2018 SPCC – Surface Preparation and Cleaning Conference

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Deposition of volatile chlorohydric acid on Copper wafer depending on humidity and HCl airborne concentration

April 10-11th, 2018 in Cambridge, MA, USA

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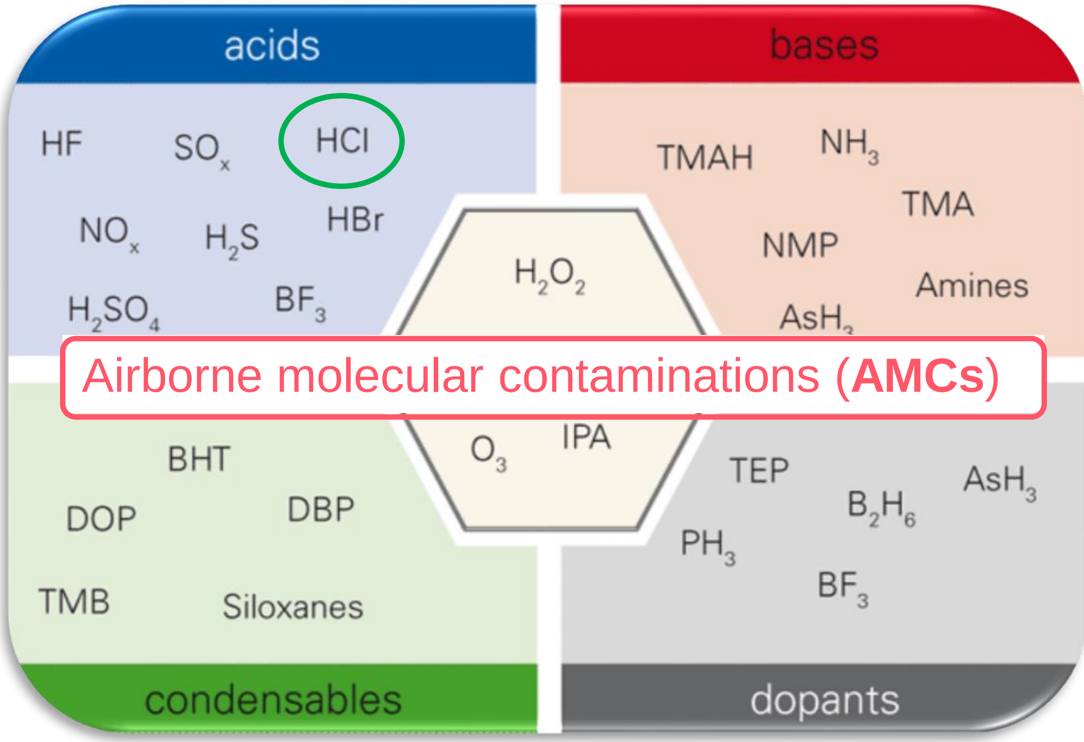
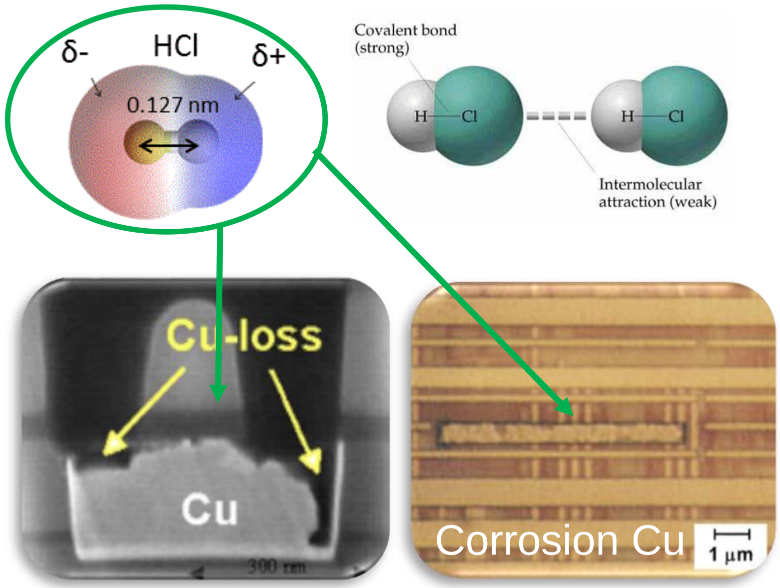
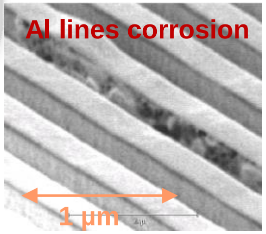
OUTLINE

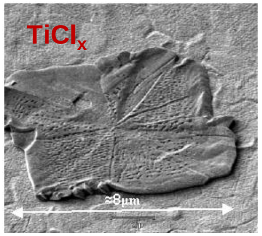
1. **Introduction**
2. **Experimental setup**
3. **Result - HCl deposition onto Cu 200 mm wafer**
   - Relative Humidity (RH<1%, RH 40% and RH 70%)
   - Airborne concentration (range of 20 – 400 ppbv)
4. **XPS characterization of contaminated Cu surfaces**
5. **HCl - Cu mathematical model**
6. **Conclusion**

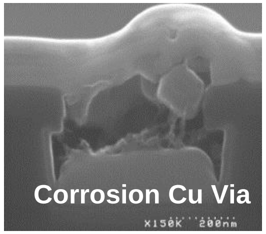
INTRODUCTION











- Cleaning: IPA, acetone, ethanol, terpenes HCl, HNO_3, NH_4OH, etc.
- Plasma etching gases/etched materials: (Cl_2/CCl_4 + Ar), HCl gas (36%) for Al
- Silicon vapor-phase epitaxy – HCl gas

Yield losses

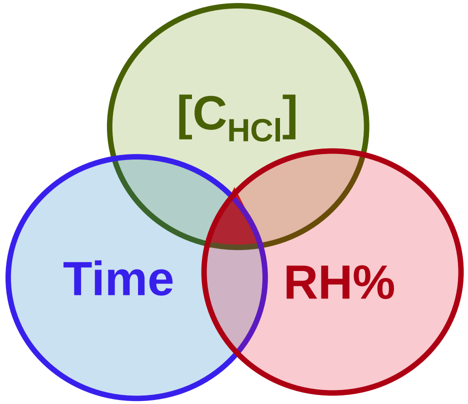
Limit AMCs effect

INTRODUCTION

0 – 400 ppbv

0 – 100 hours

0 – 70% RH



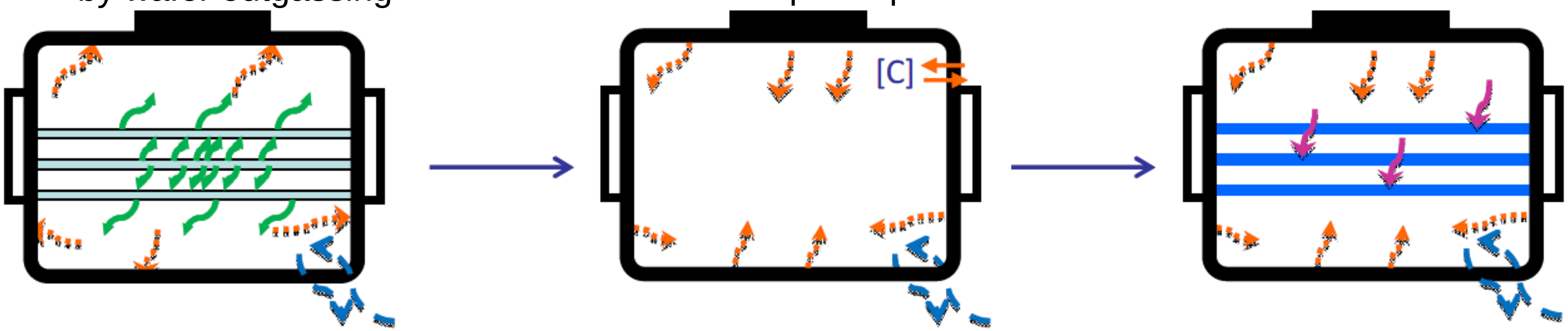
Deposition HCl on Cu

- **Fundamental research deposition HCl on Cu surface (200mm wafer)**

FOUP contamination by wafer outgassing

Contaminant outgassing FOUP → air up to equilibrium

Contamination transfer FOUP → Air → Wafer



Outgassing phase from wafer

FOUPs sorbed contaminants

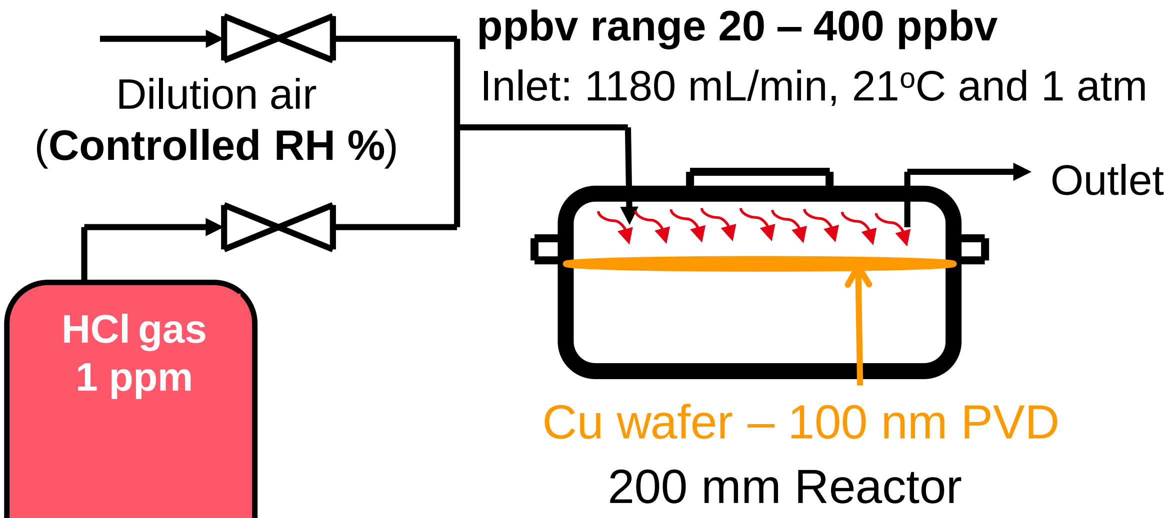
FOUPs outgassing contaminants

FOUPs outgassing

Transfer conta. on new wafers

- **Knowledge of [C_{HCl}] in airborne → minimizing defect**
- **Predicting storage time**

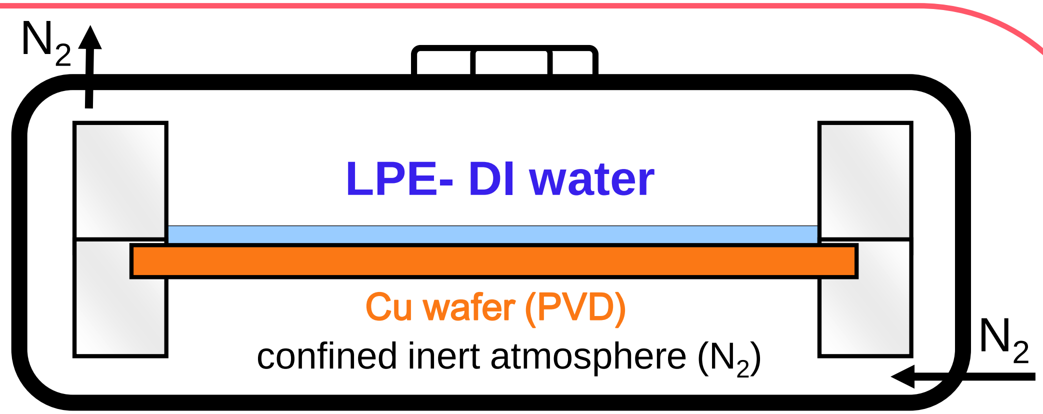
EXPERIMENTAL SETUP



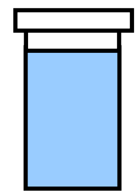
- Copper wafers: Physical Vapor Deposition (PVD) - 100nm copper
- Stored Cu wafer in polypropylene box (PVD process - HCl deposition)
- Diluted HCl gas by clean air

1st

EXPERIMENTAL SETUP



Liquid Phase Extraction
(LPE process)
Collect DI water on Cu wafer



Quantify ion Cl^- by
Ionic Chromatography (IC)

Cl^- ion deposition on Cu wafer

$HCl + H_2O \rightarrow Cl^- + H_3O^+$

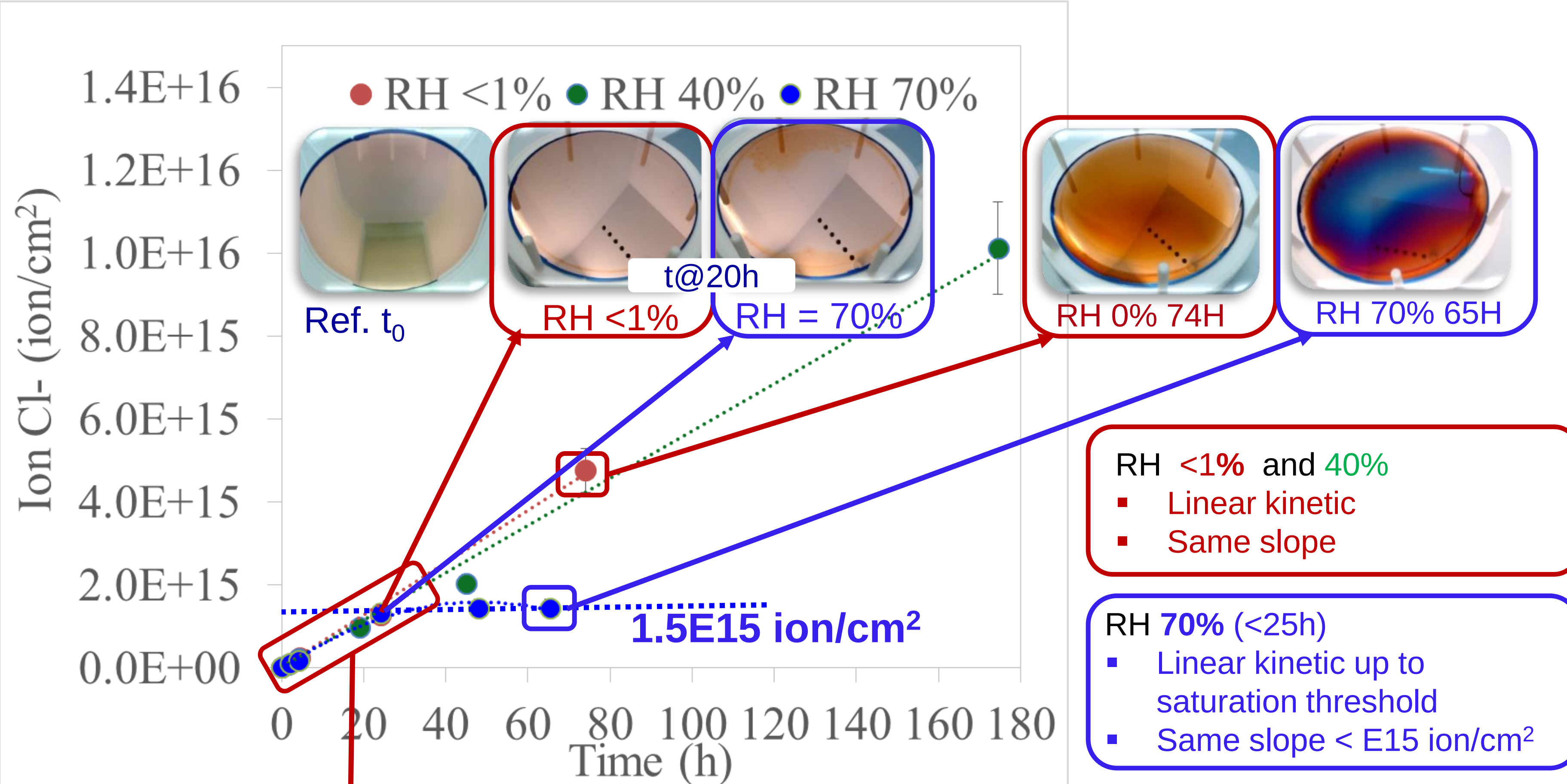
Efficiency of LPE-IC

- Collection by LPE is > 90% at first extraction(LPE1)
- LLD for Chloride: **< 1.0 x 10^{11} ion/cm^2 (0.05 ppbw)**

2nd

RESULT – HCL DEPOSITION ON CU WAFER

HCl Deposition Kinetic on Cu at 20 ppbv, **varying RH**



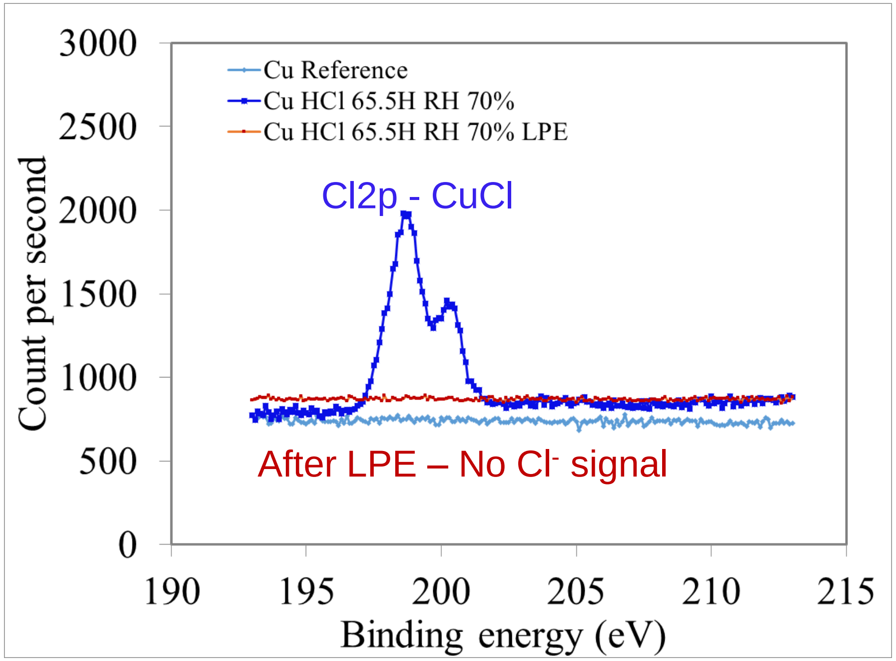
RH **<1%** and 40%
- Linear kinetic
- Same slope

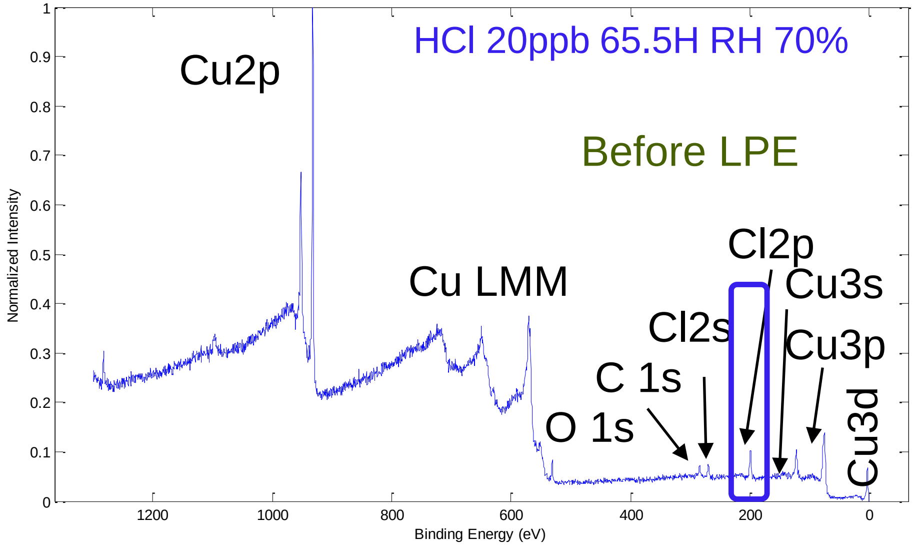
RH **70%** (<25h)
- Linear kinetic up to saturation threshold
- Same slope < E15 ion/cm²

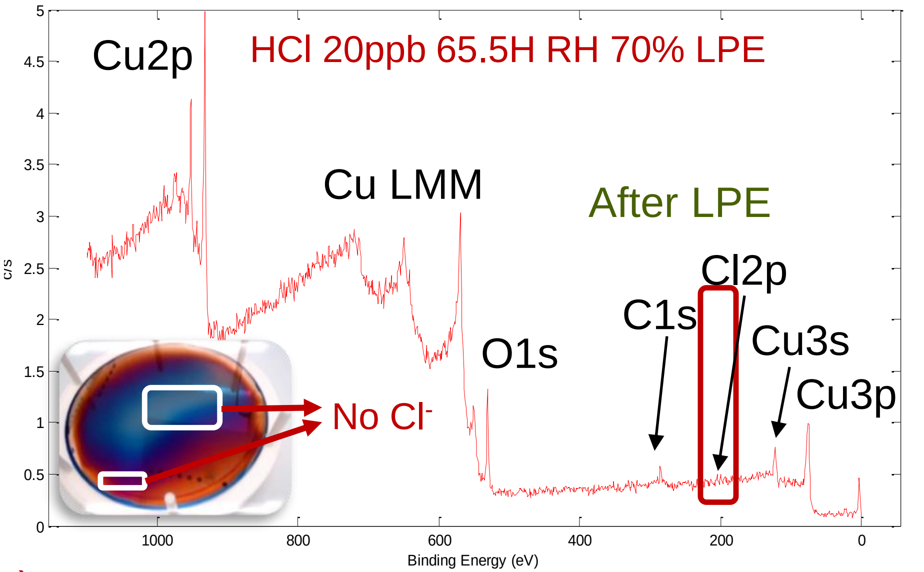
$[Cl^-]_{HCl@20ppbv} = 5.3E13*[Time] + [HCl]_{to}$

- ❑ Deposition HCl independent on RH (<40%)
- ❑ Threshold 1.5E15 ion/cm² (RH 70%) (monolayer)

RESULT - XPS ANALYSIS - EFFICIENCY OF LPE-IC





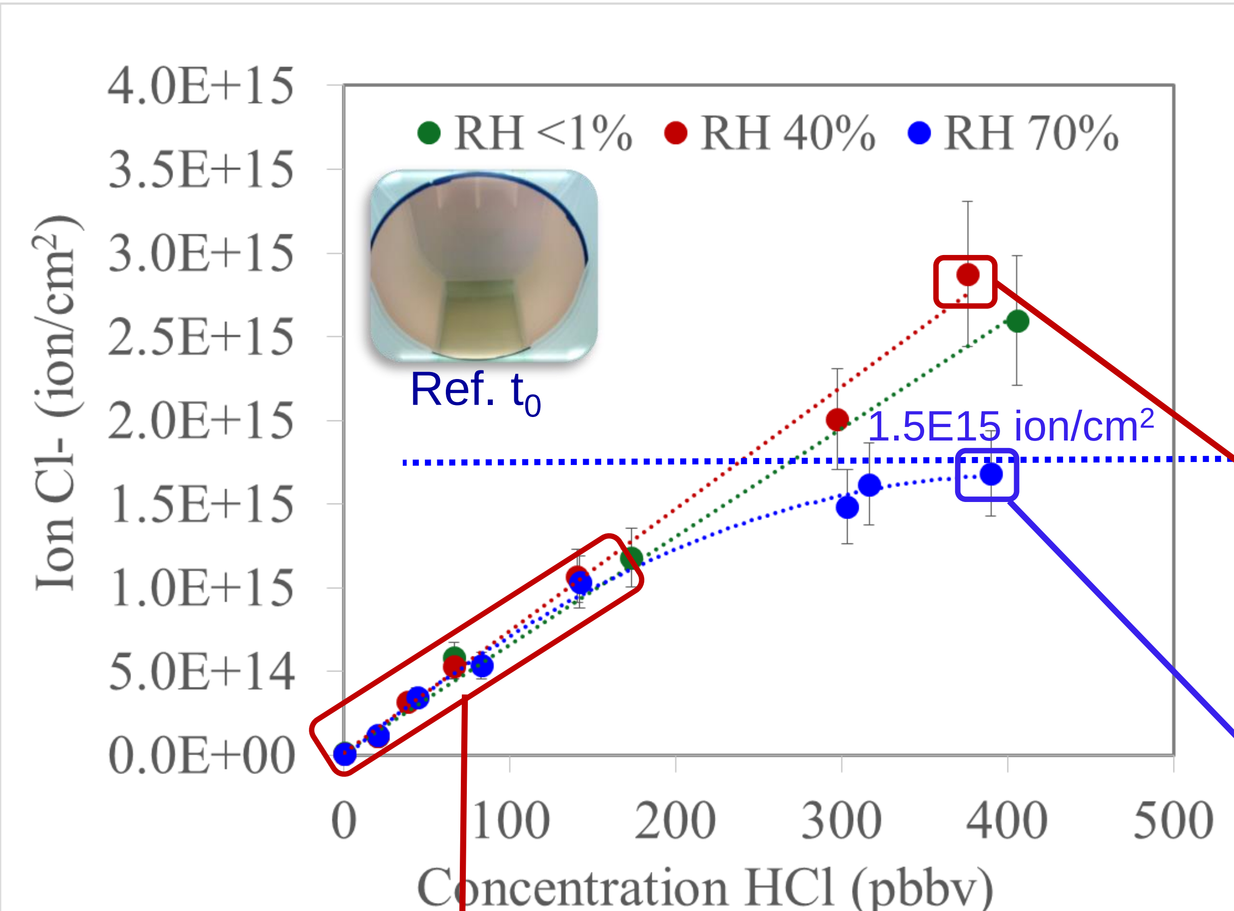


- ❑ Collection by LPE is > 95%
- ❑ Confirm by XPS (Before LPE – After LPE)
  - Before LPE: Cl2p peaks – double peak
  - After LPE: No Cl2p signal
- ❑ After LPE: No Cl2p detected signal - different spots of Cu wafer

Saturation level measured by IC is accurate
(no artifact measurement due to an insoluble Cl^- species)

RESULT – HCL DEPOSITION ON CU WAFER

HCl Deposition on Cu for 2h vs. **HCl Airborne Concentration**



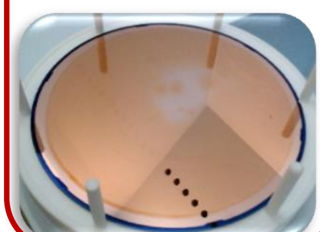
RH **<1%** and **40%**

- Linear behavior
- Slope difference not signifiant > 250 ppbv

RH = **70%** (< threshold)

- Linear behavior
- Same slope as RH **<1%** and **40%**

RH<1% 400 ppbv

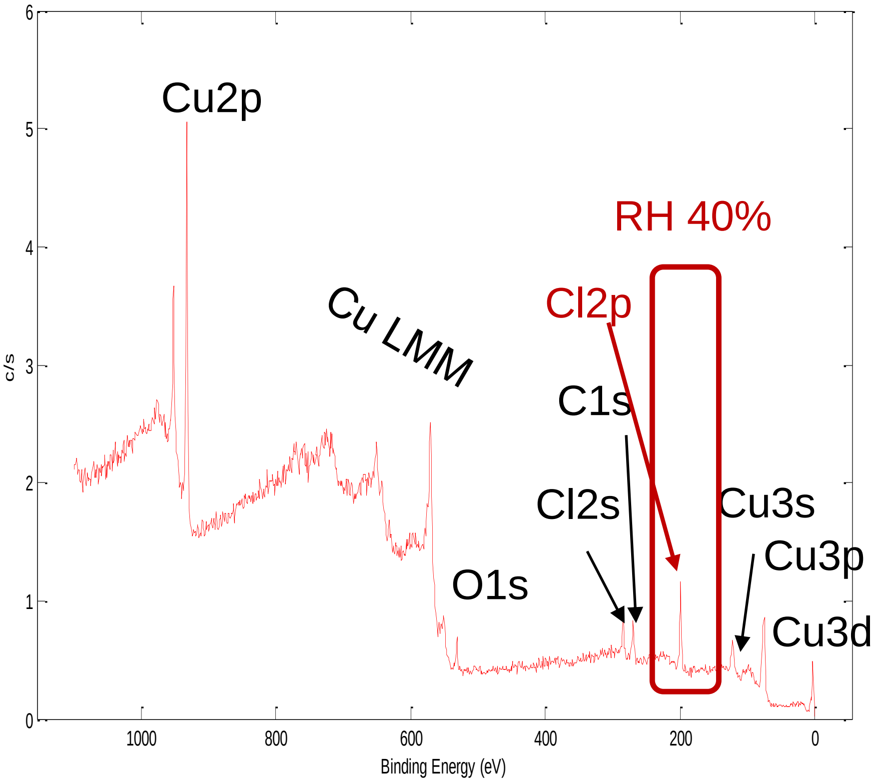


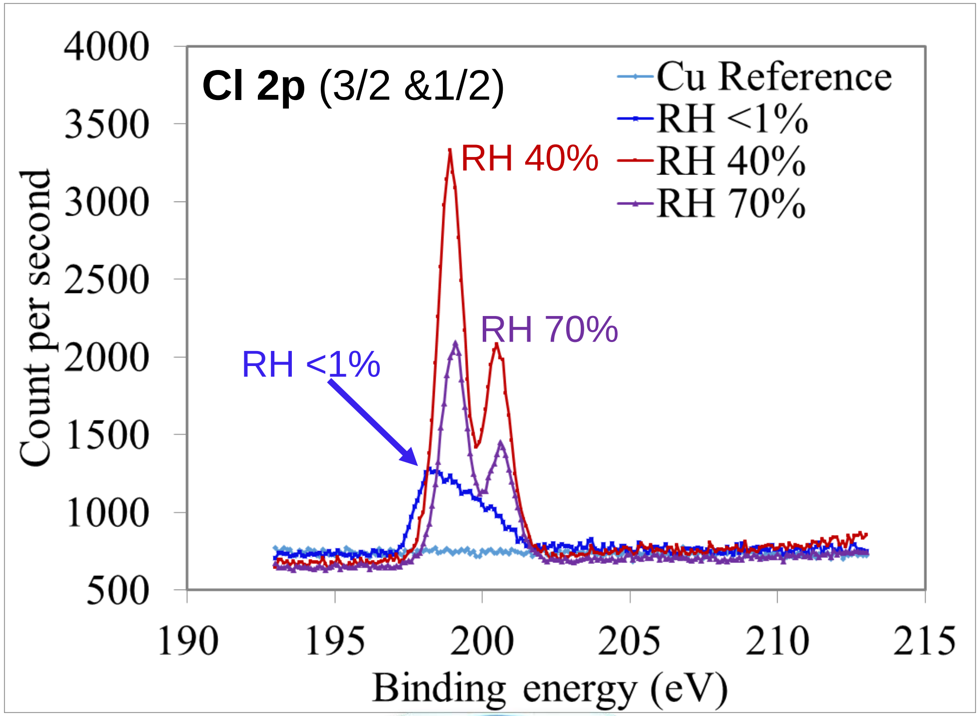
RH 70% 400ppbv

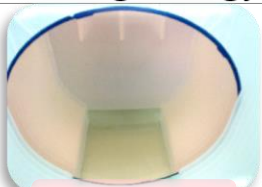
$[Cl^-]_{2H,\ time} = 6.9E12*[C_{HCl}] + [HCl]_{to}$

HCl threshold concentration showed at 1.5E15 ion/cm² (monolayer)

RESULT - XPS ANALYSIS







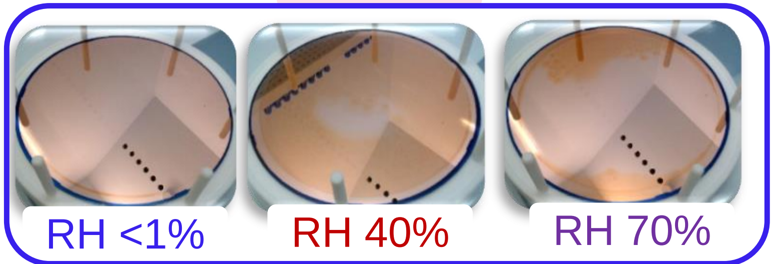
Cu Ref.

Cu contaminated at 20 ppbv, 24h, varying RH

→ IC measurement showed 1.5E15 Cl^-/cm^2 whatever RH%

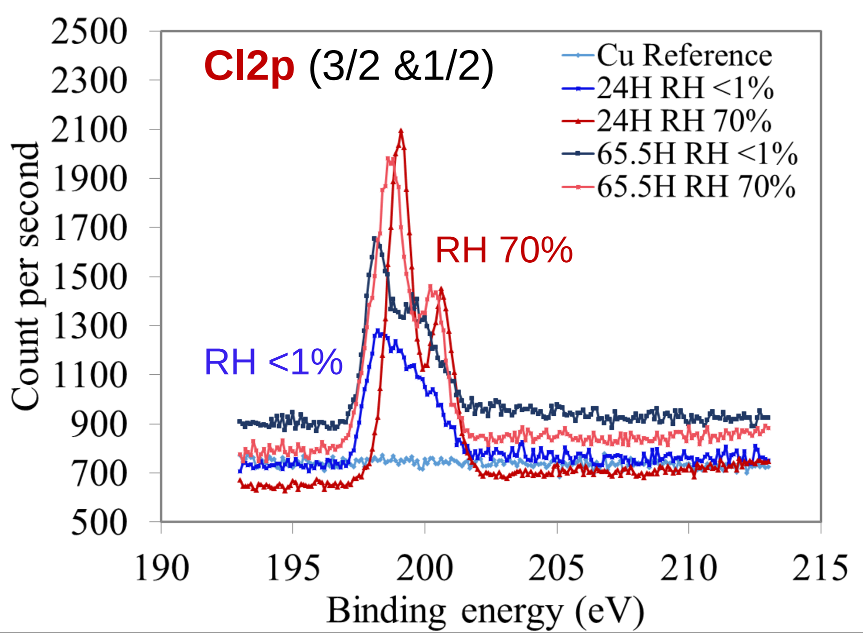
- ❑ XPS before LPE
  - → Bonding nature of Cl^- on Cu surface
- RH <1%: HCl_{gas} adsorption and Cl^- as CuCl
- RH 40%: Cl^- as CuCl
- RH 70%: Cl^- as CuCl

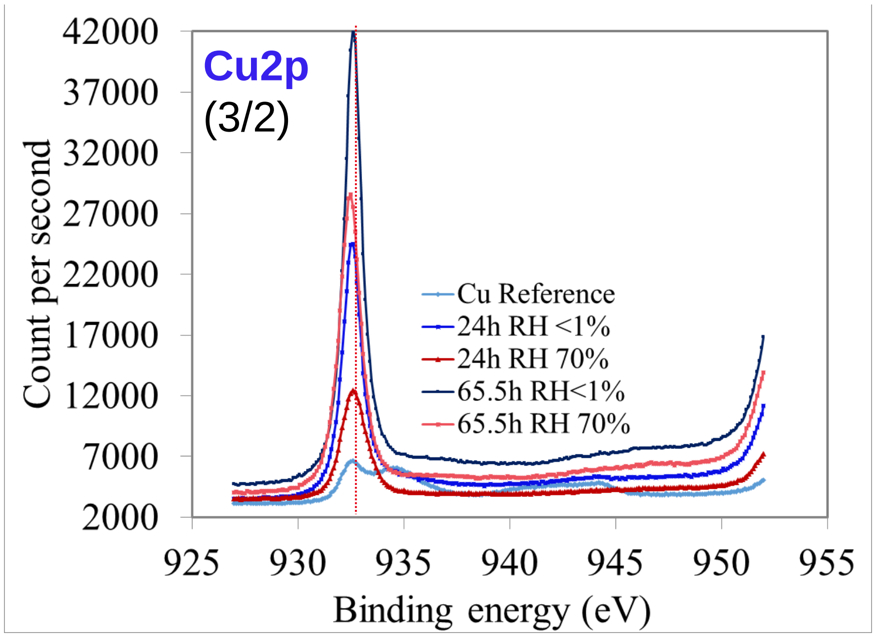
} → New Cu compounds (Color change)

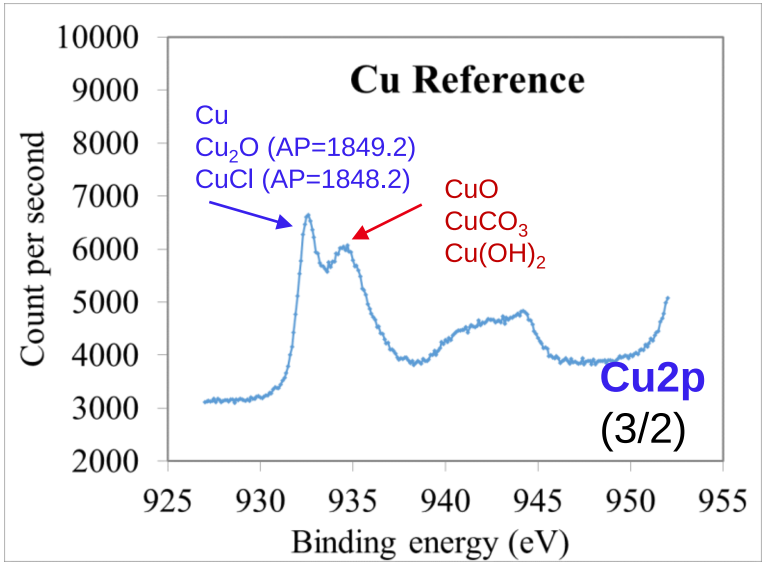


RESULT - XPS ANALYSIS

XPS results Cu-HCl – Extended exposure time: 24h vs. 66h



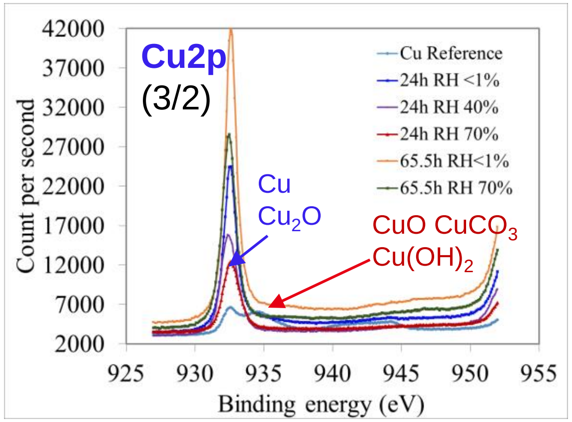


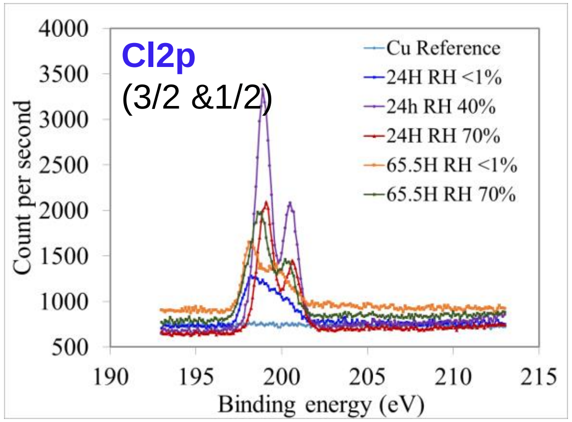


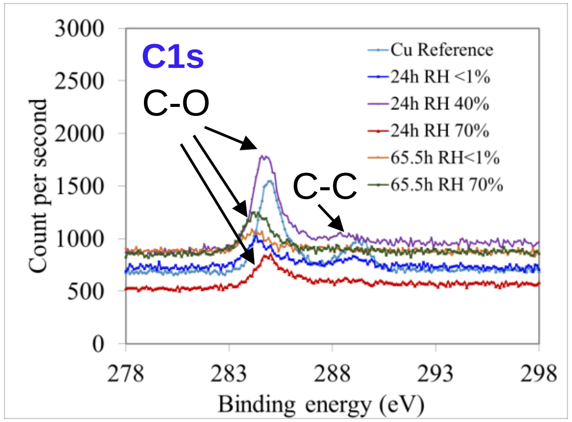
- RH 70%: Cl^- ~1.5E15 ion/cm^2 (by IC measurement)
- Extended exposure time
  - RH >1%: Cl^- as CuCl (65.5h), possibly HCl_{gas}
  - RH 70%: Cl^- as CuCl (65.5h)

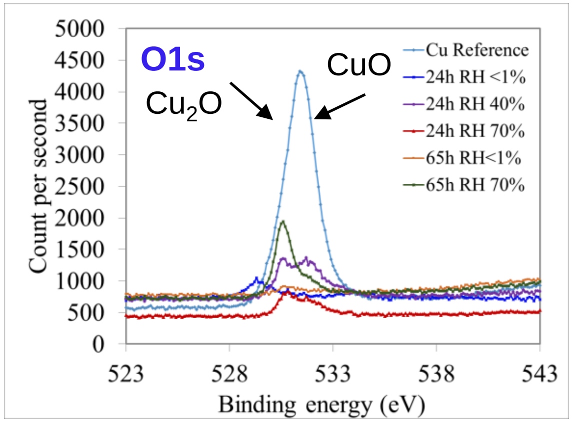
- Color
  - RH 70%→ Strong color change (multiple colors)
    → new Cu compound ($CuCl_x$,Cu_xO, Cu_xCO_3, $Cu(OH)_x$, etc.
  - RH >1% → slight color change (mostly CuCl)
- Oxidation state
  - XPS showed only Cu, Cu^+ peak (RH<1% and RH 70%) while Cu Ref. has Cu, Cu^+ and Cu^{+2}

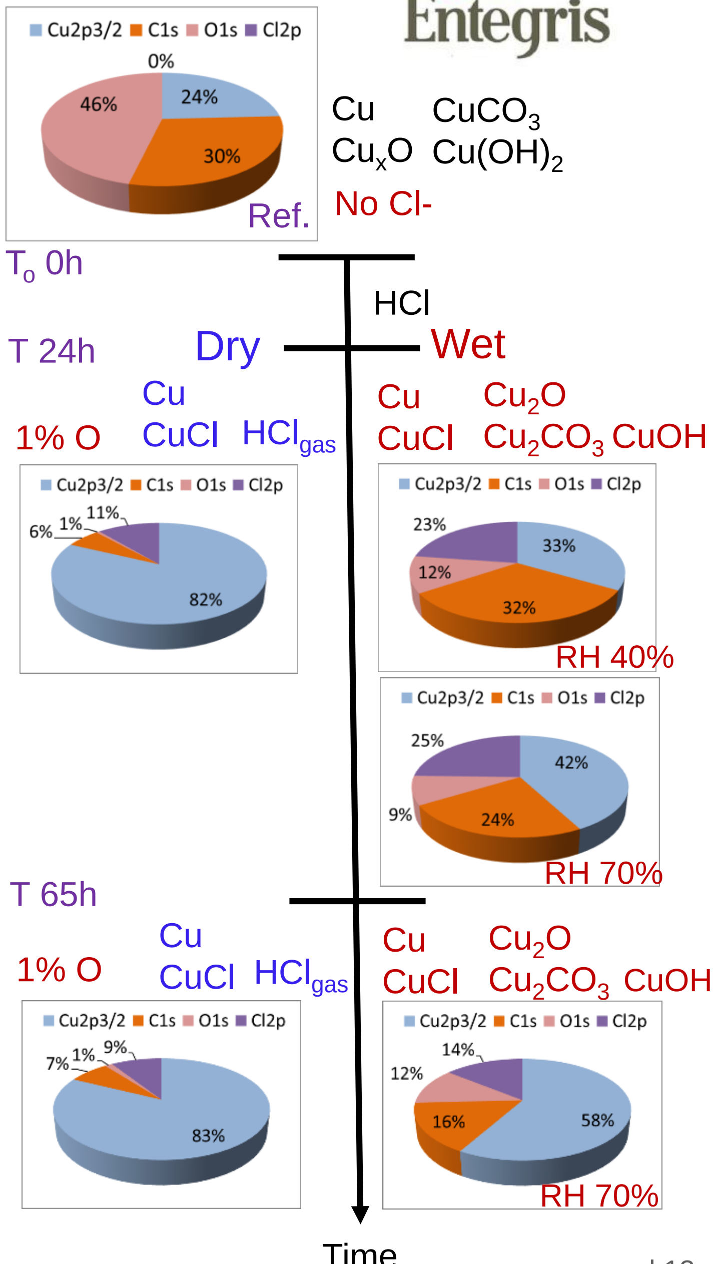
XPS ANALYSIS











Dry condition: RH<1% Cu|Cu_xO → Cu|CuCl

- HCl, Cl^- replaced Oxygen on Cu surface (Cu, CuCl, HCl, C-C organic); only Cu (I)

Wet condition: RH ≥ 40% Cu|Cu_xO → Cu|CuCl|Cu_xO|Cu_xCO_3, etc.

- HCl, Cl^- reacts CuO & Cu_2O; mainly Cu (I) (Cu, Cu_2O, CuCl, CuOH, Cu_2CO_3, possibly $CuCl_2^-$ (complex))

RESULT – HCL DEPOSITION ON CU WAFER

Linear mathematical model

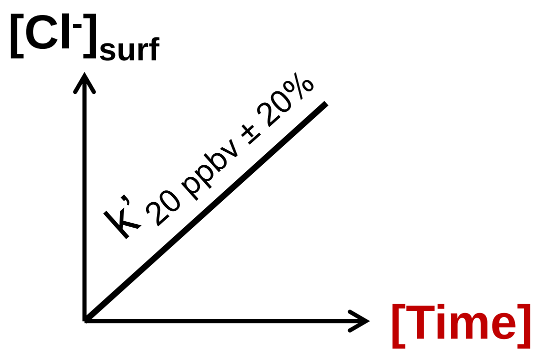
Predict HCl deposition on Cu wafer

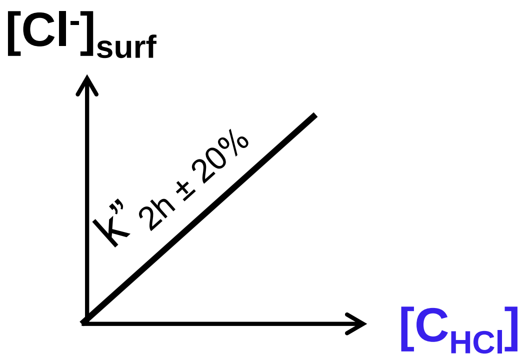
$[Cl^-]_{surf}$ = f([RH], $[C_{HCl}]$, [Time])

$[Cl^-]_{surf}$ independent [RH]

On the range [0 – 70%] RH

up to 1.5E15 at/cm^2





$[Cl^-]_{20ppbv}=5.3E13*[Time] + [Cl^-]_o$

$k'_{20\ ppbv}=k_c*20_{ppbv}$

$[Cl^-]_{2h}=6.9E12*[C_{HCl}] + [Cl^-]_o$

$k''_{2h} = k_h*2h$

$K_c = 2.65E12$

$K_h = 3.45E12$

$K_{c,h} = 3.05E12 \pm 20\%$

atom/cm^2.h.ppbv

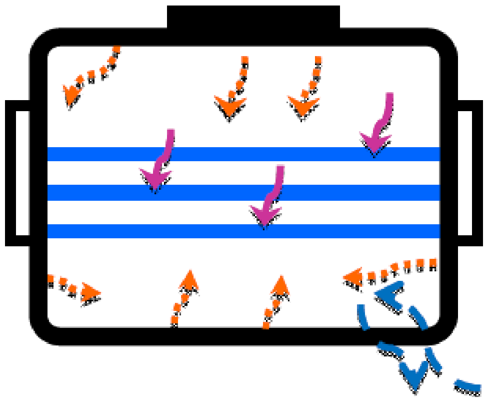
Linear model: $C_{surf} = K.C_g t$, with K = ± 20%

$[Cl^-]_{surf} = K_{C,h}[C_{HCl}][Time] + [Cl^-]_o$

With $K_{c,h} = 3.05E12 \pm 20\%$

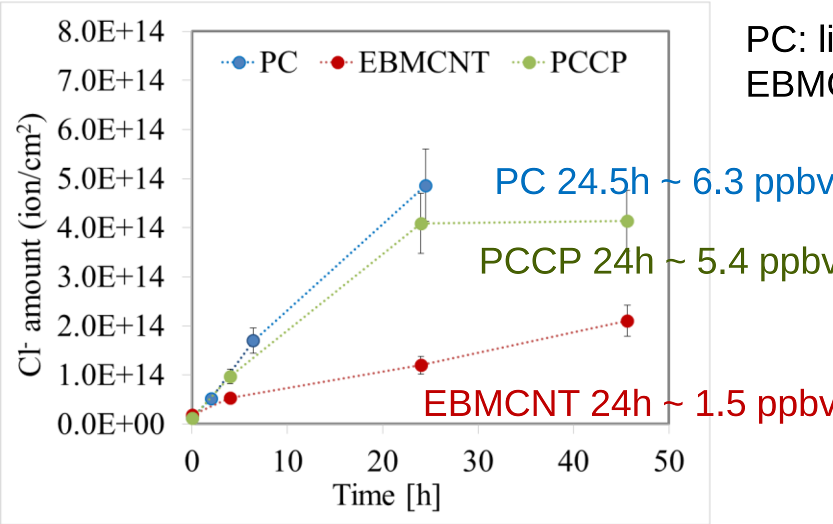
- For RH [0 – 70%] Linear model up to 1.5E15 Cl^-/cm^2
- RH < 40% : valid up to few E16 at/cm^2

APPLICATION LINEAR MODEL HCL – CU



FOUPs outgassing
Transfer conta. on Cu wafers

HCl transfer kinetic to Cu-coated wafer after FOUPs intentional contamination and purge step [*]



PC: linear
EBMCNT: linear

[*] F. Herran *et al. Micro electronic Engineering 169 (2017) 34 - 38*

- <u>Example 1</u>: Storage Cu wafer in different FOUPs (PC, PEI, PEEK, EBMCNT, etc.)
  - Known the $[Cl^-]$ amount transferred on Cu wafer at given time
    → Estimate the **average HCl airborne concentration** in FOUPs

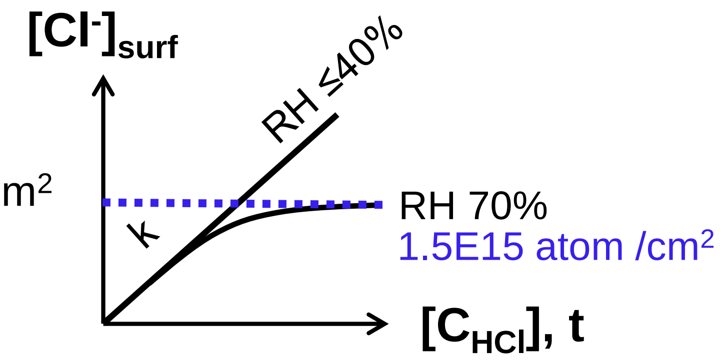
$$[Cl^-]_{surf} = k*[C_{HCl}]*[Time] + [Cl^-_o]$$

- <u>Example 2</u>: ITRS 2016 – limit Cl^- on Cu surface $E13\ Cl^-/cm^2$
  - Known the $[C_{HCl}]$ outgassing in certain FOUPs
    → Estimate the **maximum storage time**

CONCLUSIONS

- HCl deposition on Cu surface
  - Linear law versus $[HCl]_{air}$, Time
  - No dependent on RH% [0-70%] up to 1.5E15 atom /cm^2

$[Cl^-]_{surf} = k*\mathbf{[C_{HCl}]}*\mathbf{[Time]} + [Cl^-_o]$
With k = 3.05E12 ($Cl^-/cm^2.h.ppbv$) ± 20%



- Oxidation state of Cu after HCl exposition is mostly Cu^+

  Dry condition: RH <1%
  - HCl, Cl^- replaced Oxygen on Cu surface
    (Cu, CuCl, HCl, C-C organic); only Cu (I)

  Wet condition: RH ≥ 40%
  - HCl, Cl^- reacts CuO & Cu_2O; mainly Cu (I)
    (Cu, Cu_2O, CuCl, CuOH, Cu_2CO_3, possibly $CuCl_2^-$ (complex))

- Not recommend to store Cu wafer in high humidity (RH 70%)
- Model can be used as industrial tool to predict and to limit the yield losses caused by HCl in cleanroom conditions

Thanks for your attention

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