アミノシラン原料による ALD法によるSiO_2の成膜特性

Film Formation Characteristics of SiO_2 via ALD Method Using Aminosilane Precursors

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施設共用におけるALD成膜のユーザー事例紹介

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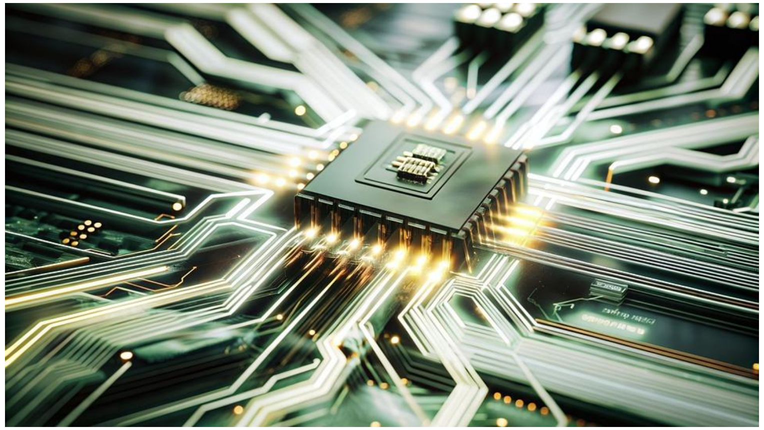
1. Introduction　ALD-SiO_2



Quoted from Pixabay

Application

- **Semiconductor Device**
  insulator / gate dielectric layer / sacrificial layer
- Optical coating
- Gas barrier coating

Advantage

- High uniformity
- Precise thickness control
- Good conformality

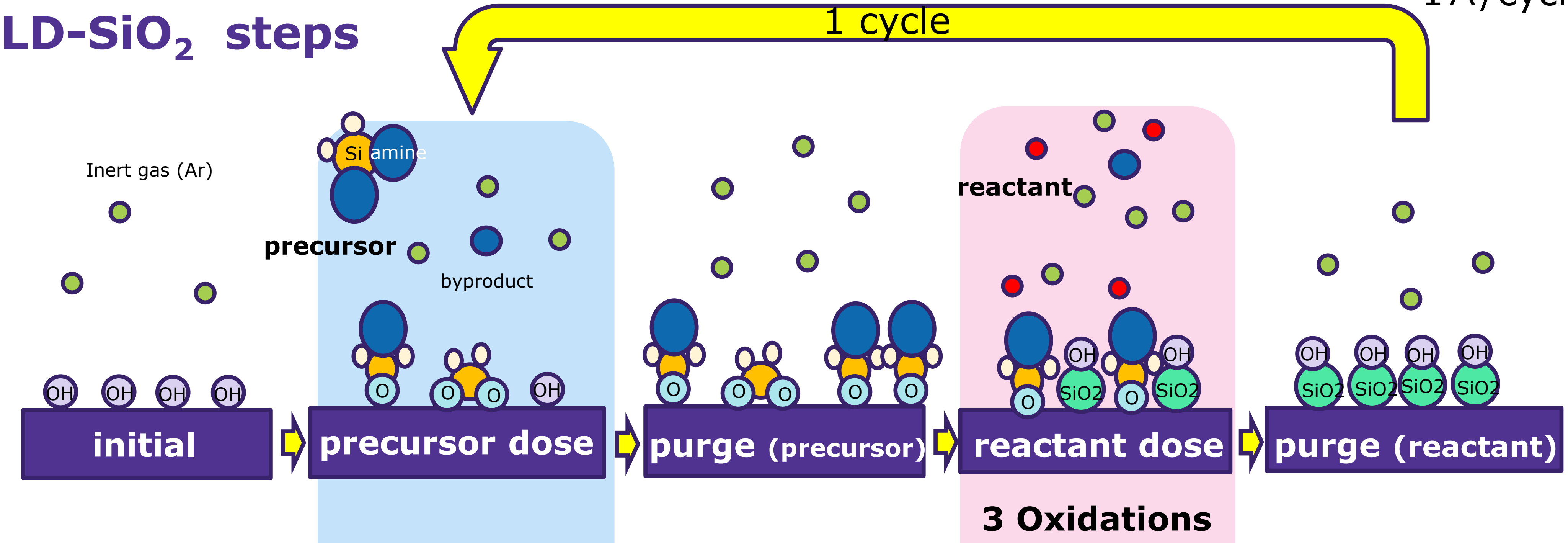
Disadvantage

- Low deposition rate
  (Growth Per Cycle)

2. Experiment

ALD-SiO_2 steps

layer by layer deposition
~ 1 Å/cycle



Chemisorption of **aminosilane precursors** onto surface OH groups.

exchange of ligands between amine and OH

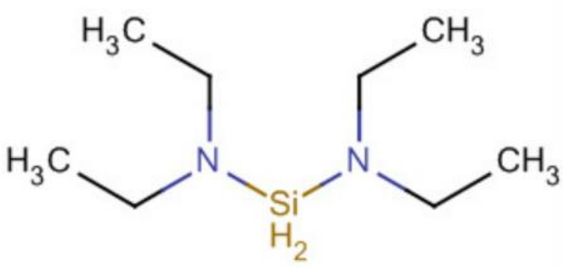
Thermal ALD – O_3 (>90%)
Direct plasma – ion, O radical
Remote plasma – O radical

Comparison oxidations

Precursor, Tool & Conditions

BDEAS
（Bisdiethyaminosilane）

2 amino group



Tool (SAMCO PEALD)
Sample size: 4 inch wafer
Plasma: ICP (13.56MHz)

Condition

Temp.	50~400C
Press.	5 Pa(dose) 12 Pa (plasma)
plasma power	50～300 W
Time dose-prg-oxidation-prg	0.2s-1s-3s-0.1s (center cond.)

NPF099 AD-100LP
(SAMCO PEALD)

Evaluation

GPC Performance, Film property

Comparison 3 oxidations

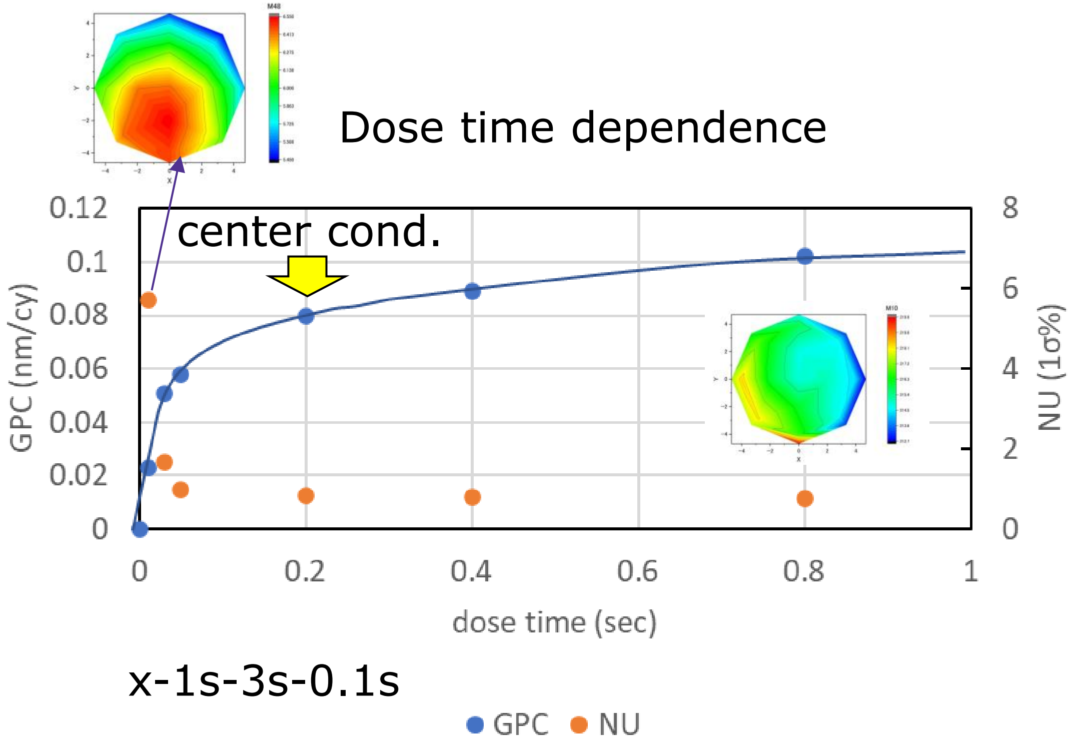
3 oxidations (Center Cond.)

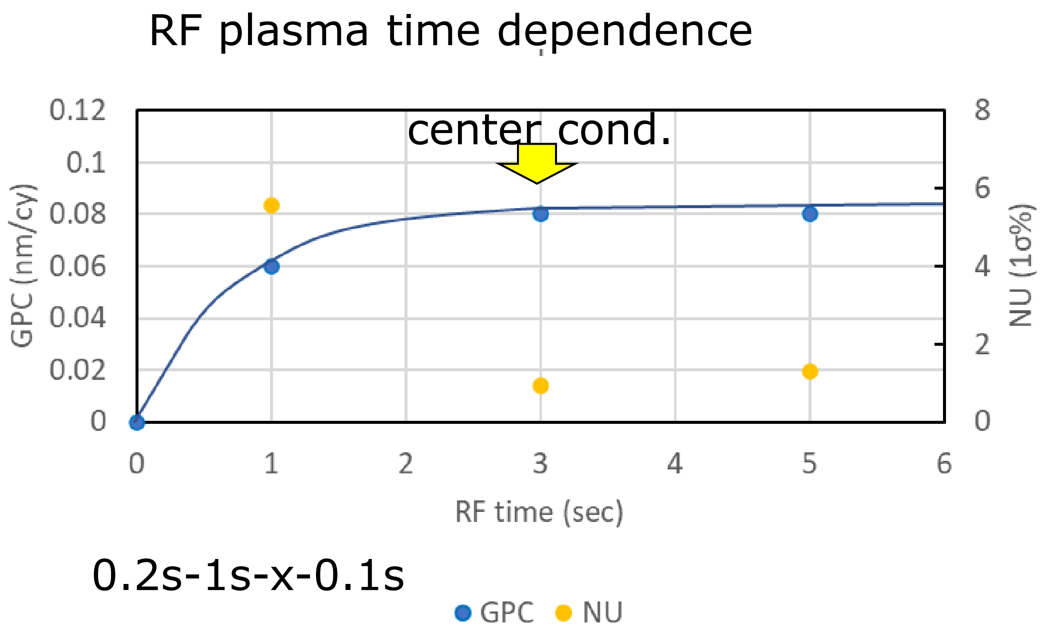
1) **O_2 direct plasma 100W 3 sec**
2) O_2 remote plasma 100W 3 sec
3) Pure Ozone (>90% O_3 2 sec)

NPF105 Pure Ozone
(Meidensha O_3 Supplier)

➔ thickness and non uniformity : ellipsometry
film property: WER, TDS, Coverage, FTIR

GPC performance



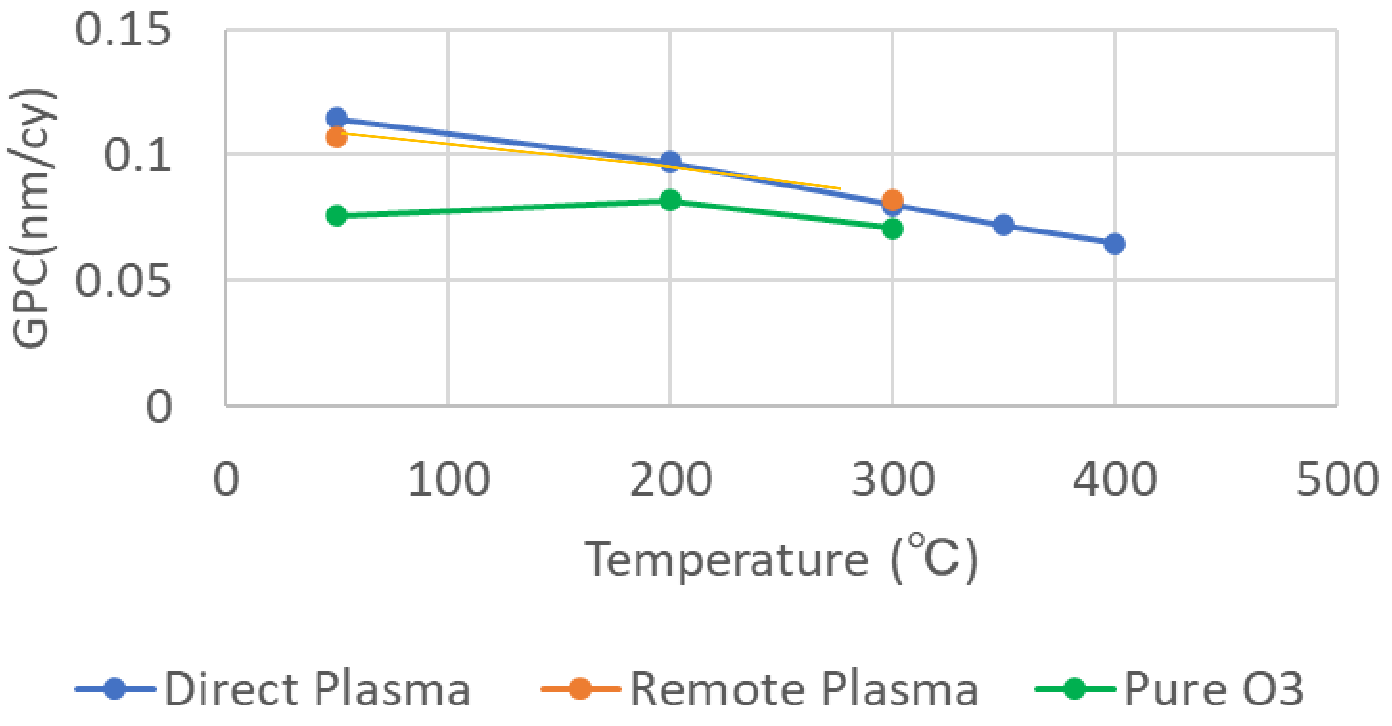


Temp.	300C
Press.	5 Pa(does) 12 Pa(plasma)
Direct plasma PW	100 W

Oxidation:O_2 direct plasma

Precursor adsorption saturates with precursor dose.
SiO_2 oxidation saturates with plasma RF time.
ALD is a self-limiting saturation process.

Temperature dependence of GPC on 3 oxidations



Press.	5~12 Pa (Plasma) 2~100 Pa (O3)
Direct plasma	0.2s-1s-3s-0.1s
Remote plasma	0.2s-1s-3s-0.1s
O3	0.2s-5.3s-2s-13s

GPC for direct and remote plasma is almost same. The GPC for O_3 is lower, especially at low temperatures, compared to plasma. The radical oxygen generated by plasma is more reactive than O_3.

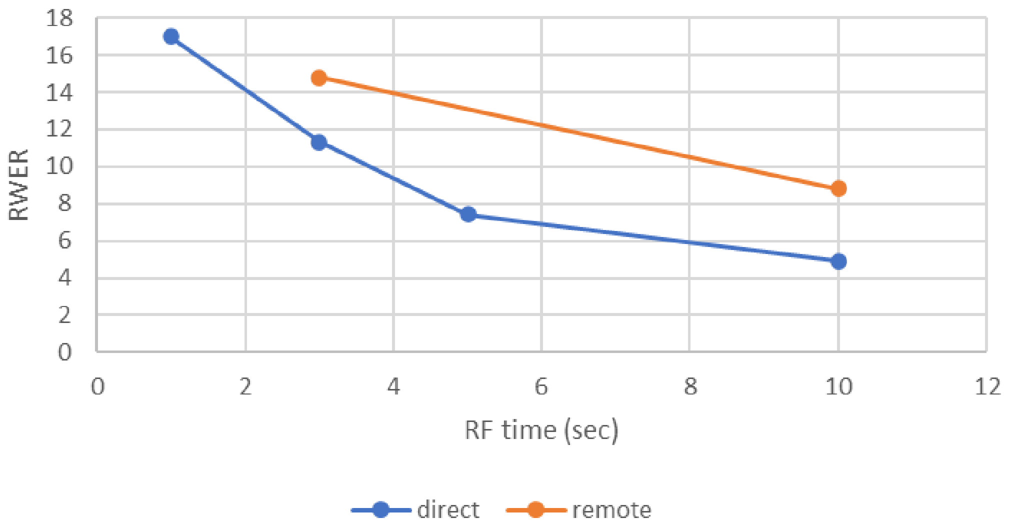
Film property
plasma dependence of WER

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

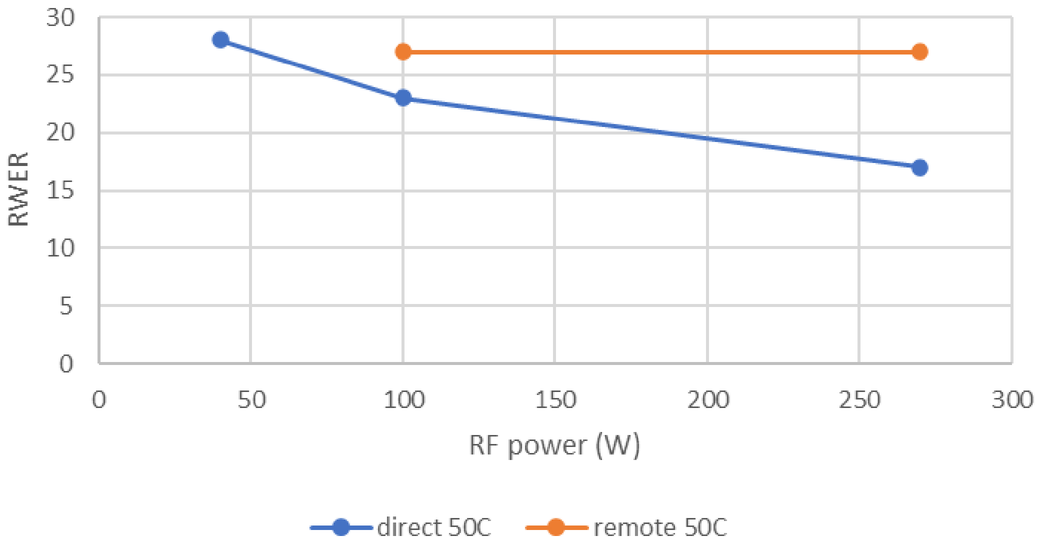
Press.	5 Pa(dose) 12 Pa (plasma)
Direct plasma	0.2s-1s-3s-0.1s
Remote plasma	0.2s-1s-3s-0.1s
Temp.	300C

plasma time

Good film

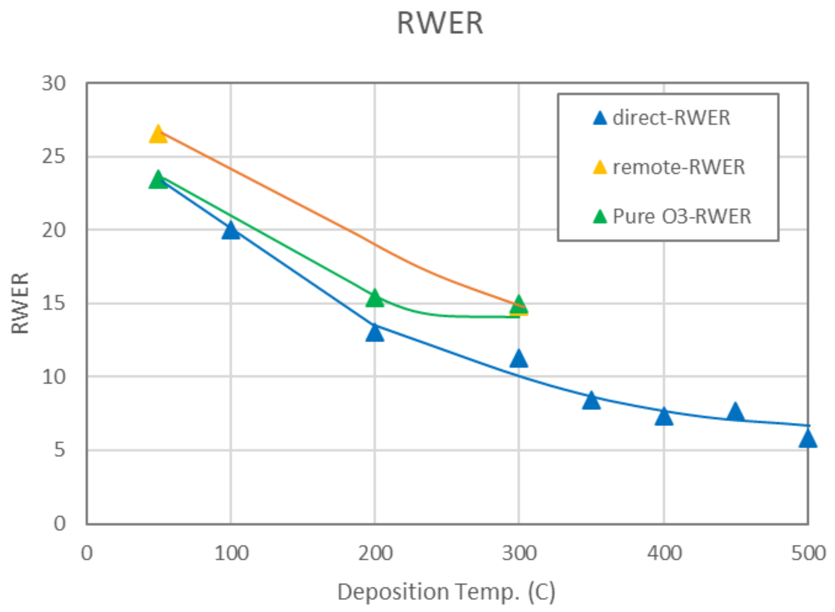


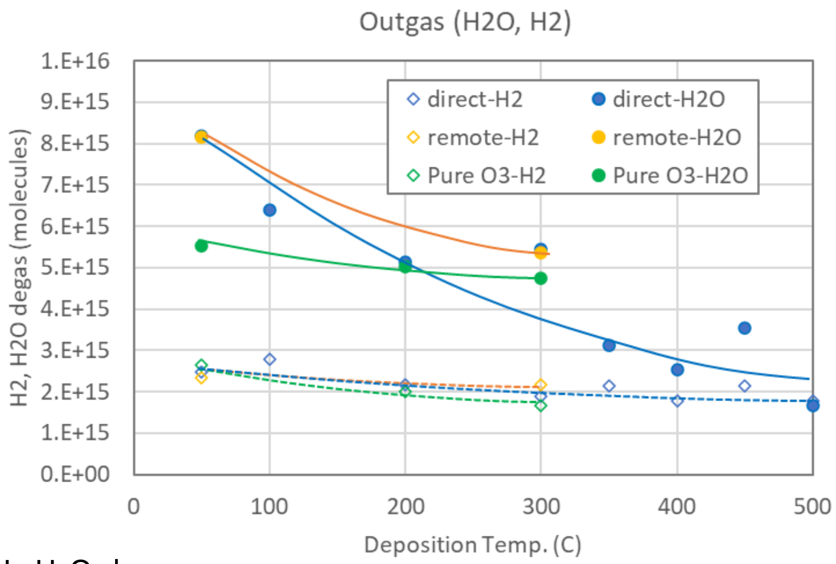
plasma power



The WER is lower for direct plasma than for remote plasma, indicating better film quality. The power dependency for remote plasma is minimal. Direct plasma ions provide greater energy, enhancing film quality.

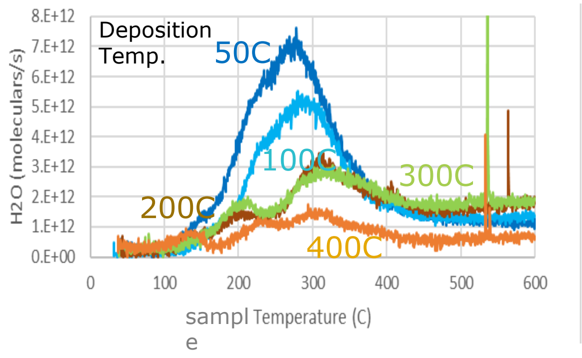
Deposition temperature dependence of film property (outgas, WER)





H_2,H_2O degas :
total gas 50~600C

TDS data
H_2O outgas dependence of sample temperature



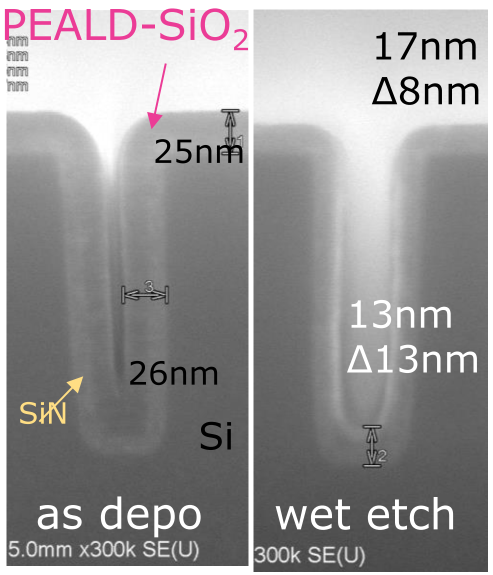
Press.	5~12 Pa (Plasma) 2~100 Pa (O3)
Direct plasma	0.2s-1s-3s-0.1s
Remote plasma	0.2s-1s-3s-0.1s
O3	0.2s-5.3s-2s-13s

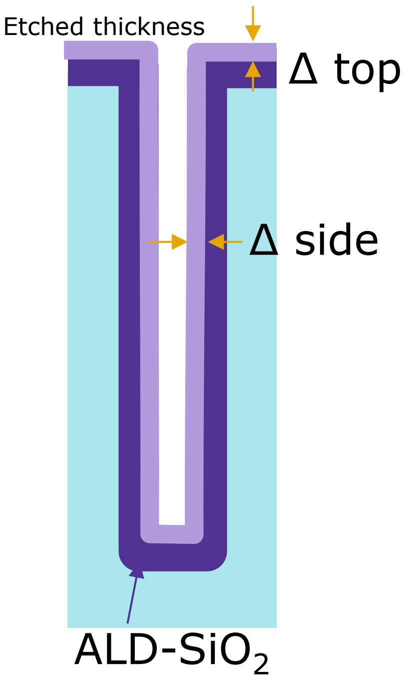
RWER and H_2O outgas show strong correlation to each other.
Higher temperature improves film property (lower RWER)

H_2 outgas is not correlated to film property and show relatively small temperature dependence.

Film quality: Direct O_2 plasma > O_3 ~ remote O_2 plasma

WER at pattern





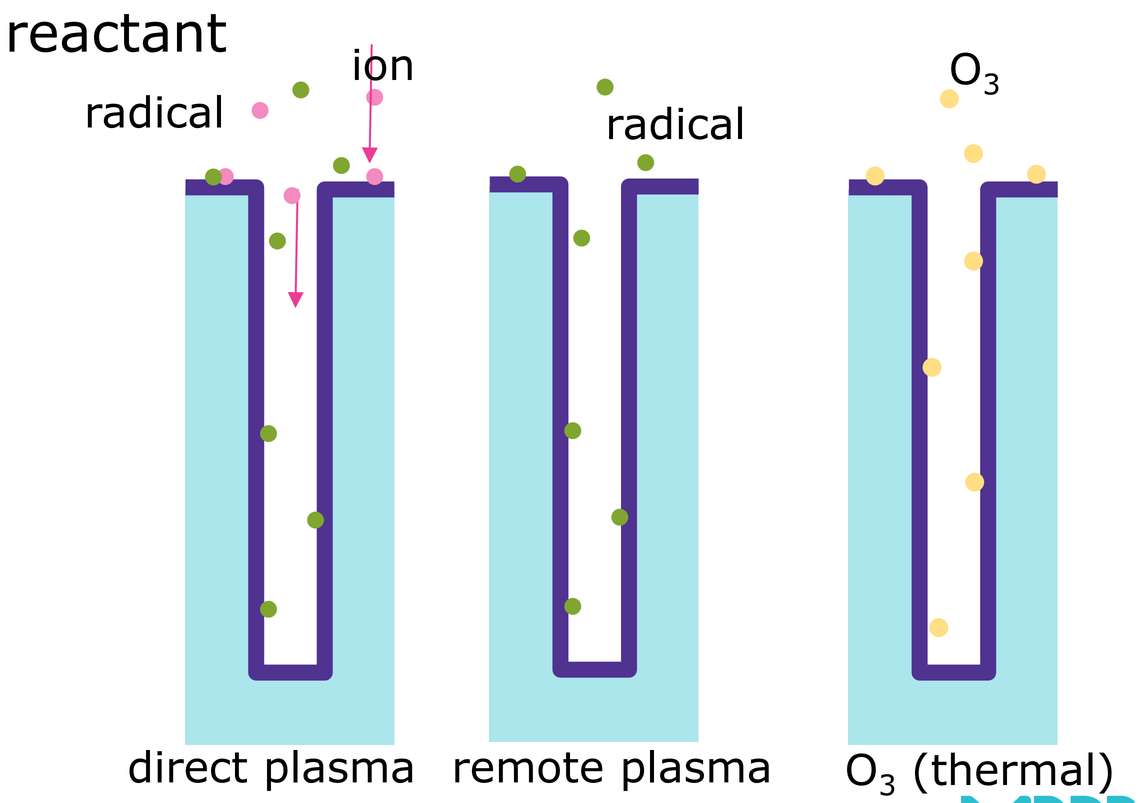
dip $DHF:H_2O$ = 1:500

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 reactants 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



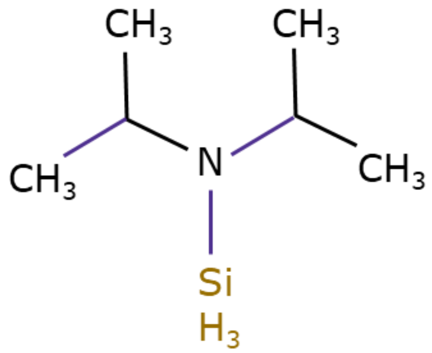
4. Discussion
Oxidation comparison

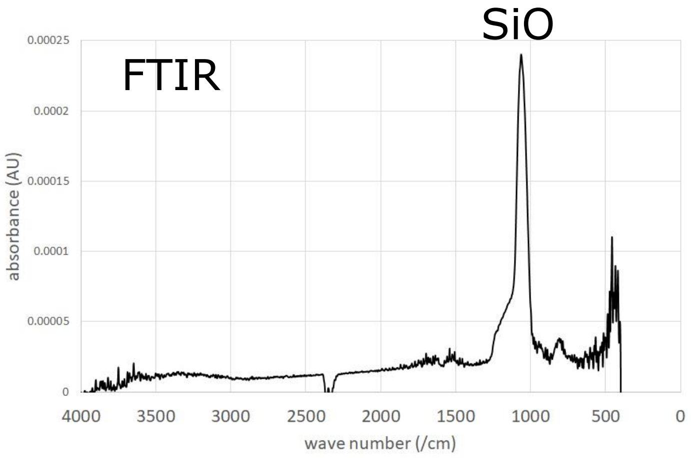
	O_2 Direct Plasma	O_2 Remote Plasma	Pure Ozone
Reactant (Oxidant)	Radical Oxygen Ion	Radical Oxygen	O_3
GPC Performance	High	High	Lower GPC than Plasma Especially at lower temp.
Film Property (WER)	Best >	~ Similar level	
WER Coverage	Bad: Large WER in the trench.	Same level WER at the top and middle of the trench.	
	Good film Ion assists to improve film quality. However, ion effect is not conformal.	O radical have very active and conformal effect.	Thermal energy is very conformal. Although reactivity is lower than that of plasma especially at low temp.

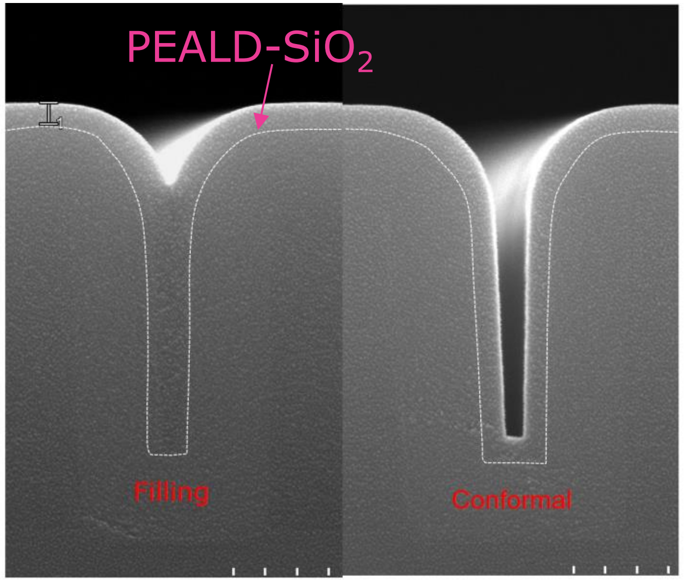
5. Precursor DIPAS
（ Diisopropylaminosilane ）

One amino group

vapor pressure (3kPa@RTM)







Tool (Oxford Instruments PEALD)
sample size: 4 inch wafer
Plasma: ICP (13.56 MHz)

Press.	10 Pa(dose) 2 Pa (plasma)
Temp.	300C
Direct plasma Pw	250 W
time	0.5s-5s-3s-5s

Confirmed SiO_2 structure (FTIR) and excellent coverage.

GPC	0.1 nm/cy
RWER	10

6. Summary

- ALD-SiO_2 film is widely used as dielectric film in various applications.
- ALD-SiO_2 film was deposited at AIST NPF with amino silane precursor.
- The saturation of GPC, a characteristic of ALD, was confirmed.
- 3 Oxidations, direct, remote plasma and O_3, were evaluated in ALD-SiO_2 film deposition. GPC with O_3 is small at low temperatures and less reactive than plasma. Film quality (RWER) is similar for O_3 and remote plasma, but better for direct processes, where film quality varies in areas like trenches due to limited ion reach.
- Amino silane precursors are used as ALD-SiO_2 precursor. DIPAS is expected to have good characteristics.

Thank you

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