Preparation and electrical characterization of CeO_2 films for gate dielectrics application: comparative study of CVD and ALD processes

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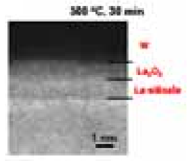
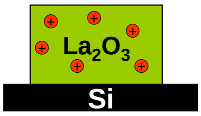
CeO_2 capping effect



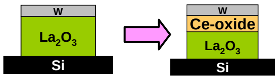
La silicate is a high-k material with k=9~12.

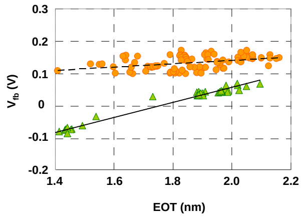
La silicate /Si direct contact has been achieved.

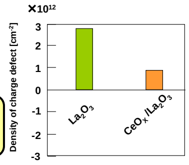
No interfacial layer



However Charged defects were formed.







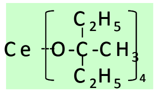
Charged defect density was reduced by the CeO_2 capping layer.

Purpose of this work

To implement the rare-earth oxide materials into semiconductor manufacturing, CVD/ALD processes are necessary.
However, CVD/ALD processes for CeO_2 were hardly investigated so far.

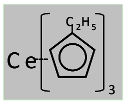
Structures of Ce sources used in this study

CVD Thermal decomposition



$Ce[OC(C_2H_5)_2CH_3]_4$ ($Ce(Mp)_4$)

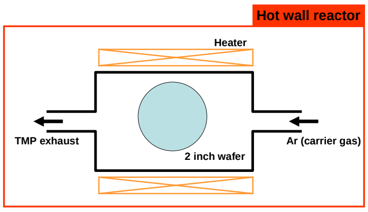
ALD-like process



$Ce[C_2H_5C_5H_4]_3$ ($Ce(EtCp)_3$)

- Preparation of CeO_2 films by CVD and ALD-like processes.
- Comparison of electrical properties of their MOSCAPs.

Device fabrication



Thermal decomposition CVD

- Growth temperature ：350℃
- Partial presser of $Ce(Mp)_4$: 2E-4 – 2E-3 Pa
- Growth rate : ~0.05 nm/s

ALD-like process

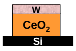
- Growth temperature ：250℃
  - Source gas feed ：10s
  - Ar gas purge ：10s
  - H_2O feed ：1s
  - Ar gas purge ：30s

1 cycle

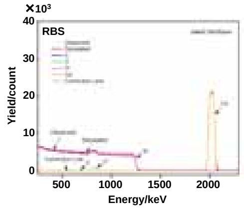
MOSCAP fabrication

- n-type Si substrate ($3x10^{15}$ cm^{-3})
- SPM, HF last treatment
- CeO_2 film deposition by CVD or ALD processes
- Tungsten (W) metal gate electrode deposition by RF sputtering
- PMA (Post Metallization Annealing) 500℃ 30min (FG:3%H_2)
- Bottom electrode Al deposition

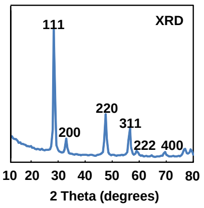
Not in-situ



Stoichiometry and structure of Ce oxide



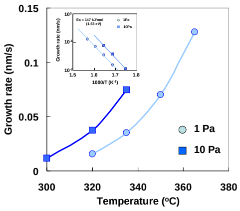
Ce:32.1%, O:64.4%, C:3.5%



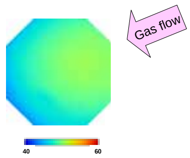
- XRD analysis ：Polycrystalline CeO_2 with the cubic phase.
- RBS/NRA showed that Ce:O ratio was 1：2.

Result

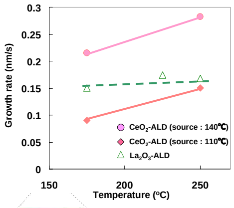
Comparison of CeO_2 films prepared by CVD and ALD-like processes



- Activation energy : 1.53 eV
  ➡ Thermal decomposition
- Sub-linear dependence on pressure
  ➡ Growth took place via surface adsorption.



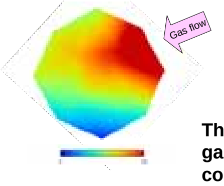
Thickness distribution
$(d_{max}-d_{min})/2d_{av}$ = 7.5%
σ = 3.9%



- Growth rate : 0.1~0.3 nm/cycle
- Small temperature dependence

No self-limiting growth (i.e., ALD-like process)

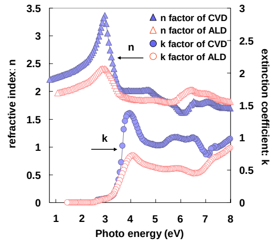
c.f. Self-limiting growth (i.e., genuine ALD process) was observed for La_2O_3



Thickness distribution
$(d_{max}-d_{min})/2d_{av}$ =48%
σ = 20%

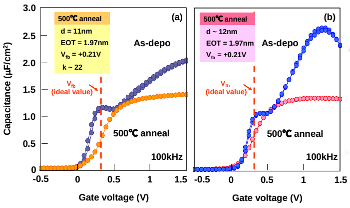
Thickness profile along the gas flow is pronounced as compared to CVD.

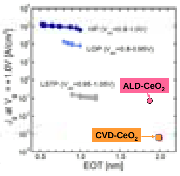
Optical properties



- E_g = 3.2 eV for both CVD and ALD-like films (good agreement with the literature data for CeO_2)
- Absorption peak for the CVD film is lager than that for ALD-like film.
  ➡ Higher crystallinity for CVD process film

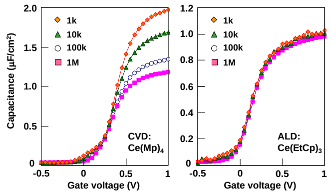
Characteristics of MOSCAP





Small hysteresis and flat band voltage shift after 500°C PMA

CVD film showed smaller leakage current than that for ALD-like process



C-V characteristics for CVD films exhibited frequency dispersion under accumulation.

Crystallization caused freq. dispersion in the dielectric response (so-called dielectric relaxation)
[Saito et al., JJAP 48 (2009) 121405]

Conclusion

CVD process :	CeO_2 polycrystalline film	△
	Small leakage current	○
	Frequency dispersion	✕
ALD-like process:	No self-limit growth	✕
	Large leakage current	✕
	No frequency dispersion	○

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