WET-CHEMICAL CLEANING OF COBALT AND MOLYBDENUM FOR ADVANCED INTERCONNECTS

Q.T. LE, E. KESTERS, A. USMAN IBRAHIM*, A. KLIPP*, H. GUEVENC*,
A. PACCO, M. VAN DER VEEN, E. ALTAMIRANO SANCHEZ, AND F. HOLSTEYNS
IMEC, LEUVEN, BELGIUM
* BASF SE, LUDWIGSHAFEN, GERMANY

Email address: QuocToan.Le@imec.be

We create chemistry

SPCC, September 1-2, 2020

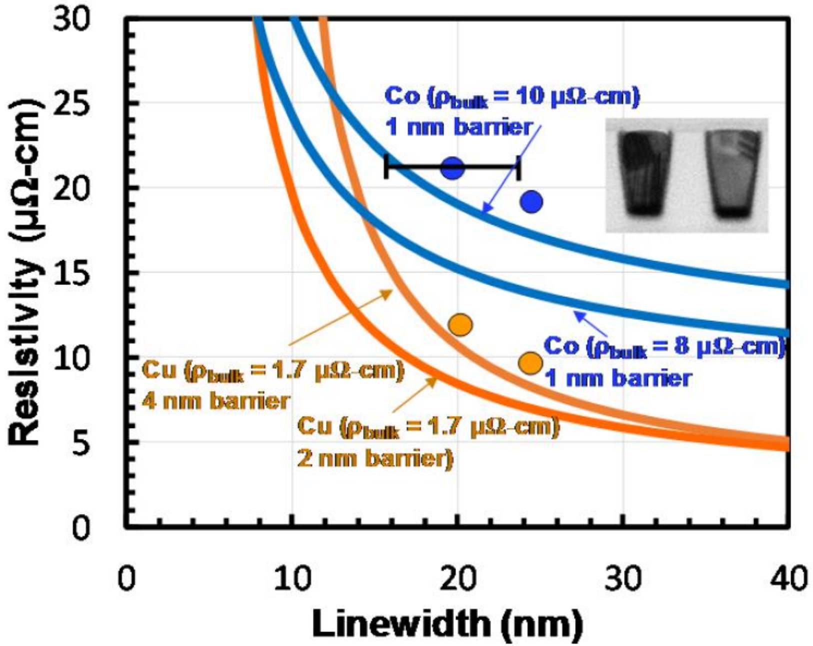
Outline

- Introduction
  - Cobalt as an alternative metal to Copper
  - Co etching: commodity vs. formulated chemicals
- Co cleaning using Fotopur RD-F mixture
  - Experimental: Cleaning chemistry and objectives
  - SEM, XPS, and TEM characterization of patterned stack structure
  - Electrical evaluation
  - Summary
- Mo cleaning: choice of chemicals
  - Effect of annealing
  - Effect of H_2O_2 as oxidizer concentration (H_2O_2)
  - Summary

INTRODUCTION

COBALT: INTERCONNECT ALTERNATIVE TO COPPER

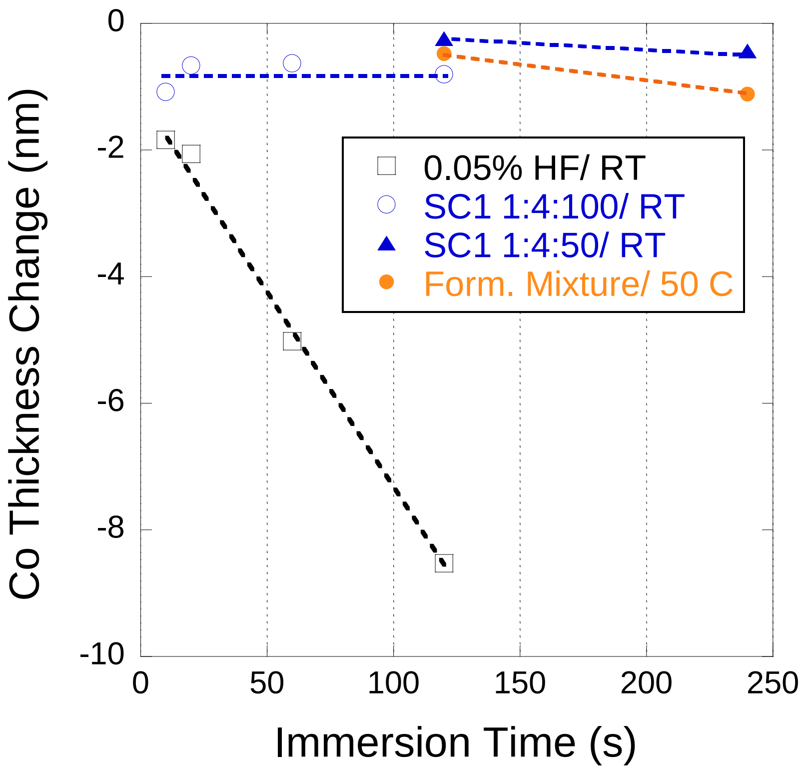
Line resistance trends for Cu vs. Co interconnects under certain assumptions



- Alternative metal(s) to mitigate Cu resistance scaling impacts for lines and vias, and from size-effects
- Co: interconnect metal
  - higher bulk resistivity, but lower size-effects and requires ultrathin barrier
  - Co vs. Cu: resistance crossover may occur below ~15 nm CD

1. J. Kelly *et al.*, and V. Kamineni *et al.*, IEEE IITC/AMC 2016.
2. D. C. Edelstein, IEDM 2017.

Co ETCHING: COMMODITY VS. FORMULATED CHEMICALS



- Co etch rate
  - 0.05% HF > Form. chem. with HF pre-treat > SC1 1:4:100 ~ SC1 1:4:50 ~ Form. chem.
  - In acidic medium

$$Co + H_2O \rightarrow Co(H_2O)_{ads} \rightarrow Co\ (OH)^+ + H^+$$

$$\downarrow$$

$$Co^{2+} + H_2O$$

- Characteristics

	Commodity	Formulation
Choice	Large	Limited choice
Co compatibility	Low	High (due to appropriate pH, additives)
Etch residue removal	Limited efficiency	Higher

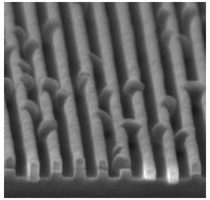
More info on Co etch/HF:

1. L. Broussous *et al.*, UCPSS 2016.
2. Y. Akanishi et al., UCPSS 2018.

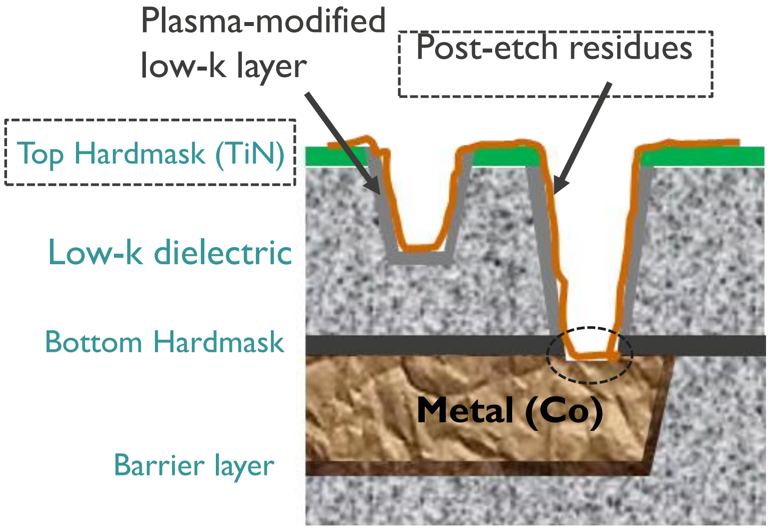
Co CLEANING USING FOTOPUR RD-F MIXTURE

BASF
We create chemistry

CLEANING CHEMISTRY AND OBJECTIVES



Typical Dual Damascene Structure



Three main objectives:

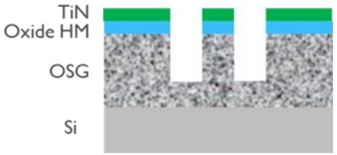
- TiN hardmask: to be removed
- Post-etch residues: to be removed before metallization
- No metal etch & no oxidation

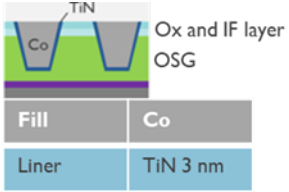
CLEANING CHEMISTRY

- Fotopur RD-F (BASF)
  - RD-F:H_2O_2 = 1:1/ 50 °C

TEST VEHICLES

- Blanket films (Co, TiN, OSG)
- Patterned structures





MATERIAL COMPATIBILITY AND TiN ETCH BY RD-F

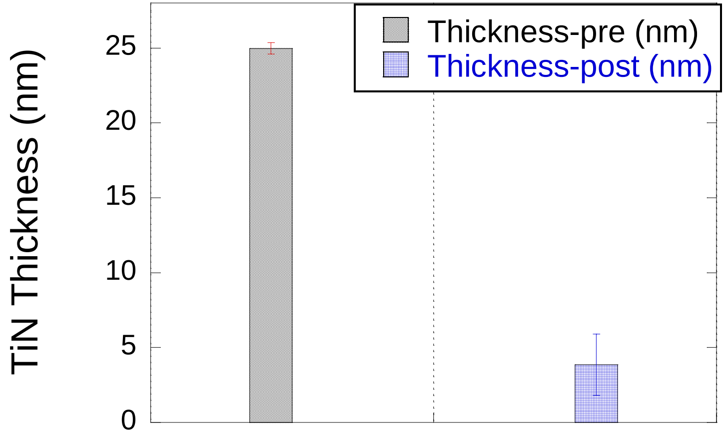
Plasma-treated OSG 2.85

	Pre clean		Post clean	
	Thickness (nm)	RI @ 633 nm	Thickness (nm)	RI @ 633 nm
Mean	53.2	1.3880	53.0	1.3891
Min	50.5	1.3871	50.0	1.3883
Max	55.2	1.3886	55.0	1.3898

ECD Co

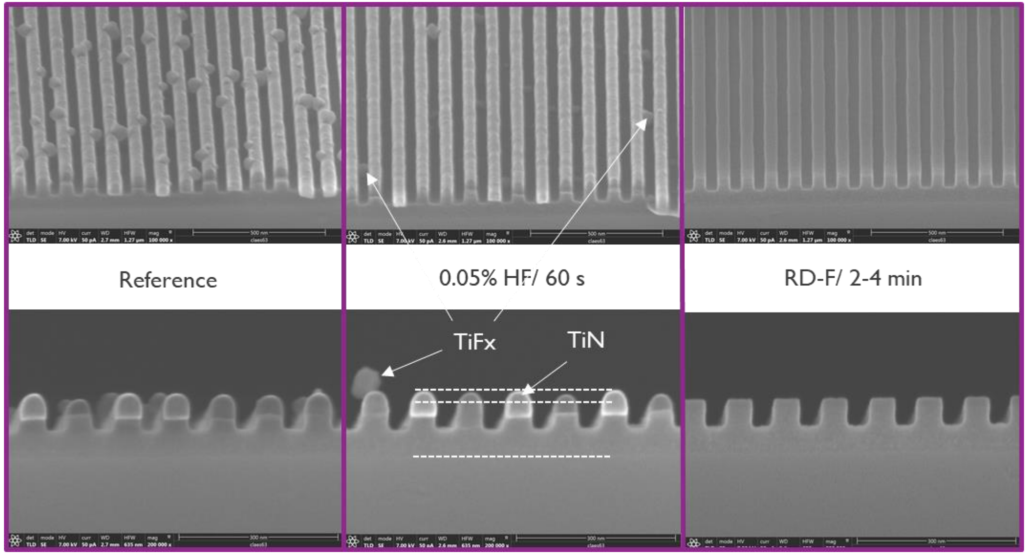
	Rs_Pre (Ohm/sq.)	Rs_Post (Ohm/sq.)
Mean	0.284	0.282
Stdv	0.021	0.012

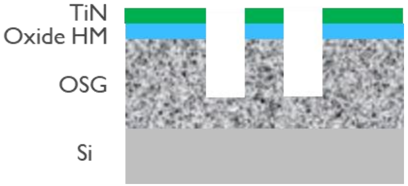
TiN etch



- RD-F:H_2O_2 1:1 @ 50 °C/ 2 min
- Good compatibility with OSG 2.85 and ECD Co
- TiN etch: ~3 nm remained for 2 min clean
  - Artifact (SE measurement)
  - Complete TiN etch confirmed using patterned structure

PERR EFFICIENCY: X-SEM AND XPS RESULTS



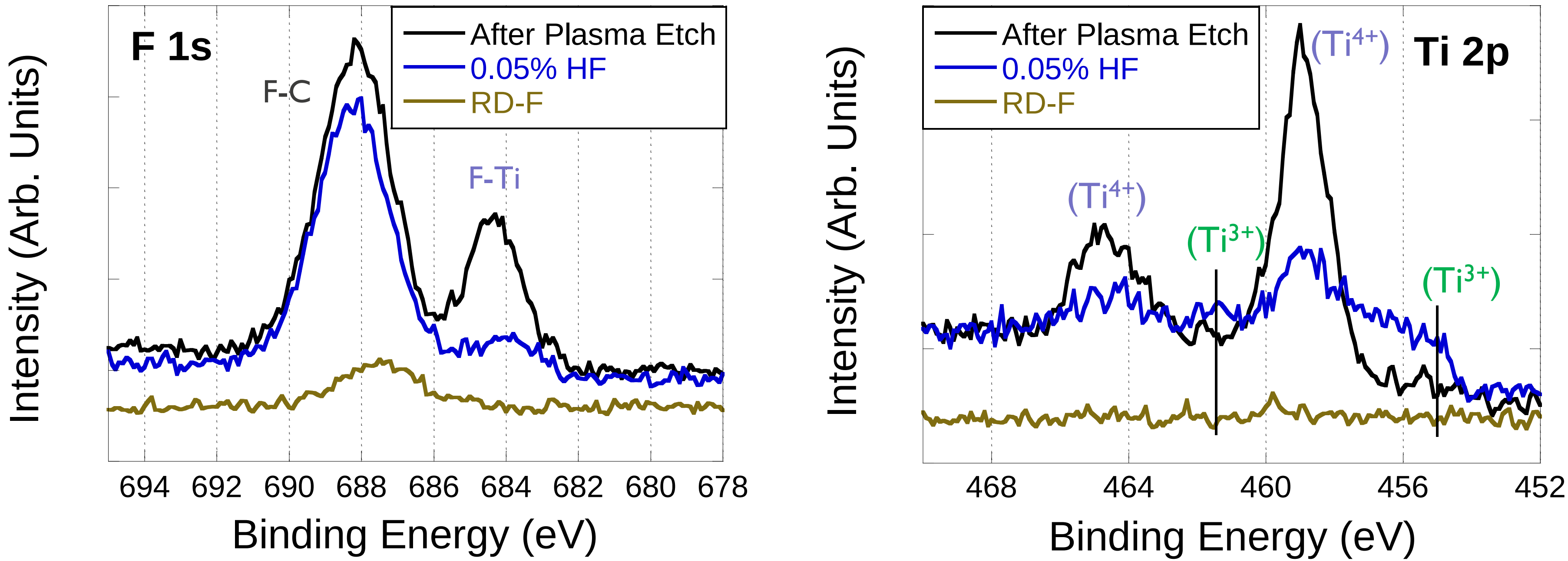


- RD-F:H_2O_2 1:1 @ 50 °C
  - TiN HM removed together with TiFx and CFx residues
  - No LK dielectrics etch after 4 min

Atomic concentrations (At.%)

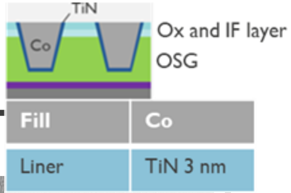
	C	O	Si	Ti	N	F
REF	26.4	27.4	8.0	8.3	6.1	23.8
0.05% HF	28.2	24.9	10.7	8.3	10.6	17.3
2min RD-F	15.9	53.5	26.1	0.1	1.1	3.3
4min RD-F	16.2	53.6	26.2	0.1	1.2	2.7

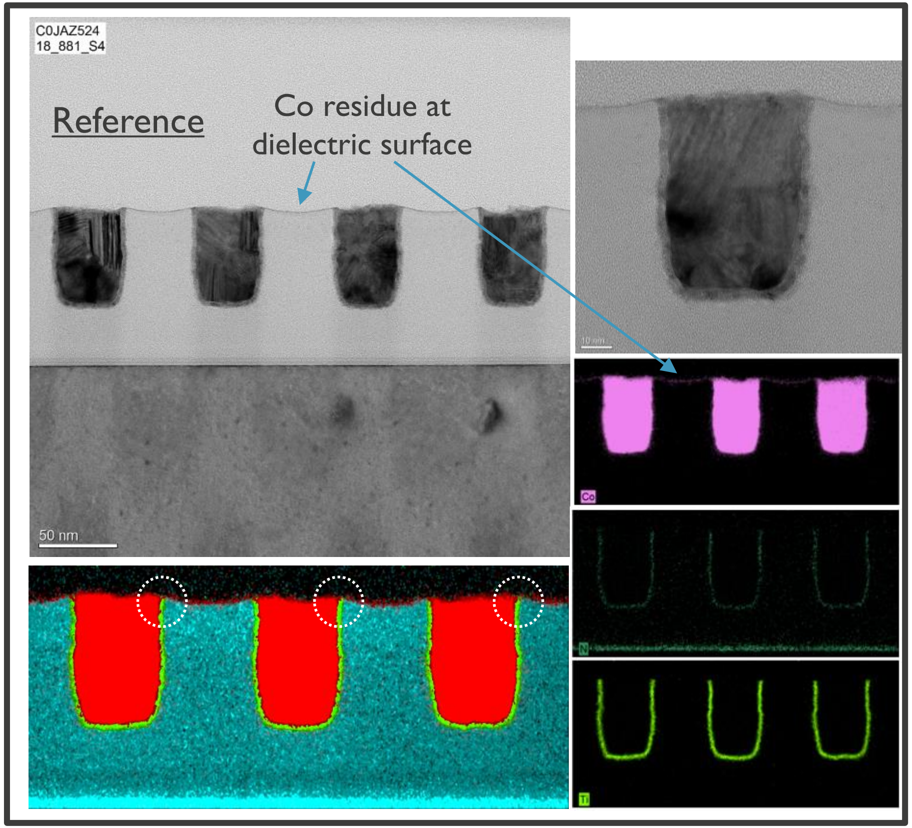
XPS CHARACTERIZATION OF PATTERNED OSG STACK

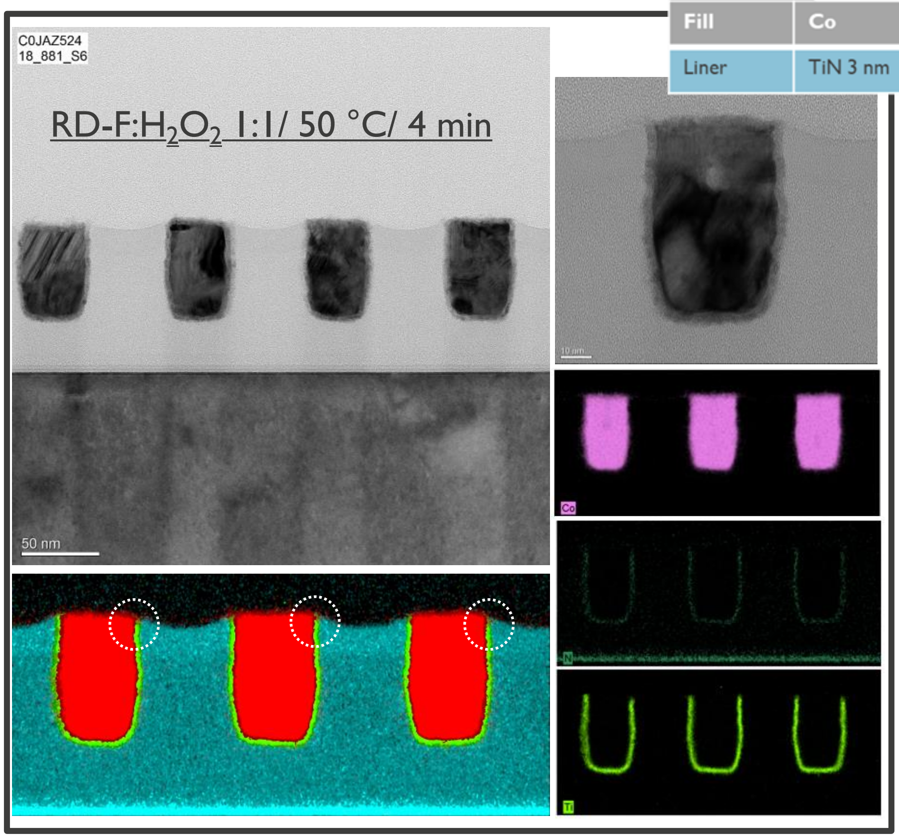


- Both TiFx residues and TiN HM were completely removed in RD-F:H_2O_2 mixture
- Small amount of fluorinated residues (detected at BE ~688 eV) still remained, which could be understood by incorporation of some residues into the OSG pores during dry dielectric etch

Co ETCH AND GALVANIC CORROSION



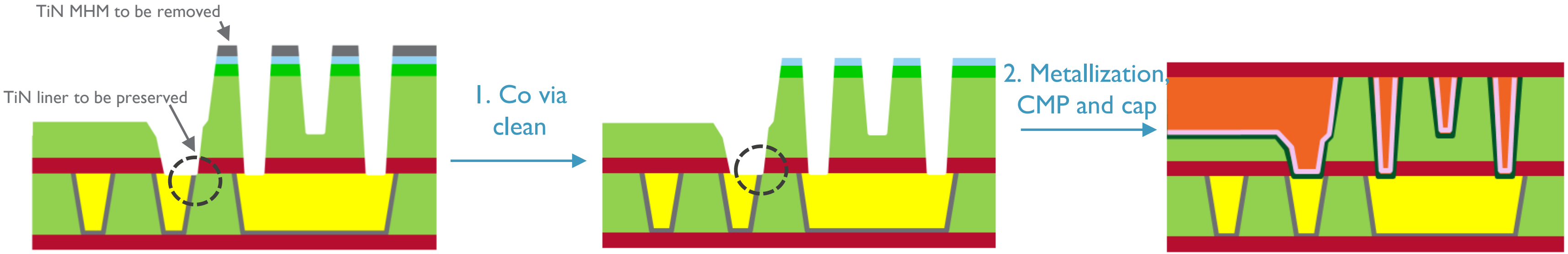




- Presence of Co residue on SiO_2 surface
- Some dishing already observed after CMP

- Co residue at surface removed by RD-F
- No Galvanic corrosion induced by RD-F chemistry

ELECTRICAL EVALUATION: EXPERIMENTAL



22 nm HP Cu Metal-2 on Co metal-1

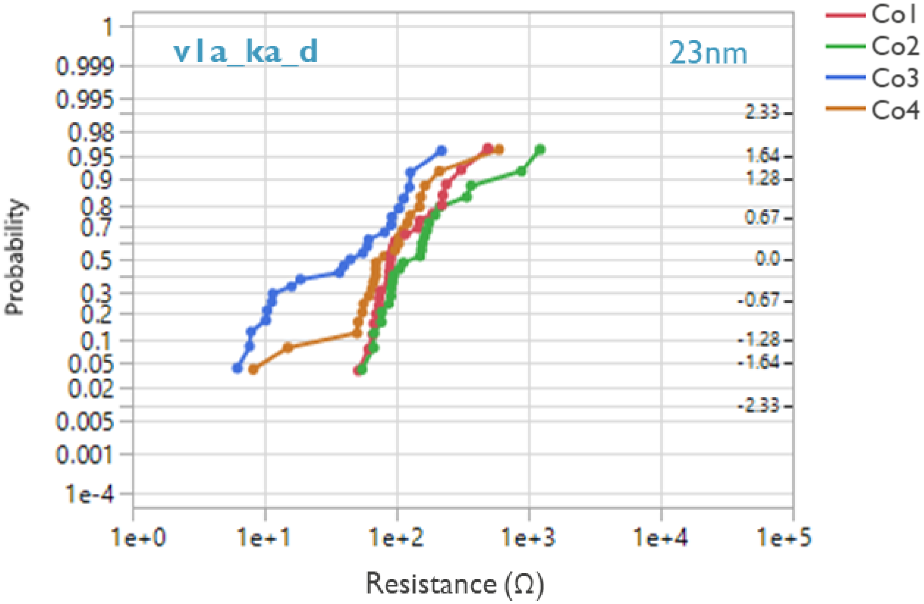
Objective: Co clean evaluation using RD-F mixture, on 22 nm HP dual damascene structure

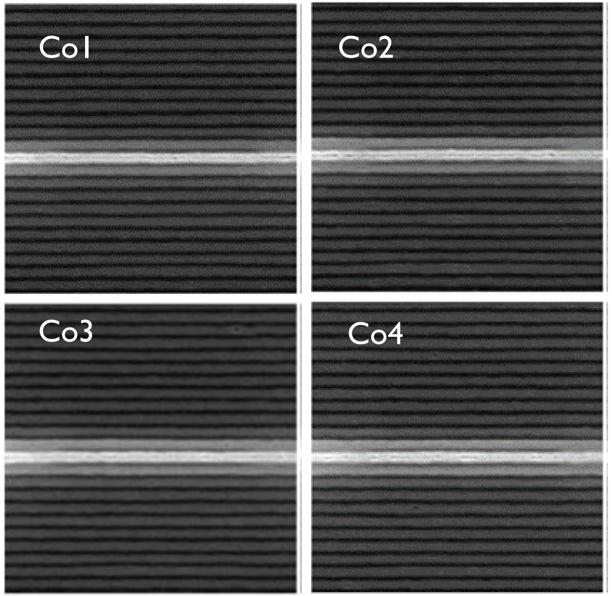
EXPERIMENT DETAIL:

#	Co Clean	Rinse
Co1	2 min RD-F	Aqueous alkaline + IPA rinse
Co2	2 min RD-F	Aqueous alkaline rinse
Co3	5 s dHF + 2 min RD-F	Aqueous alkaline + IPA rinse
Co4	5 s dHF + 4 min RD-F	Aqueous alkaline + IPA rinse

KELVIN VIA RESISTANCE

#	Co Clean	Rinse
Co1	2 min RD-F	Aqueous alkaline + IPA rinse
Co2	2 min RD-F	Aqueous alkaline rinse
Co3	5 s dHF + 2 min RD-F	Aqueous alkaline + IPA rinse
Co4	5 s dHF + 4 min RD-F	Aqueous alkaline + IPA rinse





TD-SEM after CMP

- dHF pre-treatment (Co3 and Co4) ➔ lower resistance but larger distribution
- Only a small difference between Co1 and Co2 where Co1 seems to be slightly better
  - The aqueous alkaline rinse followed by IPA-rinse (Co1) is better than without (Co2)

SUMMARY

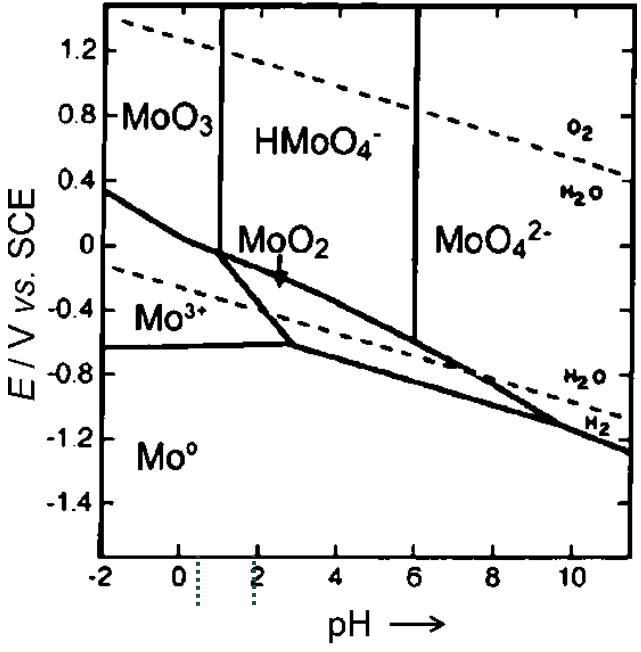
- Co cleaning using Fotopur RD-F cleaning chemistry
  - Good residues removal (both TiFx and organic residues) and TiN HM etch
  - No Galvanic corrosion induced by RD-F chemistry
  - 22 nm MP structure: good electrical performance (via resistance)
    - dHF pre-treatment of 5 s: appears to have a noticeable impact on resistance (slight etching of damaged LK layer)
      ➔ larger resistance distribution
    - An IPA rinse is necessary to obtain lower resistance

Mo CLEANING: CHOICE OF CHEMICALS

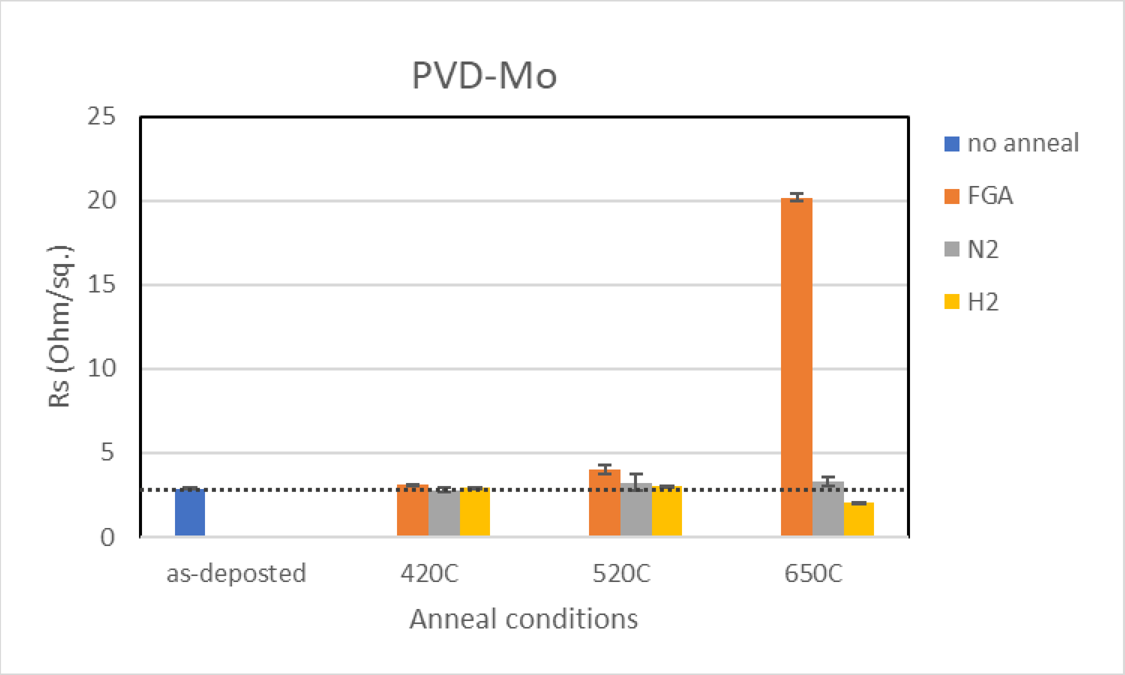
OBJECTIVE AND EXPERIMENTAL

Objective: Mo compatibility with chemical mixtures

- Mo samples: deposited by PVD
  - Nominal thickness: 50 nm
  - As-deposited and annealed at 420 and 650 °C
  - Annealing atmospheres: FG, N_2, and H_2
- Choice of chemical mixtures
  - *0.05% HF*
  - *SC1 mixture with variable [H_2O_2]*
  - *Formulated mixture, pH >12*
  - *Formulated mixture, pH <2*
- Characterization
  - XRD
  - 4-point probe: Rs ➔ conversion to thickness, assuming the initial thickness is 50 nm
  - AFM: surface roughness

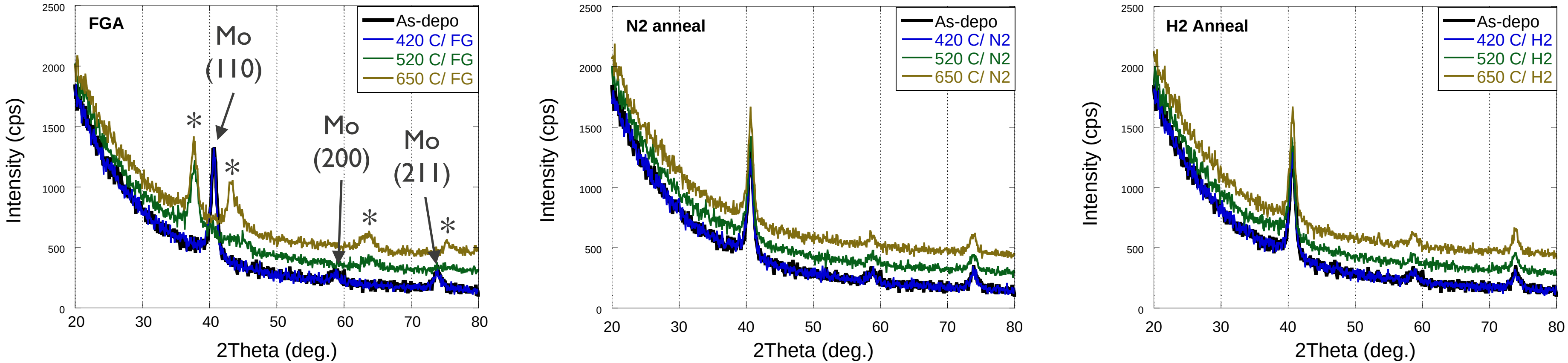


EFFECT OF TEMPERATURE ON Rs

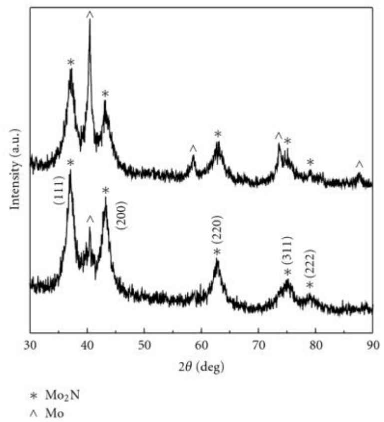


- FG anneal
  - Rs increased as a function of annealing temperature; substantial increase for 650 °C anneal
- N_2 anneal: slight increase of Rs for higher temperatures within 520-650 °C range
- H_2 anneal: significant decrease of Rs for 650 °C anneal

GI-XRD

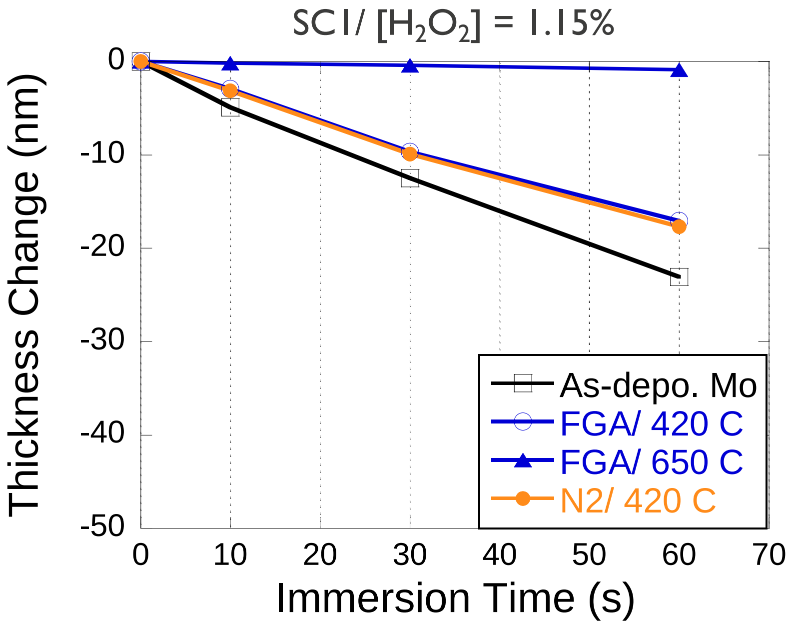


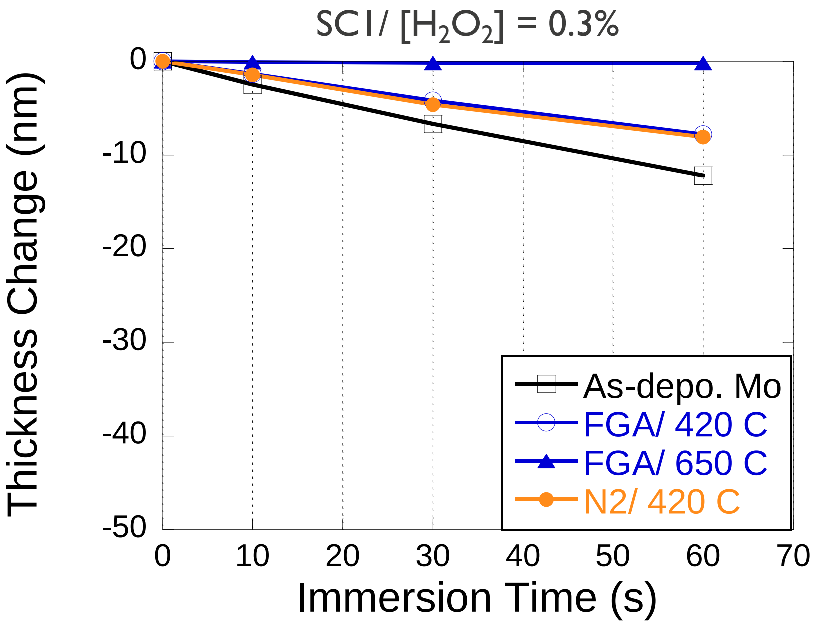
- FG anneal
  - 420 °C : no noticeable change vs. as-deposited Mo
  - 520 and 650 °C: formation of Mo nitride (*)
- N_2 and H_2 anneals: no noticeable change observed up to 650 °C



L. Shen et al., J. Nanomater. (2011) doi:10.1155/2011/781935

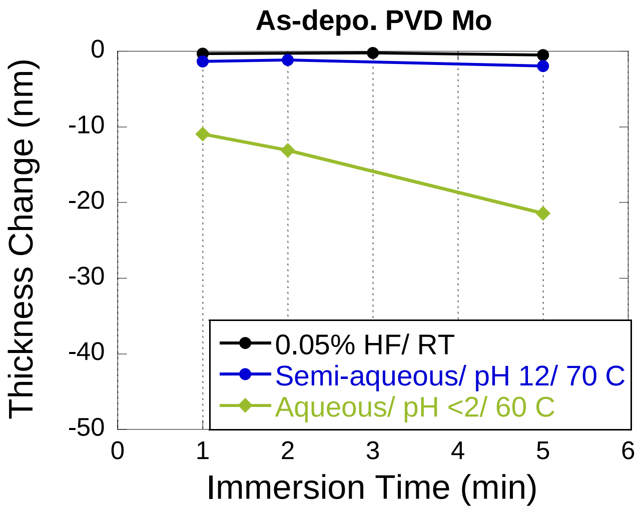
EFFECT OF OXIDIZER CONCENTRATION ON Mo ETCHING

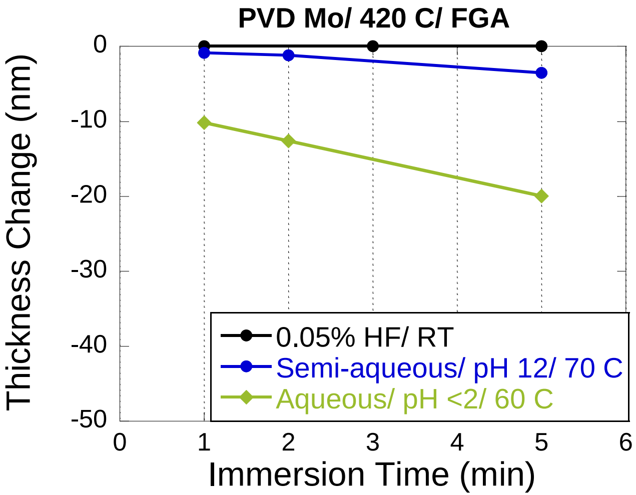




- Lower etch rate for lower concentration of the oxidizer (H_2O_2) in the mixture
- FG annealed Mo/ 650 °C: very low etching explained by the formation of Mo nitride
- Etch rate: as-depo. Mo > annealed Mo

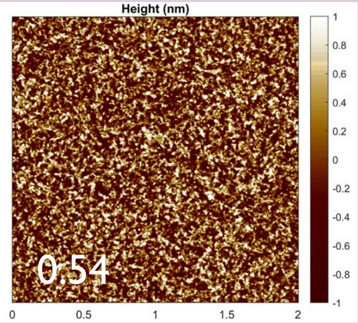
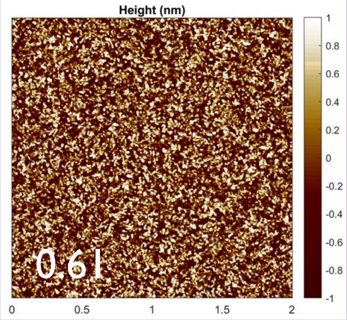
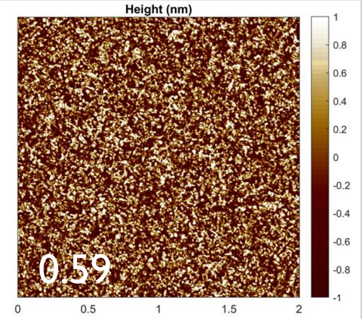
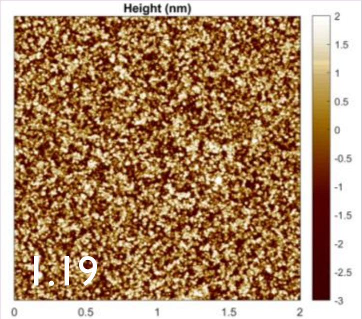
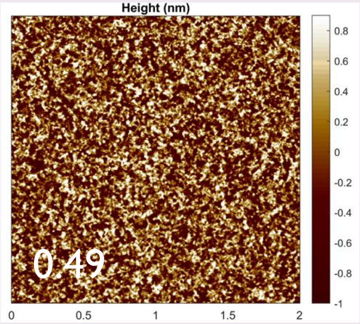
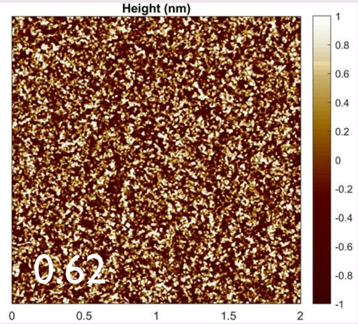
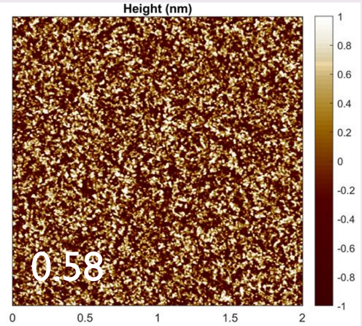
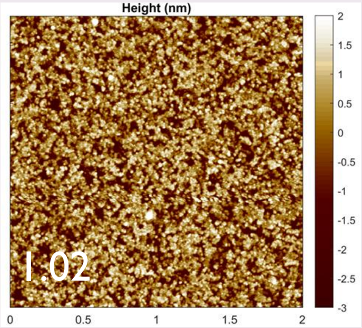
FG ANNEALING vs. AS-DEPO Mo





- As-depo and FGA
  - 0.05% HF and semi-aqueous mixture pH >12: no or very low etching
    - *Could be used for Mo cleaning; residues removal efficiency needs to be assessed*
  - Aqueous mixture pH <2: ~10 nm/min etch (as-depo and FGA/ 420 °C)
- Similar trend for N_2- and H_2-annealed Mo (results not shown)

SURFACE ROUGHNESS EVALUATION (AFM)

	No wet clean	0.05% HF/5 min	Semi-aq./2 min	Aqueous/2 min
As-depo. Rq (nm)	 0.54	 0.61	 0.59	 1.19
Forming Gas Rq (nm)	 0.49	 0.62	 0.58	 1.02

Low etching = minor increase of roughness

SUMMARY

- Annealing: formation of Mo nitride if Mo was annealed at temperatures ≥ 520 °C in forming gas, explained by a lower dissociation energy of N_2 molecule with the presence of H_2 in the mixture
- SC1: substantial etch of Mo; etch rate increased with the concentration of the oxidizer (H_2O_2) in the mixture
- 0.05% HF
  - Almost no Mo etching after 5 min
  - Could be used for PERR of Mo-containing stack, depending on (a) the stack structure (dielectrics) and (b) the plasma used for patterning
- Semi-aqueous mixture pH >12
  - Very low ER for Mo, typical ER ≤0.5 nm/min
  - Could be used for residue removal of Mo-containing stack; residue removal efficient needs to be assessed

imec

embracing a better life