Hotwire-assisted Atomic Layer Deposition of Pure Metals and Metal Nitrides

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Motivation

1. Materials

CMOS backend: seed layers & barriers

(Chipworks.com)

2. Deposition method

Group III – Nitride TFTs


High aspect ratio structures (e.g. memories)

(Chipworks.com)
Classic example of thermal ALD

Metallic TiN films

ALD:
✓ Self-limiting reactions
✓ Thickness control
✓ High aspect ratio structures

\[ \text{OH} + \text{TiCl}_4 \rightarrow \text{O} \text{TiCl}_3 + \text{HCl} \]

\[ \text{TiCl} + \text{NH}_3 \rightarrow \text{TiNH}_2 + \text{HCl} \]

Courtesy of Hao Van Bui
Need for extra activation

$M(\text{CH}_3)_3$

ALD of AlN and GaN compared

$M = \text{Al, Ga}$

$\text{CH}_3$

$\text{CH}_4$

$\text{NH}_3$

Readily occurs for Al, difficult for Ga

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Plasma-Enhanced ALD (PEALD)

1\textsuperscript{st} precursor: plasma off

2\textsuperscript{nd} precursor: plasma on
ALD classification

Atomic Layer Deposition

Thermal

Radical-Enhanced

PEALD

Making radicals w/o plasma?

Purpose: Hot-wire generated radicals (H, NHₓ, ...) for ALD w/o plasma

Cat. dissociation of H₂ on hot tungsten filament

Plasma versus Hot Wire

**Plasma**

1. Breaking molecules by electrons or excited species
2. Number of chemical reactions can be significant
3. Ions are present => more reactions & charging
4. UV light emission

**Hot Wire**

1. Catalytic dissociation by a hot (1600-2000 °C) tungsten wire
2. Lower pressures possible
3. Number of reactions is limited
4. No ions
5. No UV

Our study: Hot-wire assisted ALD (HWALD)
Outline

- Motivation

- Hotwire-Assisted Deposition:
  - Confirmation of the Presence of Atomic Hydrogen
  - HWALD of Tungsten (W) Films
  - On the Growth of Titanium (Ti) Films
  - Confirmation of the Presence of Nitrogen radicals
  - On the Growth of Aluminum Nitride (AlN) Films

- Conclusions
HWALD: Which radicals can be formed?
Confirmation of the Presence of Atomic Hydrogen
Reactor details

Is at-H delivered to the wafer surface?

- *Atomic* hydrogen reacts with Te surface producing TeH$_2$:
  
  $$2H + Te(s) \rightarrow TeH_2(g) \rightarrow$$ etching Te film

- There is no reaction between *molecular* hydrogen and Te.
Real-time monitoring of Te etching

The etching of Te was real-time monitored by in-situ SE

1. Introducing H₂, **FILAMENT OFF**
2. Stop introducing H₂, **heat up the filament**
3. Introducing H₂ with **FILAMENT ON**

Thickness verification by SEM

Etching of Te by H-pulses


Bridge to Hot Wire ALD (HWALD)

![Graph showing Te thickness over time with H-on and H-off periods.]

Te thickness (nm)

Time (min)
Delivering atomic-H goes easily

*Horizontal HW*

- Reactor 2
- Few ml

*Vertical HW (line-of-sight)*

- Reactor 3
- Few ml

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HWALD of Tungsten (W) Films
In-situ SE monitoring

- Sequential pulses of WF$_6$ and at-H
- Well-defined ALD window can be found

One ALD cycle:
1. at-H
2. Purge
3. WF$_6$
4. Purge
Properties of W

✓ High purity

✓ Excellent step coverage

Crystallinity

Growing either $\alpha$- or $\beta$-phase W possible

![X-ray diffraction patterns of $\alpha$- and $\beta$-phase W](image)

2Theta (degree)

Intensity (Arbitrary unit)

- Red: $\alpha$-W
- Black: $\beta$-W

Resistivity

Film thickness: 10-12 nm
RMS: 1.4 nm

µΩ·cm

14.8
14.9
15.0
15.0
15.2

✓ Resistivity:
- 100 µΩ·cm, β-phase
- 15 µΩ·cm, α-phase

Resistivity mapping

Resistivity (Ohm·cm)² vs. Position

HWALD: On the Growth of Titanium (Ti) Films

(Let’s replace WF₆ by TiCl₄ while keeping at-H)
Reference: ALD of TiN by TiCl$_4$/NH$_3$ pulses

TiCl$_4$/H/NH$_3$ pulses

Surface passivation by a-Si

43 at.% Ti

25 at.% N

35 at.% O (was 3-5 %)

Base pressure 2×10$^{-7}$ mbar

Arrival of contaminants: 0,1 monolayer/s

TiCl₄/H pulse sequence

- H reduces –Cl groups, releasing HCl and leaving dangling bonds…

**Case #1:** H atoms occupy dangling bonds

→ Would be great...
  but: 10⁻⁷ mbar of residual H₂O

**Case #2:** O atoms occupy dangling bonds

→ TiO₂ will continue growing but very slowly as it is limited by the supply of H₂O
It does work for W...
Why not for Ti, Al, ...?

$\text{WO}_x$ can be reduced by at-H to metallic W whereas $\text{TiO}_2$ and $\text{Al}_2\text{O}_3$ cannot
HWALD: Which radicals can be formed?

On the Presence of Nitrogen Radicals
N-radicals delivered in line of sight

Real-time SE acquisition

Nitridizing Si wafer

- HW off
- HW horizontal
- HW vertical

![Graph showing thickness over time for different hardware configurations](image)

**Adv. Mater. Interfaces 2017, 1700058**
Towards AlN: HW out of line-of-sight

Atomic %

Sputter time (min)

Towards AlN: HW out of line-of-sight

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Horizontal HW

NH₃

350 °C

Wafer

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Towards AlN: HW in line-of-sight

(b) HW on - 1800 °C

Atomic %

O\textsubscript{1s} 60

Al\textsubscript{2p} 40

N\textsubscript{1s} 20

Si\textsubscript{2p}

Sputter time (min)

350 °C Wafer

Adv. Mater. Interfaces 2017, 1700058
Conclusions

- ALD = self-limiting surface reactions => advantages
- Additional means to supply energy sometimes required
- HW can (to some extent) replace plasma:
  - Generation of at-H confirmed by etching of Te films
  - at-H: delivery in both in and out of line-of-sight possible
  - Generation of Nitrogen radicals confirmed by nitridation of Si
  - Nitrogen radicals: delivery in line-of-sight only
  - Obviously (residual) oxidants can also be activated by HW
  - Metal oxidation and reduction of the oxides should be taken into account

- HWALD enables (so far):
  - Area-selective growth of high-quality W using WF$_6$/at-H
  - Deposition of TiO$_x$ using TiCl$_4$/at-H
  - Deposition of AlN$_y$O$_z$ using TMA and NH$_3$ via HW
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