New precursor for low temperature deposition of SiO_2 layer using thermal and plasma enhanced ALD techniques

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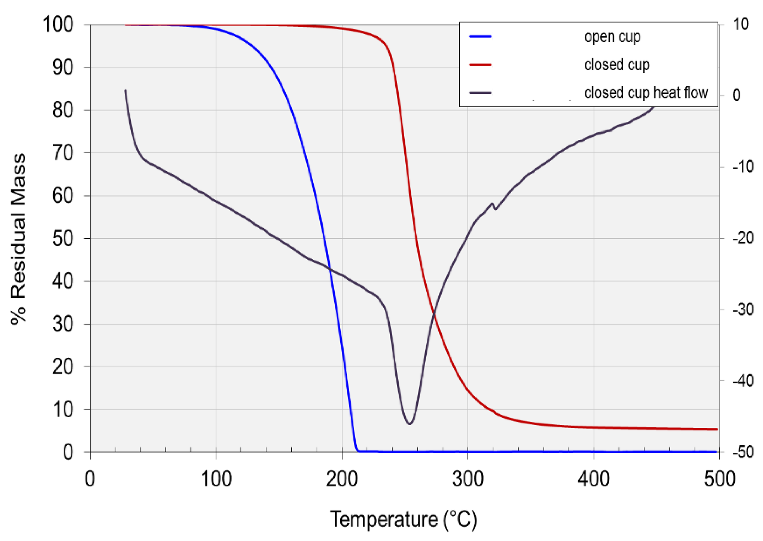
Introduction

- SiO_2 is an excellent low-*k* dielectric material for uses as gate dielectric, gate spacer, inter poly dielectric and liner
  - traditionally deposited via CVD or PVD methods at high temperatures (>500 °C) with drawbacks of poor uniformity and step coverage in high density devices as well as high thermal stress
- ALD (and particularly PEALD) provides high uniformity and layer thickness control for depositions done at much lower temperatures (<200 °C) [1]
- Some of currently used low temperature SiO_2 precursors include HCDS [2], BDEAS [3], DIPAS [4]
- In this work we introduce a recently developed precursor (VLTO-1) and present the results of deposition experiments using PEALD and ALD techniques

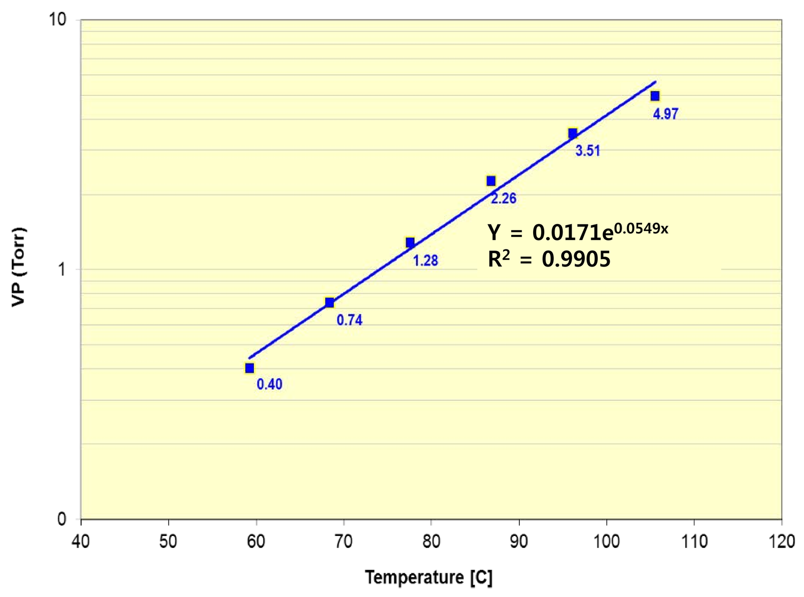
VLTO-1 physical properties

- Clear colorless liquid
- Purity: 99.0% minimum by GC; 99.9999% minimum by ICP-MS

TGA data



Vapor pressure data



- Complete evaporation in open cup TGA
  - Stable at least up to 200˚C
- Closed cup TGA residue: 5.4%
- Boiling point from closed cup heat flow curve: 235˚C

- VP: 1 torr @ 75˚C
- ΔH_{vap} 13 kcal/mol

Sufficiently stable and volatile precursor for below 200˚C processes

Molecular modeling studies

Calculations performed using Schrödinger Software Suite [5]

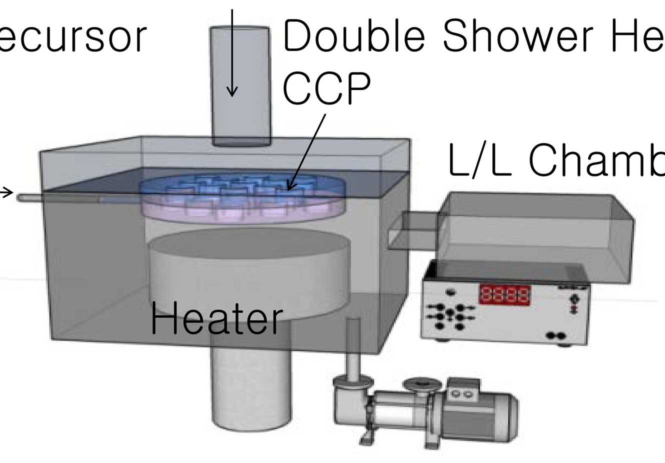
Si precursor	Si-N bond dissociation energy (kcal/mole)	Molecular level, reaction energies (kcal/mole)	Atomic level, $\Delta G^{\#}$ (kcal/mole)
VLTO-1	75.5	ΔH = -169.56 ΔG = -199.25	30.5
$SiH_3(^iPr_2N)$ (DIPAS)	76.9	ΔH = -147.40 ΔG = -157.09	24.1

$\Delta G^{\#}$ is the activation energy calculated for rate-determining step in ALD SiO_x

VLTO-1 is predicted to have thermodynamically more favorable reaction with ozone vs. DIPAS

ALD experimental conditions

Si precursor pulse → Ar purge → Oxidant pulse → Ar purge



CN1 6″ showerhead ALD equipment

Precursor supply: through vent port only (no bubbling of Ar gas)

- Precursor: DIPAS, VLTO-1
- Substrate temperature (T_{sub}) → 50 - 150°C
- O_3 concentration 6-7 % in 3 torr O_2
- O_2 plasma power 200W with 200 sccm gas flow

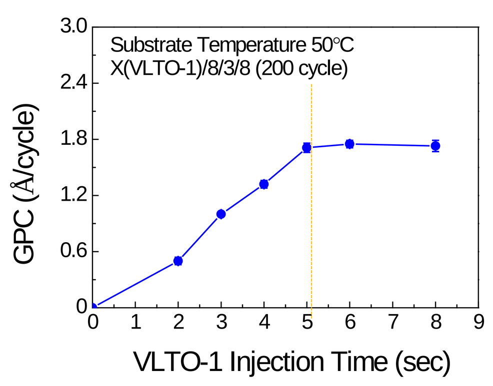
VLTO-1 vs. DIPAS SiO_2 O_2 PEALD saturation data

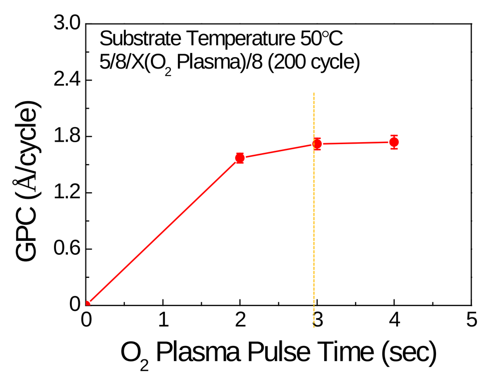
- 50 °C
- 200 cycles
- 200W O_2 plasma

VLTO-1 pulse (10 mtorr) X s → Ar purge (50sccm) 8 s → O_2 plasma pulse (200W) X s → Ar purge (50sccm) 8 s

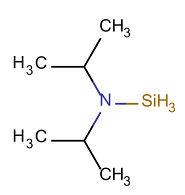
VLTO-1

- VLTO-1 saturated at:
- Precursor pulse: 5 sec
- O_2 plasma pulse: 3 sec
- GPC: 1.7 Å/cy



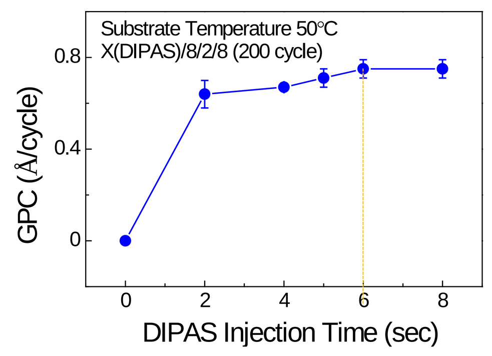


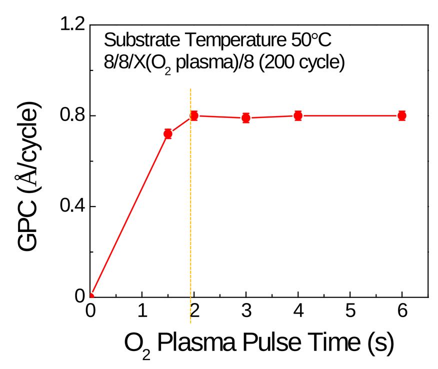
DIPAS pulse (10 mtorr) X s → Ar purge (50sccm) 8 s → O_2 plasma pulse (200W) X s → Ar purge (50sccm) 8 s



DIPAS

- DIPAS saturated at:
- Precursor pulse: 6 sec
- O_2 plasma pulse: 2 sec
- GPC: 0.72 Å/cy





Diisopropylaminosilane (DIPAS) is the current standard precursor for low-temperature SiO_2
VLTO-1 and DIPAS achieve surface saturation in comparable time

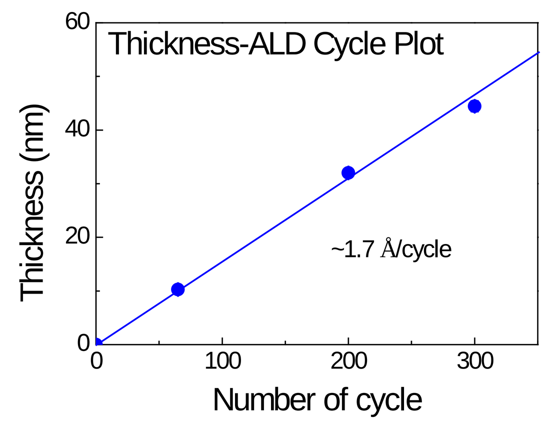
VLTO-1 vs. DIPAS SiO_2 O_2 PEALD growth rate and film purity

- 50 °C
- 200W O_2 plasma

VLTO-1 pulse (10 mtorr) 5 s → Ar purge (50sccm) 8 s → O_2 plasma pulse (200W) 3 s → Ar purge (50sccm) 8 s

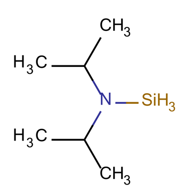
VLTO-1

- GPC: 1.7 Å/cy
  - liner growth over 300 cycles
- Film purity by XPS
  - No significant impurities
  - Si : O = 1 : 1.68 stoichiometry



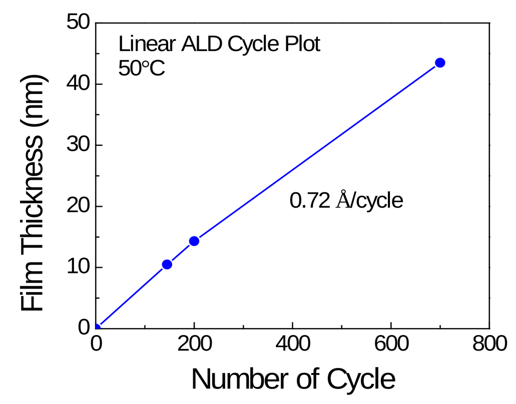
Element	atomic %
Si	37
O	62
C	< 1
N	-
B	-

DIPAS pulse (10 mtorr) 6 s → Ar purge (50sccm) 8 s → O_2 plasma pulse (200W) 2s → Ar purge (50sccm) 8 s



DIPAS

- GPC: 0.72 Å/cy
  - liner growth over 700 cycles
- Film purity by XPS
  - Small amount of C
  - Si : O = 1 : 1.59 stoichiometry



Element	atomic %
Si	37.9
O	60.1
C	< 2
N	-
B	-

VLTO-1 shows more than 2x growth rate vs. DIPAS and better purity of the deposited film

VLTO-1 vs. DIPAS SiO_2 film properties

- 50 °C; 200W O_2 plasma

Precursor	Film density, g/cm³	Thickness uniformity,%	Dielectric thickness	Dielectric constant	D_{it}, $cm^{-2}eV^{-1}$	Hysteresis, mV	Leakage current at -1MV/cm, A/cm²
VLTO-1	2.20	98.6	10 nm SiO_2	4.87	1.37×10^{12}	~ 100	1.30×10^{-7}
DIPAS	2.26	98.5	10 nm SiO_2	4.94	1.48×10^{12}	~ 300	1.30×10^{-7}

VLTO-1 150 °C SiO_2 O_3 ALD summary

VLTO-1	Growth Temperature, °C	150
Growth rate	GPC, Å/cycle	1.05
Composition & Density	Si : O Stoichiometry	1 : 1.81
	Chemical purity	C <0.5%
	Density, g/cm³	2.21
Electrical properties	*k* (dielectric constant)	4.78
	D_{it}, $cm^{-2}eV^{-1}$	2.3×10^{12}
	Hysteresis, mV	~200
	Leakage Current, A/cm²	1.84×10^{-7}

10 mtorr VLTO-1 5 s → Ar 50sccm 8 s → O_3 0.18 torr 4 s → Ar 50sccm 8 s

- VLTO-1 150 °C SiO_2 O_3 ALD shows lower growth rate vs. 50 °C O_2 PEALD
- Films of roughly the same good quality are obtained by both methods

Conclusions

- **Molecular modeling results show more favorable reaction of VLTO-1 with oxygen source vs. DIPAS**
- **VLTO-1 is sufficiently stable and volatile precursor for below 200˚C processes**
- **VLTO-1 performs better than DIPAS in low temperature SiO_2 PEALD**
  - **Growth rate is more than 2x, while producing about the same good quality SiO_2 films**
- **O_3 ALD using VLTO-1 produces good quality SiO_2 films below 200˚C, but with lower growth rates**

References

[1] S. George *Chem. Reviews,* **2010**, *110*, 111-131
[2] D. Guo *et al* (Entegris) **2017** US patent US20170103888 A1
[3] M. Karg *et al Chem. Mater.*, **2017**, *29*, 4920–4931
[4] Y-S. Lee *et al Ceramics International,* **2017**, *43*, 2095-2099
[5] Jaguar density functional theory (DFT) package (Version 8.0); Basis set: B3LYP/6-31G**