A novel Hf precursor with linked cyclopentadienyl-amido ligand for thermal atomic layer deposition of HfO_2 thin film

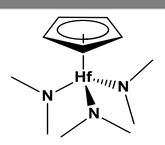
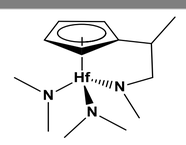
Jeong Do Oh, Min Hyuk Nim, Jae Seok An, Jang Hyeon Seok*, Jung Woo Park
Hansol Chemical, 873, Gwahak-ro, Bongdong-eup, Wanju_Gun, Jeollabuk-do, 55321, Republic of Korea

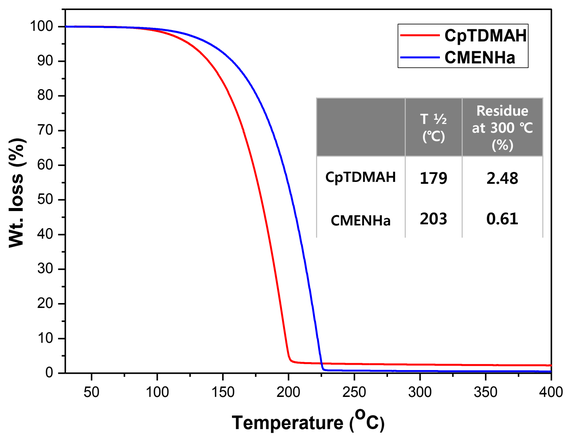
✓ INTRODUCTION

- HfO_2 has been widely used as gate oxide layer in the CMOS device as well as DRAM due to suitable band offset with Si, high thermodynamic stability on Si, and high permittivity.
- In this study, we investigated a novel Hf precursor, CMENHa, which is coordinated by cyclopentadienyl-amido ligand.
- Also we compared the properties of the HfO_2 thin film of CMENHa to those of commonly used CpTDMAH ($CpHf(NMe_2)_3$) by thermal atomic layer deposition.

✓ RESULT AND DISCUSSION

➢ Physical properties

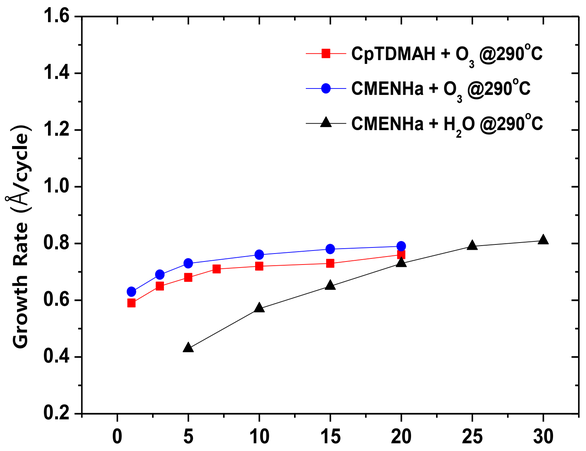
Precursor	CpTDMAH	CMENHa
Structure		
M.W	375.81 g/mol	401.85 g/mol
B.P	81℃@0.1 torr	110℃@0.25 torr
Viscosity	10.2 cP @25℃	8.9 cP @25℃



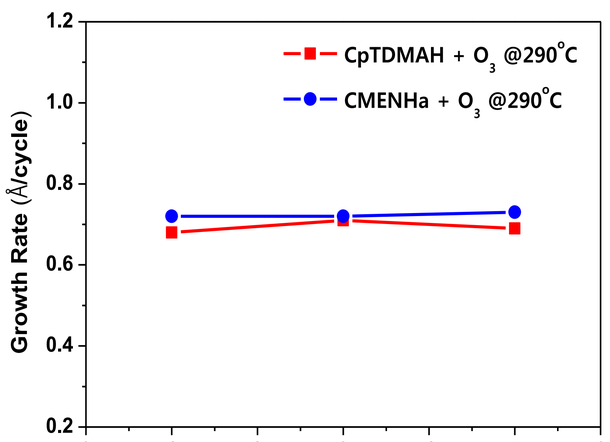
	T ½ (℃)	Residue at 300 ℃ (%)
CpTDMAH	179	2.48
CMENHa	203	0.61

➢ ALD Characteristics

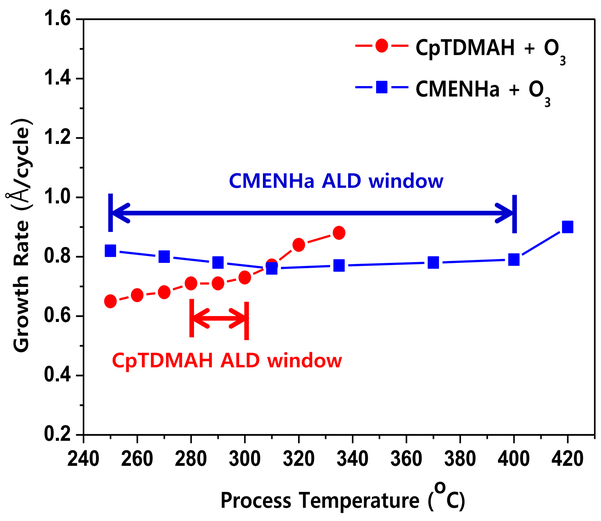
❖ Precursor saturation



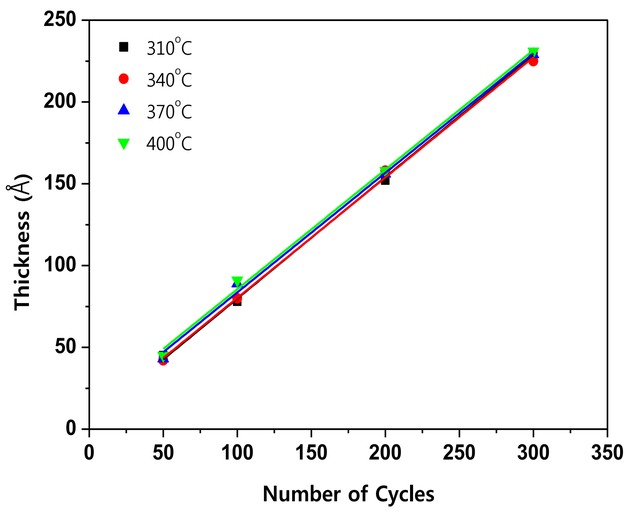
❖ Reactant saturation



❖ ALD window

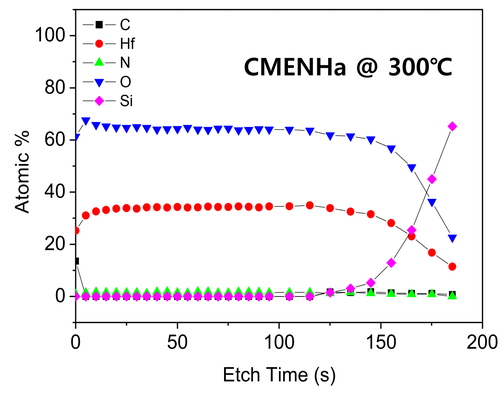


❖ Growth linearity



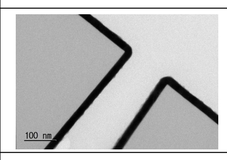
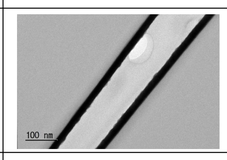
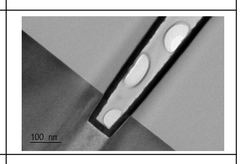
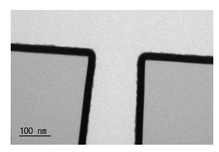
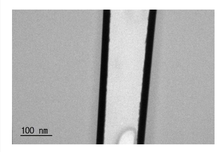
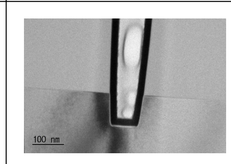
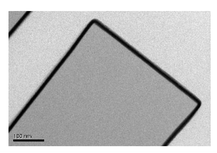
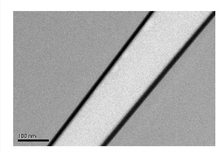
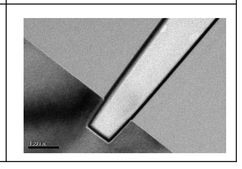
➢ Film Characteristics

❖ Film composition



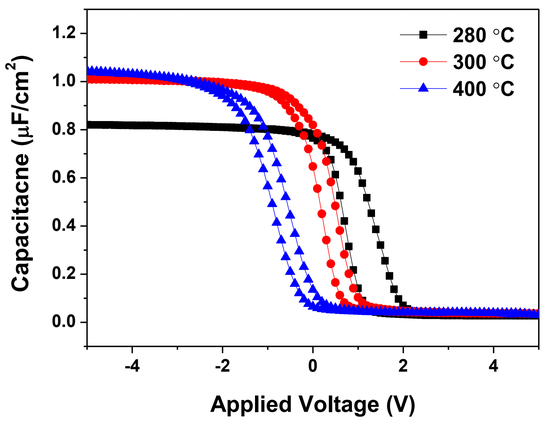
Product	Composition	
	O/Hf	C (at.%)
CpTDMAH +O_3 (@300℃)	1.9	2
CMENHa +O_3 (@300℃)	1.9	0
CMENHa +H_2O (@290℃)	1.7	5~8

❖ Step coverage

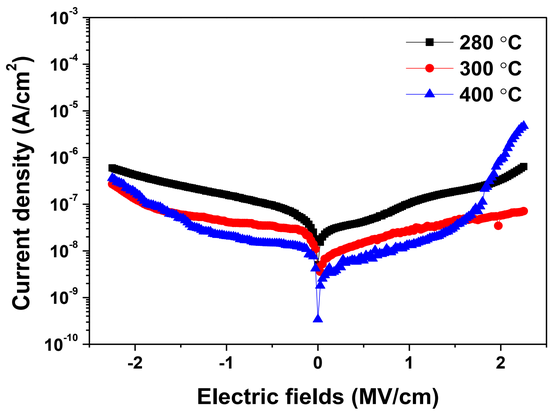
Trench (Aspect ratio, 40:1)	Step Coverage		TEM Image		
	Middle /Top	Bottom /Top	Top	Middle	Bottom
CpTDMAH +O_3 (@300℃)	95%	92%			
CMENHa +O_3 (@300℃)	100%	99%			
CMENHa +H_2O (@290℃)	82%	78%			

➢ Electrical properties

❖ C-V curves



❖ I-V curves



Process Temp (℃)	Dielectric Constant		Leakage current @ -1MV/cm (A/cm^2)	
	CMENHa	CpTDMAH	CMENHa	CpTDMAH
280	18.5	24.7	1.6×10^{-7}	2.7×10^{-5}
300	22.8	26.1	4.2×10^{-8}	3.6×10^{-7}
400	23.6	26.8	2.0×10^{-8}	3.0×10^{-8}

✓ CONCLUSION

- As compare to CpTDMAH precursor, CMENHa precursor showed higher thermal stability due to chelate effect of bidentate ligand, lower residue (0.6%) and lower viscosity (8.9 cP)
- CMENHa was observed wide ALD window in range of 250-400℃ with low carbon impurity contents and good electrical properties such as high dielectric constant and low leakage current density.
- Based on excellent step coverage, electric properties and wide ALD window, the CMENHa precursor has demonstrated potential as dielectric material for use in CMOS device and DRAM capacitor.

Hansol Chemical