AREA SELECTIVE Ru ALD FOR SUB 7 NM BOTTOM-UP METAL INTERCONNECTS

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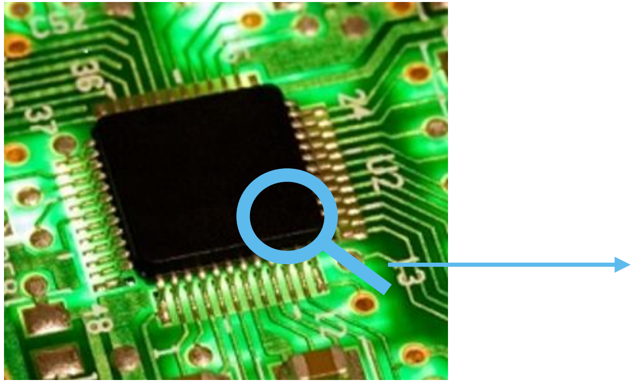
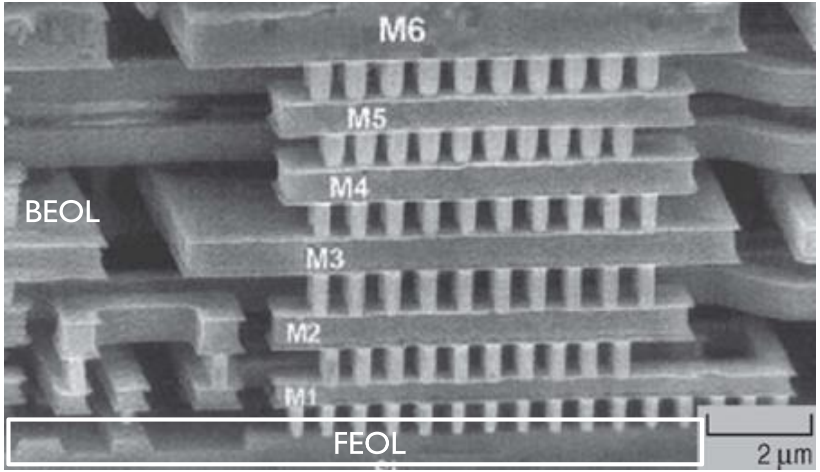
OUTLINE

- Introduction and Motivation
- Process flow
- Process fundamentals
  - Plasma interaction with SiCN/ Low-k and aC surfaces
  - Ru selectivity vs plasma treatments
  - Ru selectivity vs ALD temperature
- ASD Cu/ Ru integration (45 nm HP)
  - Test vehicle
  - Ru selectivity vs plasma treatments
  - Defectivity
- Conclusions and outlook

What are Interconnects?

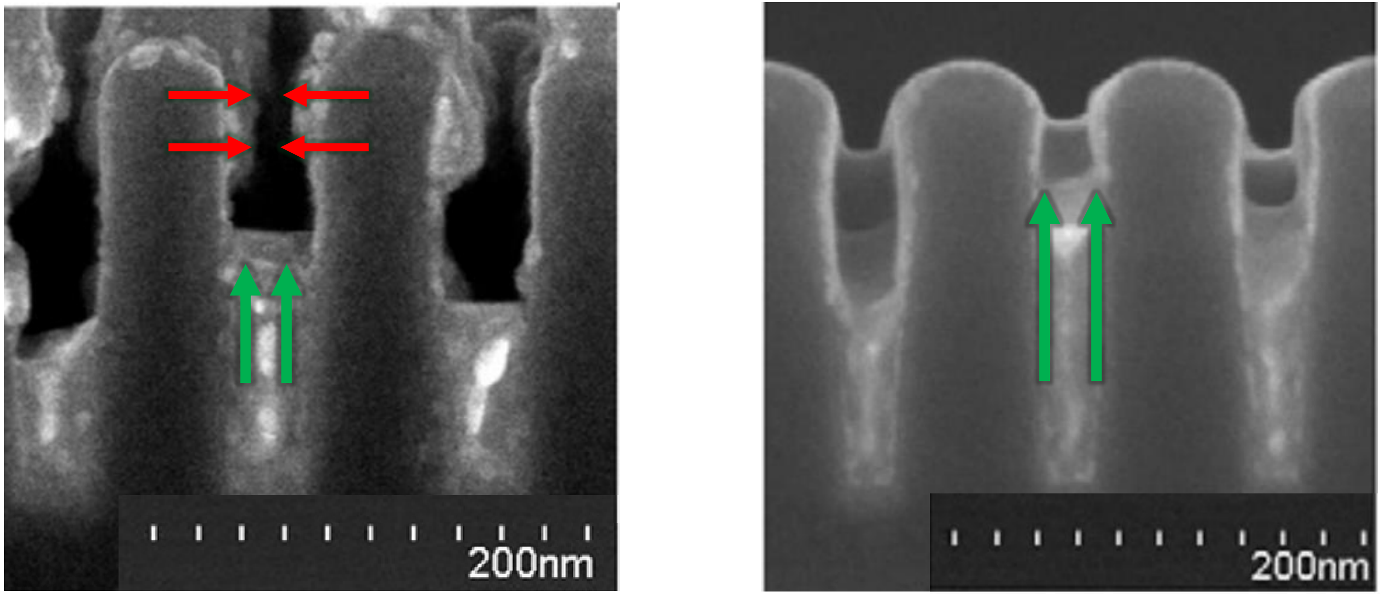




Multilevel metallization structure

- IC consists of devices (FEOL) and interconnects (BEOL)
- Interconnects consist of metal and dielectric isolation

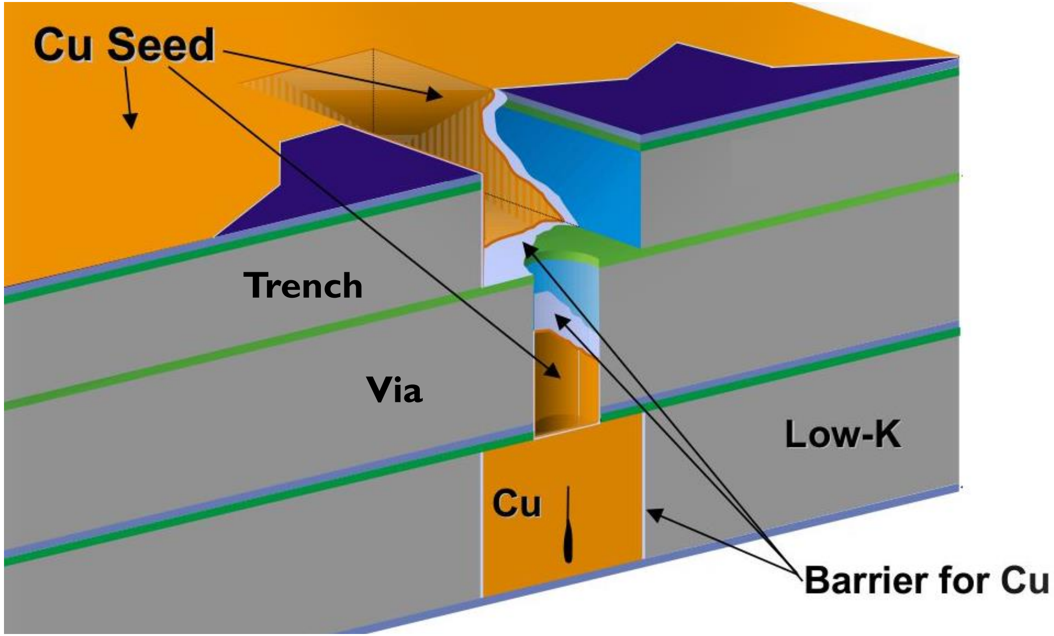
Problem statement



iPVD Cu deposition without (left) and with (right) Ru liner, Ishizaka, Tadahiro, et al., *Microelectronic Engineering* 92 (2012): 76-78

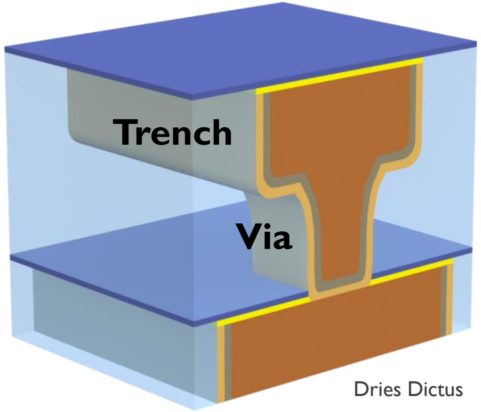
- Conventional metal fill becomes very challenging for narrow structures
- Bottom-up metal deposition can be used for defect-free fill

Interconnect structure. Dual-Damascene



Multilevel metallization structure

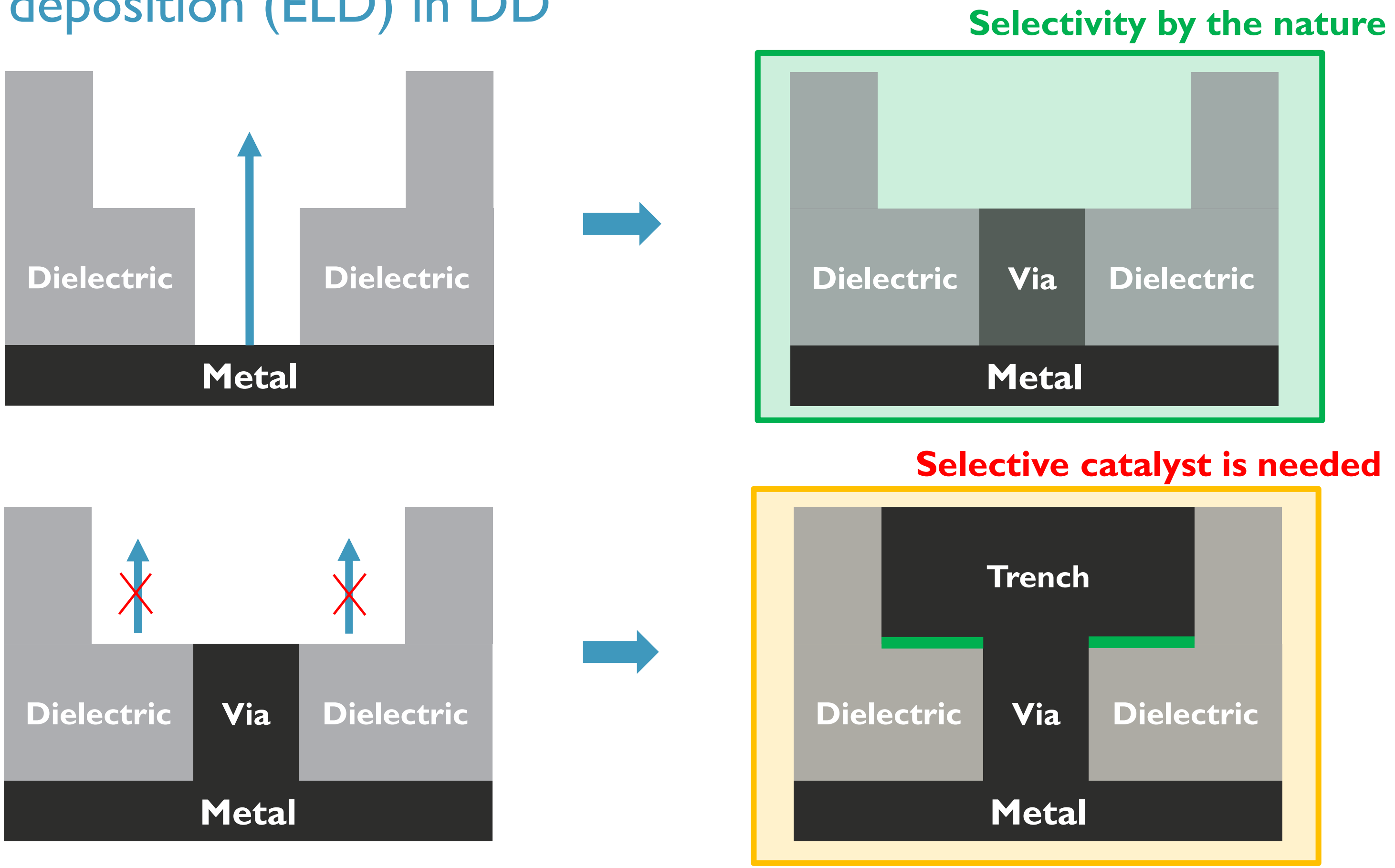
Dual-Damascene



Dries Dictus

- Metal fill is used instead of metal etch
- Metal fill of Via and Trench areas is required (bottom-up?)

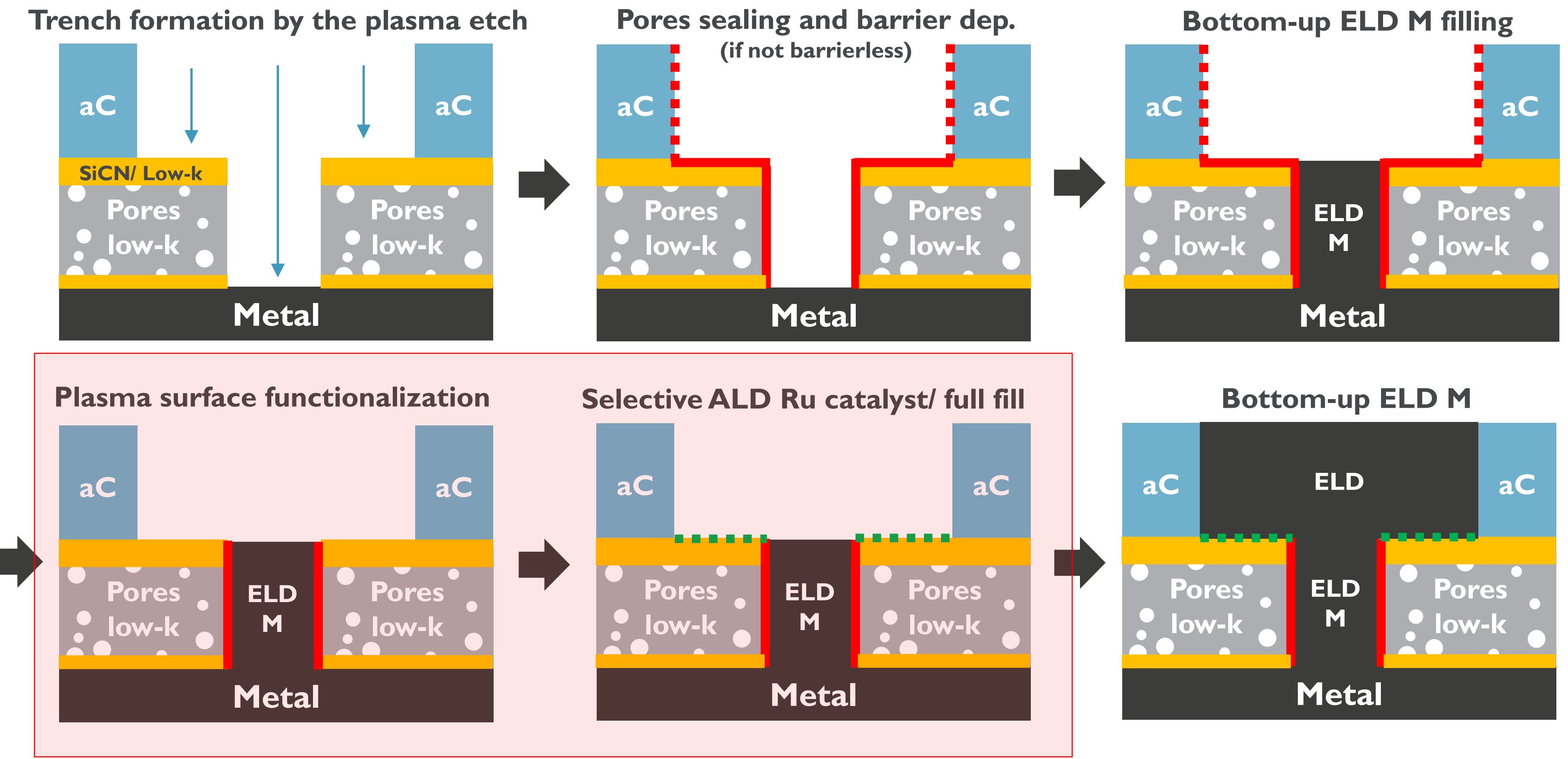
Electroless deposition (ELD) in DD



Metal catalyst is needed for Electroless deposition on the dielectric surface

Process flow

Trench-up deposition in alternative DD structure using *plasma for surface functionalization*



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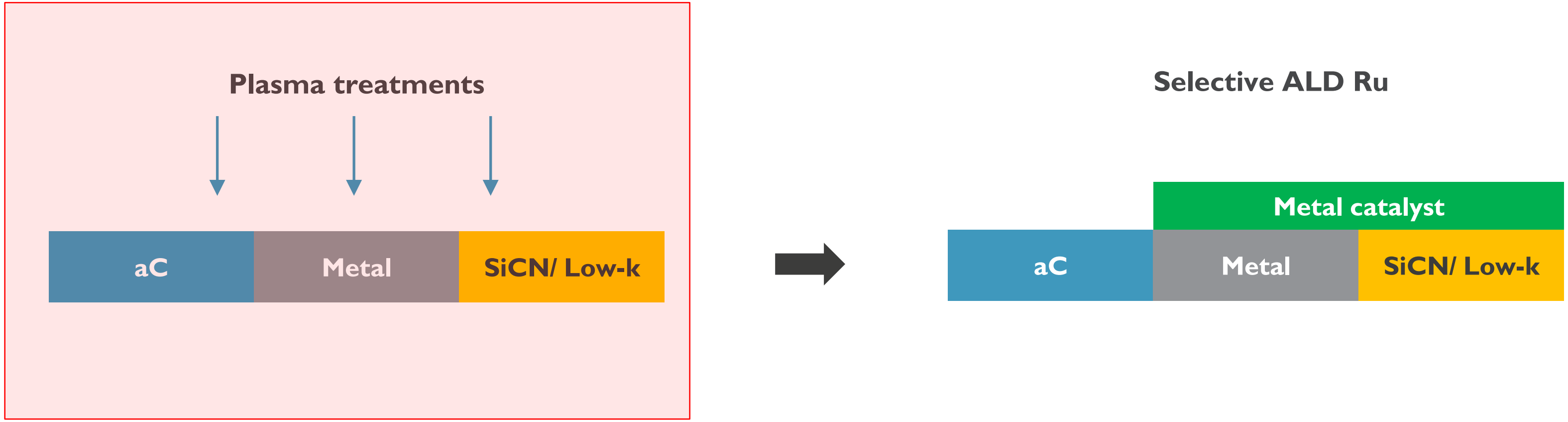
aC etch and low-k replacement

Process scheme

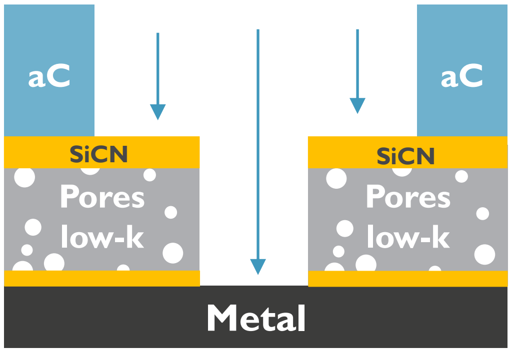


Plasma treatment is the most important step to achieve ALD Ru selectivity

Plasma interaction with SiCN/ Low-k and aC surfaces

Plasma needed for the process

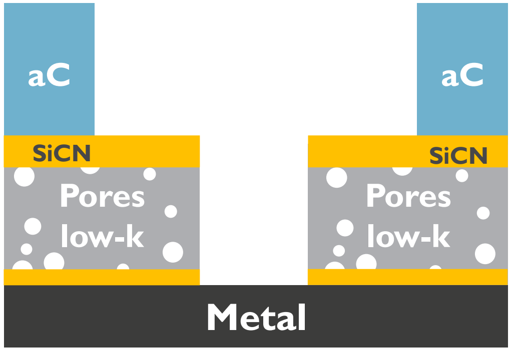
Trench formation by the plasma etch



H_2/N_2 plasma

(provides anisotropic etch of dielectrics)

Plasma surface functionalization

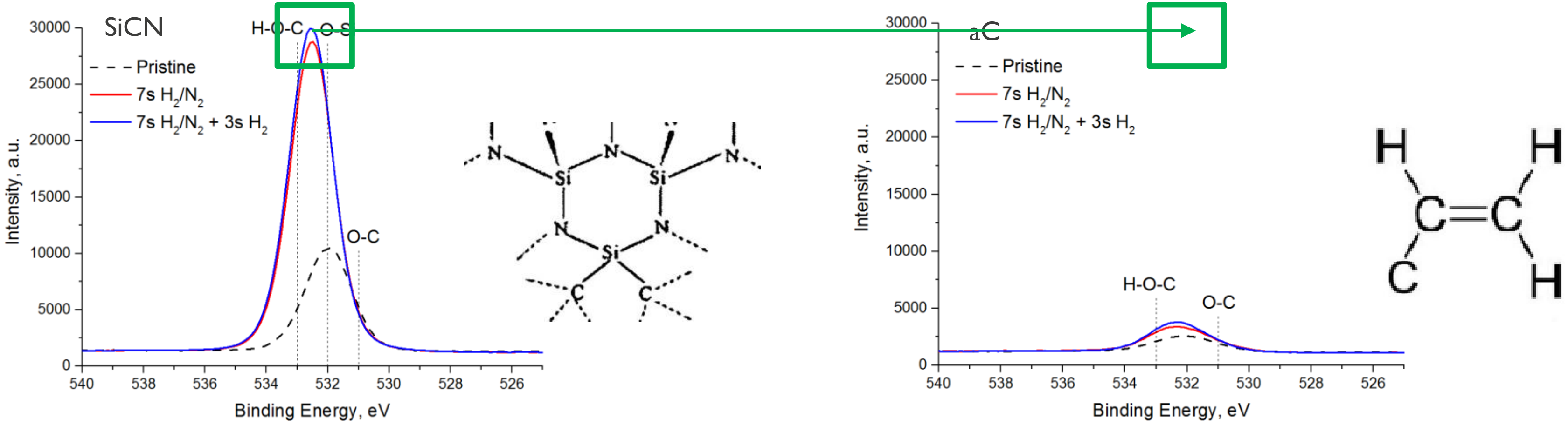


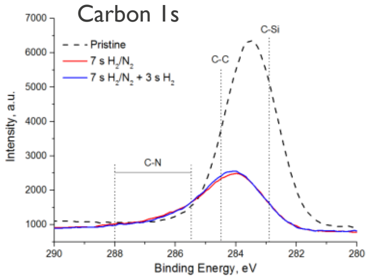
Different plasma mixtures were investigated such as: CF_4/H_2, CH_4/H_2, H_2.

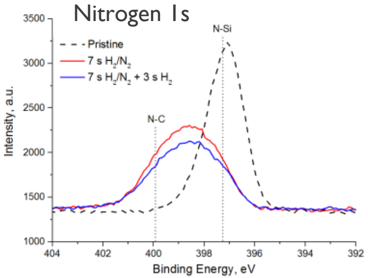
Selectivity was achieved with H_2 plasma post-treatment

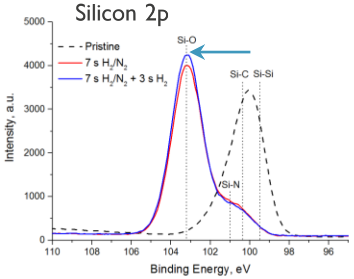
Plasma interaction with dielectric surfaces

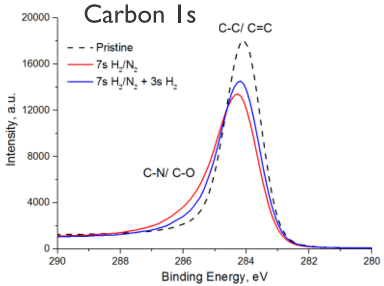
SiCN XPS Oxygen 1s peak **aC XPS Oxygen 1s peak**

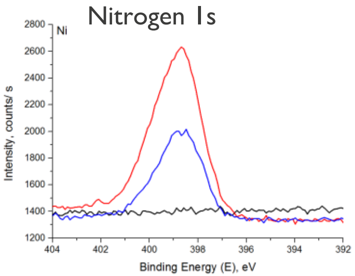












C ↓

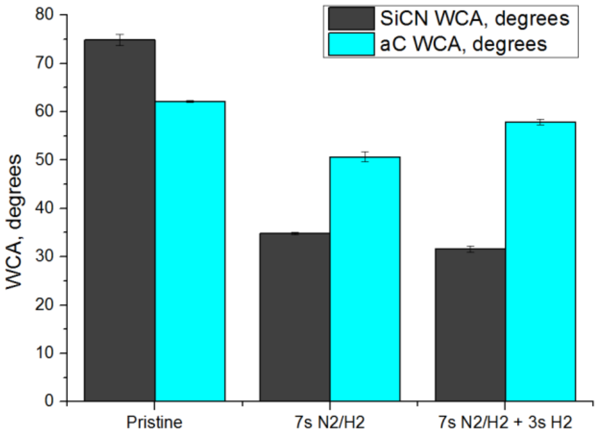
N ↓

SiO_x surface formation in atmosphere

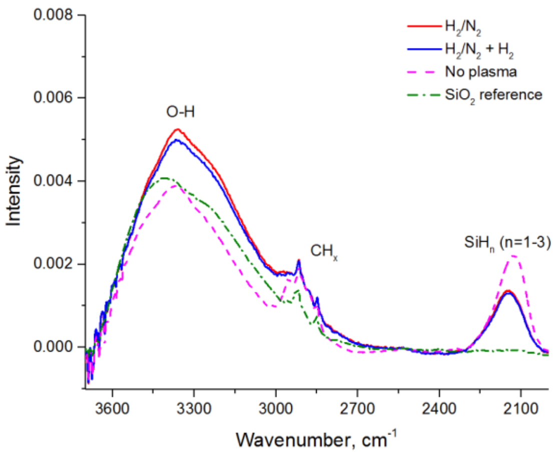
- **Amino groups formation and removal**
- **CH_3 groups formation**

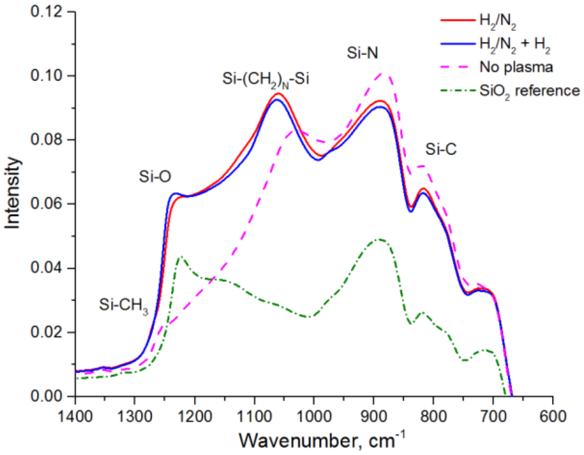
Plasma interaction with dielectric surfaces

Water contact angle measurements:



FTIR spectra of SiCN before/ after plasma treatments





- SiCN becomes more hydrophilic after the plasma treatment
- aC properties restores after H_2 plasma

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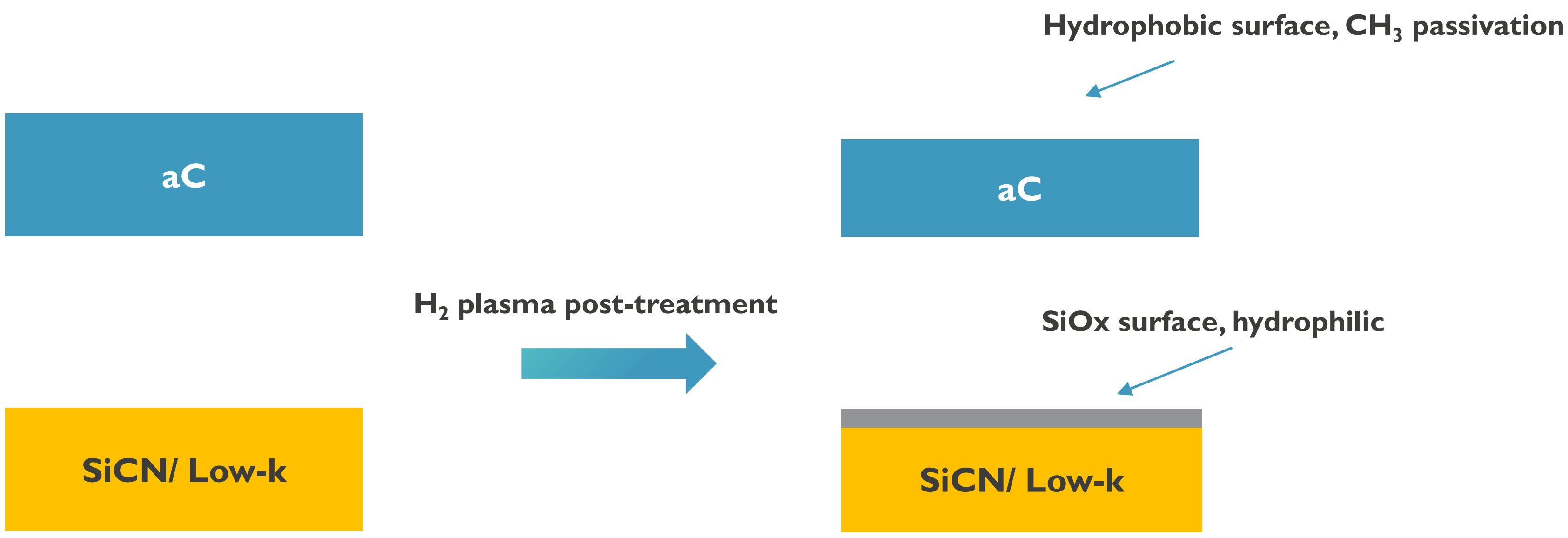
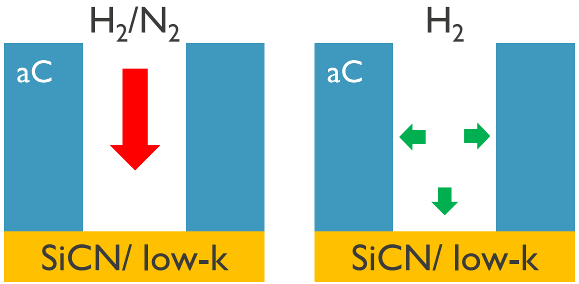
Plasma interaction with dielectric surfaces

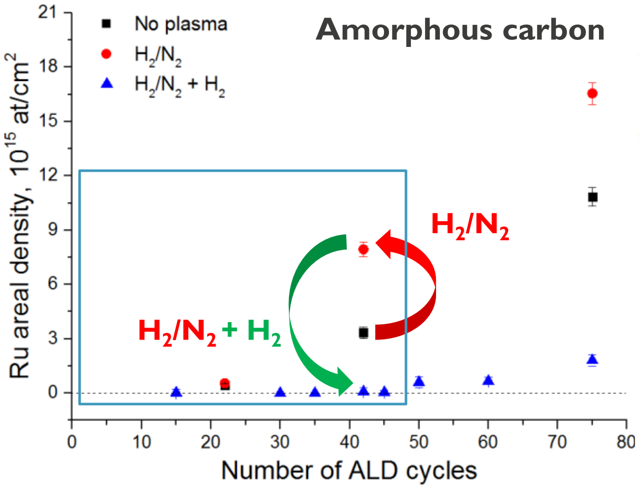


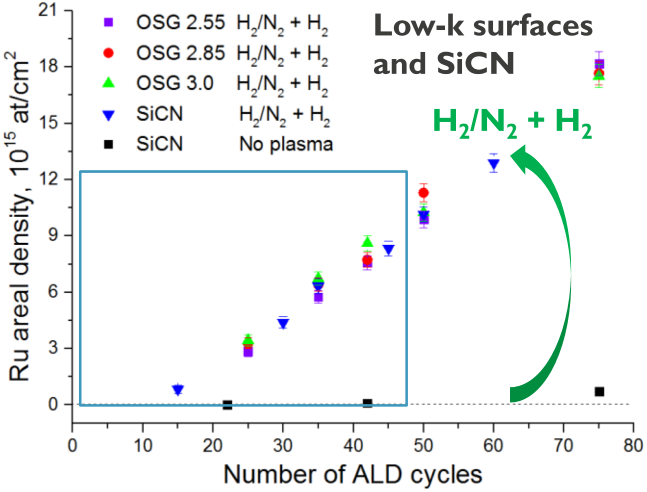
Selective ALD Ru for bottom-up metal ELD

ALD Ru selectivity vs plasma treatment

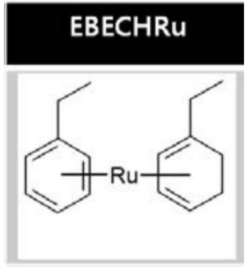
2 plasma steps in the process flow





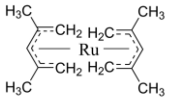


Ethylbenzen–ethylcyclohexadiene Ru(0) precursor



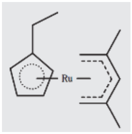
Precursor decomposition occurs at 225-325 C in the presence of oxygen

Selectivity window up to 45 cycles (~ 1 nm Ru on SiCN) @ 325 C, sel. factor 400



Heo, Jaeyeong, et al., *Electrochemical and Solid-State Letters* 11.2 (2008), G5-G8.

"surface modification by the UV-assisted O3 treatment, causing it to be denser and hydrophilic, i.e., an oxygen-rich composition. The increase in the number of reactive sites led to the easy chemisorption and cracking of the Ru precursor by the sufficient supply of oxygen"

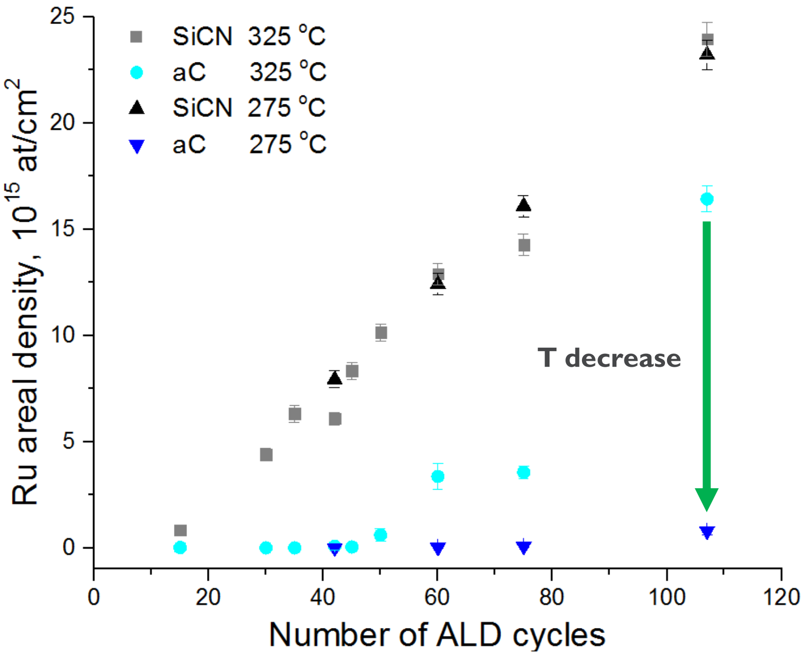


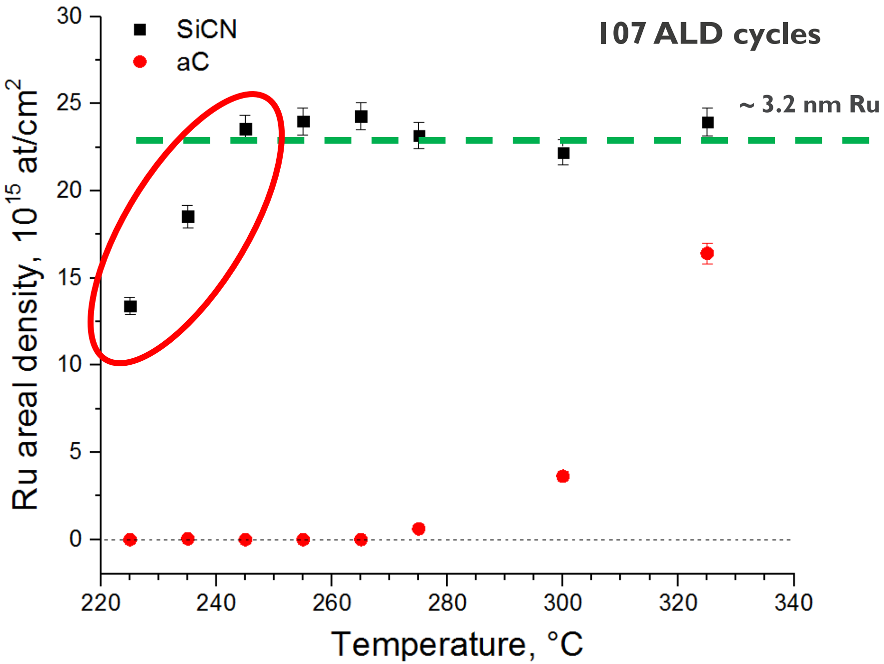
Heo, Jaeyeong, et al., *Electrochemical and Solid-State Letters* 11.8 (2008), H210-H213.

"a weak Van der Waals force may be the only interacting force between the ligand and the methyl group [..] it has been reported that the aromatic benzene molecule (C_6H_6) exhibits a strong adsorption on a silanol group.."

ALD Ru selectivity vs deposition Temperature

RBS Ru concentrations on SiCN/ aC surface



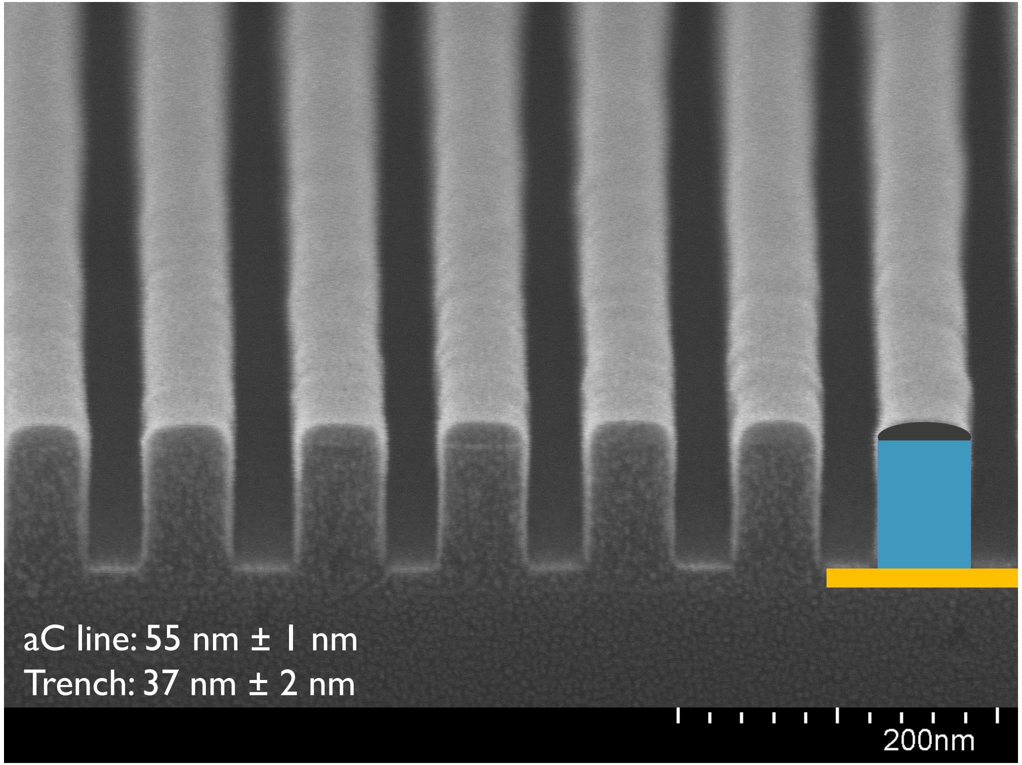


- Two deposition regimes are observed on SiCN
- Ru GR on aC constantly decreases on aC surface while Ru GR is constant on SiCN up to 250 C
- Selectivity window up to 3.2 nm Ru on SiCN (sel. factor 600) @ 275 C

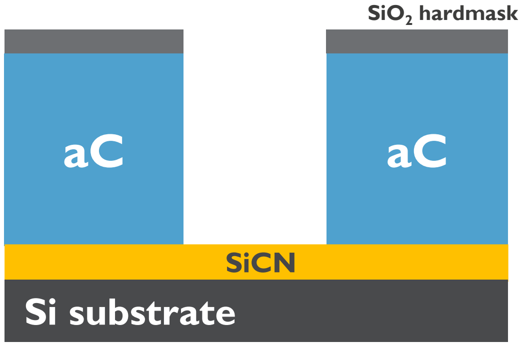
ASD Ru/ Cu on patterned substrates

Test vehicle (45 nm HP)

H_2/N_2 plasma etch of aC/ SiCN



Test vehicle

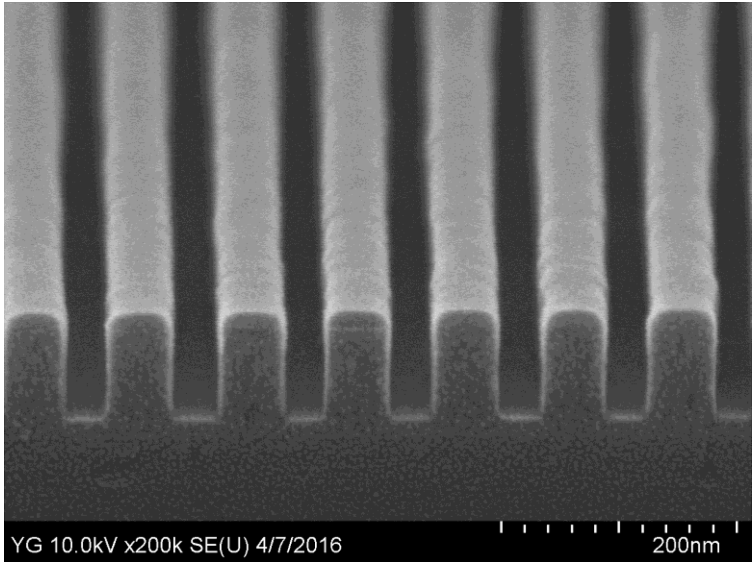


- 20 nm SiO_2 hardmask
- 80 nm PECVD aC
- 15 nm PECVD SiCN

H_2/N_2 plasma is very anisotropic and selective to aC with respect to SiCN

Test vehicle (45 nm HP)

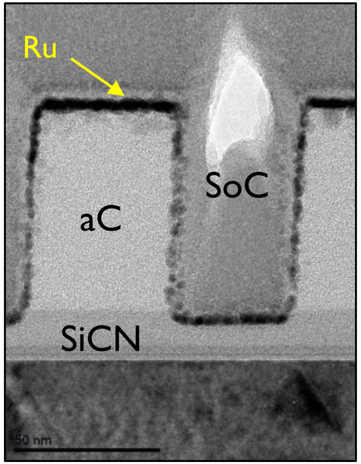
H_2/N_2 plasma etch of aC/ SiCN:

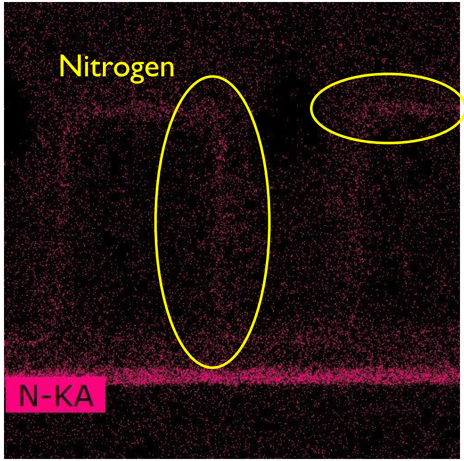


90 cycles ALD Ru @ 250 C

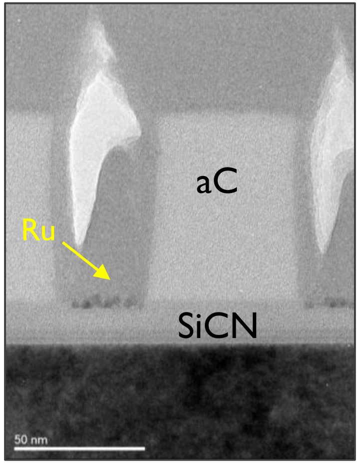
EDX Nitrogen map

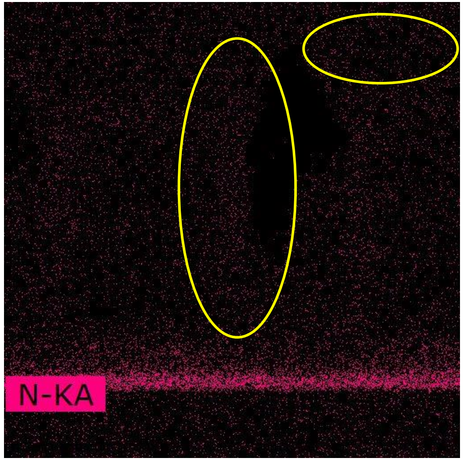
HF clean + 3 s H_2 plasma





HF clean + 10 s H_2 plasma





Short H_2 plasma (3 s)
- ALD Ru is not selective
- N is detected on aC sidewalls and aC lines top

Long H_2 plasma (10 s)
- ALD Ru is selective at the trench bottom
- N content is close to the noise signal

Electroless Cu on ALD Ru seed

Model ELD Cu chemistry

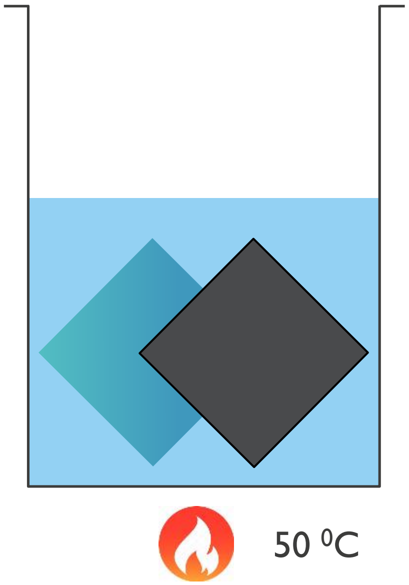
At 50 ^{0}C in a glovebox (concentration of oxygen did not exceed 10 ppm)

The ELD solution contains:

- 0.036 mol/L Cu sulfate
- 0.24 mol/L ethylenediaminetetraacetic acid (EDTA) as a complexing agent
- 40 ppm of 2-2 dipyridyl as a stabilizer
- 0.19 mol/L glyoxylic acid as a reducing agent
- 500 ppm of polyethylene glycol (PEG Mw 4000)

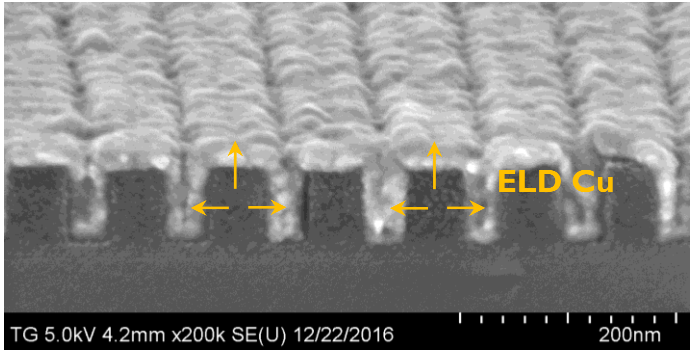
The pH of the bath was adjusted by tetramethylammonium hydroxide (TMAH; Fujifilm, Silicon Etch)

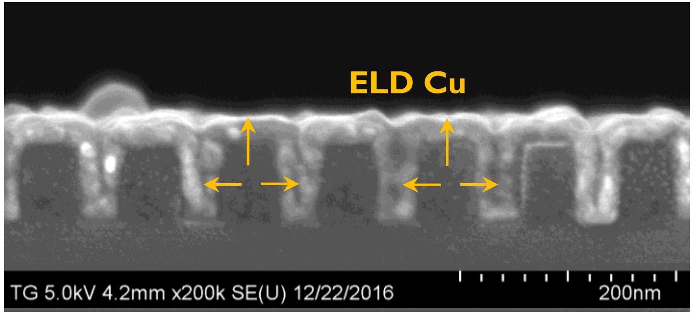
Coupons were dipped in the ELD bath simultaneously for the same deposition time



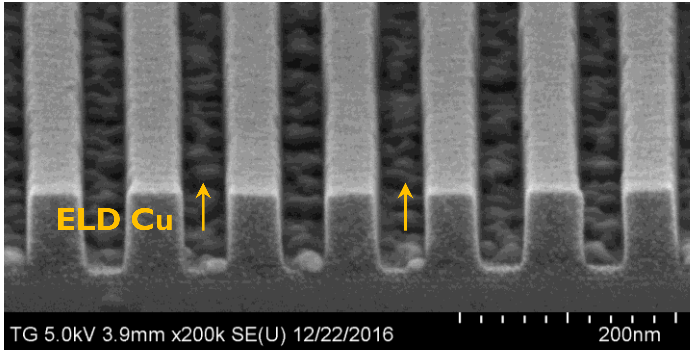
ELD Cu (5 min)

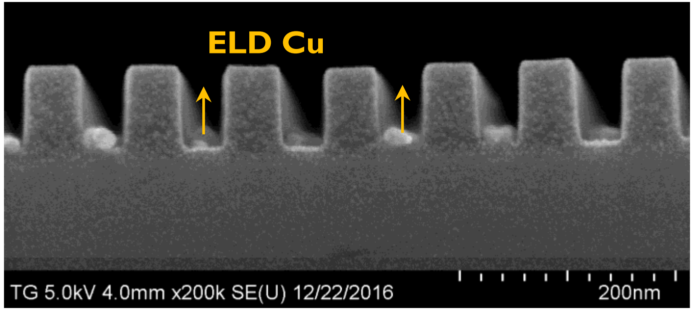
Short H_2 plasma





Long H_2 plasma

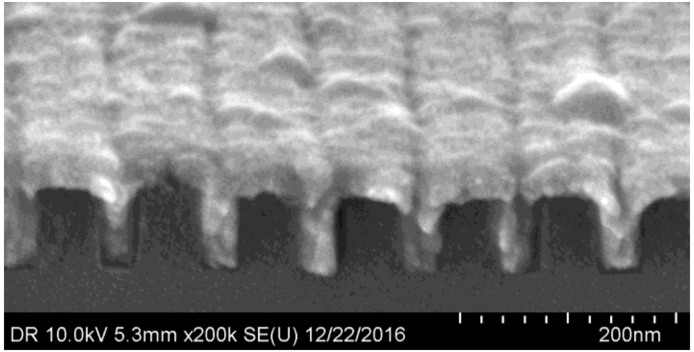


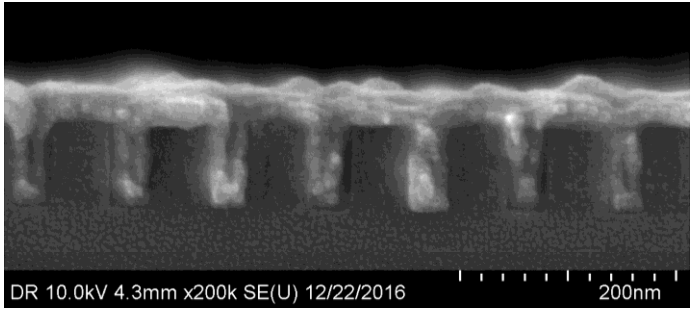


D09 (standard etch) – no selectivity, voids are formed
D10 (shorter H_2/N_2, longer H_2) – nucleation only at the trench bottom

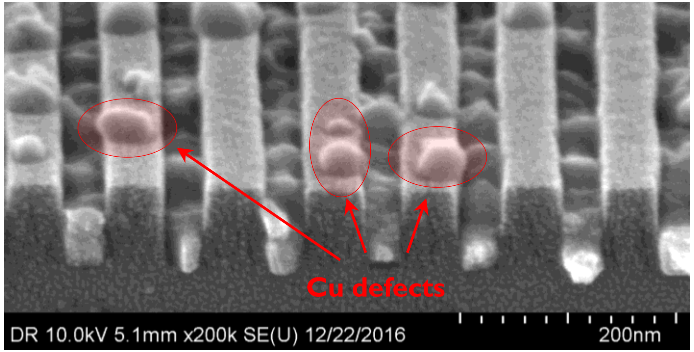
ELD Cu (10 min)

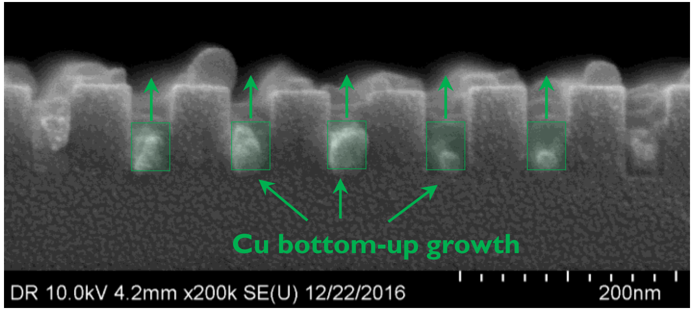
Short H_2 plasma





Long H_2 plasma

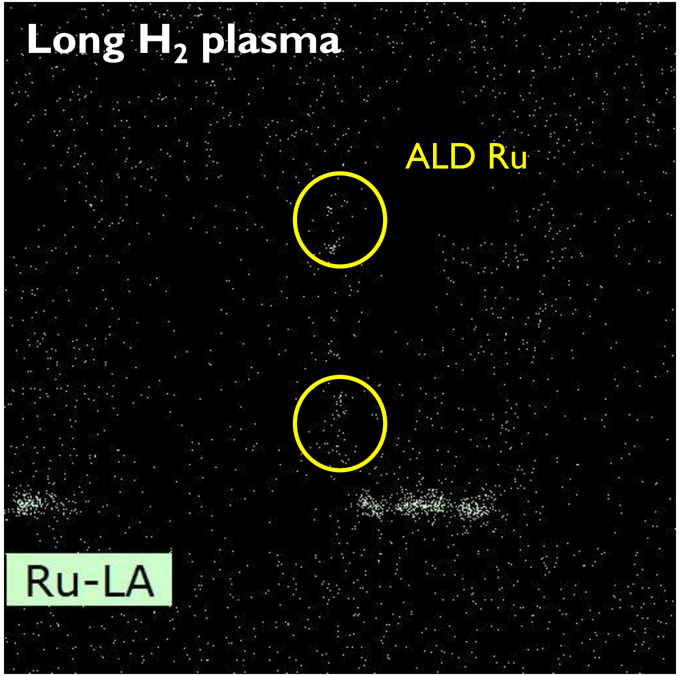




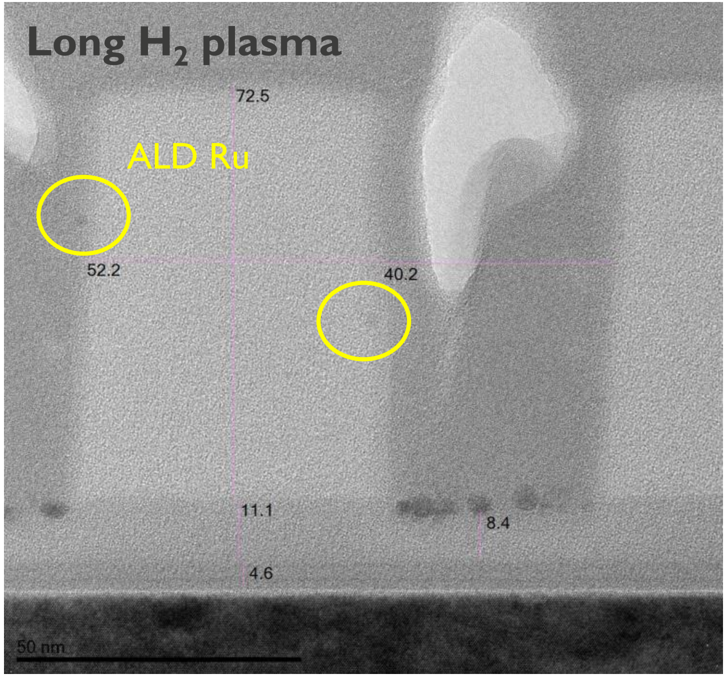
Cu defects are formed on aC lines
ELD or ALD defects?

Defectivity

EDX Ruthenium map

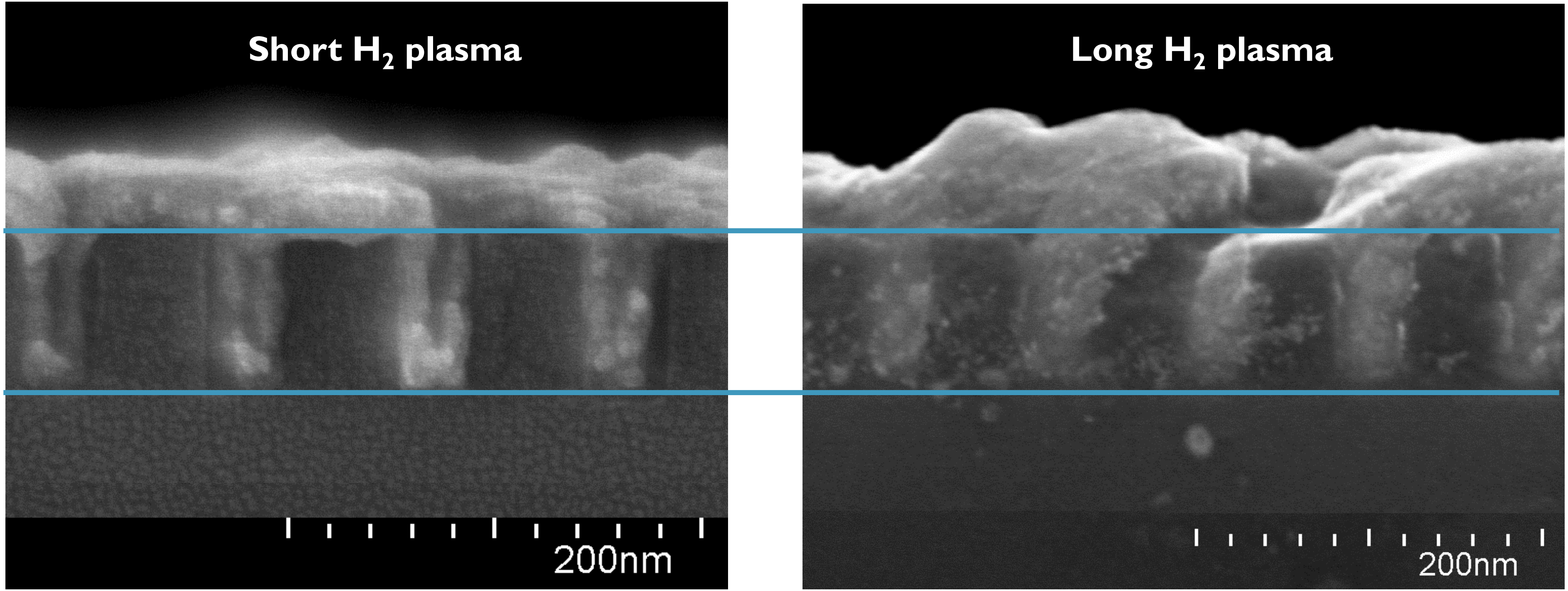


TEM image



- There are Ru defects on aC (both sidewalls and lines top).
- ALD Ru seed is not uniform at the bottom of the trench.

ELD Cu full fill



No central seam is formed in the case of Long H_2 plasma treatment

CONCLUSION

- ALD Ru selectivity is achieved with sel. factor 600 (3.2 nm of Ru on the SiCN)
- ALD Ru is deposited selectively into aC trench on the SiCN surface using additional 10s H_2 plasma
- ELD Cu growths bottom-up, but defectivity should be improved

embracing a better life