ALDのメカニズムとプロセスの紹介

ALD mechanism and process introduction

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2022.12.22 第１回ARIM量子・電子マテリアル領域セミナー
ALD（原子層堆積）による成膜技術

Contents

1. ALD introduction

1) ALD characteristics

Mechanism

1. cycle deposition
2. 1 mono layer precursor adsorption (self-limiting)
3. saturated growth rate

Advantage

4. good step coverage
5. thin film deposition by atomic level

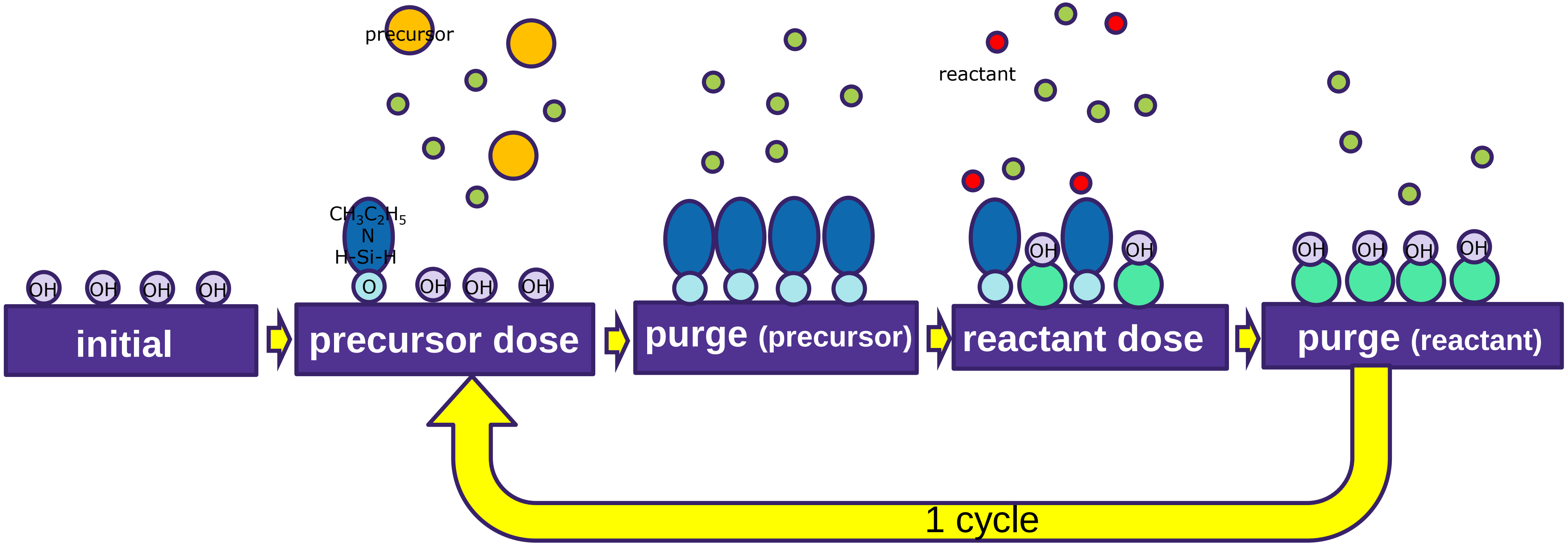
Disadvantage

6. low deposition rate

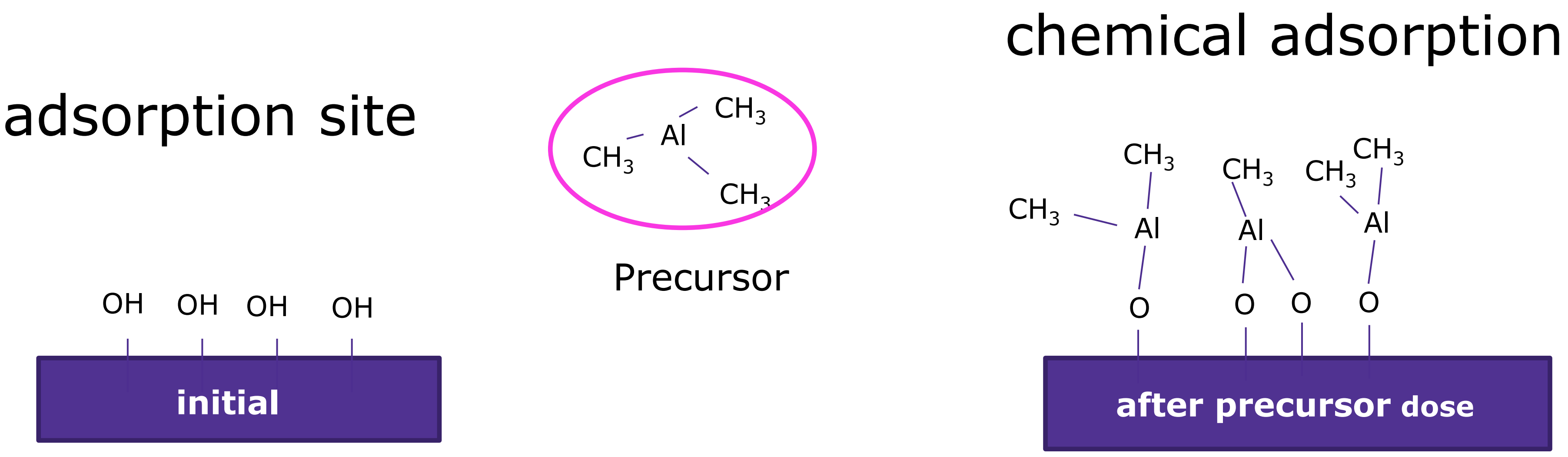
Atomic Layer Deposition

Cycle deposition consist some steps.

layer by layer deposition
~ 1 Å /cycle



2)Chemical adsorption



$$AlOH^* + Al(CH_3)_3 \rightarrow [Al\text{-}O\text{-}Al(CH_3)_2]^* + CH_4.$$
$$2AlOH^* + Al(CH_3)_3 \rightarrow [Al\text{-}O\text{-}Al(CH_3)]^* + 2CH_4$$

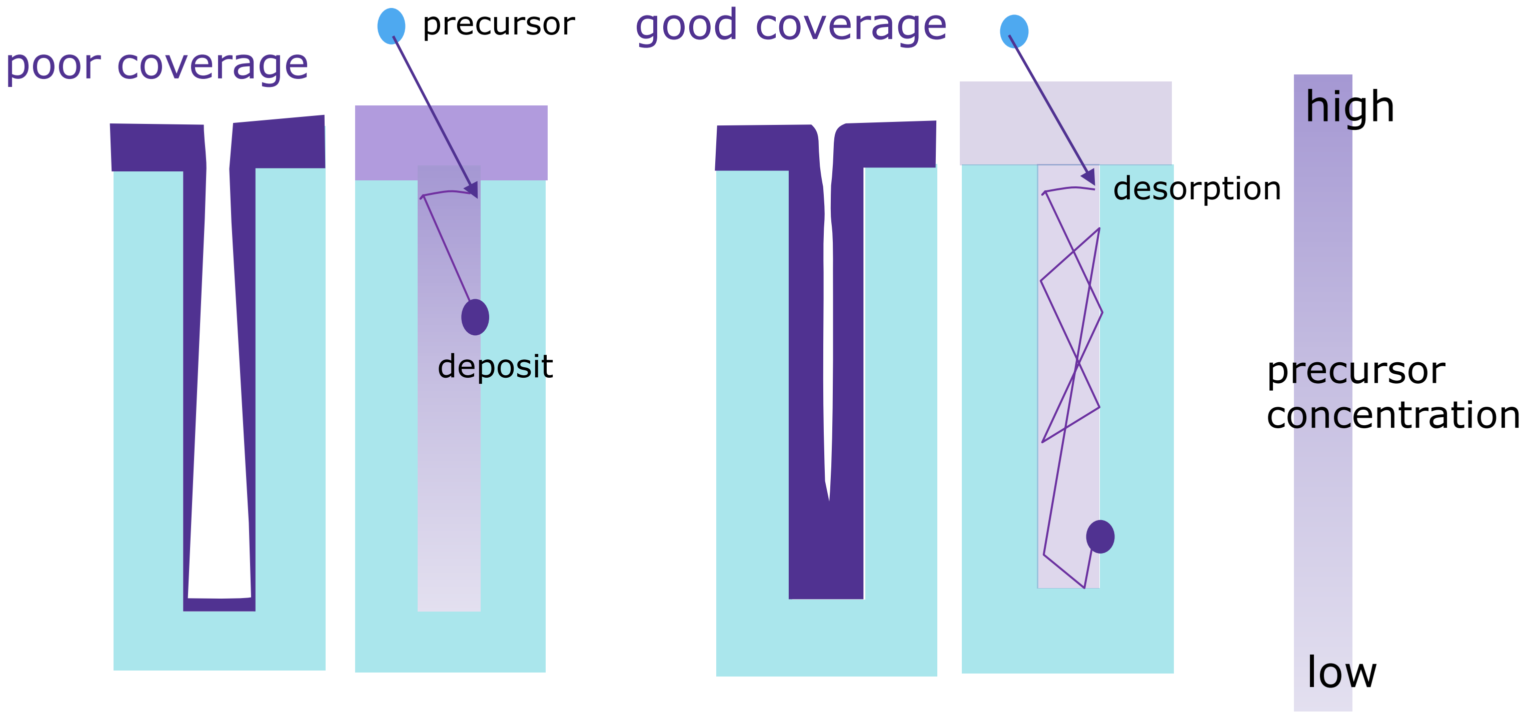
irreversible reaction

only one layer adsorption (=self limiting)

3) Step coverage

CVD Case

Why is coverage different?



mean free path >> pattern size

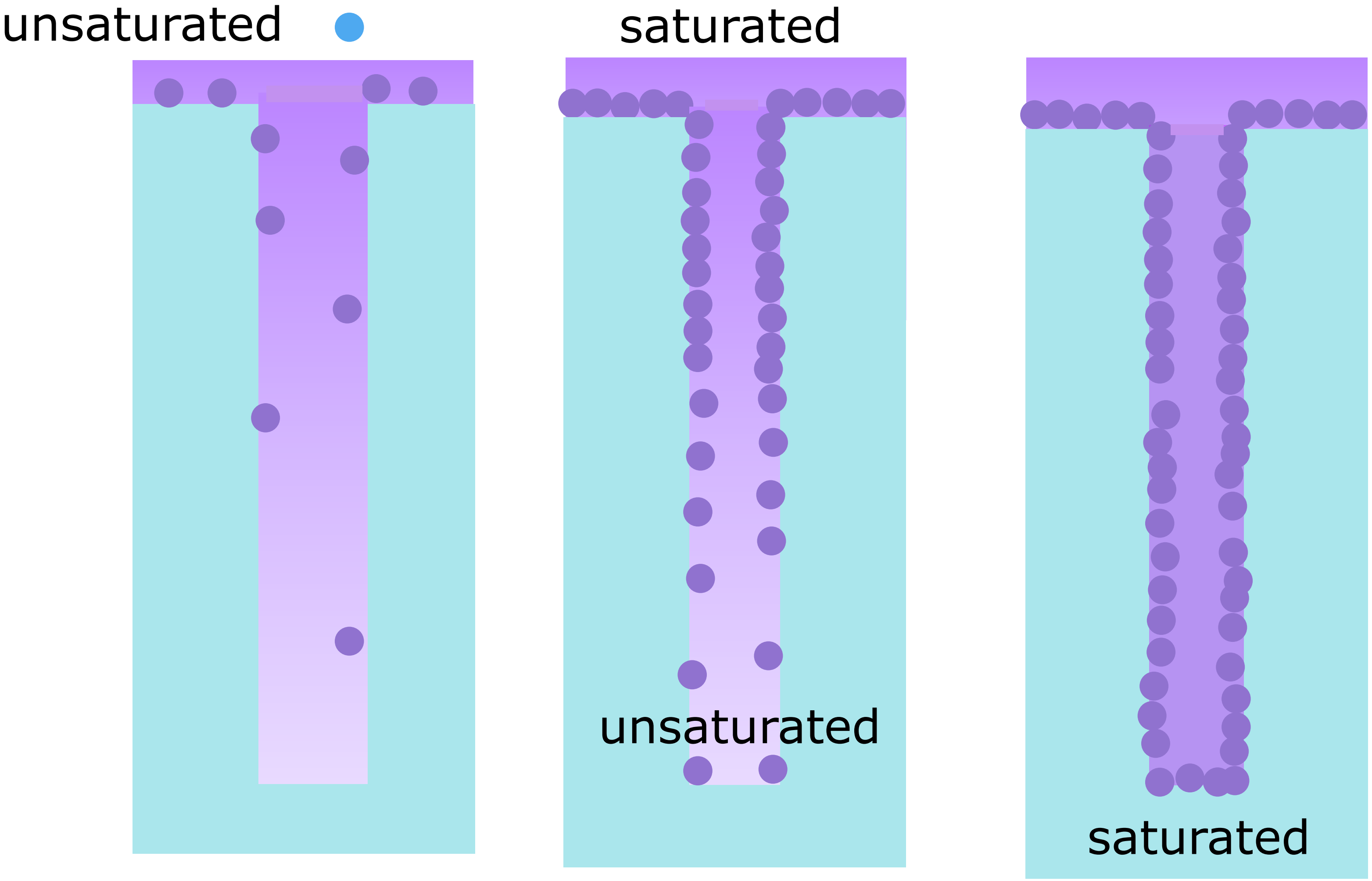
precursor collides pattern side wall

deposition rate
$\propto$ precursor concentration

sticking probability high → high difference concentration between top and bottom in the pattern
➔ poor coverage

low → low difference.
➔ good coverage

Sticking probability and coverage in ALD case

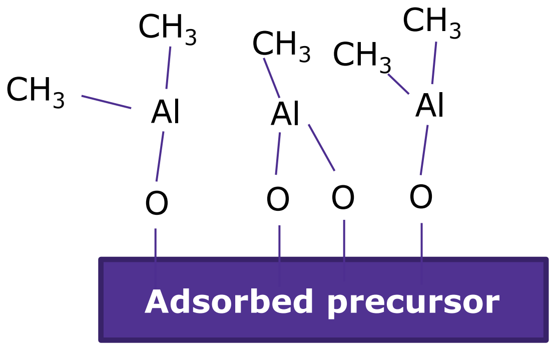


When precursor adsorption is saturated, precursor adsorbed conformal.

If they react with reactant, film is deposited conformal.

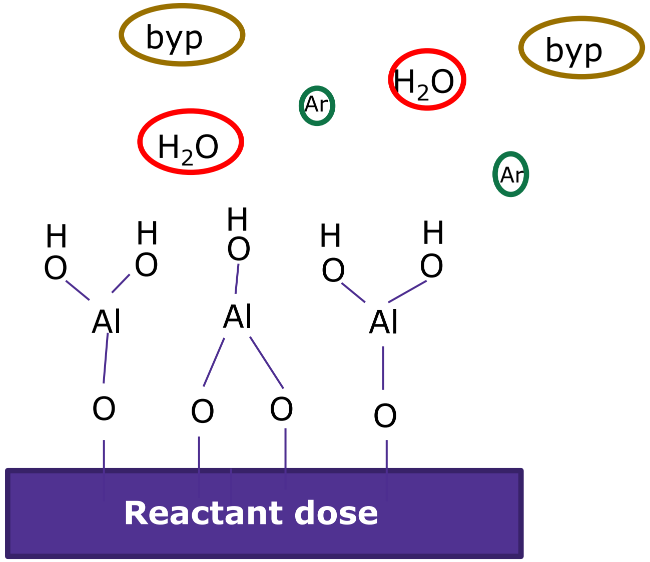
4) Reactant dose -- Thermal ALD

chemical adsorption



reactant: H_2O

react with reactant



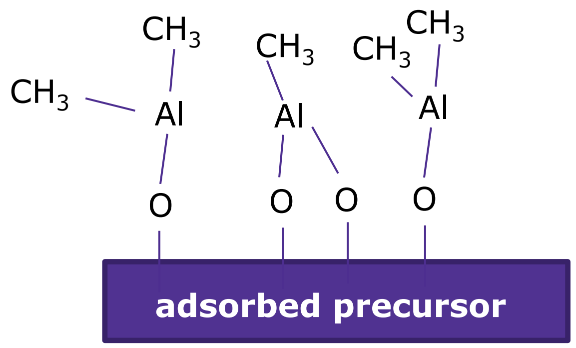
$[Al\text{-}O\text{-}Al(CH_3)_2]^* + 2H_2O \rightarrow [Al\text{-}O\text{-}Al\text{-}(OH)_2] + 2CH_4$

$[Al\text{-}O\text{-}Al(CH_3)]^* + H_2O \rightarrow [Al\text{-}O\text{-}Al\text{-}OH] + CH_4$

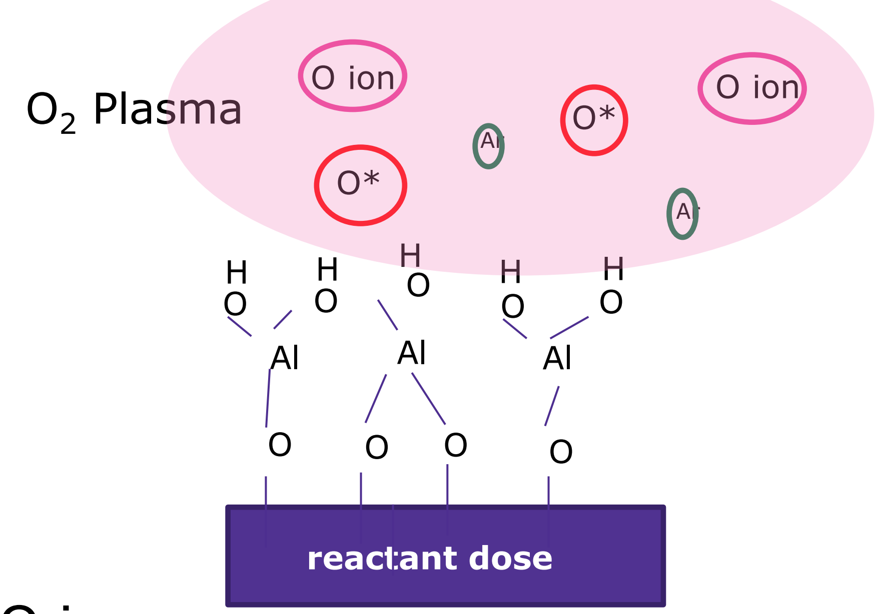
thermal ALD: react with reactant by thermal energy.

Reactant dose -- Plasma Enhanced ALD (PEALD)

chemical adsorption



react with reactant



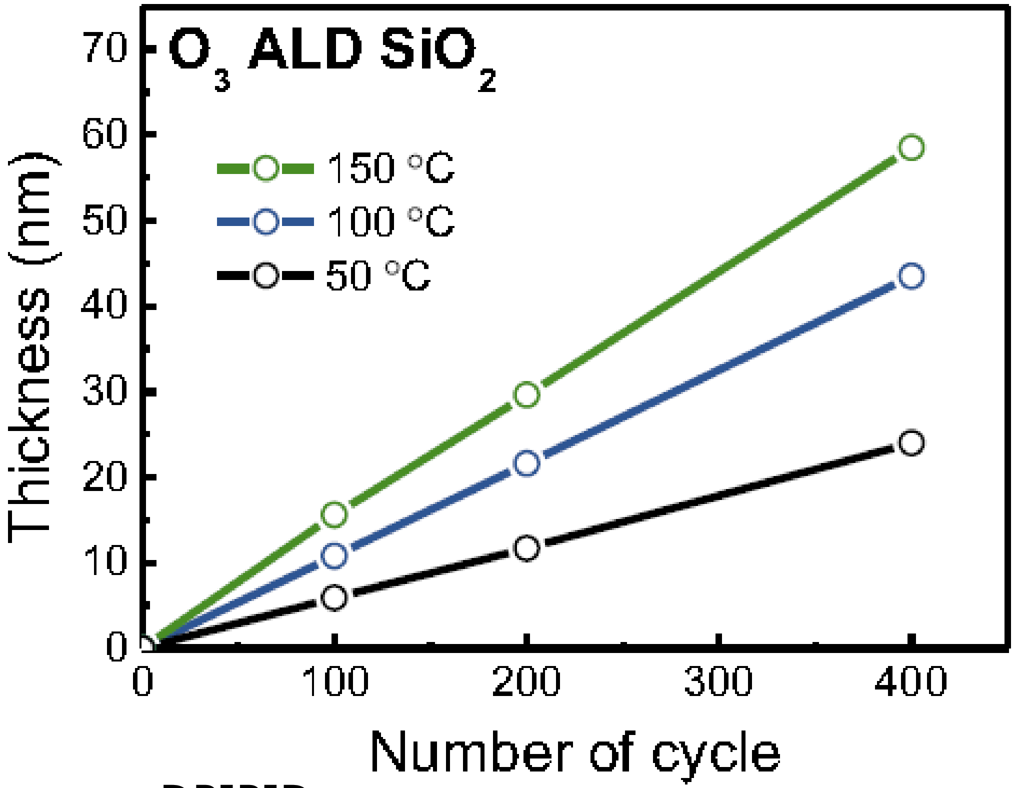
direct plasma ： O radical, O ion
remote plasma：O radical

PEALD：react with radical and ion
plasma energy and thermal energy
deposition at lower temperature

5) Deposition time
cycle number

deposition time = cycle number x cycle time

Thickness is proportional to cycle number.



Precursor DPIPID

T.Nam and et. al., applied surface science 485 (2019)381.

Deposition rate is shown by GPC:
Growth Per Cycle (nm/cycle)

150C 60nm/400cy
GPC 0.15 nm/cy

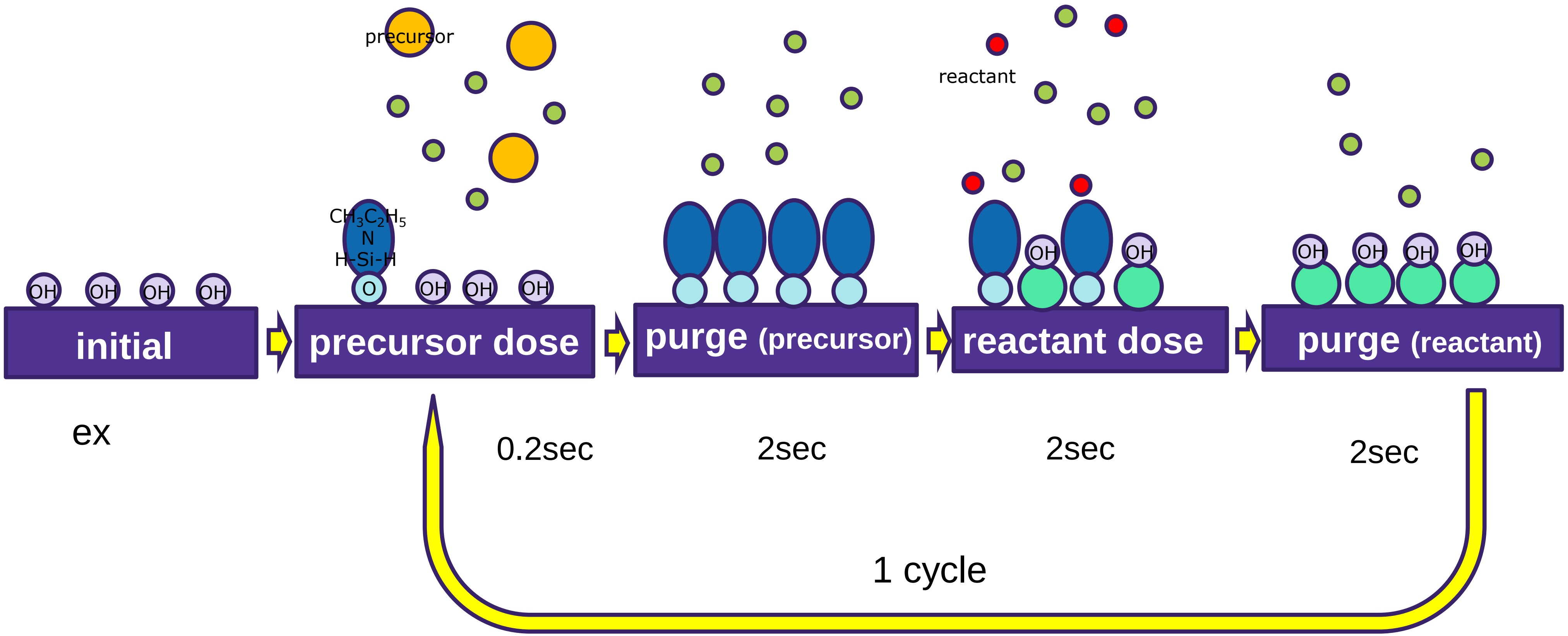
Normally
GPC is around 0.1 nm/cy
1 mono layer adsorption

cycle number = thickness /GPC

GPC < 0.2 nm/cy
increase GPC → decrease cycle number

Cycle time

deposition time = cycle number x cycle time



initial	precursor dose	purge (precursor)	reactant dose	purge (reactant)
ex	0.2sec	2sec	2sec	2sec

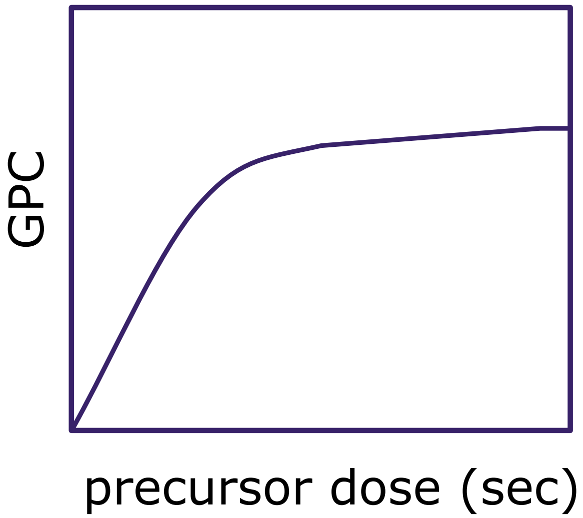
1 cycle

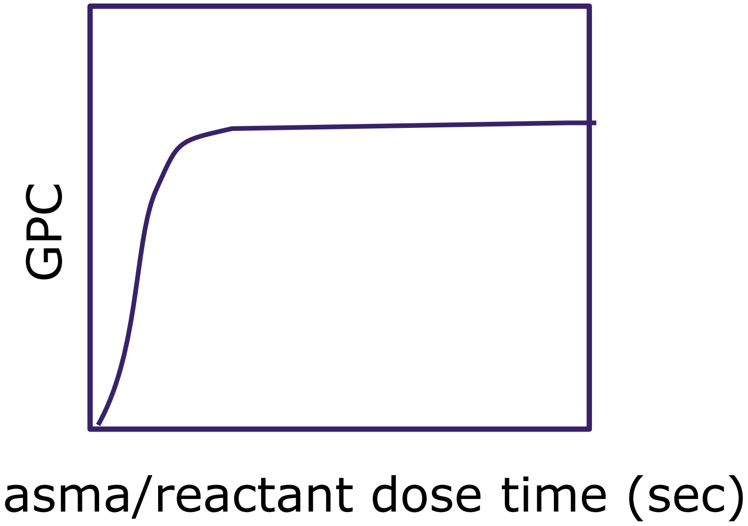
total 6.2 sec/cycle

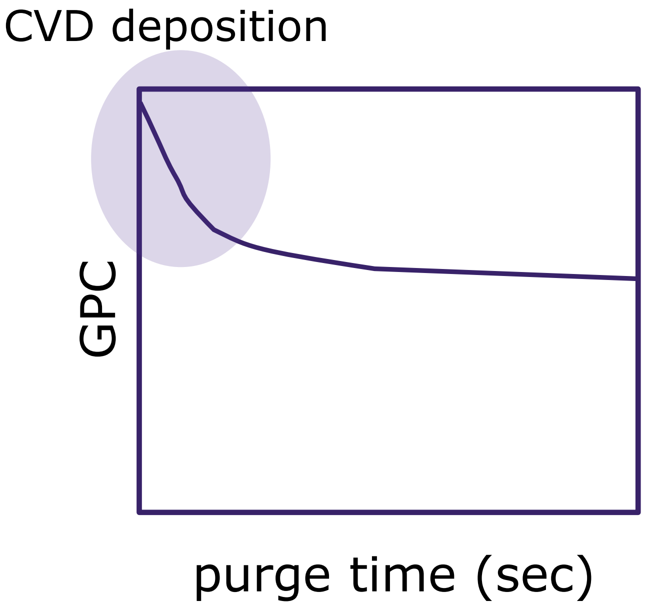
cycle time

6) Saturation process

GPC (Growth Per Cycle) : thickness on 1 cycle (nm/cycle)







Precursor adsorption saturated

Reaction is saturated.

In CVD region residual precursor or reactant react in gas phase.

Poor coverage and large non-uniformity in unsaturated region (in case).

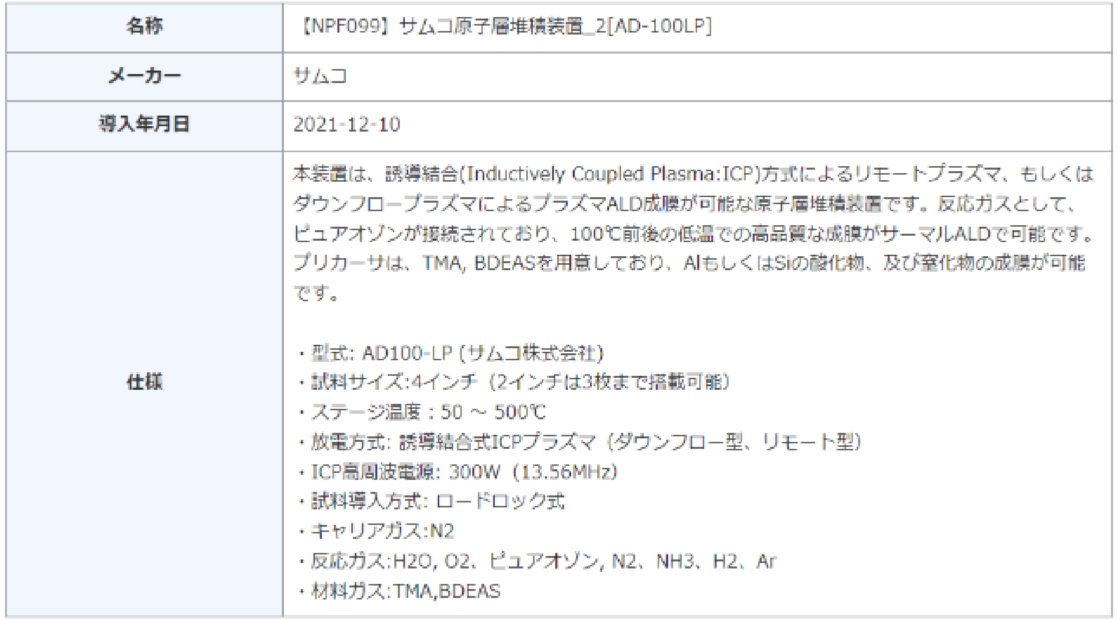
2. ALD-SiO_2
Samco ALD tool in AIST NPF

【NPF099】サムコ原子層堆積装置_2[AD-100LP]

PEALD- SiO_2, Al_2O_3, AlN_x
thermal-ALD SiO_2, Al_2O_3

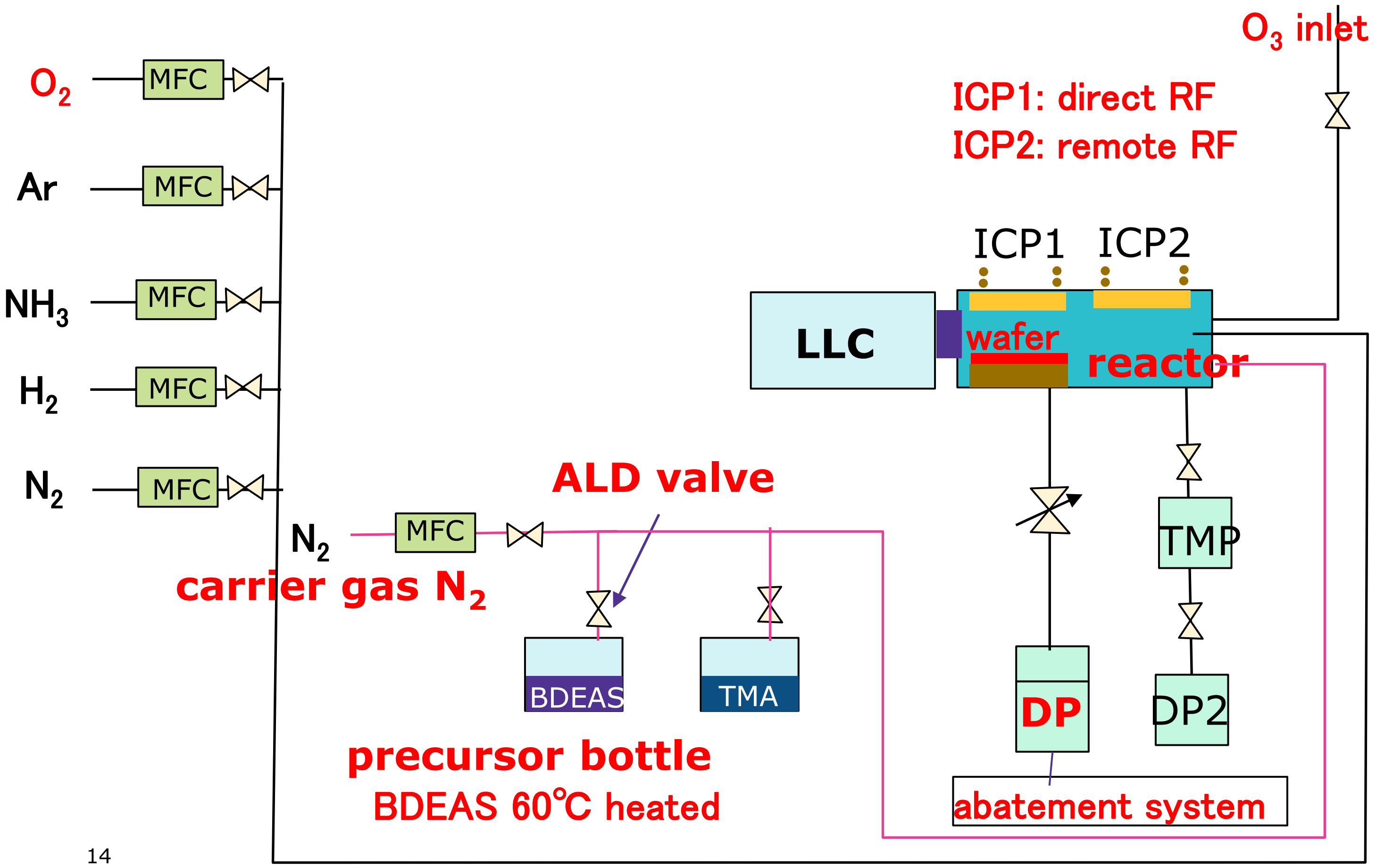
precursor: BDEAS / TMA
oxidation: O_2 plasma (remote and direct)
O_3 or Pure O_3, H_2O
nitridation: NH_3, N_2 Plasma

4 inch Si wafer
temp.: 50~500C



名称	【NPF099】サムコ原子層堆積装置_2[AD-100LP]
メーカー	サムコ
導入年月日	2021-12-10
仕様	本装置は、誘導結合(Inductively Coupled Plasma:ICP)方式によるリモートプラズマ、もしくはダウンフロープラズマによるプラズマALD成膜が可能な原子層堆積装置です。反応ガスとして、ピュアオゾンが接続されており、100℃前後の低温での高品質な成膜がサーマルALDで可能です。プリカーサは、TMA, BDEASを用意しており、AlもしくはSiの酸化物、及び窒化物の成膜が可能です。 ・型式: AD100-LP (サムコ株式会社) ・試料サイズ:4インチ（2インチは3枚まで搭載可能） ・ステージ温度：50 ～ 500℃ ・放電方式: 誘導結合式ICPプラズマ（ダウンフロー型、リモート型） ・ICP高周波電源: 300W（13.56MHz） ・試料導入方式: ロードロック式 ・キャリアガス:N2 ・反応ガス:H2O, O2、ピュアオゾン, N2、NH3、H2、Ar ・材料ガス:TMA,BDEAS

Samco ALD tool gas line



gas：lateral flow

plasma
  ICP1：direct
  ICP2：remote

O_3 & pure O_3 (>90% O_3)

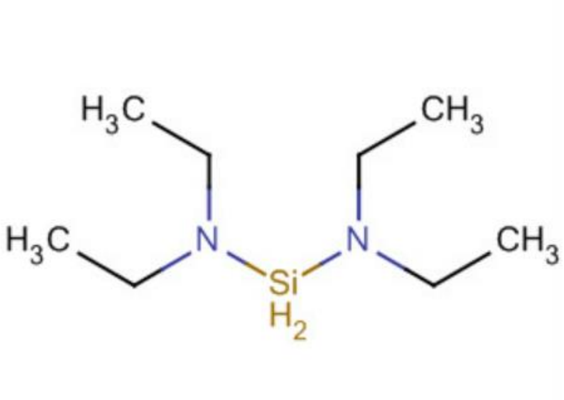
precursor
  BDEAS (Si source)
  TMA (Al source)

sub. temp. 50~500C

other gas: Ar, N_2, O_2, NH_3, H_2

ALD-SiO_2 Experiment

BDEAS （Amino Silane precursor）



BDEAS GPC ~0.1nm/cy

- GPC saturation curve
- film property

center condition

temp. 300℃
Press. 5~12Pa
dose time 0.2sec
direct plasma 100W 3sec

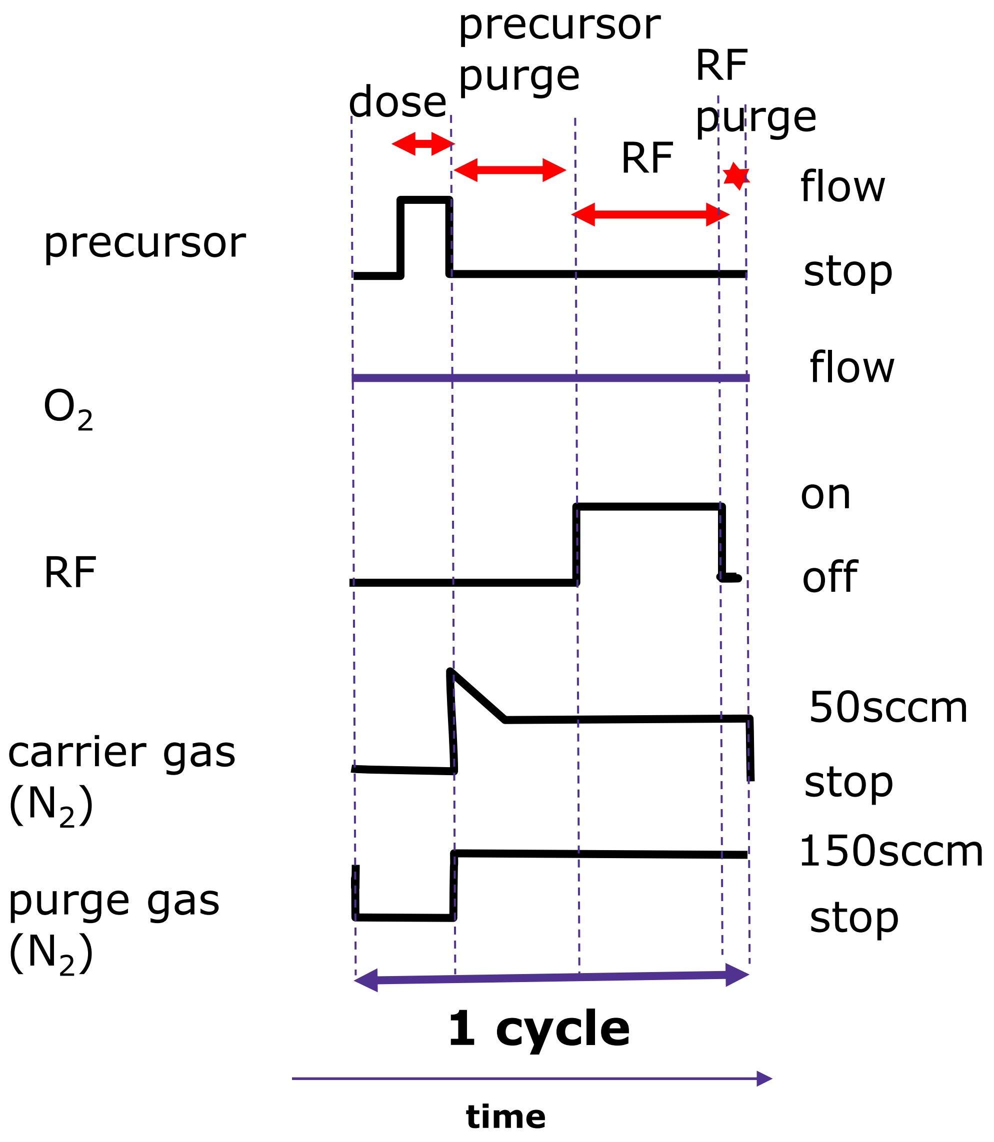
other oxidation
remote plasma 100W 3sec
Pure O_3 (>90% O_3 2sec)

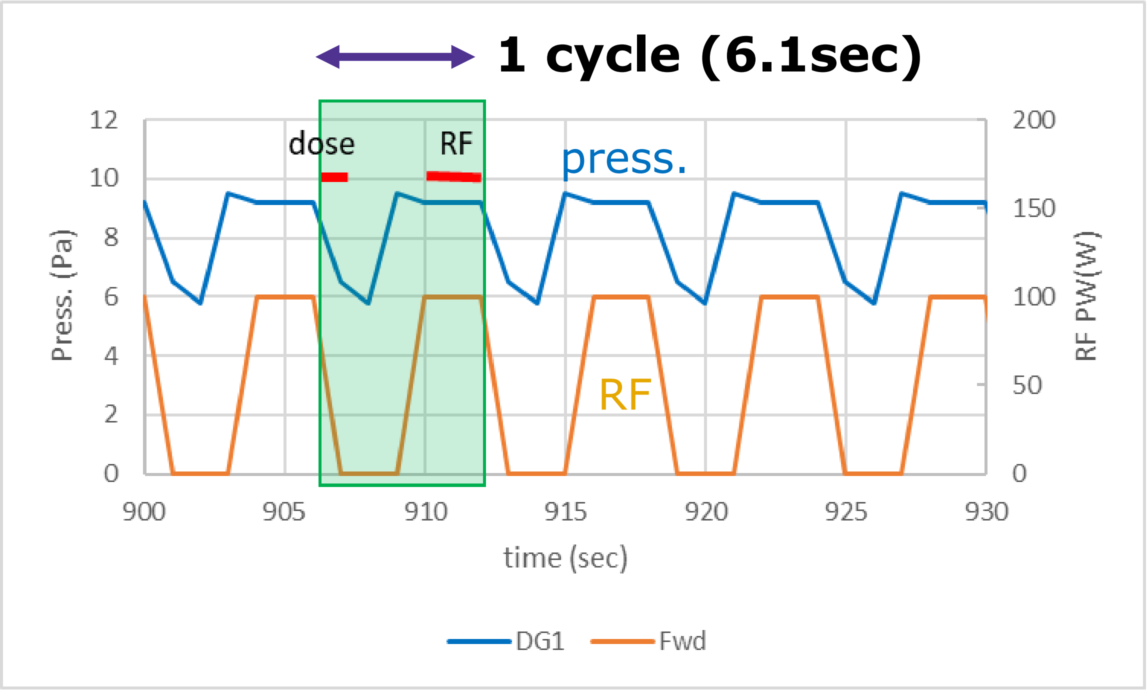
evaluation

thickness (ellipsometry) NU(non uniformity)

WER (DHF 1:500 dip)

Sequence (center condition)



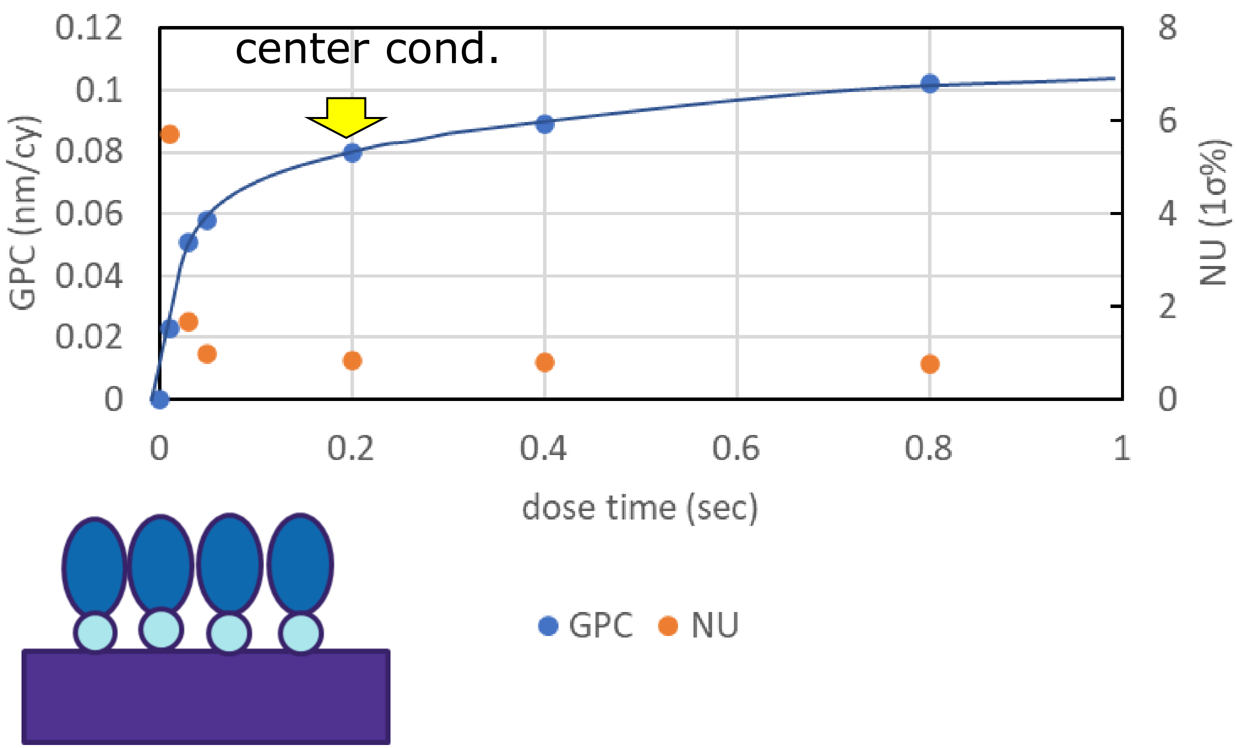


cycle time	6.1 sec/cy
center GPC	0.08 nm/cy

➡ 30nm ~ 400 cycle

➔ 2400 sec ~~ 40min

1) GPC saturation curve precursor dose



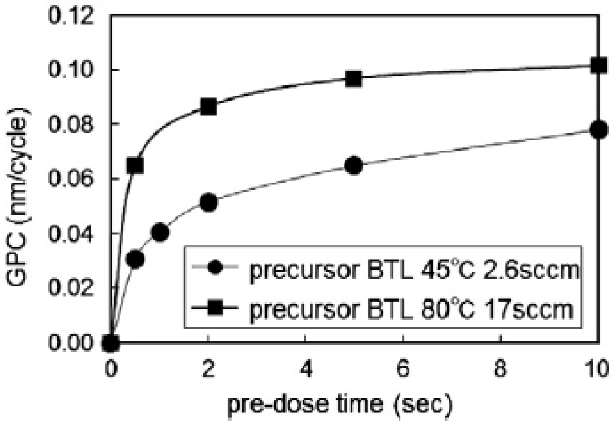
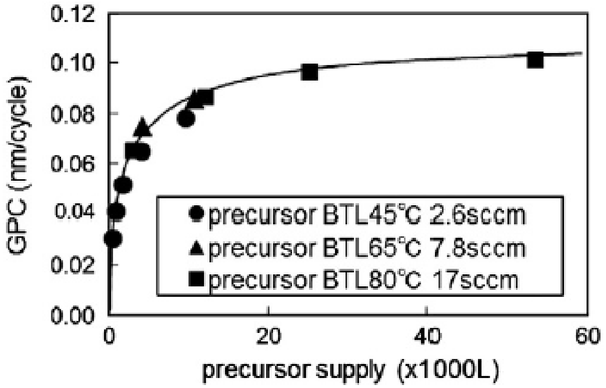


Fig. 4. GPC as a function of precursor dose (pre-dose) time. The deposition temperature was 300 °C, and precursor bottle temperatures were 45 and 80 °C as stated.

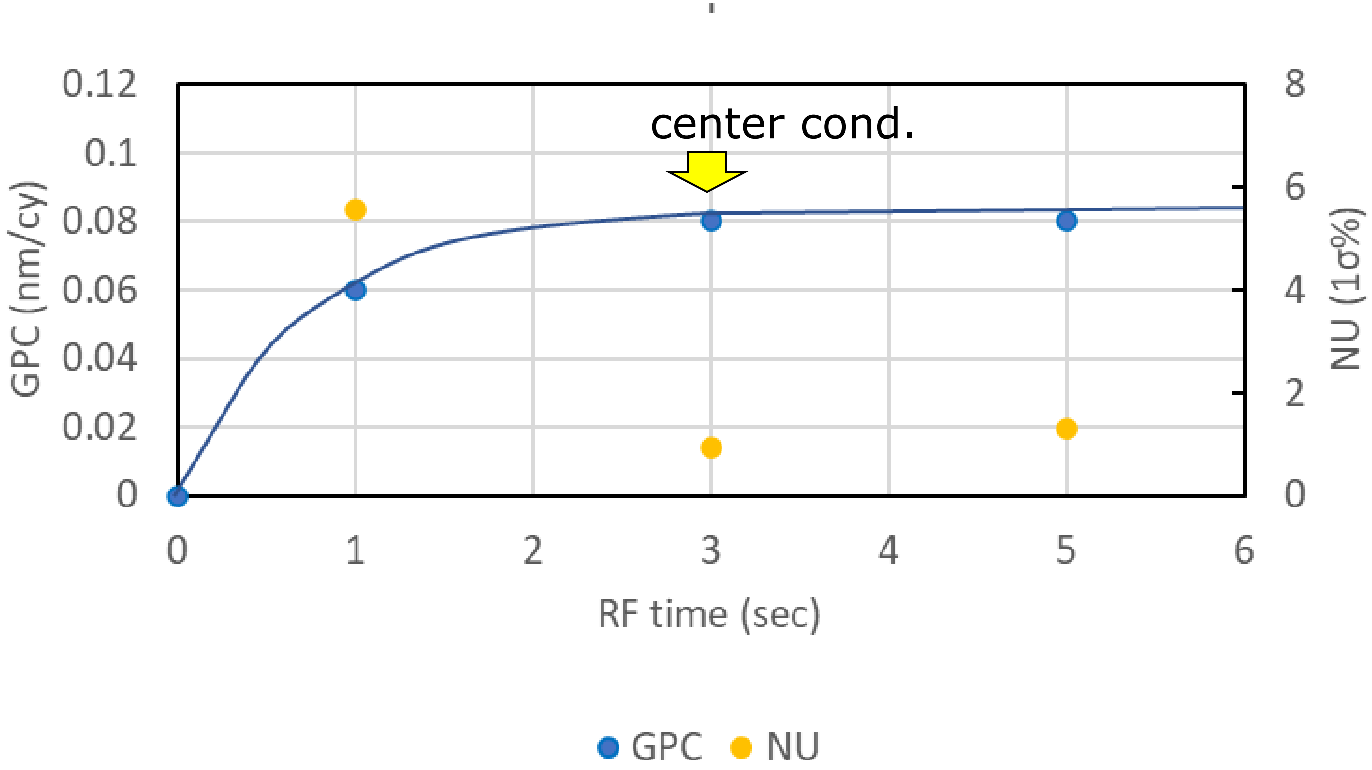


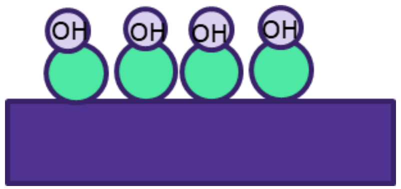
dose time x precursor partial pressure (∝ flow rate)

Precursor adsorption saturates with precursor dose.

A. Kobayashi, and et. Al., thin solid films 520 (2012)3994.

Saturation curve
reactant dose (RF time)

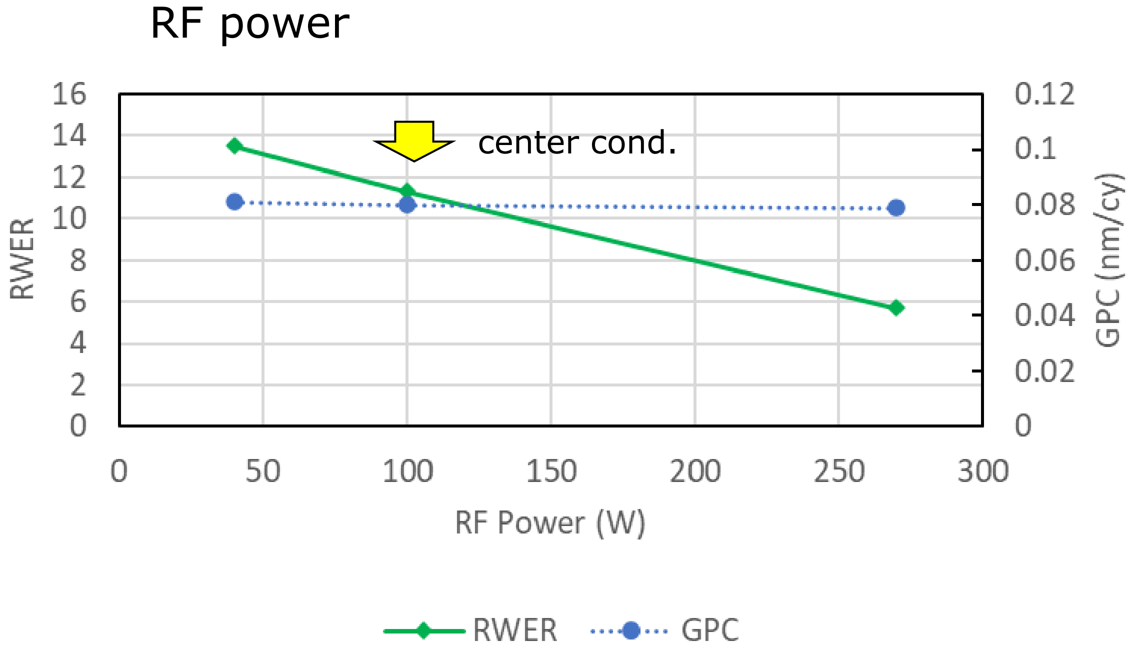


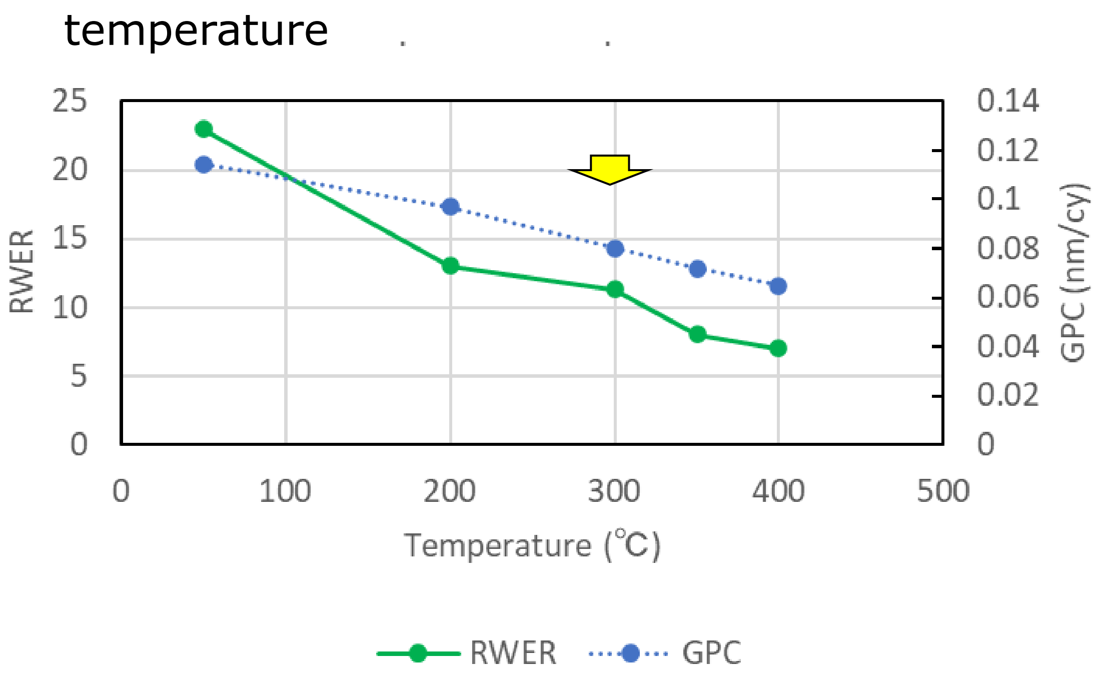


Oxidation saturates with RF time.

2) Film property (WER)

RWER: Relative Wet Etch Rate
dip dHF:H_2O-1:500 TOX 0.2nm/min(=RWER 1.0)

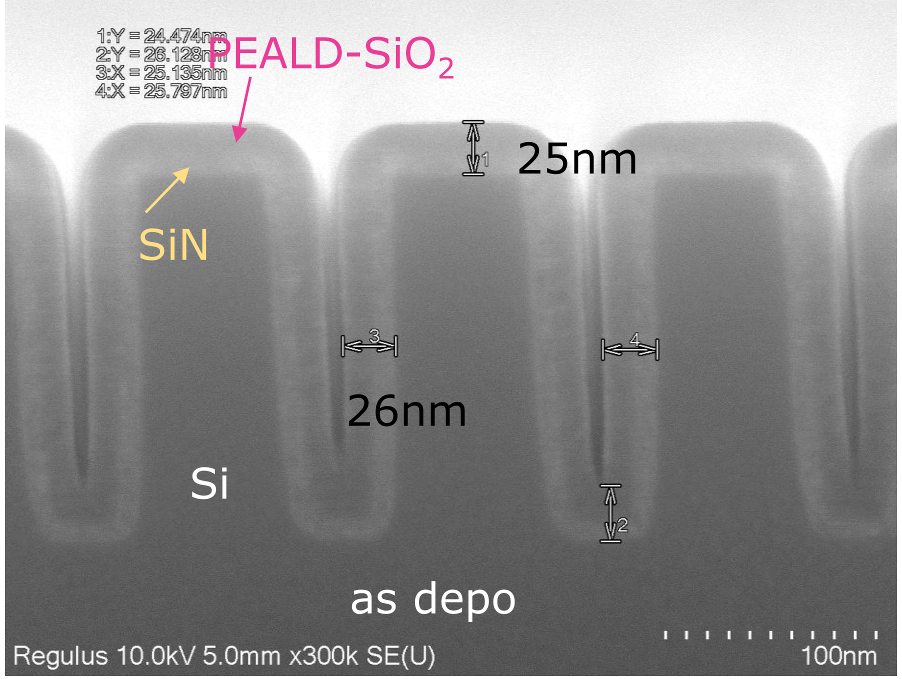


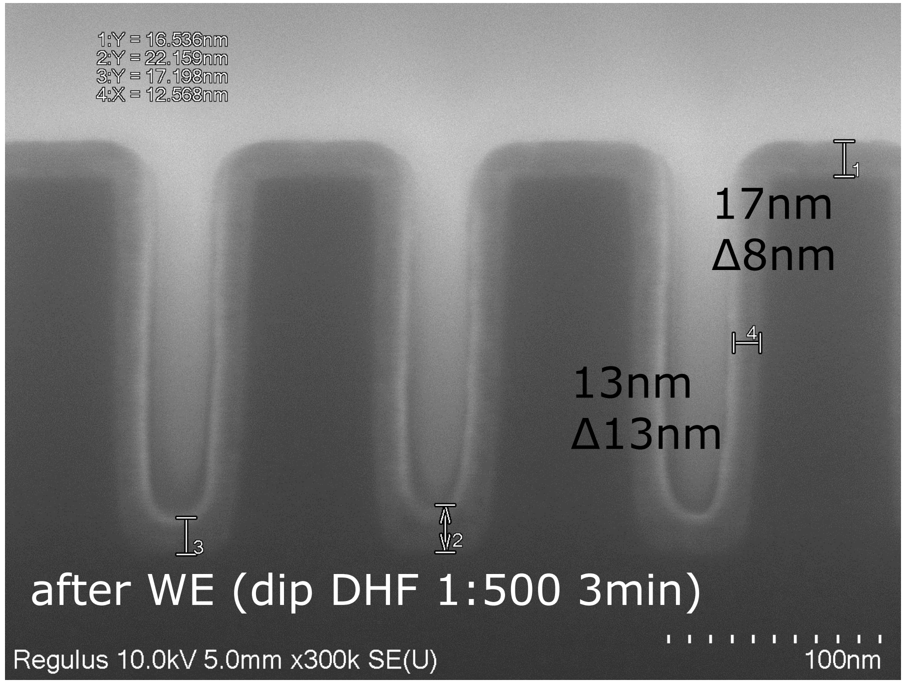


RWER depends on RF time, RF power and temperature.
Film property depends on plasma and thermal energy.

WER at pattern

PEALD-SIO$_2$ STD 300℃ direct RF 100W 3sec RWER11



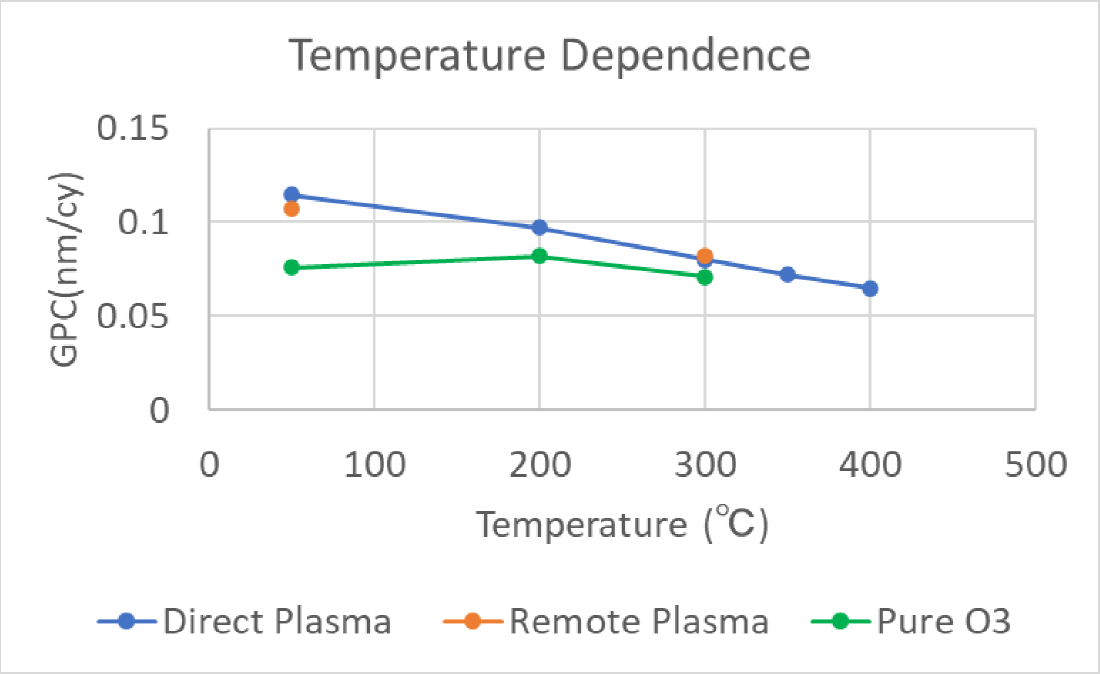


WER on top is smaller than that on side.
Ion effect is smaller on side than that on top.

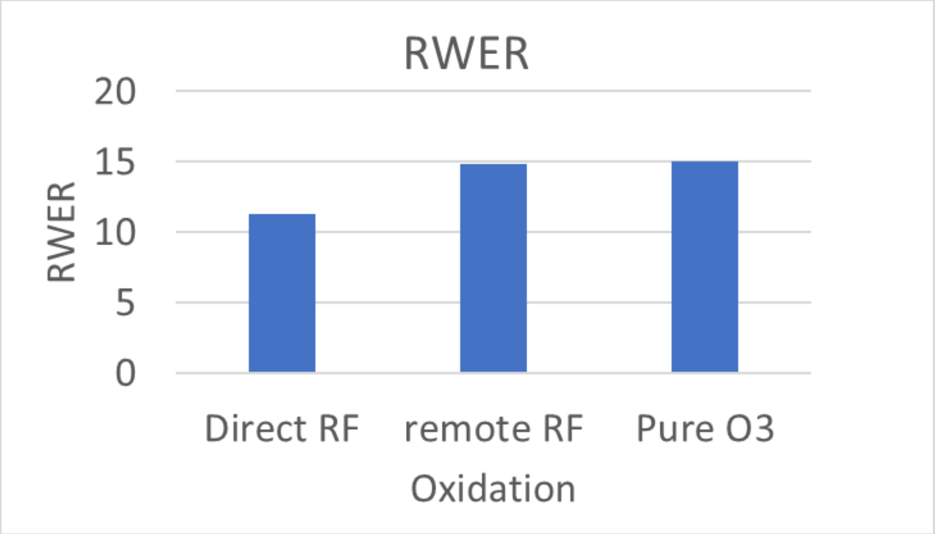
thickness (nm)

	as depo	after WE	etched Δ
Top	25	17	8
Side	26	13	13

3) Oxidation



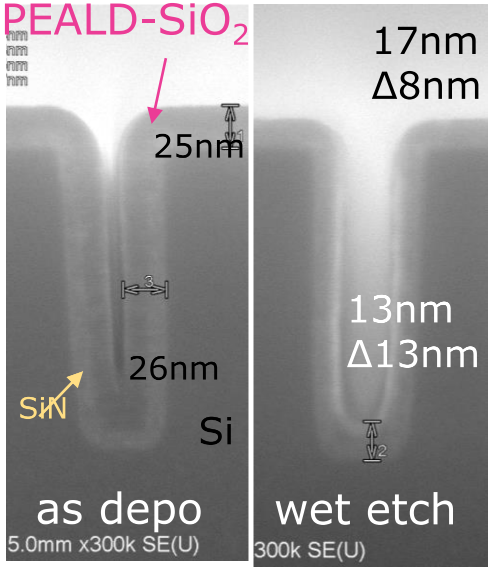
300℃ data

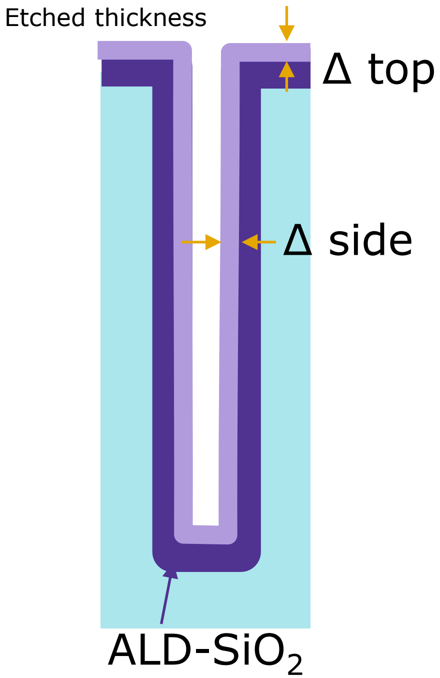


GPC in the case of direct and remote PEALD are almost same.

RWER is the smallest with direct PEALD. It depends on RF power and RF time.

WER at pattern





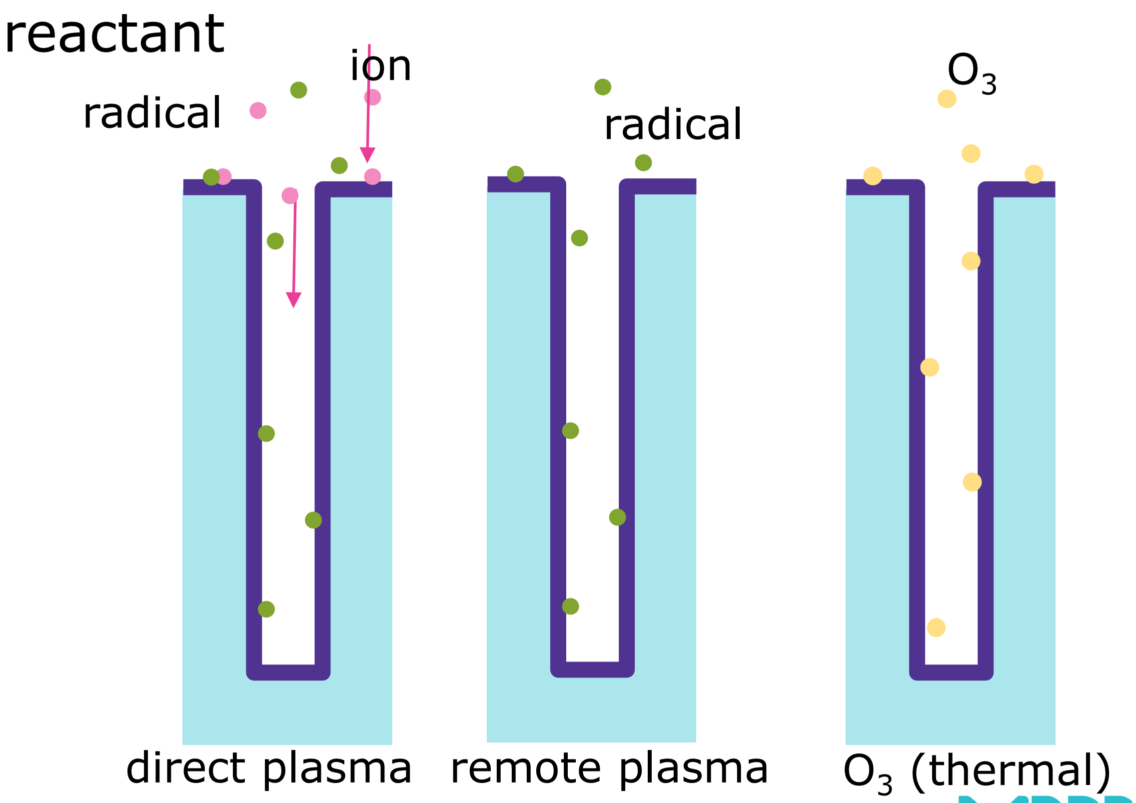
dip DHF:H_2O = 1:500

Direct plasma PEALD-SiO_2 film on side wall has larger WER than that on top. It is caused by ion effect.
Radical and O_3 reactant are isotropic.

300℃ pattern Etch thickness (nm)			
	direct PE	remote PE	Pure O3
Δ top (nm)	8	5	7
Δ side (nm)	13	7	6

large side WER

same level



3. ALD oxide & nitride

Typical Process

	precursor	Reactant	Temp.	GPC
SiO_2	BDEAS	O_2 plasma 1) O_3 2)	>50C >300C	0.12 nm/cy 0.1 nm/cy
TiO_2	$TiCl_4$ TDMAT	O_2 Plasma / H_2O O_2 Plasma 5)	>RTM 150℃、300C	 0.05 nm/cy
HfO_2	TDMACpH	O_2 plasma 5)	150℃	0.1 nm/cy

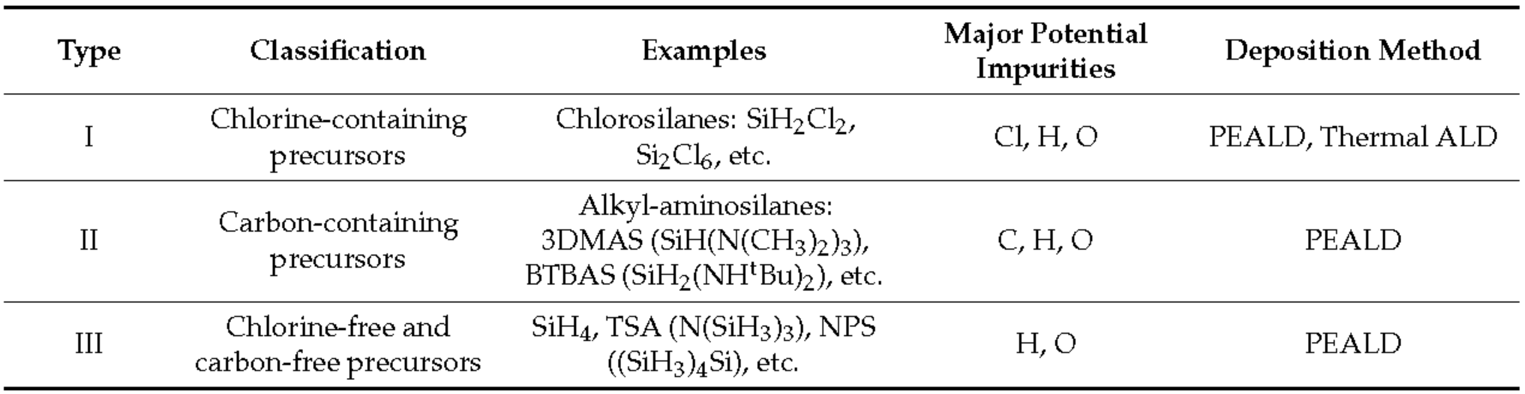
1) A. Kobayashi, and et. Al., thin solid films 520 (2012)3994.
2) H. Roh, and et. Al., Applied Surface Science 571(2022)151231
3) K.Koehler and et. Al., IOP Conf. Series: Materials Science and Engineering 41 (2012) 012006
4) 大陽日酸技報 No. 33(2014)
5) T. Faraz, and et. Al., ACS Appl. Mater. Interfaces 10 (2018)13158

	precursor	reactant	Temp.	GPC
SiN_x	DCS	NH_3 Plasma 3) NH_3 4)	(>450C) >600C	0.05 nm/cy
TiN_x	$TiCl_4$ TDMAT	NH_3 6) H_2 plasma 5)	400C 200℃	0.03 nm/cy 0.05 nm/cy
HfN_x	TDMACpH	H_2 plasma 5)	450℃	0.035 nm/cy

Oxide film can be deposited easier than nitride film.
Nitride film need high energy like higher temperature and higher power plasma.

ALD-SiN

Table 3. Classification of the silicon precursors used in SiN_x ALD process.



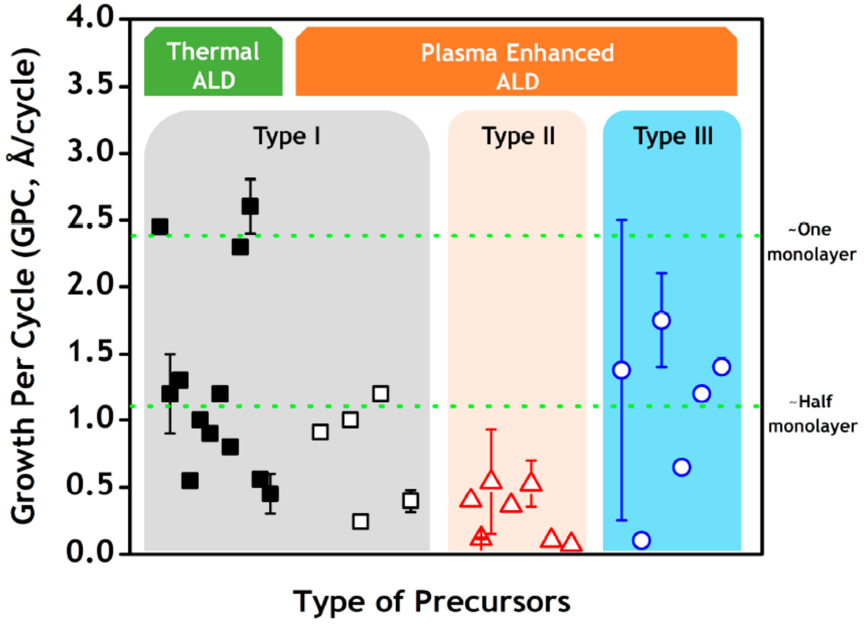
Cl included

Amino-silane

C & Cl free

Type	Classification	Examples	Major Potential Impurities	Deposition Method
I	Chlorine-containing precursors	Chlorosilanes: SiH_2Cl_2, Si_2Cl_6, etc.	Cl, H, O	PEALD, Thermal ALD
II	Carbon-containing precursors	Alkyl-aminosilanes: 3DMAS ($SiH(N(CH_3)_2)_3$), BTBAS ($SiH_2(NH^tBu)_2$), etc.	C, H, O	PEALD
III	Chlorine-free and carbon-free precursors	SiH_4, TSA ($N(SiH_3)_3$), NPS ($(SiH_3)_4Si$), etc.	H, O	PEALD

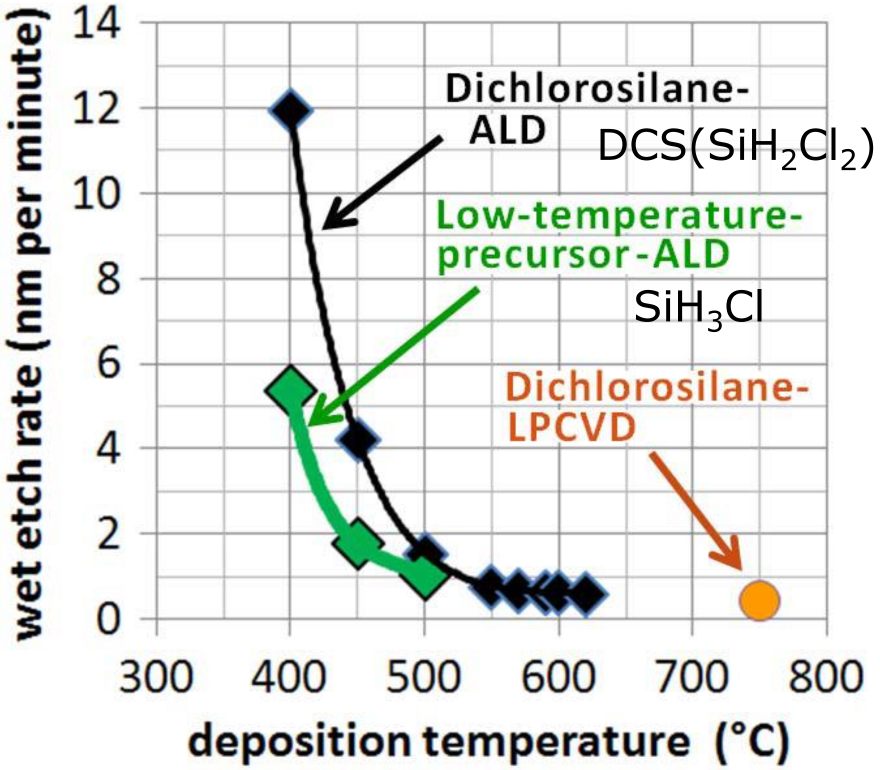
Xin Meng and et. Al., Materials **2016**, 9, 1007



Plot of SiN_x ALD growth per cycle (GPC) data (from Tables 1 and 2) vs. differ
cursors using thermal ALD (solid symbol) and plasma-enhanced ALD (open sy

Chlorine-containing precursor deposited with high GPC (~0.05nm/cy).
Amino-silane precursor typically have very low GPC.

ALD-SiN



1. K.Koehler and et. Al., IOP Conf. Series: Materials Science and Engineering 41 (2012) 012006

BTBAS :$SiH_2(NHBu)_2$ + N_2 plasma

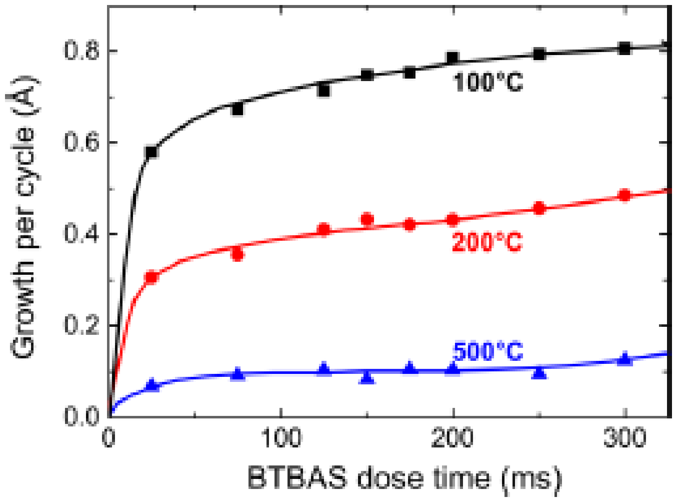


Figure 3. Growth per cycle (GPC) as a function of the precursor dosing time for a table temperature of 100 °C, 200 °C, and 500 °C. The GPC was determined using a 3 s plasma exposure time. The lines serve as a guide to the eye.

H.C.M.Knoops and et. Al., ACS Applied Materials & Interfaces, 7, 35 (2015) 19857.

ALD-SiN film quality is better at high deposition temperature.
GPC @ 500 ℃
DCS (Chloride) : 0.05 nm/cy
BTBAS (amino silane) :0.01 nm/cy.

Summary

・ALD is cycle deposition having good coverage with atomic level thickness control. It is self-limiting process thanks to mono layer precursor adsorption.

・ALD-SiO_2 film was deposited at AIST NPF. GPC is saturated with precursor dose and RF time. Film property depends on RF time and power with direct plasma. Pattern WER on side wall is larger than that on top because of ion bombardment effect.

・Several oxidants, direct, remote plasma and $O_{3,}$ are evaluated in ALD-SiO_2 film deposition. WER with remote plasma and O_3 are similar and larger than that with direct plasma. Pattern WER with remote and O_3 are conformal.

・Nitride ALD is the next target to oxide ALD.

Thank you

AIST
Dr. Arimoto, and Mr. Yamazaki for supporting ALD work at AIST.

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