EuroCVD 22-Baltic ALD 16 Conference

Kinetic analysis on TiAlN-CVD to construct reaction model

Jun Yamaguchi[1], Tomoko Hirabaru[1], Hayato Kubo[2], Momoko Deura[1], Takeshi Momose[1], Takahito Tanibuchi[2], Yukihiro Shimogaki[1]

1. Department of Materials Engineering, The University of Tokyo, Japan

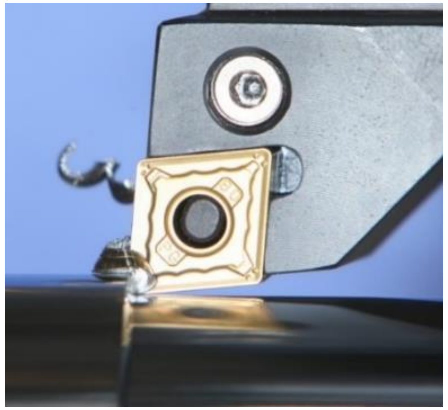
2. Cutting Tool R&D Division, Kyocera Corporation, Japan

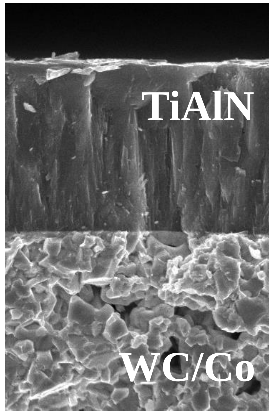
About titanium aluminum nitride

■Cubic titanium aluminum nitride(c-TiAlN)

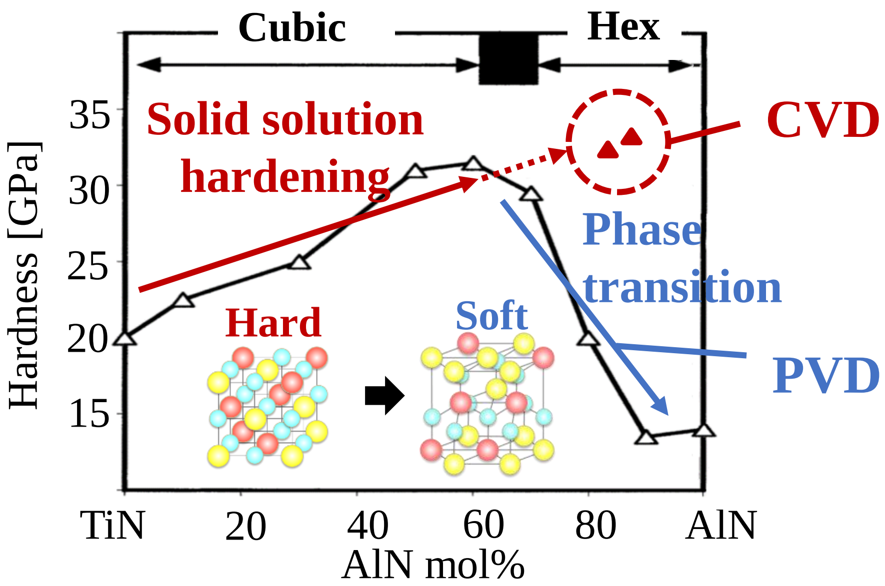
- High hardness
- High thermal resistance
- Chemical stability

→ C-TiAlN is applied to cutting tool coating





■Relationship between process and characteristics [1]



In PVD, hardness decreases significantly when Al composition exceeds 60%

In CVD, cubic-TiAlN with Al composition 90% can be synthesized and hardness more increases

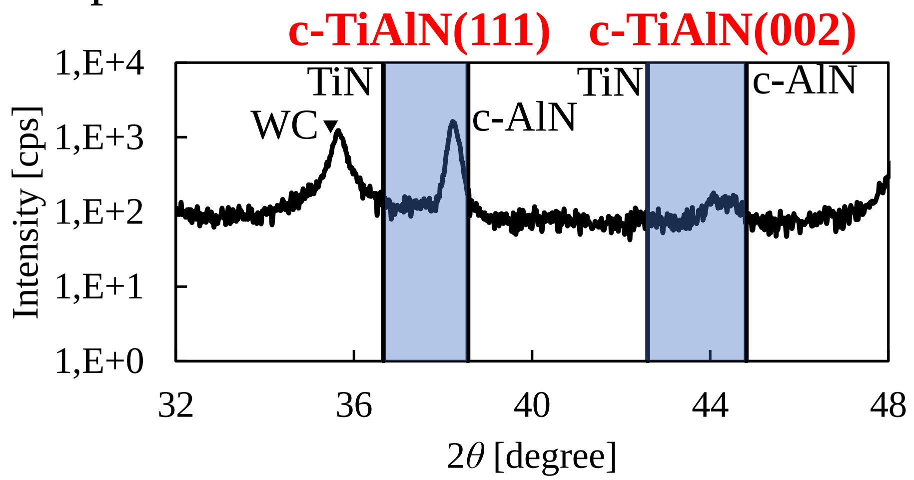
[1] S. PalDey and S.C. Deevi, Mater. Sci. Eng. (2003) [2] I. Endler *et al.*, Surf. Coat. Technol. (2008)

■Evaluation of our CVD-TiAlN sample

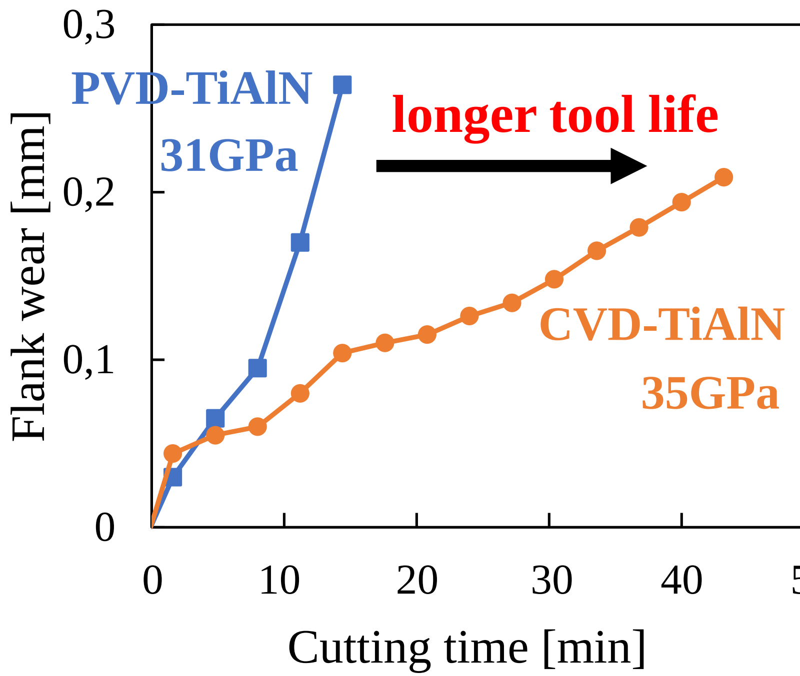
Film properties

Al [at%]	Ti [at%]	N [at%]	Al/(Al+Ti) [%]	Hardness [GPa]
47	4	43	92	35

XRD profile



Result of cutting test

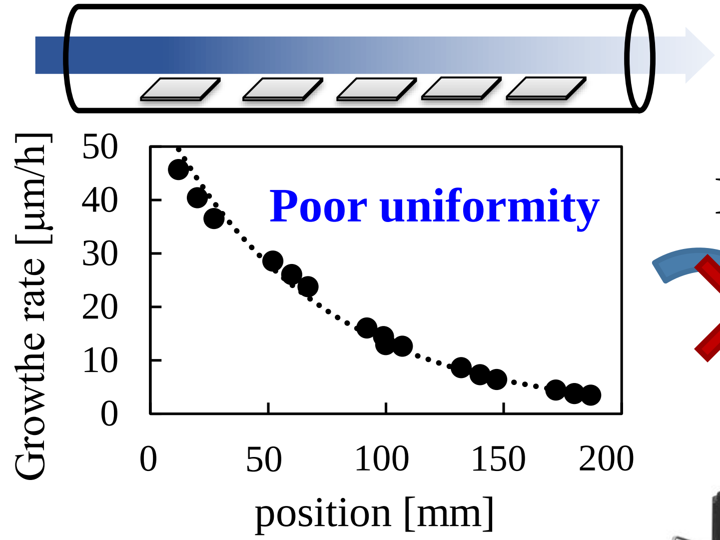


Succeeded in synthesizing Al rich cubic-TiAlN and achieved 3 times longer tool life than PVD-TiAlN

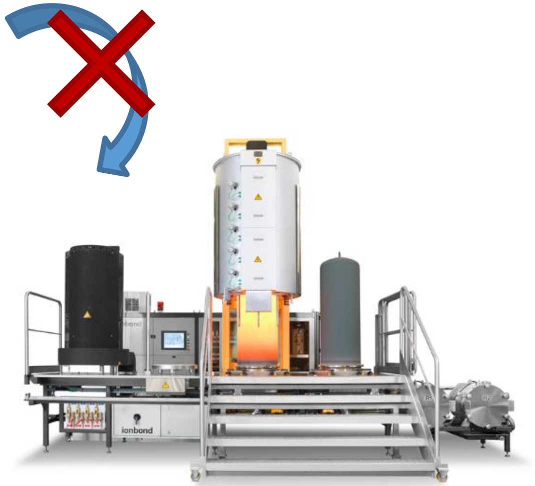
Problem of TiAlN-CVD and purpose of this research

■Challenge

Growth rate distribution occurs even in lab-scale reactor



Impossible to scale up



Mass production reactor [1]

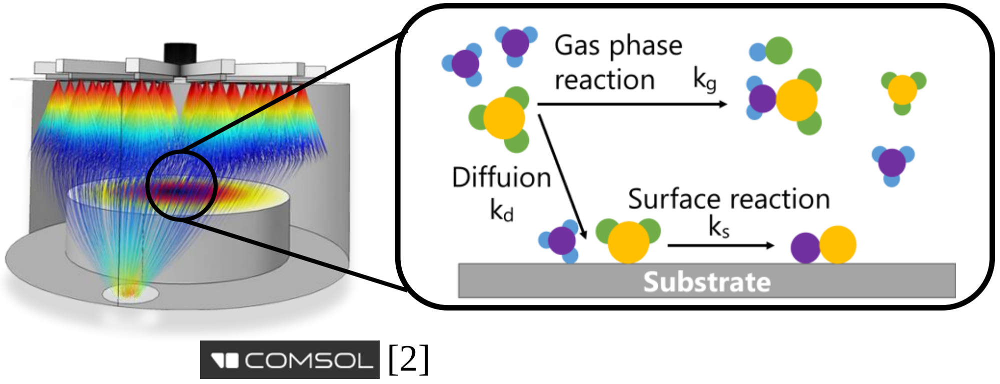
Process design is necessary

■Solution

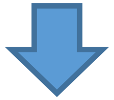
❌Optimization by trial and error

- Too many parameter (Temp., Press., Precursor conc., …)
- Impossible to change reactor shape easily

〇Computer-aided process design



[2]

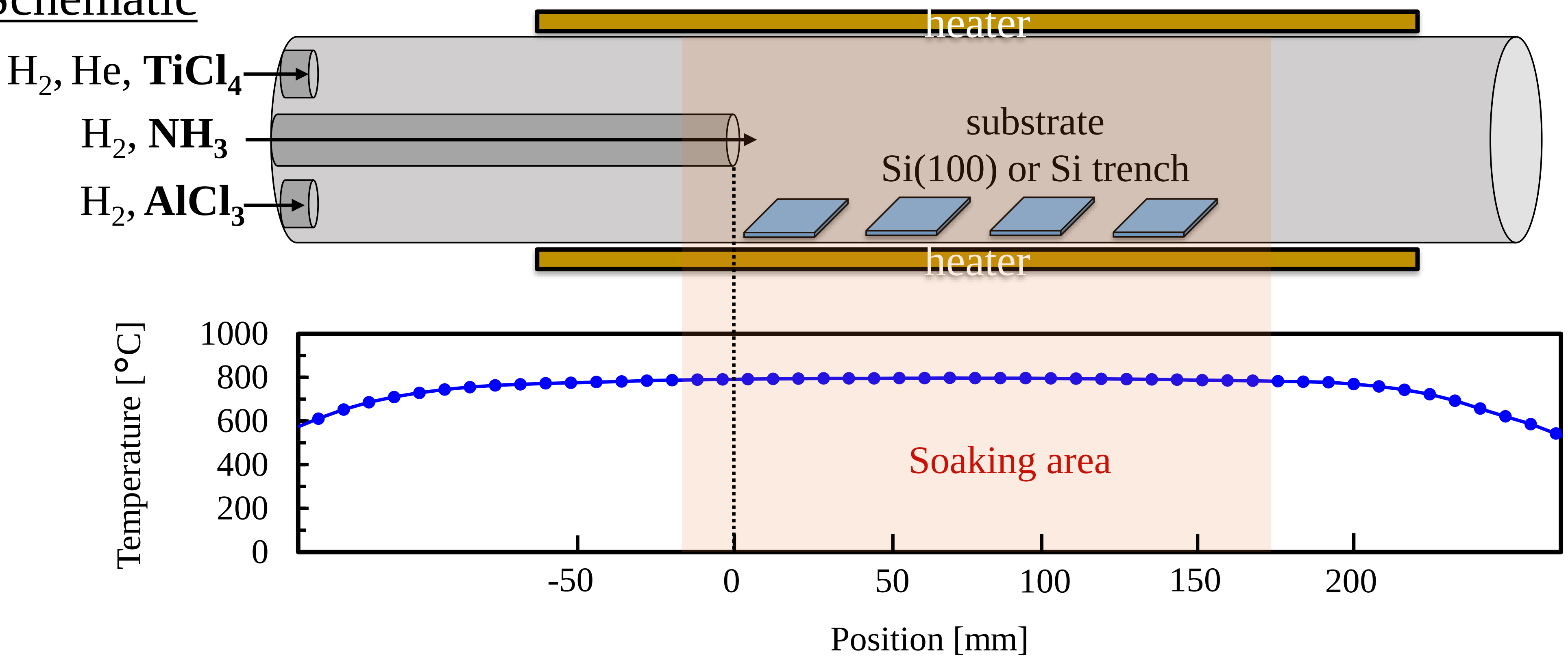


Necessary to understand reaction phenomena and to construction model

[1] https://www.ionbond.com/coating-equipment/cvd/
[2] Image made using COMSOL Multiphysics® software and provided courtesy of COMSOL.

Experimental method

Schematic



- Hot wall
- Circular tube reactor
- NH_3 is mixed just before the reaction region

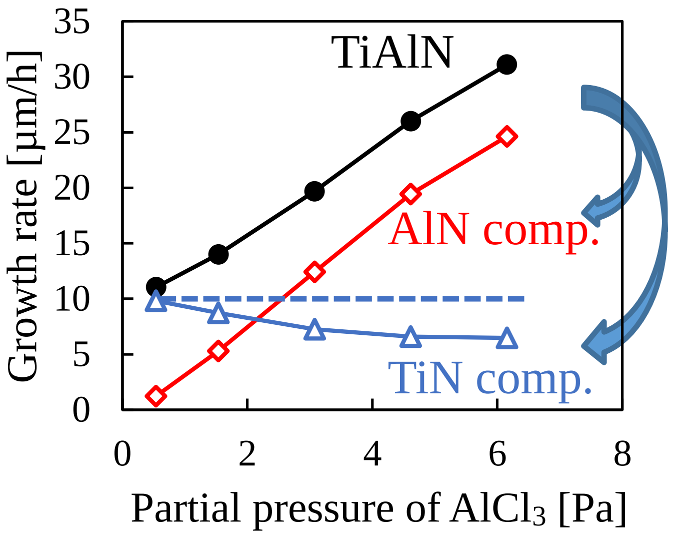
Process condition

Temperature [°C]	Total pressure [Pa]	Partial pressure [Pa]				
		H_2	He	$AlCl_3$	$TiCl_4$	NH_3
800	1000	balance		0-6.2	0-3.1	19.2

Interaction of Ti and Al

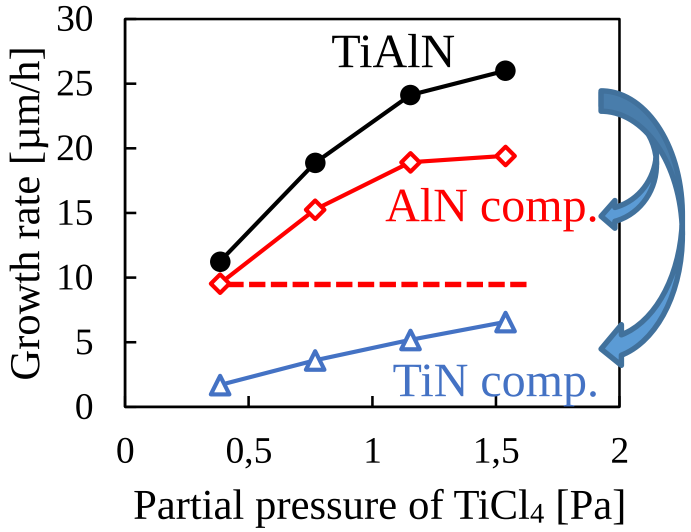
■Complexity of TiAlN system

◇Dependence on $AlCl_3$ partial pressure
(P_{TiCl_4}=1.5 Pa, P_{NH_3}=19.2 Pa)



Decomposed into AlN and TiN by XPS analysis

◇ Dependence on $TiCl_4$ partial pressure
(P_{AlCl_3}=4.6 Pa, P_{NH_3}=19.2 Pa)



TiN growth rate decreases despite constant supply of Ti source

AlN growth rate increases despite constant supply of Al source

TiAlN growth involves some interactions among Ti and Al precursors

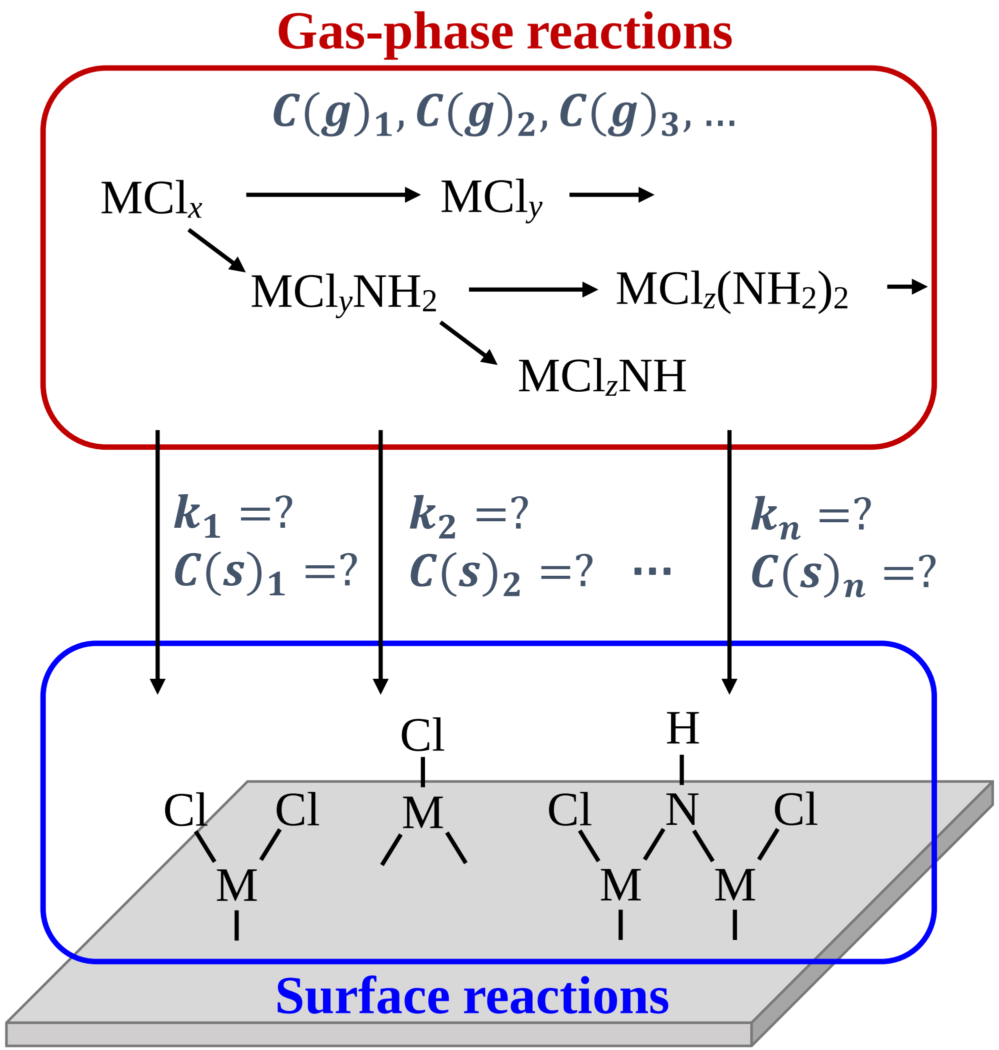
⇩

Reaction mechanism of AlN and TiN was individually investigated

Strategy of this research

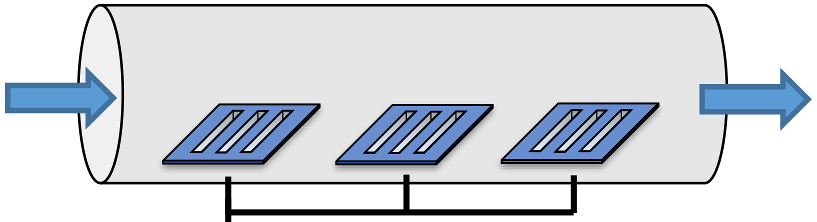
Analysis of reaction mechanism is performed by the following step

1. Determine the number of growth species(n)
2. Calculate rate constant(k) and concentration of growth species(C)
3. Identify growth species
4. Examine limiting step

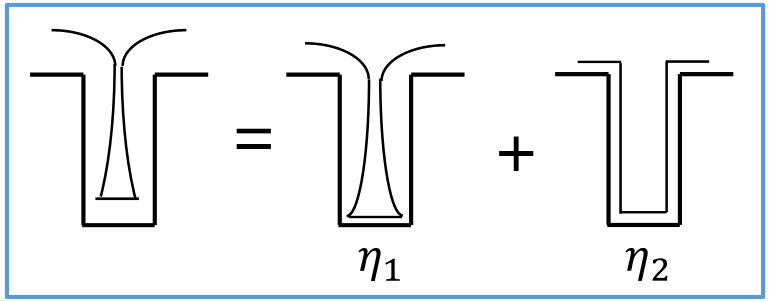


Multi-scale analysis

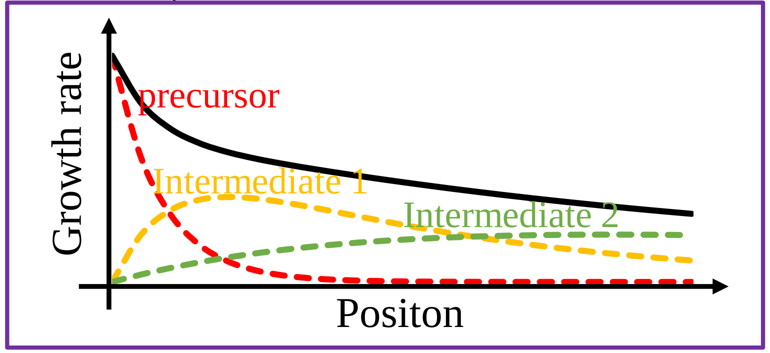
■Analytical method



Analyze the number and proportion of growth species at each position



Analyze kinetic data of each growth species



micro-scale

$$D\frac{d^2C}{dx^2} = -\frac{2k_s}{W}C$$

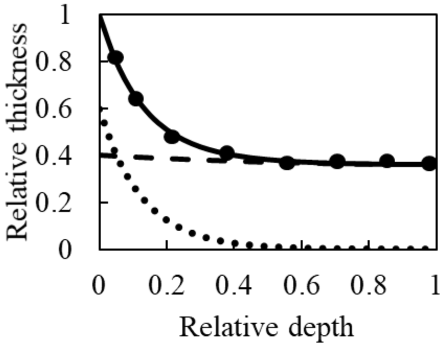
$$\rightarrow \frac{T(x)}{T_L} = \frac{\cosh\left(\phi\frac{x}{L}\right) + \frac{W}{2L}\phi\sinh\left(\phi\frac{x}{L}\right)}{\cosh(\phi) + \frac{W}{2L}\phi\sinh(\phi)}$$

$\phi = \frac{L}{W}\sqrt{\frac{3}{2}\eta}$: Thiele number

η: Sticking probability

Estimate η by fitting experimental data

Determine the number of growth species from the number of fitting parameters



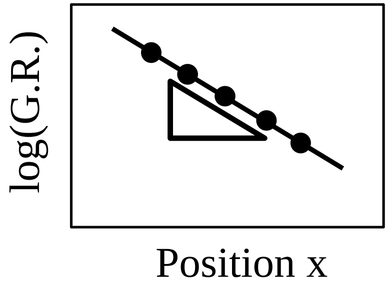
macro-scale

$$u\frac{dC}{dx} = -\frac{4k}{d}C$$

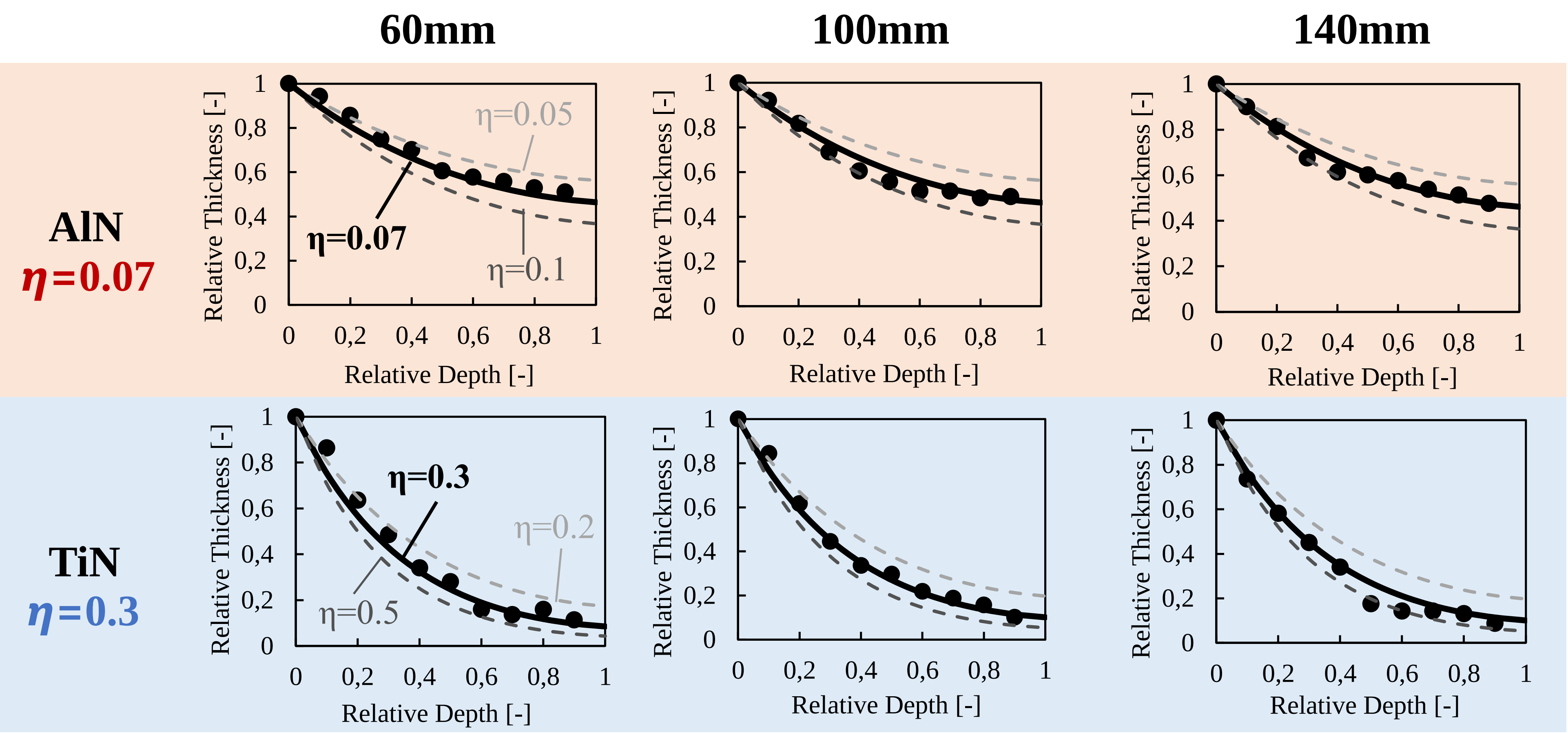
$$\rightarrow \text{Growth rate} = kC_0\exp\left(-\frac{4k}{du}x\right)$$

d: Inner diameter u: linear velocity

Calculate rate constant from slope



■Result



Fitted by a single parameter at each position

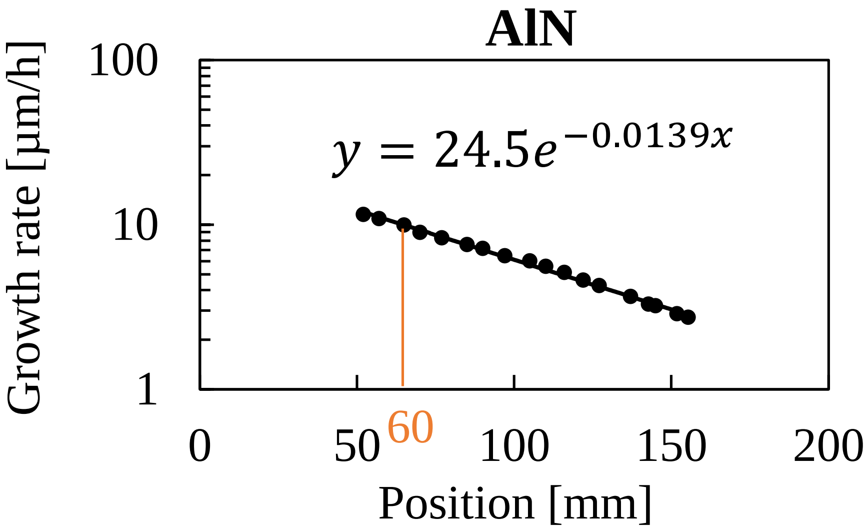
→ **The number of growth species is one**

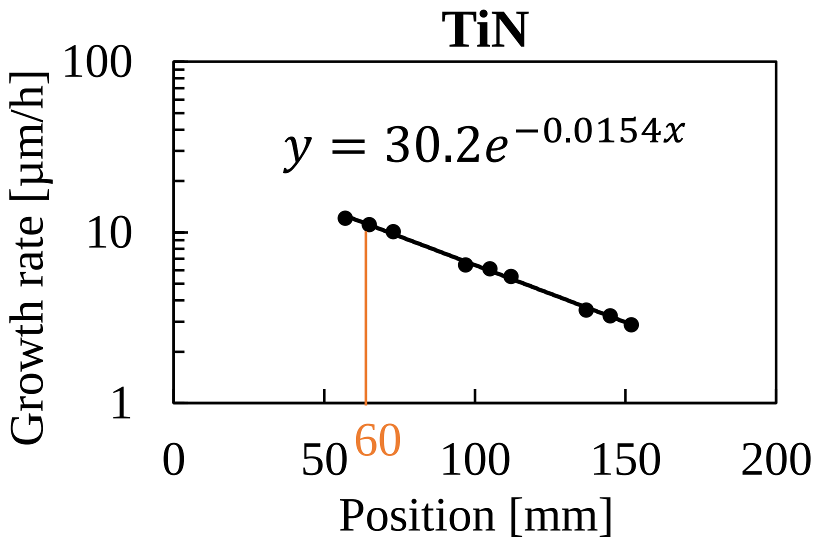
2. Calculate rate constant and concentration (by macro-scale analysis)

■Result

$$\text{Growth rate} = kC_0 \exp\left(-\frac{4k}{du}x\right)$$

d: Inner diameter= 55 mm
u: liner velocity= 7.26 m/s





	AlN	TiN
overall rate constant k [m/s]	1.4	1.5
growth species concentration C at 60 mm [mol/m^3]	1.6×10^{-4}	1.7×10^{-4}

Compare these concentrations with gas-phase species concentrations calculated by simulation

3. Identify growth species (by calculation of gas-phase reaction)

■Reaction model

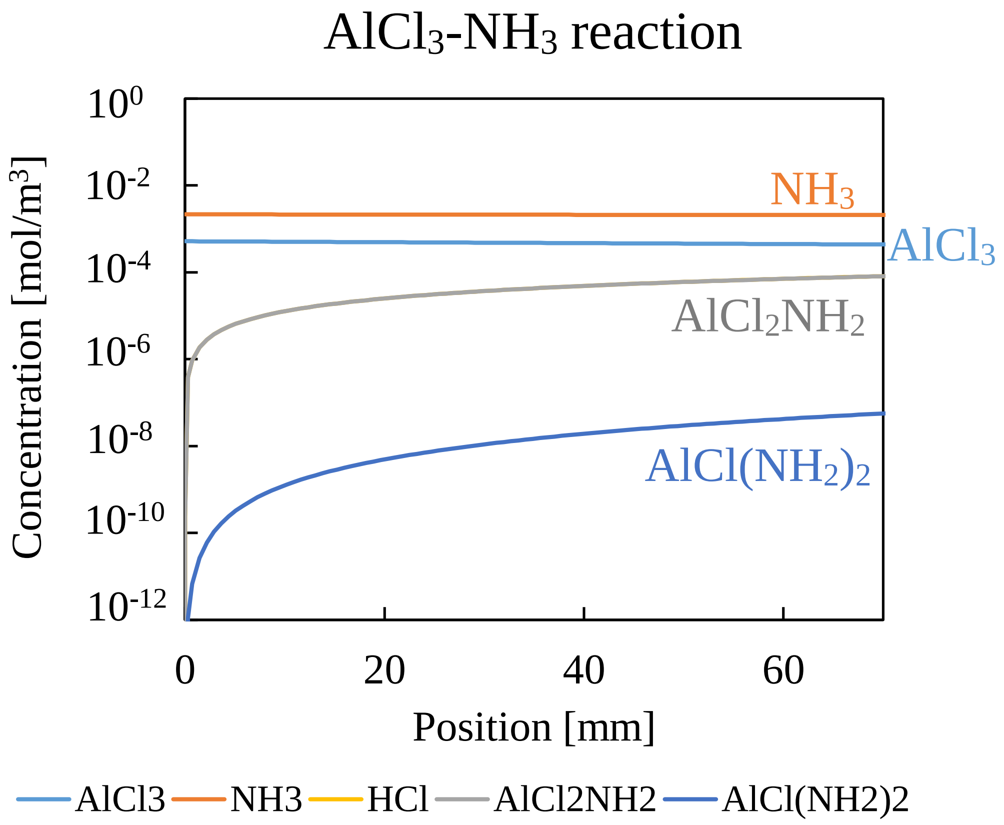
No.	Reaction	A	Ea	Ref.
1	$AlCl_3 + NH_3 \rightarrow AlCl_2NH_2 + HCl$	4.21×10^5	8.35	[1]
2	$AlCl_2NH_2 + NH_3 \rightarrow AlCl(NH_2)_2 + HCl$	3.88×10^5	18.5	[1]
3	$AlCl(NH_2)_2 + NH_3 \rightarrow Al(NH_2)_3 + HCl$	3.88×10^5	18.5	[1]
4	$AlCl_2NH_2 \rightarrow AlClNH + HCl$	10^{12}	77.3	[1]
5	$NH_3 \rightarrow NH_2 + H$	2.5×10^8	93.47	[1]
6	$AlCl_3 \rightarrow AlCl_2 + Cl$	2.5×10^8	93.47	[1]
7	$H + Cl \rightarrow HCl$	3×10^8	0	[1]
8	$TiCl_4 + NH_3 \rightarrow TiCl_3NH_2 + HCl$	3.86×10^{13}	22.8	[2]
9	$TiCl_3NH_2 + HCl \rightarrow TiCl_4 + NH_3$	1.51×10^{11}	9.5	[2]
10	$TiCl_3NH_2 + NH_3 \rightarrow TiCl_2(NH_2)_2 + HCl$	2.03×10^{15}	15.4	[2]
11	$TiCl_2(NH_2)_2 + HCl \rightarrow TiCl_3NH_2 + NH_3$	6.15×10^{14}	1.1	[2]

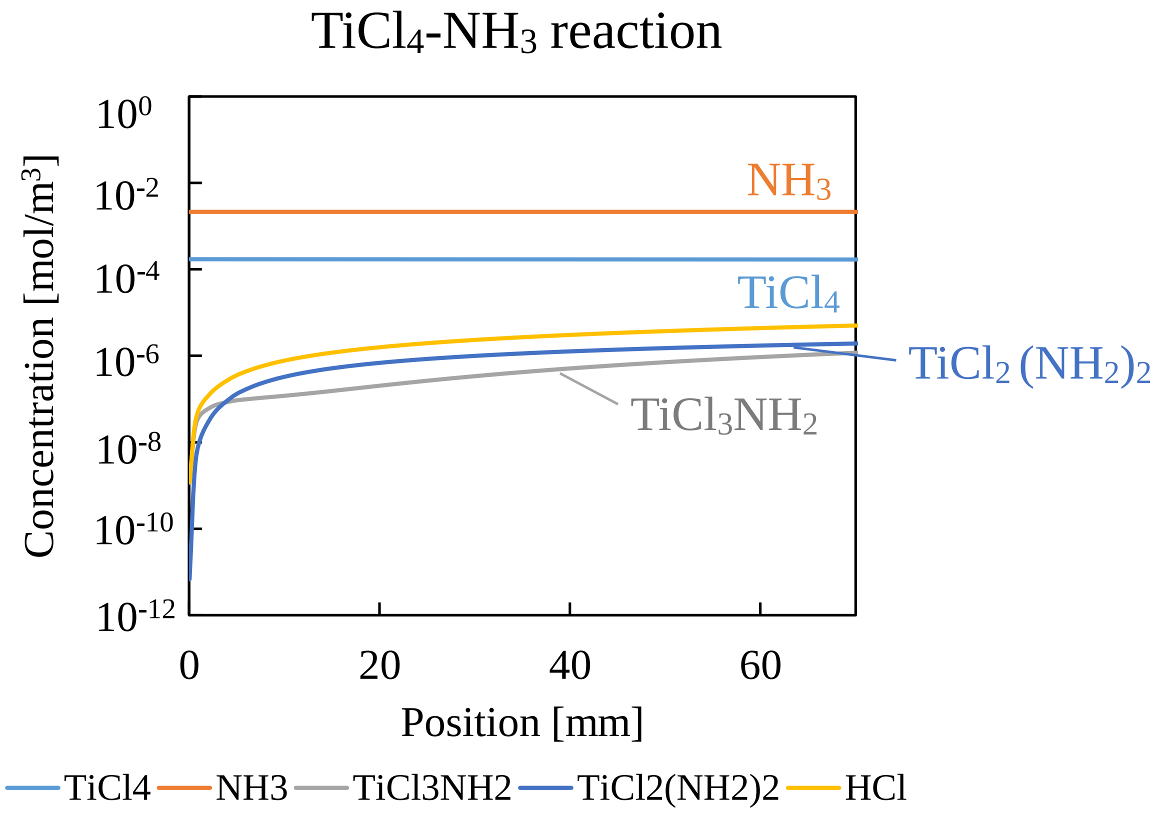
[1] A. Dollet *et al.*, Thin Solid Films 406 (2002)
[2] S. Umanskii *et al.*, J. Com. Chem. 22 (2001)

unit A: s^{-1} or $m^3mol^{-1}s^{-1}$ Ea: kcal/mol
unit A: $cm^3mol^{-1}s^{-1}$ Ea: kcal/mol

3. Identify growth species (by calculation of gas-phase reaction)

■Result

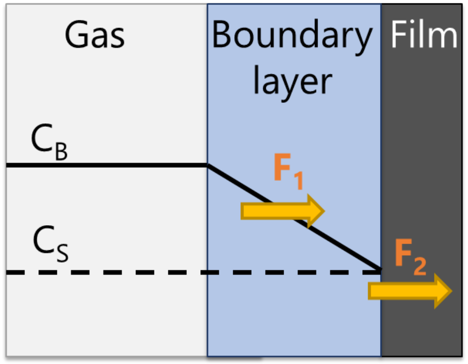




The concentrations of $AlCl_3$ and $TiCl_4$ are close to the growth species concentrations obtained from the experimental values(~10^{-4} mol/m^3)

→ The growth species is $AlCl_3$ and $TiCl_4$ in AlN and TiN deposition, respectively

4. Examine rate-limiting step



Diffusion rate $F_1 = k_d(C_B - C_S)$

Surface reaction rate $F_2 = k_s C_S$

$F_1 = F_2$

$$\rightarrow \text{Growth rate } r = \frac{k_d k_s}{k_d + k_s} C_B$$

$k_d \gg k_s \quad r = k_s C_B$ reaction limited

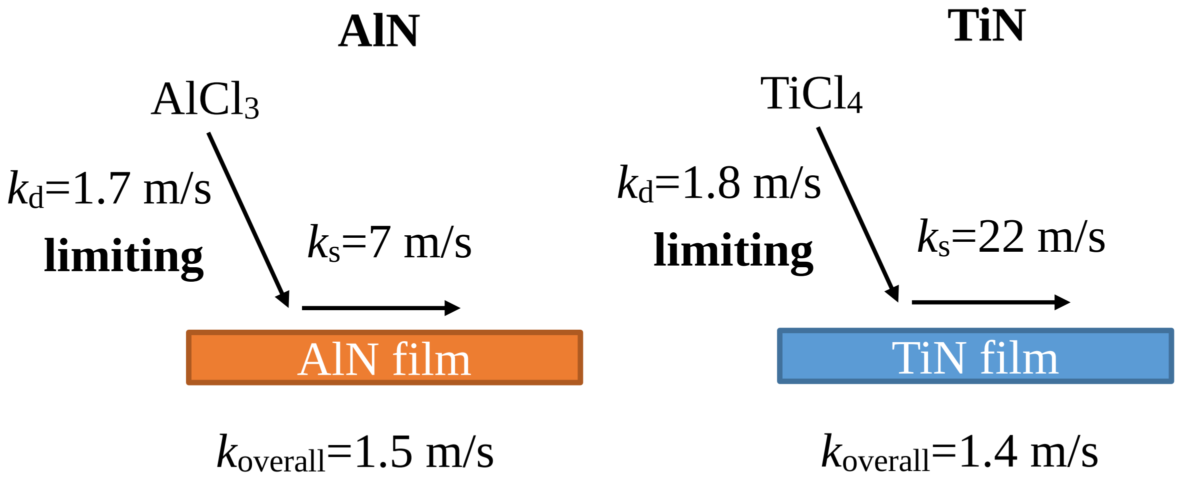
$k_s \gg k_d \quad r = k_d C_B$ diffusion limited

	AlN	TiN
Surface reaction rate constant by micro-scale analysis $k_s = \frac{\eta}{4-2\eta}\bar{v} \quad \bar{v} = \sqrt{\frac{8RT}{\pi M}}$	7 m/s	26 m/s
Mass transfer coefficient by Chapman-Enskog theory $k_d = Sh\frac{D}{d} \quad D_{Aj} = \frac{3}{16}\frac{\sqrt{2\pi k_B^3 T^3 m_{Aj}{}^{-1}}}{P\pi\sigma_{Aj}{}^2\Omega_{Aj}}$	1.7 m/s	1.8 m/s
Overall rate constant by macro-scale analysis k	1.5 m/s	1.4 m/s

$\boldsymbol{k_s \gg k_d \fallingdotseq k}$ **Diffusion limited**

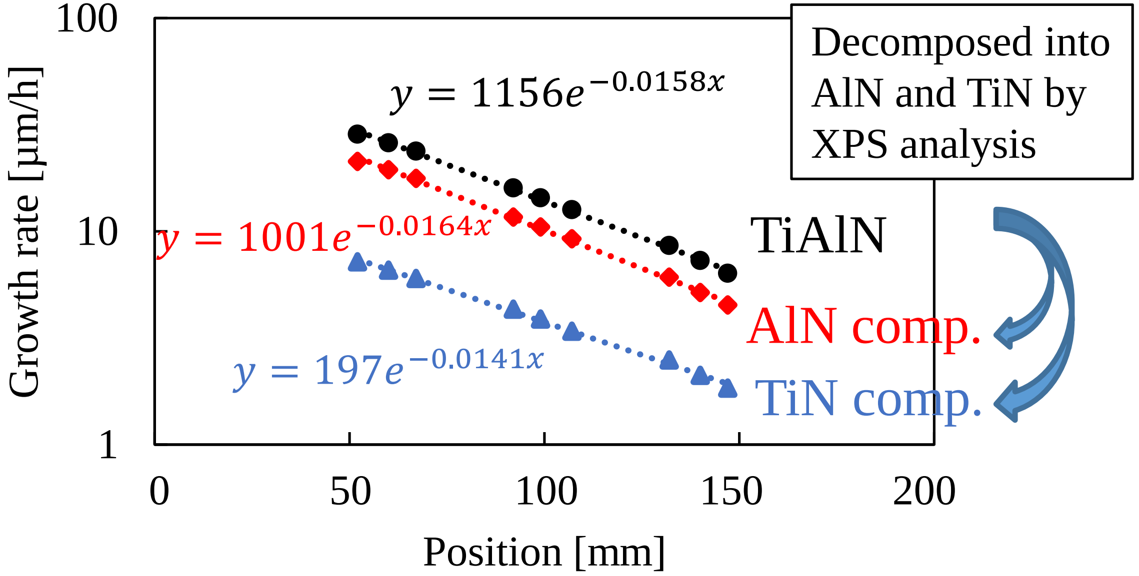
Summary of reaction mechanism analysis

■Reaction scheme



In both cases, precursors directly contribute to growth without gas-phase reaction

■Analysis of TiAlN

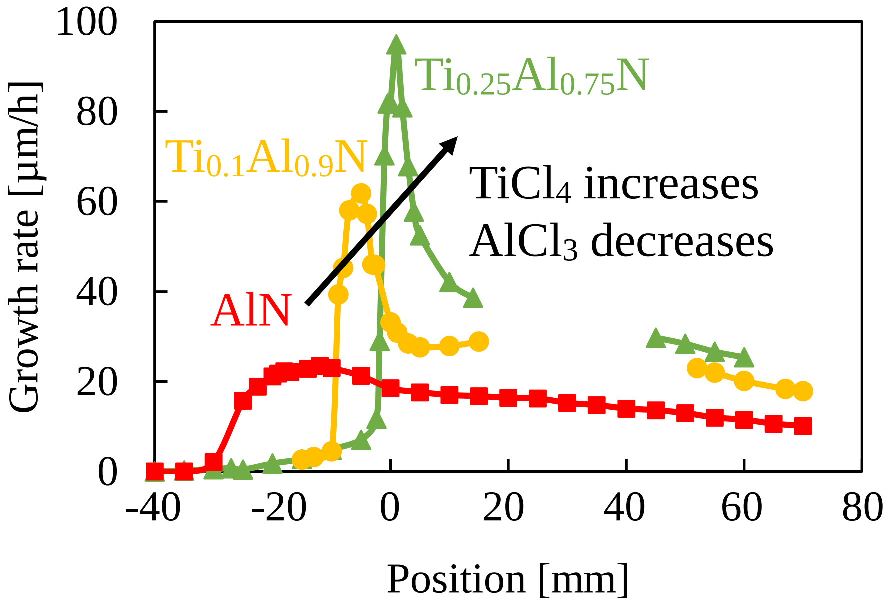


	AlN	TiN
$k_{overall}$ [m/s]	1.6	1.4

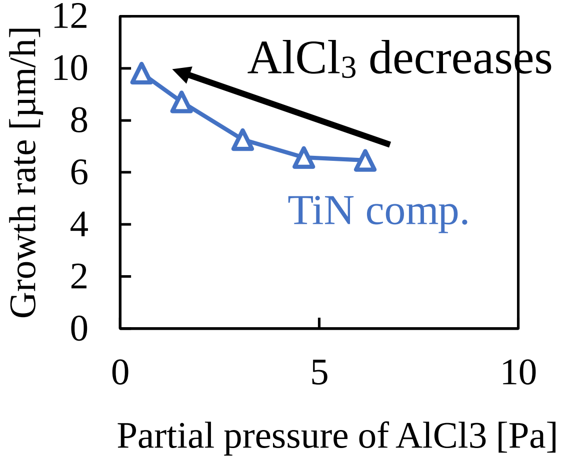
The reaction mechanism of AlN and TiN in TiAlN does not differ AlN and TiN in individual

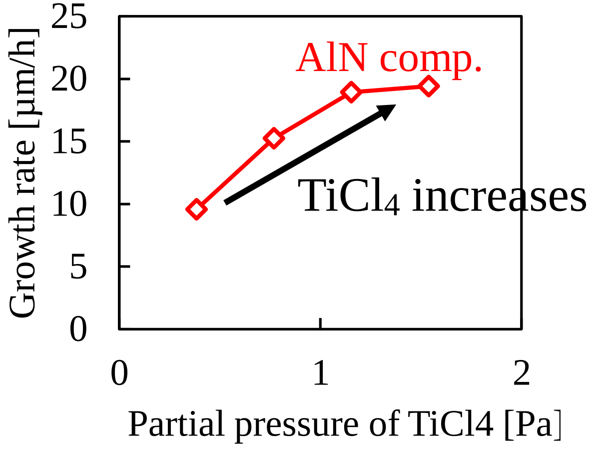
→What is the cause of the interaction?

Prediction of interaction



@60mm





The peak is shifted backward as Ti precursor is increased and Al precursor is decreased

When decreasing $AlCl_3$ or increasing $TiCl_4$, the consumption of $AlCl_3$ and $TiCl_4$ at upstream decreases

→ Growth rate of AlN and TiN at 60 mm increase

Conclusions

- Reaction mechanism of TiAlN-CVD was analyzed for mass production process design.
- TiAlN growth involves some interactions among Ti and Al precursors, and therefore reaction mechanism of AlN and TiN was individually investigated.
- In both AlN and TiN, precursor directly contribute to growth without gas-phase reaction and process is limited by diffusion.
- Although the details of the interaction are still unknown, the cause is likely to be upstream and we will focus on it in the future.