Self-limited growth of La oxides with ALD

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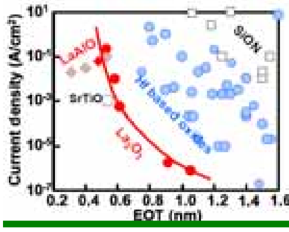
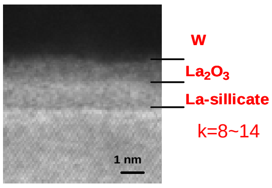
Background

La_2O_3 is a promising material for EOT scaling toward 0.5 nm

・High-k value of 23
・Wide band gap of 5.6 eV
→Leakage current can be suppressed at small EOT



・Forms silicate at the interface
⇒Direct contact High-k/Si can be formed
⇒High-quality MOS interfaces at small EOT



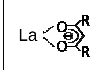
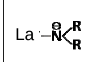
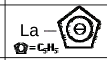
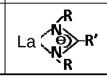
Necessary of ALD

ALD process is an essential techniquefor CMOS manufacturing

・A uniform film can be formed over the wafer
・A precise control of film thickness by the cycle number
・Alloy composition can be designed by flow sequence
・Applicable to 3D structures such as FinFET and nanowire

Pressent issues in La_2O_3-ALD

・Optimal source material and process conditions are not clear
・Difficult to achieve small EOT with good MOS properties

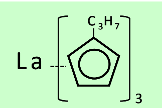
Materials	Structural formula	Properties
β-diketonate		Too stable →O_3 is necessary to form oxide. →EOT increases due to Si oxidation
silylamide		Films contain high Si concentration → k values are rather low
Cyclo-pentadienyl		Relatively new material High vapor pressure Modest reactivity with water (H_2O) →Strong candidates for ALD-source
amidinate		

Purpose of this study

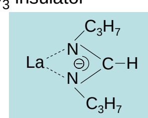
La_2O_3 growth of
- Cyclo-pentadienyl: La(^{i}PrCp)$_3$
- amidinate: La(^{i}PrFAMD)
- Oxygen Source: H_2O

・Clarify the process window to achieve self-limiting ALD with La(^{i}PrCp)$_3$ and H_2O
・Evaluate electrical characteristics of ALD La_2O_3 insulator

La(^{i}PrCp)$_3$



La(^{i}PrFAMD)$_3$



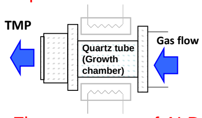
Experimental procedure

MOS capacitor

・n-Si(100) substrate
・The sample was exposed to atmosphere between ALD and electrode formation
・PMA 500 ℃ (3%H_2/N_2 30min)

・Growth temperature(T_s)=125~250 ℃
・Source temperature
- La(^{i}PrCp)$_3$: 135 ℃
- La(^{i}PrFAMD)$_3$: 80 ℃
- H_2O : RT

Experimental device



・Displacement is good
・Problem of gas can narrow down one way along the gas flow

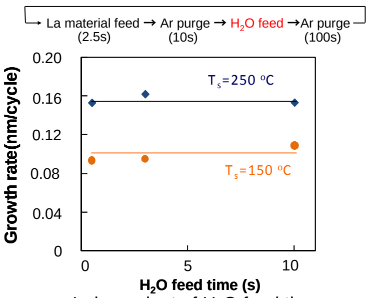
Flow sequence of ALD

①La gas feed → ②Ar purge → ③H_2O feed → ④Ar purge

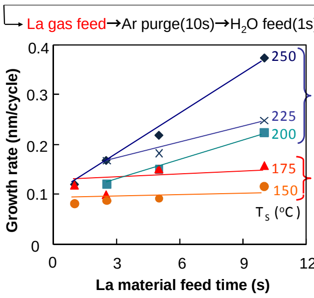
Gas flow 100 sccm, 300 sccm, 100 sccm, 300 sccm

Results and discussion

ALD growth characteristics with La(^{i}PrCp)$_3$

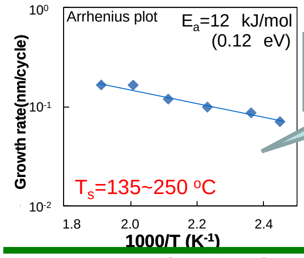


Independent of H_2O feed time

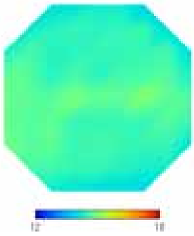


200 ℃ or higher ➡ Growth rate increases with feed time (CVD-mode)

175 ℃ or lower ➡ Growth rate hardly depends on La gas feed time (ALD-mode)



Small activation energy of 0.12 eV can be derived

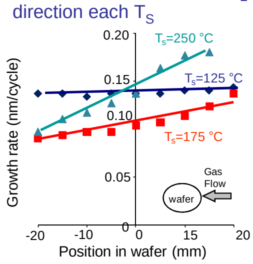


Under the self-limiting growth condition, thickness uniformity was very good

$(d_{max}-d_{min})/2d_{av}$ = 4.5%
σ = 1.8%

ALD growth characteristics with La(^{i}PrFAMD)$_3$

Thickness profiles of the La_2O_3 film along the gas-flow direction each T_s



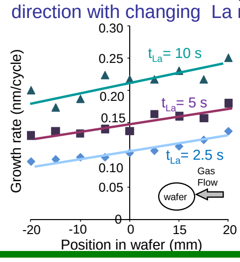
T_s is higher

Increasing of growth rate at upper stream
⇒Capability of CVD growth

T_s is lower

Thickness uniformity is improved

Thickness profiles of the La_2O_3 film along the gas-flow direction with changing La material feed time (Ts=175℃)



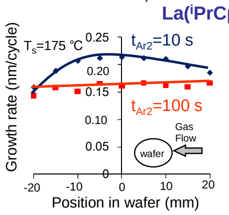
Growth rate increases with feed time

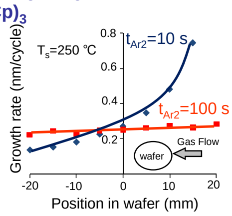
Self-limiting growth condition is not found by La(^{i}PrFAMD)$_3$

Importance of purge time after H_2O feed

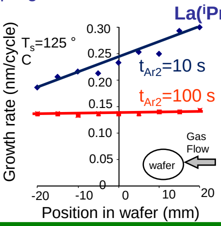
Growth rate profiles along the gas direction as Ar purge time 10 and 100s

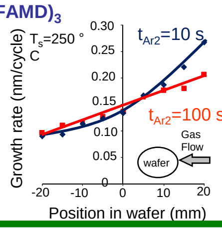
La(^{i}PrCp)$_3$





La(^{i}PrFAMD)$_3$





La(^{i}PrCp)$_3$:

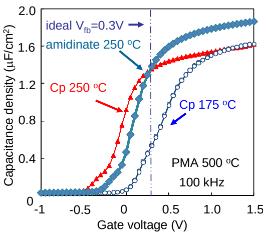
・Case of T_s=175 ℃ that is self limiting growth:
It is necessary to purge it for long time of 100 seconds
・Case of 250 ℃
Growth rate increases rapidly with short purge time

La(^{i}PrFAMD)$_3$:

The result that was similar to above was observed

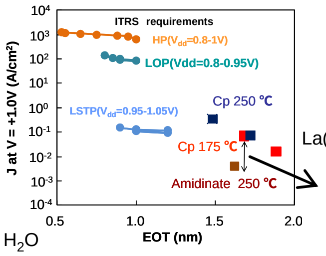
It is thought that this is essential problem case of using H_2O as oxygen material

MOS Capacitor Electrical characteristics



	Growth rate (nm/cycle)	Thickness (nm)	EOT (nm)	k	V_{fb} (V)
Cp (T_s=175 ℃)	0.15	5.2	1.68	~12	0.26
Cp (T_s=250 ℃)	0.17	5.5	1.73	~12	-0.26
Amidinate (T_s=175 ℃)	No Data (increased in Leakage)				
Amidinate (T_s=250 ℃)	~0.14	–	1.45	–	-0.09

・La(^{i}PrCp)$_3$,175 ℃
⇒ Near ideal V_{fb}
・Lower κ
⇒Oxidation source used for H_2O



Gate leakage current
La(^{i}PrFAMD)$_3$ < La(^{i}PrCp)$_3$
$>10^2$

Conclusions

We clarify realizing self-limiting condition about La(^{i}PrCp)$_3$Self-limiting

About electrical characteristics:
There is the point that La(^{i}PrFAMD)$_3$ is better on leakage characteristic

Merits and demerit of both material are being examined without atmosphere