ALD of Copper and Copper Oxide Thin Films for Applications in Metallization Systems of ULSI Devices

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Outline

• Goals of the work
• Our approach for Cu ALD
• ALD results on Ta, TaN, Ru and SiO₂
• Reduction of ALD films
• Summary

4", single-wafer, vertical flow reactor used for ALD / CVD
Why copper ALD?

- Seed layer for Cu damascene process
- Metallization of narrow holes and trenches, e.g. through-silicon vias (TSV)
- Conformally coating 3D nanostructures (porous materials, nanowires, CNTs, ...)

Requirements for the seed layer:

- Highly conformal in aspect ratios of 4 to 5 and lines of 15 to 20 nm width (ITRS projection for 2020)
- Must grow on diffusion barriers
- Continuous and sufficiently conductive for ECD
- Good adhesion to diffusion barrier

Goals of the work

see for example:
Our approach for Cu ALD

Non-fluorinated, liquid Cu(I) β-diketonate precursor

- Fluorine free
- Liquid under standard conditions → liquid delivery for ALD

ALD processes

- Temperature < 160°C
- ALD of oxidic copper films on Ta, TaN, Ru, and SiO₂
- Wet O₂ as oxidizing agent
- Subsequent reduction

Vapor pressure 14.5 mTorr at 98°C
Our approach for Cu ALD

Process Flow

- Precursor Pulse: 3 to 8 seconds
- Argon Purge: 5 seconds
- Oxidation Pulse: 5 to 11 seconds
- Argon Purge: 5 seconds

ALD cycles

Reduction after ALD
**Results**

**ALD on Ta and TaN**

**TaN, 125°C:**

TEM cross section of ALD film on TaN. Ellipsometric thickness: 3.6 nm.

**TaN, 135°C:**

TEM cross section (Ellipsometric thickness of ALD film: 4.9 nm)

→ Smooth, continuous films on TaN
→ Tendency to form clusters on TaN as temperature increases
→ Cluster formation even more pronounced on Ta

**Ta, 135°C:**

SEM top view with partially etched ALD film
Results

ALD on Ta and TaN

- CVD effects on Ta above 125°C due to high reactivity towards metal-organics ([E. Machado et al., Langmuir 21, 7608 (2005)])
- TaN less reactive – less CVD effects – ALD window up to ~130°C
- Degree of nitridation of the TaN important for ALD growth
- Nearly saturated growth on TaN at 135°C
**Results**

**XPS of ALD films on TaN**

- Composites of metallic and oxidic Cu
- Increased metallic fraction with increased processing temperature (→ beginning CVD growth modes)
- Increased metallic fraction on stronger metallic TaN
- Generally good adhesion of the films (tape test)

**ALD process temp.:**
- 115°C (purple)
- 125°C (light blue)
- 135°C (red)
- 145°C (dark blue)
- 155°C (green)
**Results**

**ALD films on Ru and SiO\textsubscript{2}**

- Smooth, adherent films obtained both on Ru and SiO\textsubscript{2}
- GPC on SiO\textsubscript{2} even lower than on TiN, higher GPC on Ru
- ALD window at least up to 135°C on SiO\textsubscript{2} and 125°C on Ru
- Composition similar to films on TaN (Cu/Cu\textsubscript{x}O composites)

AFM image of 3 nm ALD film on SiO\textsubscript{2}. RMS roughness: of 0.25 nm (SiO\textsubscript{2}: 0.21 nm)
Possible methods:

• Thermal treatment in H₂
  - High process temperature required
  - No effective reduction
  - Agglomeration of the films

• Hydrogen plasma

• Thermal treatment with organic reducing agents
  - Isopropanol
  - Formic acid
  - Aldehydes

Initial state after ALD on Ta:
Continuous film with clusters

After reduction in H₂ for 30 min:
Strong agglomeration
**Possible methods:**

- Thermal treatment in H$_2$
- **Hydrogen plasma**
- Thermal treatment with organic reducing agents
  - Isopropanol
  - Formic acid
  - Aldehydes

**Reduction of oxygen content obtained (EDX)**

- Tendency of agglomeration although processing at lower temperature (plasma effect?)
- Disadvantages of plasma reduction processes compromise benefits of thermal ALD
Possible methods:

- Thermal treatment in H2
- Hydrogen plasma
- Thermal treatment with organic reducing agents
  - Isopropanol
  - Formic acid
  - Aldehydes

- Reduction of oxygen content obtained both with IPA and formic acid
- Elevated temperature required for effective IPA treatment → increase of sheet resistance
- More promising results obtained with formic acid already at temperatures < 120°C
Reduction of oxidic ALD films

Formic acid treatment – most promising method so far

- No agglomeration on TaN up to 150°C
- More severe cluster formation on Ta
Reduction of oxidic ALD films

Formic acid treatment of ALD films on TaN

XPS analysis:

- Significant enhancement of metallic Cu content after treatment with formic acid
- Some oxidized Cu detected – possible re-oxidation after reduction due to air exposure (~ 7 weeks between reduction process and XPS analysis)

Blue curve = after ALD and 25 weeks storage in air

Red curve = status of blue curve + reduction and 7 weeks storage in air
Summary

Thermal ALD of Cu/CuₓO composites on Ta, TaN, Ru and SiO₂
- Smooth, adherent films at least up to 135°C on TaN, Ru and SiO₂
- Saturated growth confirmed on TaN – further study on other substrates
- ALD window at moderate temperatures of ≤ 130°C

Reduction processes under study to form metallic Cu on Ta and TaN
- Different approaches investigated
- Formic acid treatment most promising
  - Strong agglomeration tendency of films on Ta during reduction treatment
  - No agglomeration of ALD films on TaN up to 150°C

Outlook
- Ongoing study of ALD on Ru and SiO₂
  - Possibility of direct reduction of the precursor, especially on Ru
- Further work on reduction processes
- Application of ALD films as seed layers for Cu electroplating
- Functionalization of CNTs
Summary

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