Inhibiting Thermal and Plasma Enhanced Atomic Layer Deposition of SiO$_2$ using Fluorothiol Passivation layer on Cu

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**ECS 2021**  
G01 Tuesday Session 2  
Nanoelectronics 2  
18:00 p.m. MDT
How do we continue further downscaling?

**Top-down Processing**
- Deposited Film
- Resist Film
- Patterned Substrate
- Edge Placement Error
- Extremely challenging to align nanoscale features

**Area-Selective Deposition**
- Patterned Substrate
- Bottom-up approach to reduce photolithography challenges associated with current top-down fabrication
- Operated in a strictly surface-reaction-controlled regime, ALD is ideal for developing area-selective deposition processes

Hashemi et al., ACS Appl. Mater. Interfaces 2016, 8, 33264
Parsons et al., Chem. Mater. 2020, 32, 4920
Area Selective ALD of SiO$_2$ on SiO$_2$ with Cu as Nongrowth Surface

- No reports on ASD of SiO$_2$ on dielectric substrates with a metal as the nongrowth surface
- Reported ASD processes of dielectrics use mild oxidants such as H$_2$O

**Conventional wisdom**

- SiO$_2$ ALD requires O radicals for low-temperature growth
- Strong oxidants can undergo combustion like reaction with hydrocarbon blocking layers

Hashimi et al., ACS Appl. Mater. Interfaces 2016, 8, 33264
Liu et al., ACS Appl. Mater. Interfaces 2020, 12, 42226
Lecordier et al., J. Vac. Sci. Technol., 2018, A 36, 031605

Thiols can attach to both Cu and CuO$_x$

Bergsman et al., Chem. Mater. 2018, 30, 5694
Love et al., Chem. Rev. 2005, 105, 1103
Wang et al., Langmuir 2016, 32, 3848
Selection of Thiol Inhibitor for Cu Passivation in ASD of SiO₂

1. High vapor pressure for gas phase functionalization → No. of C atoms ~10

2. Thermally stable on surface and resistant to atmospheric exposure and strong oxidants → ALD temperature < 150 °C for thiol inhibitors

3. Resistant to O radicals during ALD → minimize C-H bonds in the blocking molecules

Perfluoroalkyl groups are resistant to combustion

\[(\text{CF}_3\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{SH})\]

1H,1H,2H,2H-perfluorodecanethiol (PFDT)

Lemal et al., J. Org. Chem. 2004, 69, 1, 1
Scherer et al., J. Am. Chem. Soc. 1985, 107, 3
Plasma ALD Reactor with *in situ* RAIRS

**ALD Reactor**

- **Pumping System**
- **O$_3$**
- **SiH$_4$**
- **IR Source**
- **Thiol Inhibitor**
- **RF Power**
- **Ar/O$_2$**
- **Heater**
- **IR Detector**
- **Si Precursor**

**In situ** Reflection-Absorption Infrared Spectroscopy (RAIRS)

- **Paraboloid**
- **Mirror**
- **Polarizer**
- **IR Detector**
- **85° Metal substrate**

Only sensitive to dipoles perpendicular to the surface

- **CMP Cu**
- Nongrowth surface
- **PECVD SiO$_2$**
- Growth surface
O₂ Plasma Enhanced ALD of SiO₂ on PECVD SiO₂

**Di-sec-butyl aminosilane (DSBAS) half cycle**
- 1.5 Torr·s dose at 100 °C

**O₂ plasma half cycle**
- 70/30 sccm O₂/Ar plasma, 150 W, 1 s

**GPC:** 1.7 ± 0.1 Å
(Ex-situ ellipsometry)
PFDT Functionalization of CMP Cu and Effect of O₂ Plasma Exposure

PFDT exposure at 100 °C
- 50 Torr·s

O₂ plasma at 100 °C
- 70/30 sccm O₂/Ar plasma, 150 W, 1 s

RMS roughness ~ 8 nm
(Bare CMP Cu: 0.4 nm)

Multilayer adsorption of thiols

O₂ plasma removes ~5-7% of thiol which can be redosed in the subsequent cycle

High roughness reported for dodecanethiol multilayers in Bergsman et al., Chem. Mater. 2018, 30, 5694−5703
A-B-C (A: PFDT, B: DSBAS, C: O\textsubscript{2} plasma) ALD Process

Can PFDT block SiO$_2$ growth and prevent oxidation of Cu?

In situ RAIRS for 35th ABC cycle (A: PFDT, B: DSBAS, C: O$_2$ plasma)

No -SiH$_3$ species observed on the surface in the DSBAS partial cycle
XPS analysis after (A: HT/ PFDT  B: DSBAS C: O₂ plasma/O₃) ALD cycle

A: PFDT, B: DSBAS C: O₃ (50 ALD cycles)

A: PFDT, B: DSBAS C: O₂ plasma (35 ALD cycles)
Can PFDT be Removed to Recover the CMP Cu Surface?

**HR-XPS of F 1s**

- Decrease in F (~85%) intensity after high temperature annealing and BHP 851 (post etch cleaning formulation) clean

**HR-XPS of Cu 2p**

- Reduced Cu with no oxide after high temperature annealing and chemical cleaning
Does the Cleaning Process Recover the Smooth CMP Cu Surface?

Bare CMP Cu

Root mean square roughness: 0.4 nm

35 A-B-C cycles + Clean

Root mean square roughness: 1.1 nm

Change in RMS roughness after cleaning ~ 1 nm
Selective Deposition of SiO₂ on Patterned Substrates

Bare Cu/SiO₂

60 A-B-C type ALD cycles

Selective Growth of SiO₂: ~10 nm)

EDAX Mapping after clean

No SiO₂ growth on Cu

ASD of SiO₂ achieved in Cu-SiO₂ pattern
Conclusions

• PFDT not only inhibited $O_3/O_2$ plasma based ALD on Cu but also prevented oxidation of Cu during the ALD process.

• The A-B-C type (A: PFDT, B: DSBAS, C: $O_2$ plasma) ALD process selectively deposited ~10.0 nm of SiO$_2$ on SiO$_2$ on Cu-SiO$_2$ pattern.

• High temperature annealing and cleaning using BHP 851 removed PFDT and recovered the CMP Cu surface.

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