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

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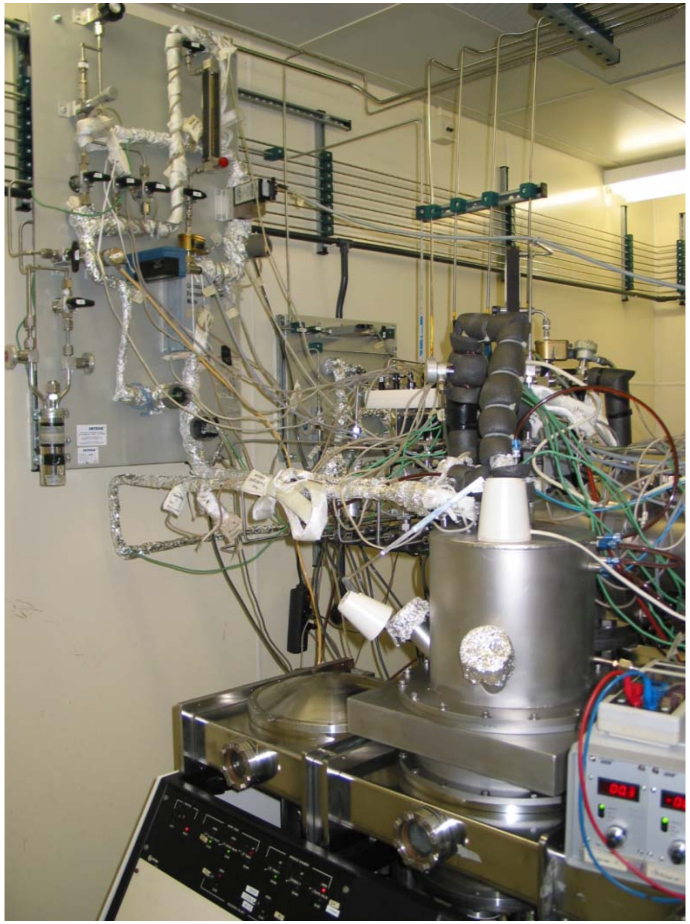
# Outline

- Goals of the work
- Our approach for Cu ALD
- ALD results on Ta, TaN, Ru and $SiO_2$
- Reduction of ALD films
- Summary



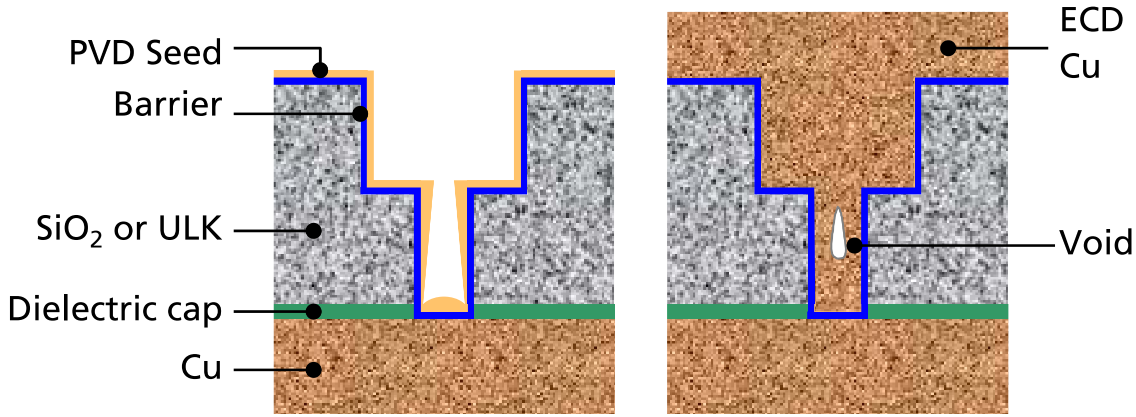
4", single-wafer, vertical flow reactor used for ALD / CVD

# Goals of the work

## Why copper ALD?

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

  see for examle:
  D.B. Farmer and R.G. Gordon,
  *Electrochem. Solid-State Lett.* **8**, G89 (2005)
  – SWNT of 22 nm diameter coated with $Al_2O_3$ by ALD

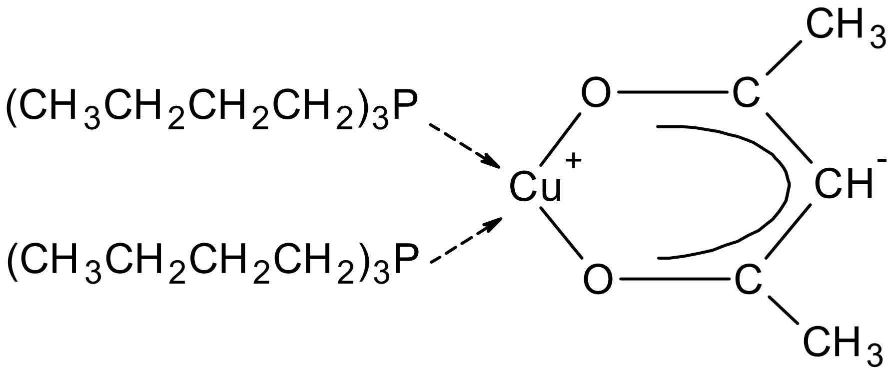


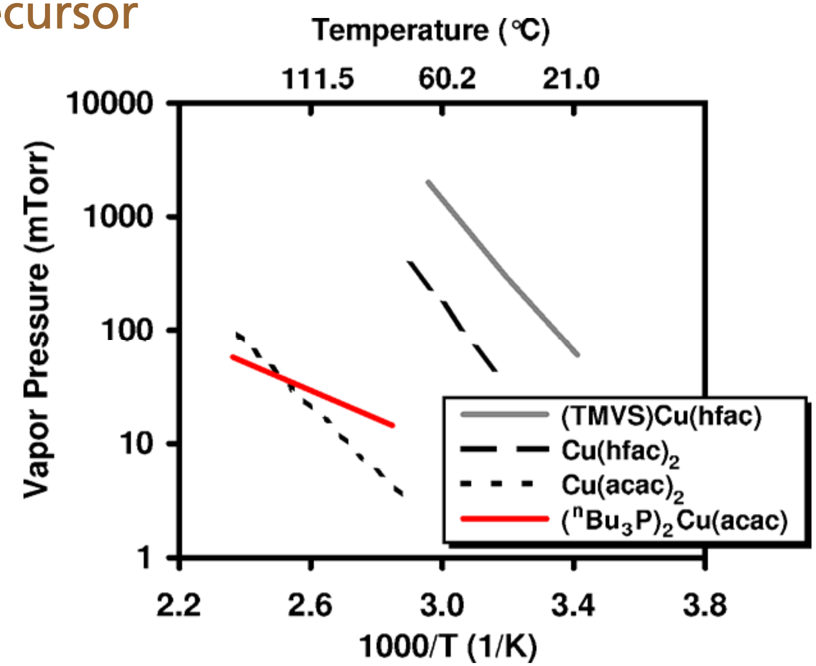

<u>Requirements for the seed layer:</u>

- 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

# Our approach for Cu ALD

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




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

Vapor pressure 14.5 mTorr at 98°C

## ALD processes

- Temperature < 160°C
- ALD of oxidic copper films on Ta, TaN, Ru, and $SiO_2$
- Wet $O_2$ as oxidizing agent
- Subsequent reduction

# 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

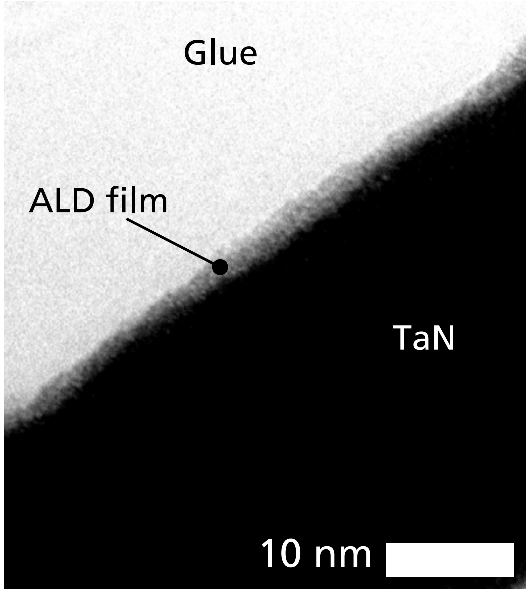
↓

Reduction after ALD

# Results

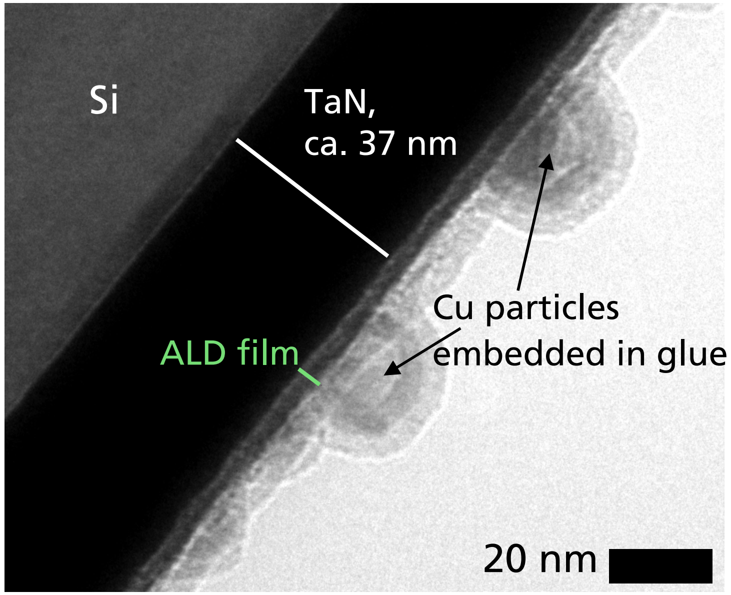
## ALD on Ta and TaN

### TaN, 125°C:



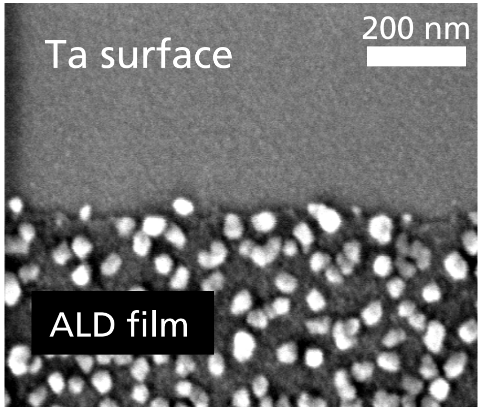

TEM cross section of ALD film on TaN. Ellipsometric thickness: 3.6 nm.

### TaN, 135°C:




TEM cross section (Ellipsometric thick-ness of ALD film: 4.9 nm)

### Ta, 135°C:




SEM top view with partially etched ALD film

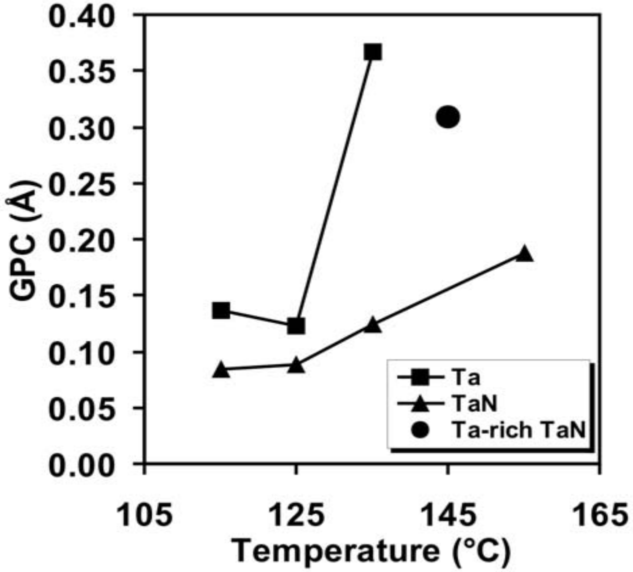
→Smooth, continuous films on TaN

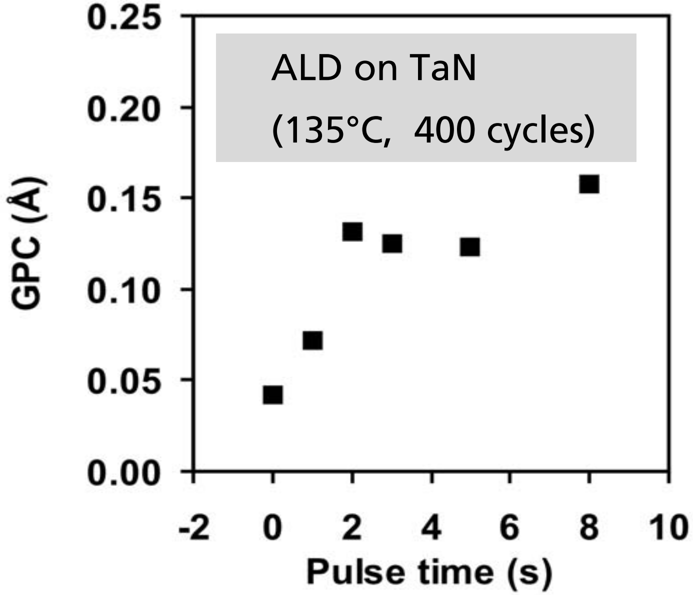
→Tendency to form clusters on TaN as temperature increases

→Cluster formation even more pronounced on Ta

# Results

## ALD on Ta and TaN

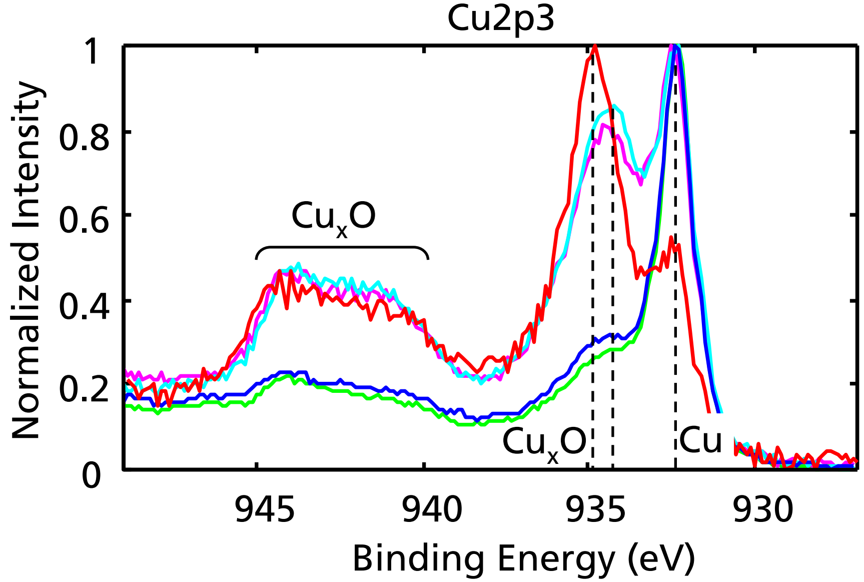


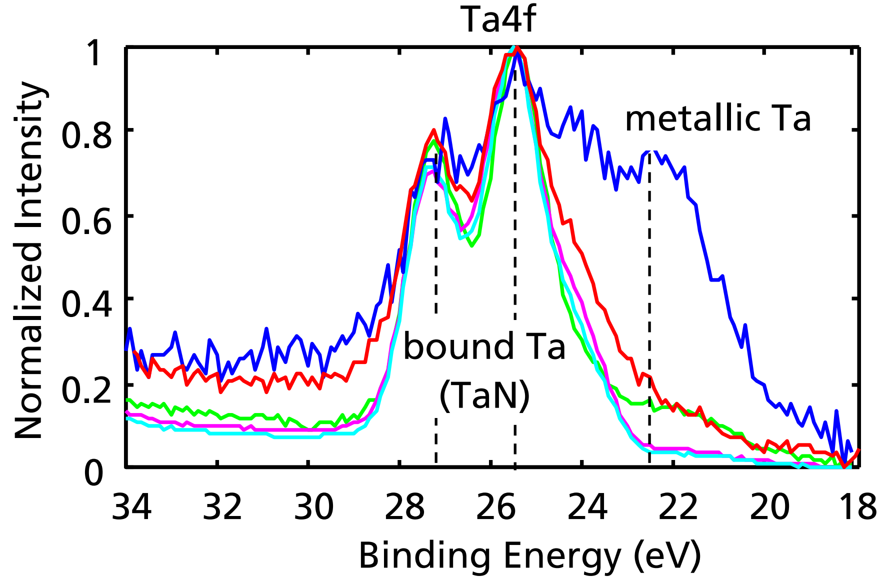




- CVD effects on Ta above 125°C due to high reactivity towards metal-organics [E. Machado et al., Langmuir 21, 7608 (2005)]
- TaN less reactive – less CVD effects – ALD window up to ~130°C
- Degree of nitridation of the TaN important for ALD growth
- Nearly saturated growth on TaN at 135°C

# Results

## XPS of ALD films on TaN



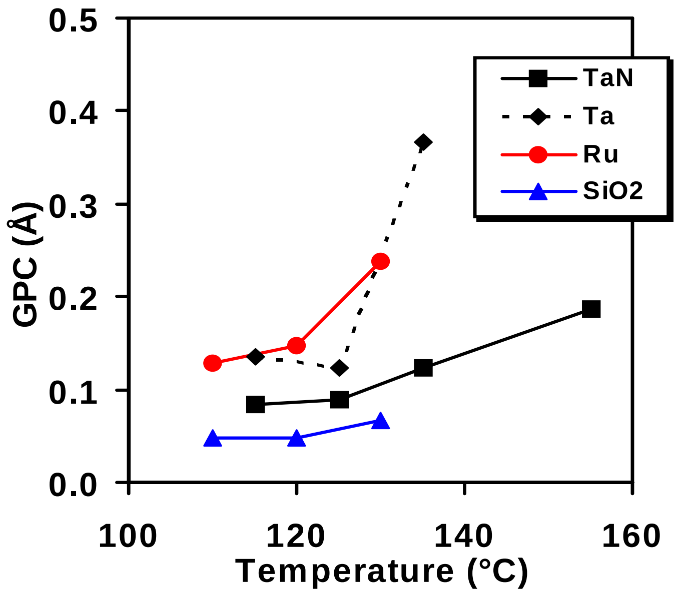

- Composites of metallic and oxidic Cu
- Increased metallic fraction with increased processing temperature (→ beginning CVD growth modes)
- Increased metallic fraction on stronger metallic TaN
- Generally good adhesion of the films (tape test)

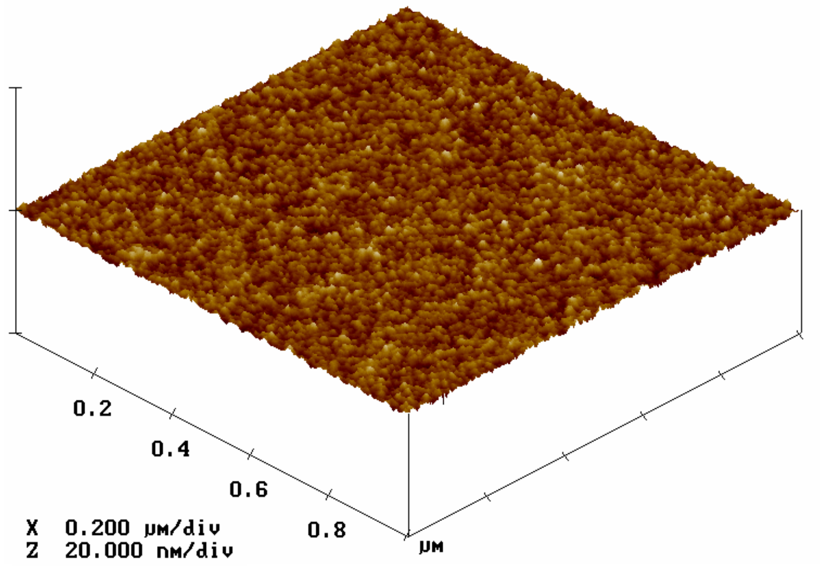
ALD process temp.:

115°C (purple)
125°C (light blue)
135°C (red)
145°C (dark blue)
155°C (green)

# Results

## ALD films on Ru and $SiO_2$




AFM image of 3 nm ALD film on $SiO_2$.
RMS roughness: of 0.25 nm ($SiO_2$: 0.21 nm)

**Results:**

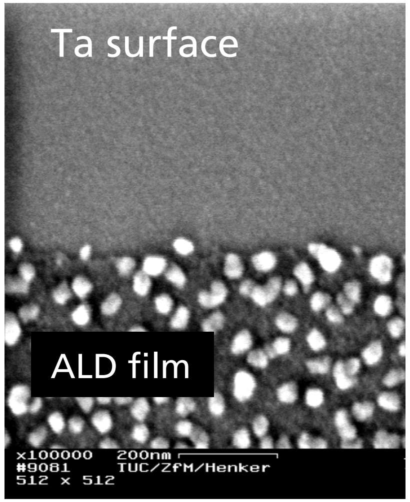
- Smooth, adherent films obtained both on Ru and $SiO_2$
- GPC on $SiO_2$ even lower than on TiN, higher GPC on Ru
- ALD window at least up to 135°C on $SiO_2$ and 125°C on Ru
- Composition similar to films on TaN ($Cu/Cu_xO$ composites)

# Reduction of oxidic ALD films

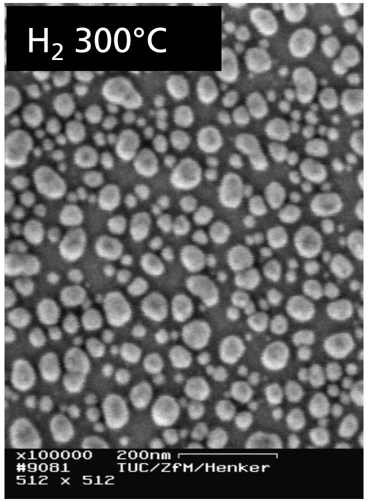
Possible methods:

- Thermal treatment in $H_2$
- Hydrogen plasma
- Thermal treatment with organic reducing agents
  - Isopropanol
  - Formic acid
  - Aldehydes

- High process temperature required
- No effective reduction
- Agglomeration of the films




Initial state after ALD on Ta: Continuous film with clusters




After reduction in $H_2$ for 30 min: Strong agglomeration

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# Reduction of oxidic ALD films

**Possible methods:**

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

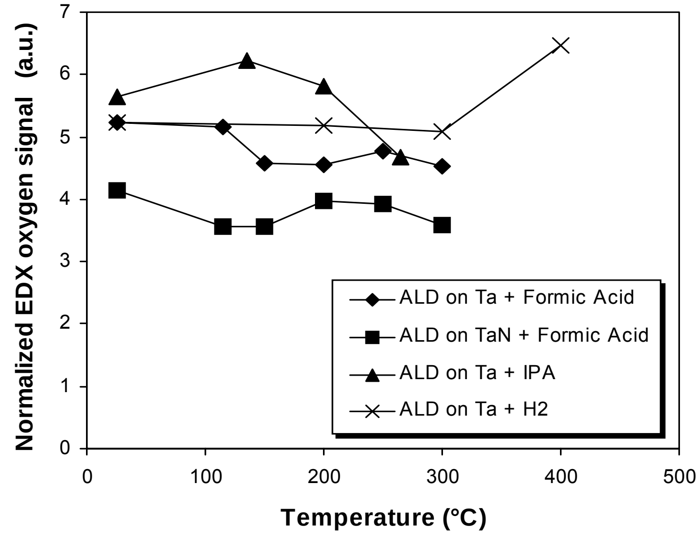
- Reduction of oxygen content obtained (EDX)
- Tendency of agglomeration although processing at lower temperature (plasma effect?)
- Disadvantages of plasma reduction processes compromise benefits of thermal ALD

# Reduction of oxidic ALD films

Possible methods:

- Thermal treatment in $H_2$
- Hydrogen plasma
- Thermal treatment with organic reducing agents
    - Isopropanol
    - Formic acid
    - Aldehydes

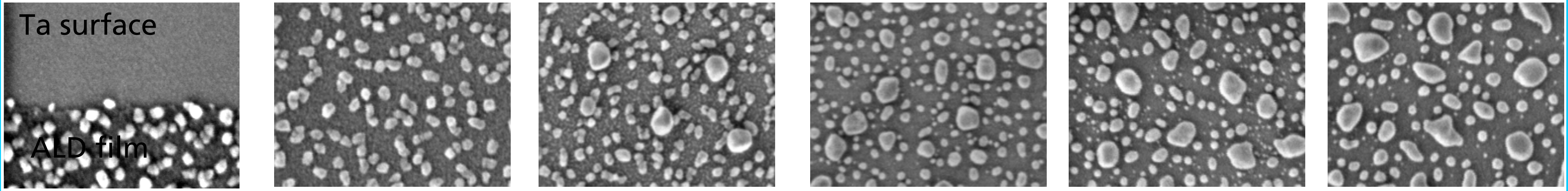
- Reduction of oxygen content obtained both with IPA and formic acid
- Elevated temperature required for effective IPA treatment → increase of sheet resistance
- More promising results obtained with formic acid already at temperatures < 120°C



# Reduction of oxidic ALD films

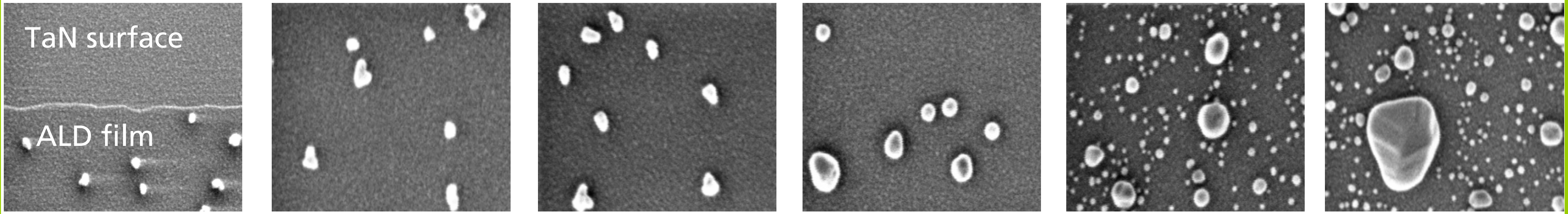
## Formic acid treatment – most promising method so far

Initial state after ALD | 20 min, 115°C | 20 min, 150°C | 20 min, 200°C | 20 min, 250°C | 20 min, 300°C




ALD on Ta

Initial state after ALD | 20 min, 115°C | 20 min, 150°C | 20 min, 200°C | 20 min, 250°C | 20 min, 300°C




ALD on TaN

- No agglomeration on TaN up to 150°C
- More severe cluster formation on Ta



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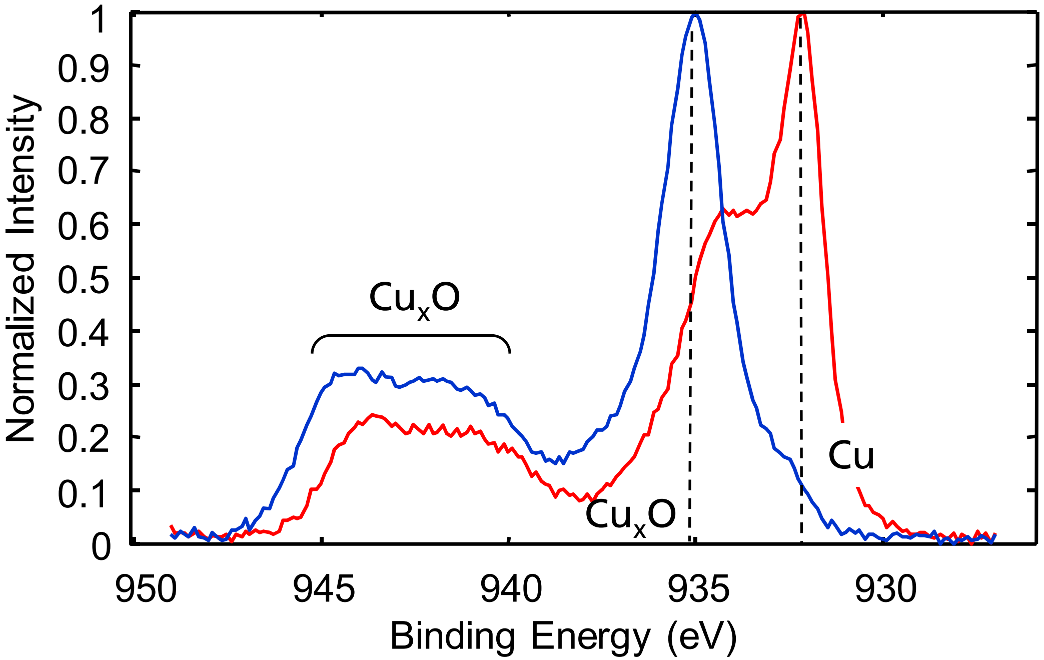
# Reduction of oxidic ALD films

## 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 $Cu/Cu_xO$ composites on Ta, TaN, Ru and $SiO_2$

- Smooth, adherent films at least up to 135°C on TaN, Ru and $SiO_2$
- 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 $SiO_2$
  - 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

TEM analyses: Anastasia Moskvinova and Dr. Steffen Schulze,
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# Thank you
# for your attention!