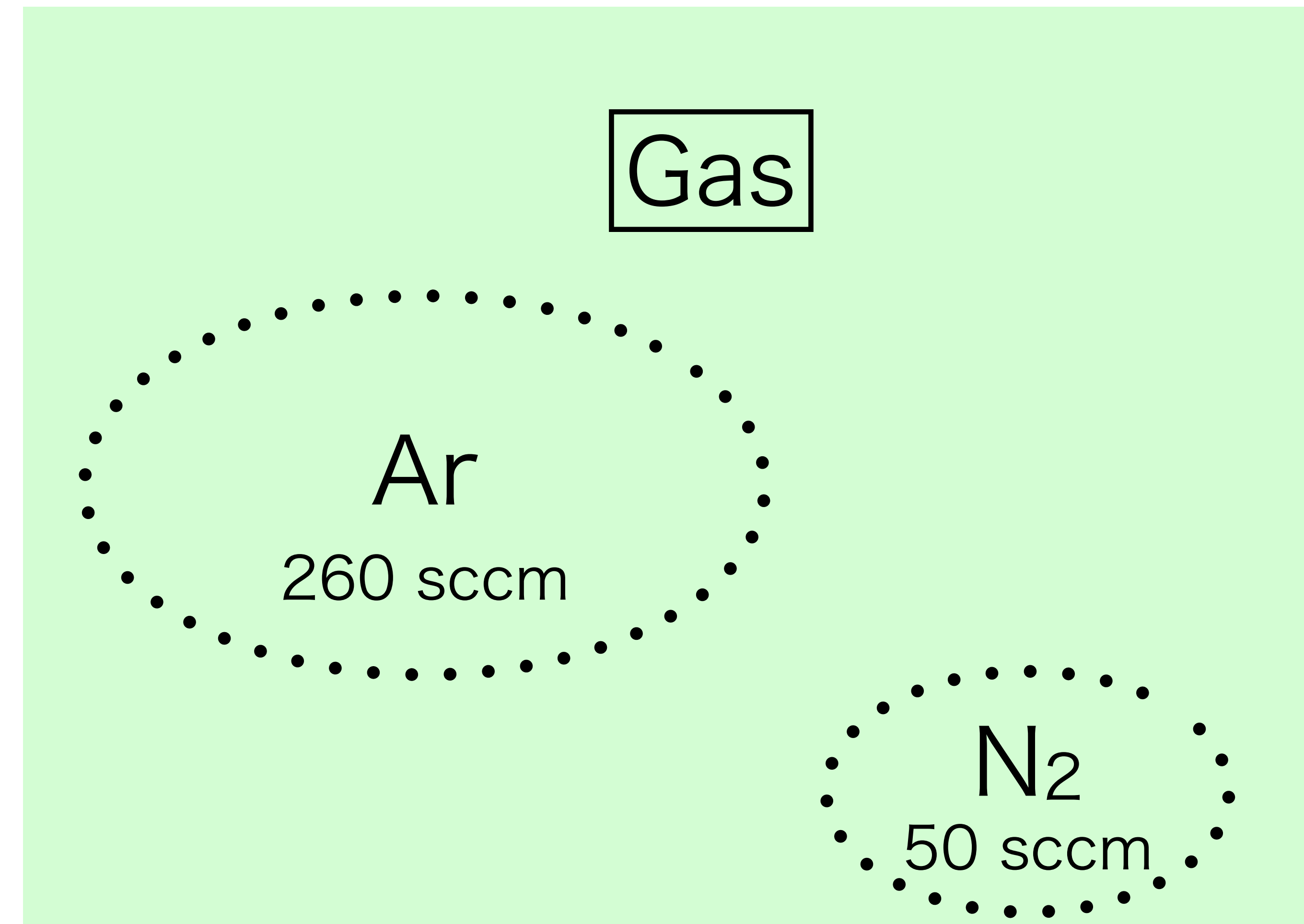
Prometrix

measures sheet resistance



Fiji Plasma TiN Recipe





Notice there is no O in the recipe

O…Must be due to (1) poor vacuum or (2) O contamination in gas and/or precursor

C…Likely due to precursor not fully reacting

Semi-Exhaustive Potential O Leak Sources

Precursor Delivery Tubes/Connections

Precursor Source

Gas Source/ Tubes/Connections

Top Chamber Seal

Oxide on Chamber Surface

*Not vacuum related, but is unlikely

Load Lock Seal

Main Chamber Seal

Vacuum Pump Limited

Bottom Chamber Seal

ALD Valves

Precursor Delivery

Reactor 1&2

Chuck

PrecursorJackets

Cone

A

B

blue ··· pre-Fiji issues

red ··· in-Fiji issues = vacuum issues

*Font size indicates my personal concern level

Solution Algorithm

Check N_2 & Ar purity at point A & B

similar

not similar

pre-Fiji limited

Vacuum limited

check all seals

go down 2nd

go right 1st

supply gas not pure enough

upgrade vacuum pump

unresolved

Add O_2 and H_2O filters to N_2 and Ar line

resolved

EAT
SLEEP
CONQUER
REPEAT

nature limited

try different precursor

unresolved

The TiN Recipe

	Instruction	#	Value	Units	
0	heaters	12-15	250 (250~270)	℃	set temperature
1	wait		7200	sec	pre bake
2	flow	0(Ar)/1(Ar)/2(N	60/200/50	sccm	specify gas & flow rate
3	pulse	1	0.06	sec	pulse TDMA-Ti precursor
4	wait		5	sec	
5	plasma		300	Watts	turn on plasma
6	wait		20 (20~300)	sec	specify plasma duration
7	plasma		0	Watts	turn off plasma
8	wait		5	sec	
9	goto	3	400	cycles	
10	end				

☐ … variables

(x~y) … range

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ID#	Fiji	tem	ptim	gas	RC	pr/	(Ω/□) flat	(Ω/□) center	(Ω/□) opp flat	5ptst	nm	g/cm	date	precursor
y44/2														
y43/2														
y42/2	2	270	5	N	y	y/y	82.53	84.55	-	3.829 4.373%			5/31	121213
y40/2	1	270	5	N	y	y/y	-	83	102.4	10.06 10.932%	28.2	4.70	5/30	40114
y39/2	1	270	5	N	y	y/y	78.57	80.29	98.69				5/30	40114
y37	2	250	0.33	N	n	n/n	-	823.9	707.2	113.6 13.320%			5/30	121213
y36	2	300	2	N	n	y/y	-	-	-	-			5/24	92413
y35	1	270	0.33	NH	n	y/y	-	595.4	-	104 17.710%			5/24	40114
y34/2	1	270	1	NH	n	y/y	-	372	225.				5/23	40114
y33/2	1	270	1	NH	y	y/y	278.7	244.7	274.				5/23	40114
y32/2	2	260	3	N	n	y/y	-	200k	-	5471. K 160.569%			5/23	92413
y31.5	2	260	3	N	y	y/y	-	-	-				5/23	92413
y31	2	270	0.33	N	n	y/y	518.5	529.9	673.6				5/18	40114
y30/1	2	270	1	N	n	y/y	222.7	223.0	266.6				5/18	40114
y29/1	1	270	1	N	n	y/y	180.7	200.6	269.1				5/18	40814
y28/1	2	270	3	N	n	y/y	92.28	92.82	111.1				5/17	40114
a-y27 /2	1	270	3	N	n	y/y	169.9	169.87	179.7				5/17	40114
y26/1	2	260	2	N	n	y/y	115.3	114.4	131.5				5/4	40114
y24/1	2	250	1	N	n	y/y	246.8	231.5	257.0				5/4	40114

234 μΩcm

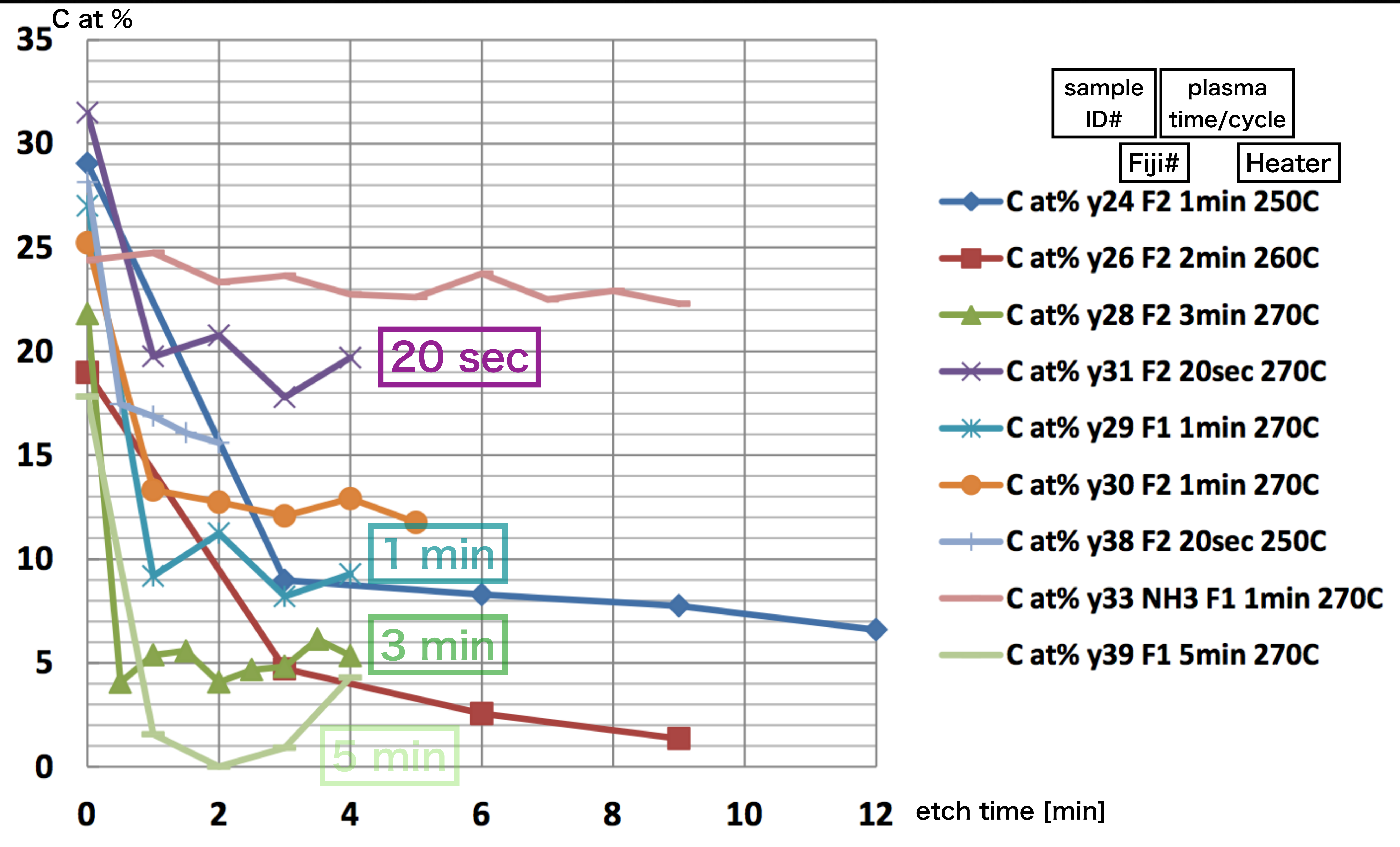
270 ℃ sheet resistance

Ω/□

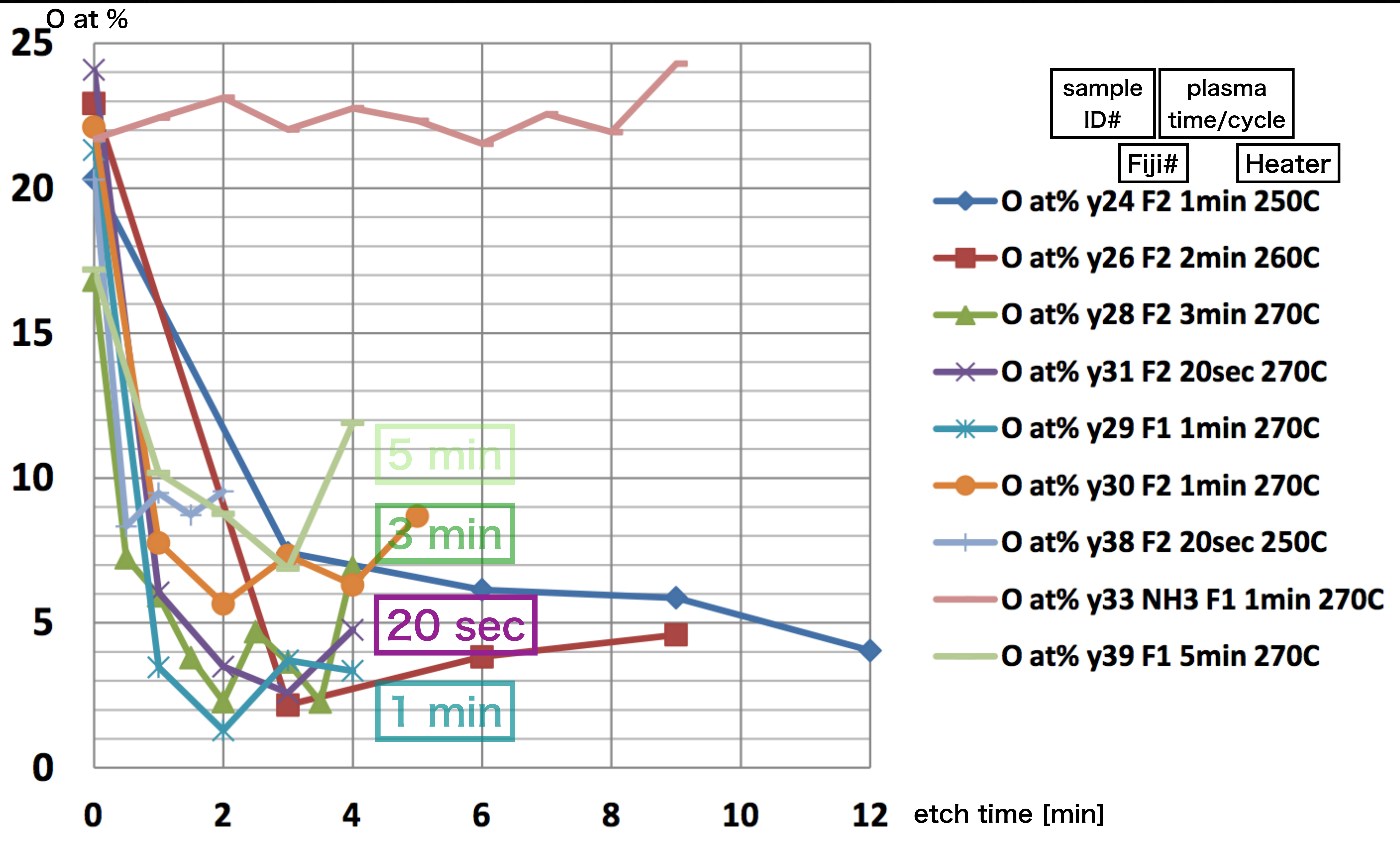
600
500
400
300
200
100
0

0 1 2 3 4 5

plasma
min/cycle



$t_{plasma} \uparrow \rightarrow C_{at\%} \downarrow$



$t_{plasma} \uparrow \rightarrow O_{at\%} \rightarrow$ or $\uparrow$

conclusion

- nearly x10 reduction in resistivity with new protocol
- longer t_{plasma} detaches the CH_3 bonds from TDMA-Ti
- O can replace the CH_3 bonds

wish list

- plate with wafer cuts in Fiji
- higher plasma capability
- shorter distance between plasma & substrate
- O_2 filters on gas and precursor lines
- turbo pump
- valves in Ar line

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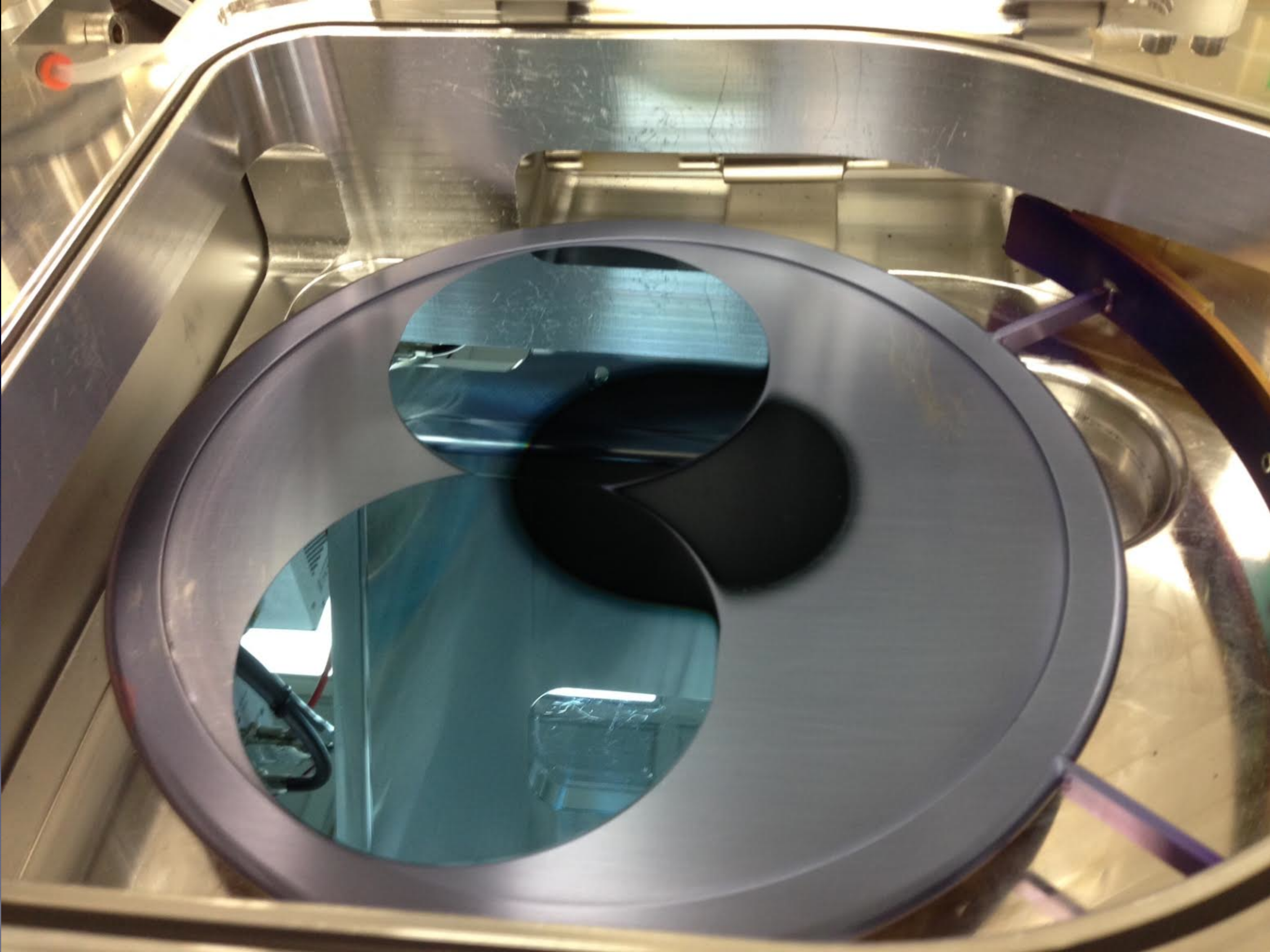
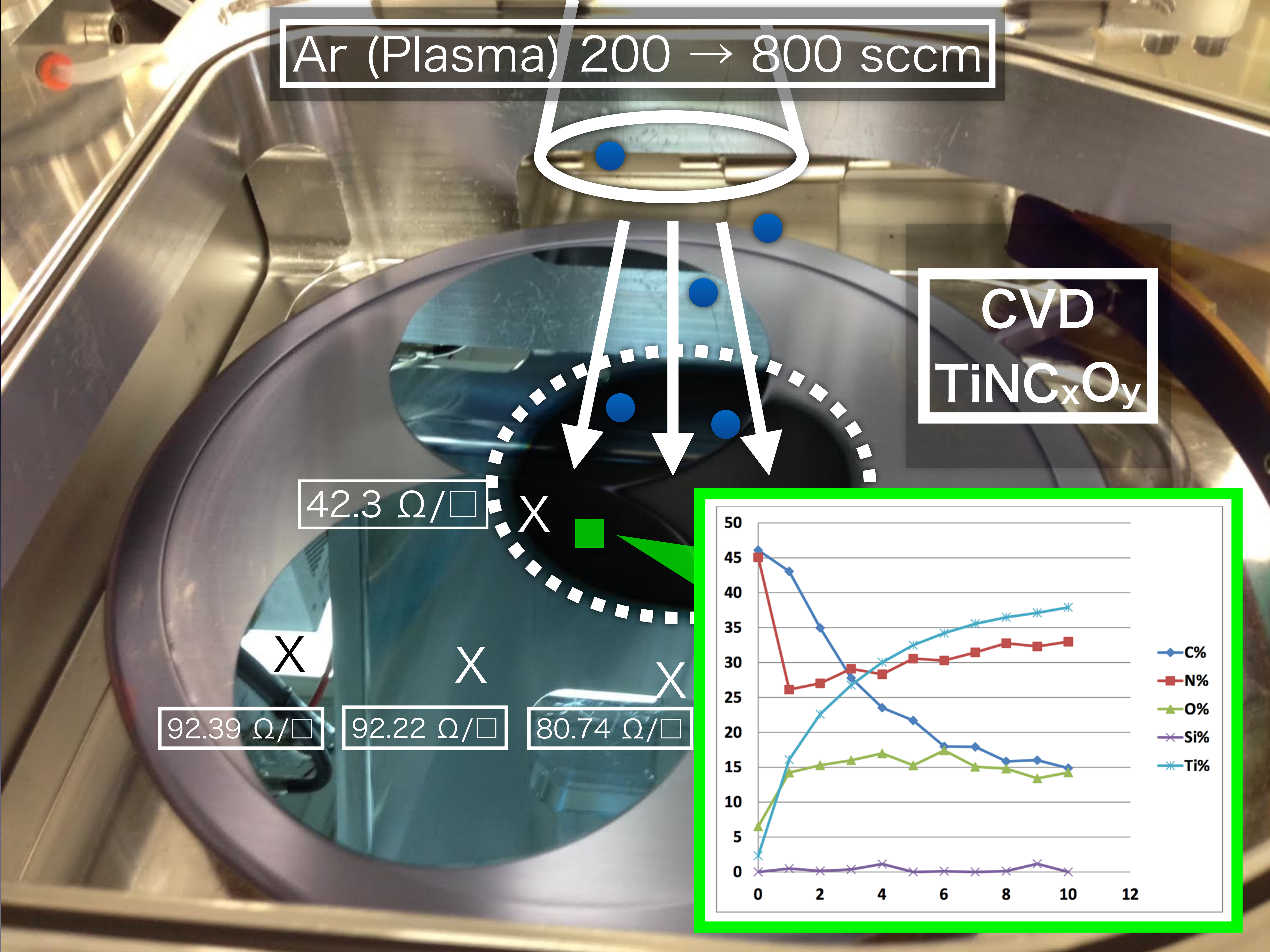
With the current hardware,
ρ may have been minimized

can we reduce time?




Ar (Plasma) 200 → 800 sccm
CVD
TiNCxOy
42.3 Ω/□
X
X
X
X
92.39 Ω/□
92.22 Ω/□
80.74 Ω/□
50
45
40
35
30
25
20
15
10
5
0
0
2
4
6
8
10
12
C%
N%
O%
Si%
Ti%

ID#	Fiji	tem	ptim	gas	RC	pr/	(Ω/□) flat	(Ω/□) center	(Ω/□) opp flat	5ptst	nm	g/cm	date	precursor
y46	2	270	0.33	N	y	y/y	-	139	180	18.58 11.864%				
y44/2	2	270	0.33	N	y	y/y	100.9	84.54	131.7	21.22 19.318%				
y43/2	1	270	2	N	y	y/y	80.74	92.22	92.39	5.746 6.349%				
y42/2	2	270	5	N	y	y/y	82.53	84.55	-	3.829 4.373%			5/31	121213
y40/2	1	270	5	N	y	y/y	-	83	102.4	10.06 10.932%	28.2	4.70	5/30	40114
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end