Area-selective atomic layer deposition for self-aligned fabrication

Adrie Mackus
Eindhoven University
a.j.m.mackus@tue.nl
Area-selective ALD for bottom-up processing

**Top-down**
- Excavated from solid rock

**Bottom-up**
- Bricks as building blocks

**Building technology**
- Subtractive processing
- Additive processing

**Semiconductor fabrication**
What is area-selective ALD?

Area-selective ALD = bottom-up fabrication by deposition of atoms at specific locations

Lecture Richard Feynman “There is plenty of room at the bottom”

What could we do with layered structures with just the right layers? What would the properties of materials be if we could really arrange the atoms the way we want them? ..... when we have some control of the arrangement of things on small scale, we will get an enormously greater range of possible properties that substances can have...

Haider et al., RSC Adv. 6, 106109 (2016)

Weber et al., Nanotechnology 26, 094002 (2015)

Lee et al., Nano Lett. 13, 457 (2013)

Kim et al., ACS Nano 10, 4451 (2016)

Cao et al., Small 17006483 (2017)
The challenge of alignment at the nanoscale

- Alignment becomes extremely challenging in future technology nodes

Alignment

Resist film patterned by lithography

Edge placement error

After etching + resist strip
Motivation: Enabling self-aligned fabrication

Area-selective ALD:

- Fewer lithography and etch steps
- Eliminates alignment issues
- Self-aligned fabrication scheme
Extension of area-selective ALD to plasma ALD

Thermal ALD processes are typically used as starting point for area-selective ALD

- Plasmas destructively interact with a self-assembled monolayer (SAM)
- Plasma-assisted ALD processes readily nucleate on most substrates

Development of area-selective ALD approaches based on plasma-assisted ALD processes will extend the set of materials that can be deposited selectively

Lee et al., J. Korean Phys. Soc. 56, 104 (2010)
Outline

• **Area-selective ALD of SiO$_2$ – using inhibitors in ABC-type cycles**
  – Proof-of-principle results
  – *In-situ* Fourier transform infrared spectroscopy

• **Area-selective ALD of Ru – combination with selective etching**
  – Selective etching of Ru
  – Demonstration on patterned samples

• Conclusions
Regeneration of self-assembled monolayers

Reference

Re-dosing

• Results in area-selective ALD of 3 x thicker ZnO films

Area-selective ALD using inhibitors in ABC-type cycles

A. Inhibitor selectively adsorbs on the non-growth area
B. Adsorbed inhibitor blocks the adsorption of the precursor
C. Inhibitor molecules and precursor ligands are removed during co-reactant exposure

Benefit: compatible with plasma-assisted or ozone-based ALD

Mameli et al., ACS Nano 11, 9303 (2013)
Area-selective growth of SiO$_2$

- Fast nucleation on SiO$_2$, SiN$_x$, GeO$_2$, WO$_x$
- Delay of 10-15 cycles on HfO$_2$, TiO$_2$, Al$_2$O$_3$
- **Unique selectivity**: distinguishes between different metal oxide starting surfaces
Sub-cycle ellipsometry data: case of Al$_2$O$_3$ and SiO$_2$

A = Acetylacetone (Hacac)

C = O$_2$ plasma

AC cycles
- Selective adsorption of Hacac on Al$_2$O$_3$ and removal by O$_2$ plasma

Mameli et al., ACS Nano 11, 9303 (2013)
Sub-cycle ellipsometry data: case of Al$_2$O$_3$ and SiO$_2$

A = Acetylacetone (Hacac)

B = BDEAS

C = O$_2$ plasma

ABC cycles
- Adsorbed Hacac on Al$_2$O$_3$ blocks adsorption of BDEAS

Mameli et al., ACS Nano **11**, 9303 (2013)
Sub-cycle ellipsometry data: case of $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$

BC cycles
- Growth rate equal to ABC cycles on $\text{SiO}_2$

$\text{Al}_2\text{O}_3$

$\text{SiO}_2$

B = BDEAS
C = $\text{O}_2$ plasma

$0.09 \text{ nm/cycle}$
**In-situ** Fourier transform infrared spectroscopy

**SiO$_2$**

- Almost no adsorption of Hacac on SiO$_2$
- Unrestricted adsorption of BDEAS

**Al$_2$O$_3$**

- Hacac adsorbs on Al$_2$O$_3$
- BDEAS adsorption is blocked by Hacac

TOF-SIMS on $\text{Al}_2\text{O}_3/\text{GeO}_2$ patterned samples

$\text{Al}_2\text{O}_3$ patterned on $\text{GeO}_2$ substrate.

15 ABC-type cycles of $\text{SiO}_2$ carried out.

TOF-SIMS demonstrates:

- $\text{SiO}_2$ growth on $\text{GeO}_2$ regions.
- Almost no $\text{SiO}_2$ ALD observed on $\text{Al}_2\text{O}_3$ regions.

Outline

• Area-selective ALD of SiO$_2$ – using inhibitors in ABC process
  – Proof-of-principle
  – *In-situ* Fourier transform infrared spectroscopy

• Area-selective ALD of Ru – combination with selective etching
  – Selective etching of Ru
  – Demonstration on patterned samples

• Conclusions
Main challenge: achieve high selectivity

- It is extremely challenging to obtain area-selective ALD with a high selectivity due to growth initiation at defects and impurities.
- Focus on metal-on-metal deposition, i.e. area-selective ALD of Ru.
- Potential solution: combine area-selective ALD with selective etching.

Combination of ALD with selective etching

- Starting point: deposition occurs at a faster rate on the metal surface
- An etch step is performed to remove any deposited atoms from metal oxide surface
- Supercycle is repeated until the desired thickness is reached
- **Etch step should be self-limiting** to preserve conformality and thickness control
Etching of Ru

- Ru can be etched using an O$_3$ or O$_2$ plasma: RuO$_4$ formed as volatile product
- O$_3$ does not etch RuO$_2$ → Ru etching might be self-limiting
- Supercycle recipe developed

ABC-type ALD cycle:
A. (ethylbenzene)-(1,3-cyclohexadiene)Ru(0) precursor
B. O$_2$ gas
C. H$_2$ gas

Etch cycle: O$_2$ plasma + H$_2$ gas
Ru ALD supercycle results

In-situ spectroscopic ellipsometry

- Ru etch cycle after every 100 ALD cycles
- 15 s O₂ plasma required to eliminate growth on SiO₂
- O₂ plasma etch saturates (at 0.08 nm per step)
Demonstration of selectivity

Patterning of Pt seed layers using electron beam induced deposition (EBID)

- Negligible Ru deposition on SiO₂ observed when using supercycles
ALD for semiconductor fabrication

Key ALD-enabled innovations in semiconductor fabrication

2007
45 nm node

High-κ dielectric

2014
14 nm node

Double patterning

2021?
5 nm node?

Area-selective ALD

Area-selective ALD for self-aligned fabrication has the potential to become the next ALD-enabled innovation in semiconductor fabrication
Conclusions

- Area-selective ALD will enable self-aligned fabrication in future technology nodes.

- New approach developed for area-selective ALD based on selective adsorption of inhibitor molecules in ABC-type cycles.

- Supercycles of Ru ALD and O\textsubscript{2} plasma etching allow for area-selective ALD of Ru with high selectivity.

- Focus in area-selective ALD community is shifting:
  - Deactivation of growth prior to deposition
  → Adding steps during deposition to improve selectivity.
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