Effect of Additives in Diluted HF Solutions on Removal of Metal Contaminants and Particles on Silicon Wafer

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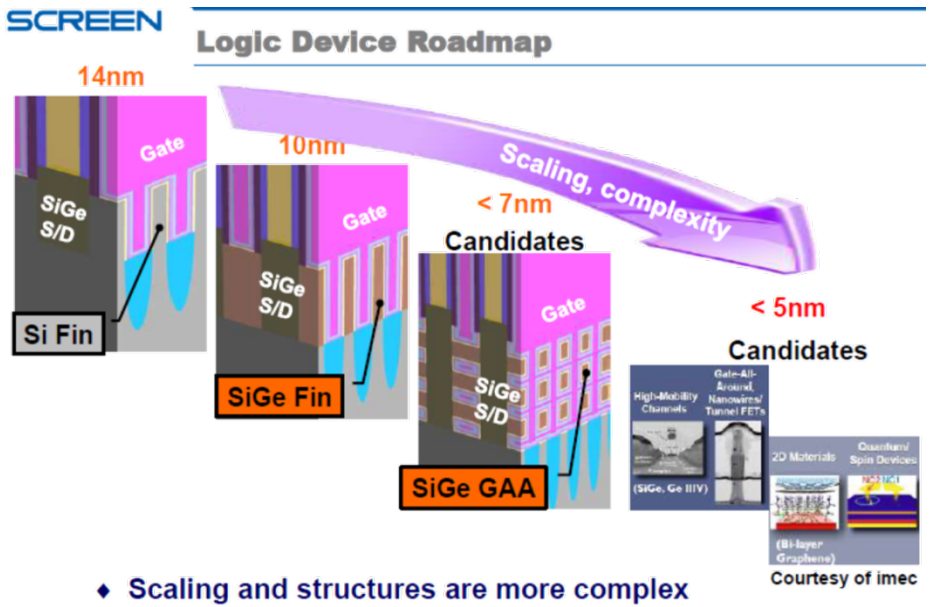
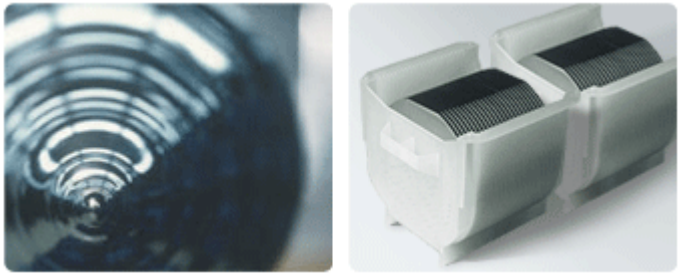
OUTLINE

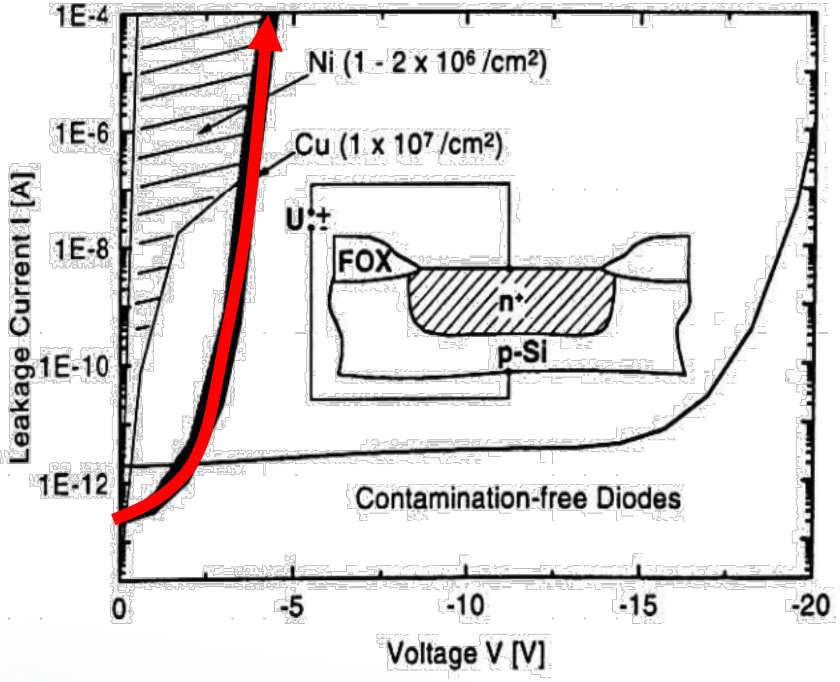
1. Research Background
   1) Research motivation
   2) Research objectives
2. Experimental Materials/Procedure
3. Experiment Results and Discussion
   1) Si surface change observation in HF/chelating agent
   2) Metal contamination cleaning by HF-based solution
4. Summary

Demands on particle/metal-free wafer in sub 10 nm devices



- Scaling and structures are more complex
- Damage-free particle removal much more important





- Electrical device degradation by metal contamination
  - Leakage current ↑ : Threshold voltage(V_T) ↑
- Requiring extremely low metal concentration in FOUP
  - Below **10^8 atoms/cm^2** is required in practice

Gargini, P. The International Technology Roadmap for Semiconductors (2015).
Takiyama, M. (2001). Influence of Metallic Contamination on LSI Fabrication. Nippon Steel Technical Report, 95-99.

Issues in conventional RCA cleaning

SC1 last: Metal ions (10^8 atoms/cm^2)

- **Dissolved metal precipitation** (Al, Cu, Ni…)
- Subsequent metal cleaning process is necessary

SC2 last : Particle redeposition (<50nm, no particles)

- Inefficient for noble metal cleaning (e.g. Cu, Ti, Ni)

  ➔ Remaining residual metal contaminants
- **Particle redeposition** by acidic atmosphere

Simultaneous Removal of both metal and particles,

Chemical Modification of SC1 or SC2

Gottschalk, C., & Schweckendiek, J. (2004). Paper reprinted from MICRO, Canon Communications LLC Publication, March.

Research objective

To control the metallic/pariculate contaminants on the silicon wafer surface by optimizing the concentration of HF, DIO_3 and chelating agent

1. Cu and Al metal contamination method and detection by AFM
2. Evaluation chelating agent and ozone in DHF solutions

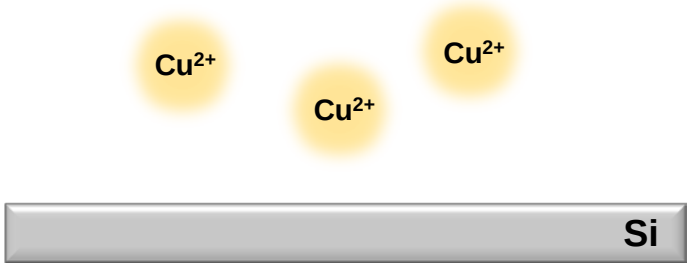
This research reports only on metal removal!

Experiment Materials And Procedure

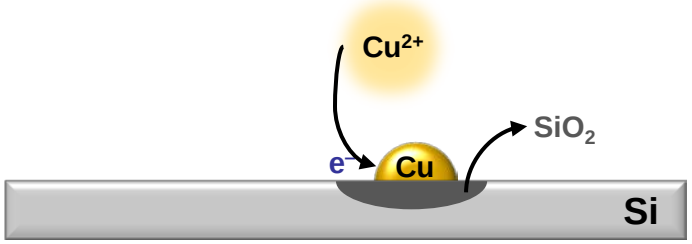
Copper growth on Si wafer

Cu formation :: Electrochemical reaction

1) Presence of Cu^{2+} and Si wafer



2) Cu nucleation by oxidizing Si through high reduction potential



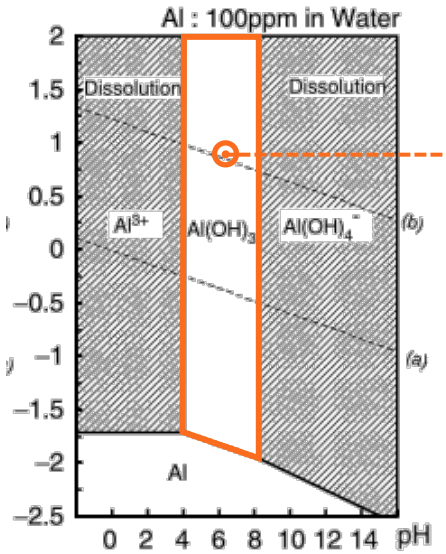
Standard reduction potential (V vs. NHE)	
$Cu^{2+} + 2e^- \rightleftarrows Cu$	0.34
$SiO_2 + 4H^+ + 4e \rightleftarrows Si + 2H_2O$	– 0.84

3) Continuous Cu particle growth

Hitoshi Morinaga, Makoto Suyama, and Tadahiro Ohmi, J. Electrochem., Vol. 141, No. 10 (1994)

Aluminum growth on Si wafer

Aluminum hydroxide formation



< Aluminum Pourbaix diagram (25 °C) >

- **$Al(OH)_3$** : Stable phase of Al in neutral solution

$$Al\ (s) + OH^- \rightarrow Al(OH)_{ads} + e^-$$

$$Al(OH)_{ads} + OH^- \rightarrow Al(OH)_{2ads} + e^-$$

$$Al(OH)_{2ads} + OH^- \rightarrow Al(OH)_{3ads} + e^-$$

Standard reduction potential (V vs. NHE)	
$SiO_2 + 4H^+ + 4e \rightleftarrows Si + 2H_2O$	– 0.84
$Al_2(OH)_3 + 3e^- \rightleftarrows 2Al + 3OH^-$	– 1.66

Aluminum oxide transformation

- $Al(OH)_3$ transformation into $Al_2O_3{\cdot}3H_2O$ compound in neutral solution
- **Precipitation formation** within SiO_2 film

$$2Al + 6H_2O \rightarrow 2Al(OH)_{3ads} + 6e^- + 6H^+ \rightarrow Al_2O_3{\cdot}3H_2O + 3H_2$$

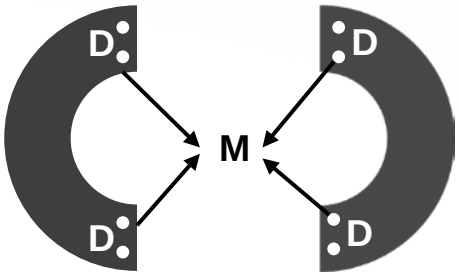
Beardmore, J., Lopez, X., Mujika, J. I., & Exley, C. (2016). What is the mechanism of formation of hydroxyaluminosilicates?. Scientific Reports, 6.
Giza, Effect of Aging on the Corrosion of Aluminum Alloy 6061, Faculty of Engineering Cairo University (2010)

Chelating agent

Chelating effect

- **What is chelate?**

  Complex compound formation with metal ion making covalent bonds by polydentate ligand (Electron donors)



< Formation of chelate by polydentate ligand >

- **Chelating effect**

  1) Stability improvement of complex by chelate rings when metal ion and ligands are combined

  2) The more ligands exist, the more reactions occur

<Chelating agents according to the metal species >

Metal	Chelating reagents
Al	F^-, $C_2O_4^{2-}$, OAc^-, cit, tart, EDTA, OH^-, BAL, NTE
Cu	NH_3, I^-, SCN^-, CN^-, $S_2O_3^{2-}$, TU, EDTA, S^{2-}, DTC, DHG, BAL, $C_2O_4^{2-}$, cit, tart, NTA, TG, NTE, tren, penten

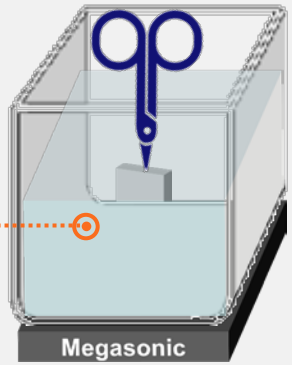
K. Burger, Organic Reagents in Metal Analysis, Vol. 54, p 39~41 (1973)

Metal contamination method

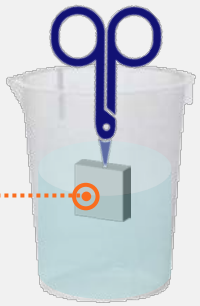
Experiment procedures

Pretreatment

SC1



DHF



Metal contamination

Condition

1. **Temperature :** 70°C
2. **Time :** 10 min.
3. **Concentration :**

   $NH_4OH:H_2O_2:DIW = 1:2:50$
4. **Megasonic power :** 1MHz, 600W

Condition

1. **Temperature :** 25°C
2. **Time :** 5 min.
3. **Concentration :**

   HF : DIW = 1:100

Condition

1.Cu contamination :

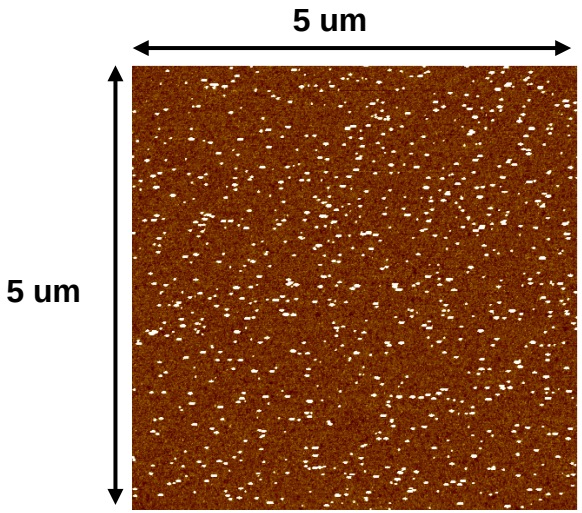
Wafer dipping in **$CuCl_2$ 500ppb** solution for 1min.

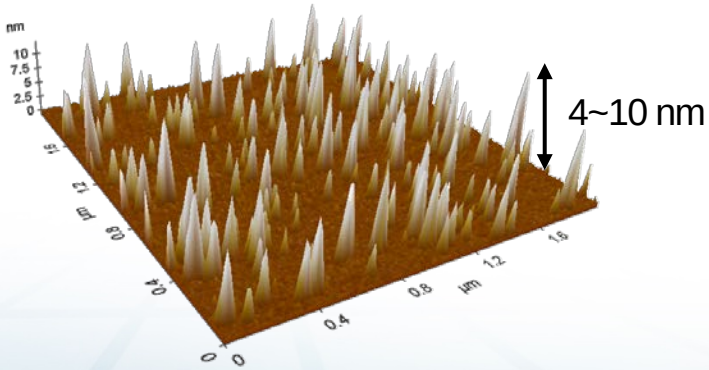
2. Al contamination :

Wafer dipping in **$AlCl_3$ 100~300ppm** solution for 1min.

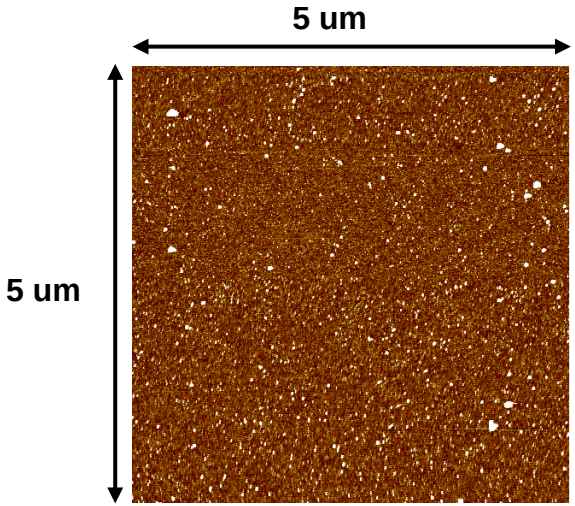
AFM images after metal contamination

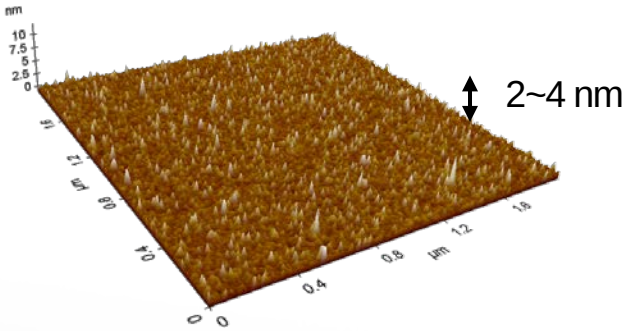
Cu contamination
(500 ppb, dipping for 1 min.)





Al contamination
(100~300 ppm, dipping for 1 min.)

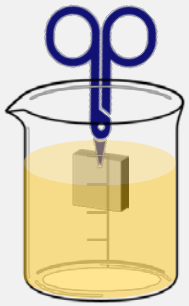




Metal removal by chelating agents

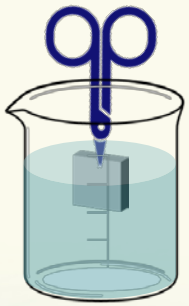
Experiment procedures

Metal particle contamination



Cu Contamination solution

- Solution : **$CuCl_2$ + DIW, 500ppb**
- Dipping for **1** min.
- Subsequent analysis using **AFM**



Al Contamination solution

- Solution : **$AlCl_3$ + DIW, 100-300ppm**
- Dipping for **1** min.
- Subsequent analysis using **AFM**

Contamination cleaning

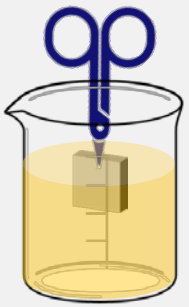
HF + Chelating agent

- **0.05wt% HF + Chelating agent**
- Dipping for **5** min.
- DIW rinsing for 1 min.
- Subsequent analysis using **AFM**

Metal removal by HF/DIO_3

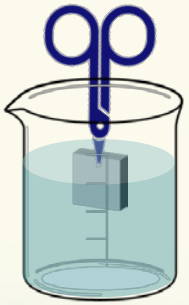
Experiment procedures

Metal particle contamination



Cu Contamination solution

- Solution : **$CuCl_2$ + DIW, 500ppb**
- Dipping for **1** min.
- Subsequent analysis using **AFM**



Al Contamination solution

- Solution : **$AlCl_3$ + DIW, 100-300ppm**
- Dipping for **1** min.
- Subsequent analysis using **AFM**

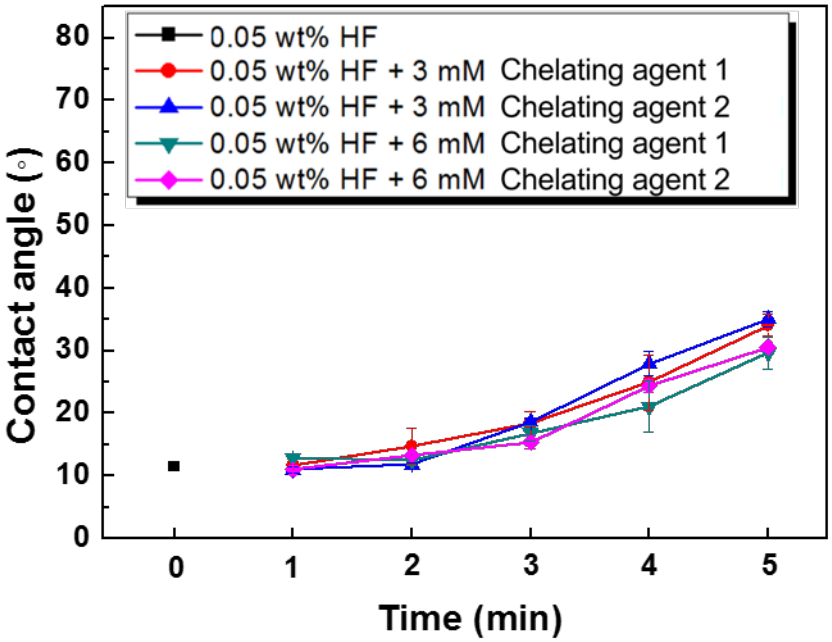
Contamination cleaning

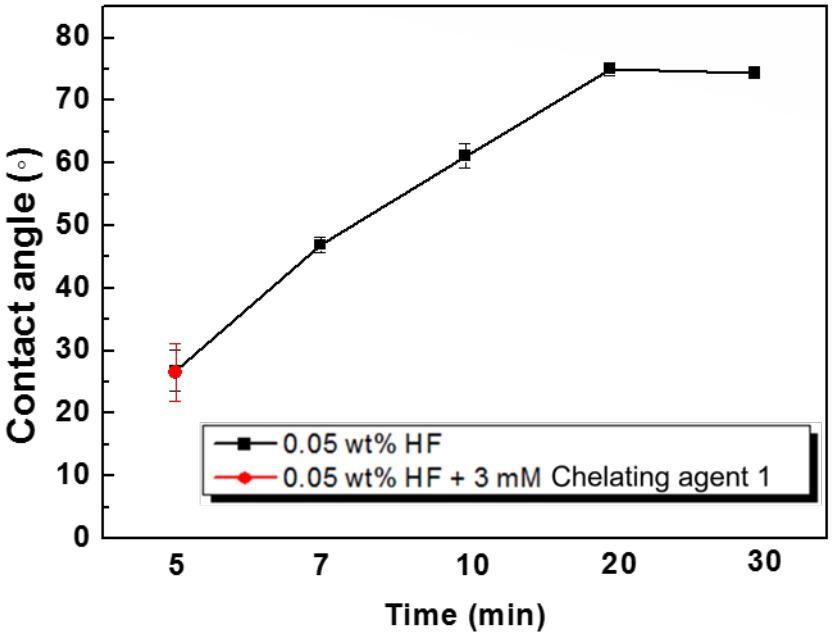
HF + DIO_3

- **0.05wt% HF + 10ppm DIO_3**
- Dipping for **5** min.
- Etch rate = 2.3 Å/min.
- Subsequent analysis using **AFM**

Experiment Results and Discussion

Effect of Chelating agent on Contact angle





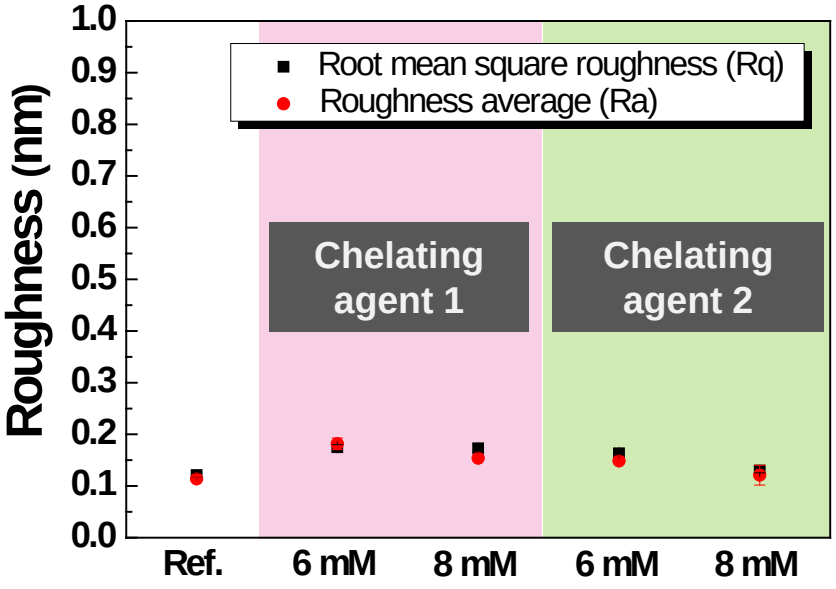
- No contact angle change by chelating agents

➔ **No surface modification effects** by chelating agent species and concentration

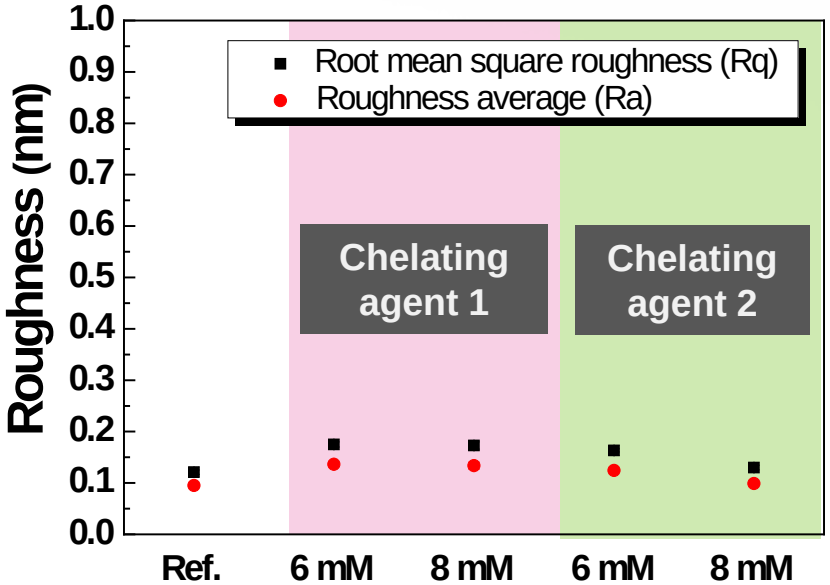
- Hydrophobic change by applying HF based solution

➔ Residual SiO_2 exists until 5 min : Minimum cleaning condition to maintain **hydrophilicity**

Surface roughness change



In 1 um X 1 um (in 0.05 wt% HF, 5 min)

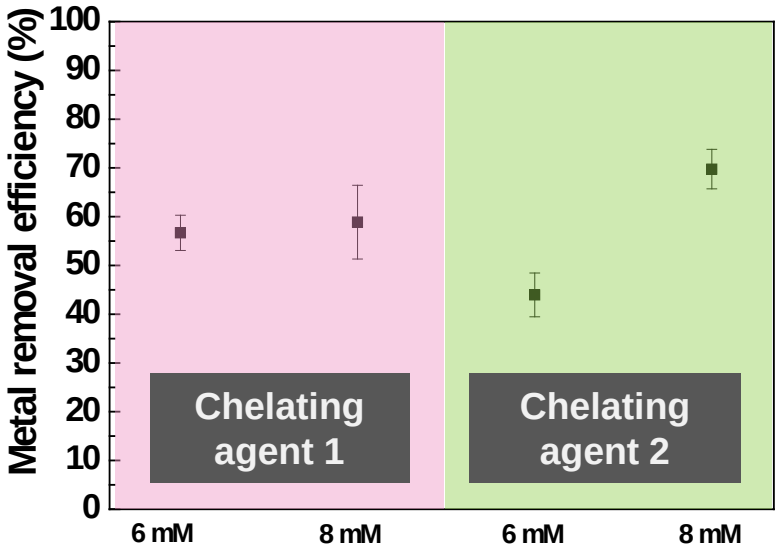


In 5 um X 5 um (in 0.05 wt% HF, 5 min)

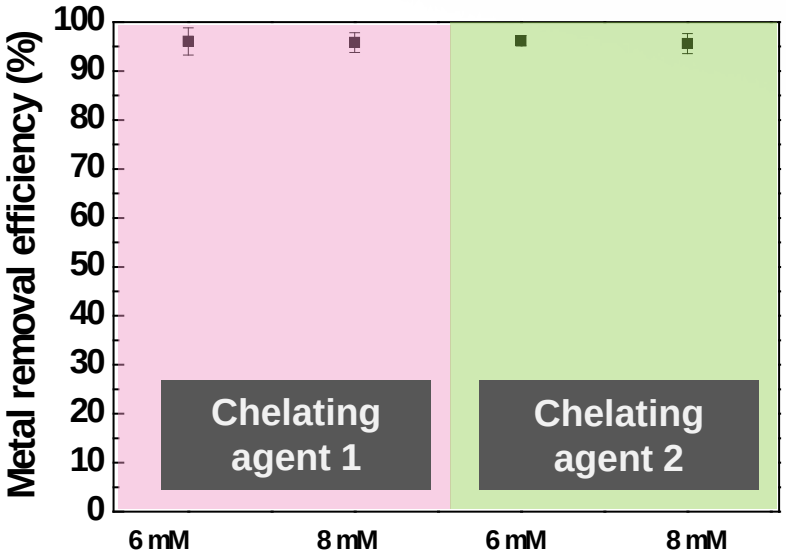
- Roughness measurement after treating the surface with HF/chelating agent using AFM
- **No roughness change** despite the chelating agent species and concentration change

Metal removal by Chelating agents

Metal removal efficiency evaluation



Cu removal in 0.05 wt% HF, 5 min



Al removal in 0.05 wt% HF, 5 min

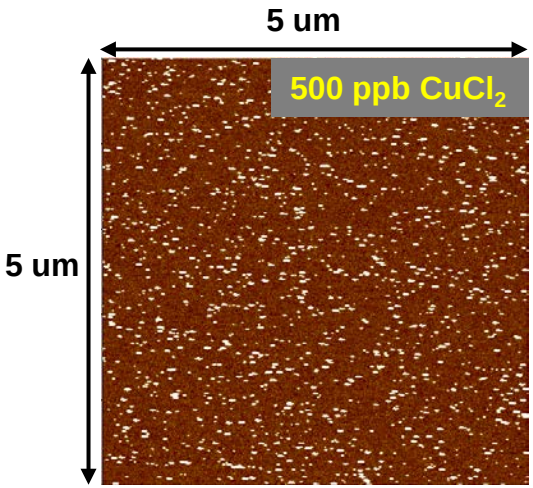
- Cu MRE at 6 mM : **Chelating agent 1 (57%)** > Chelating agent 2 (44%)

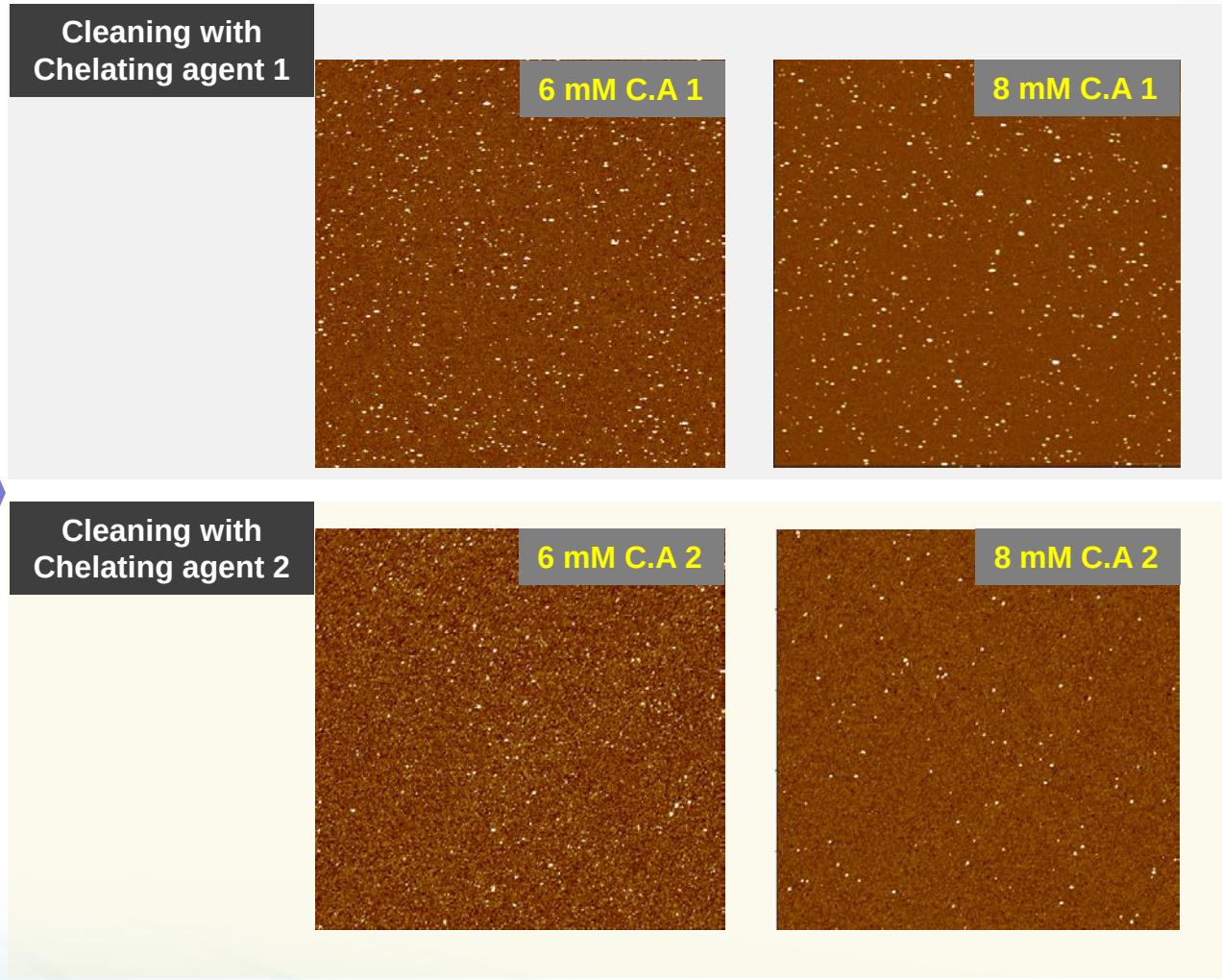
  → More functional groups in chelating agent 1 ⇔ Higher metal removal efficiency
- Cu MRE at 8 mM : Chelating agent 1 (59%) < **Chelating agent 2 (70%)**

  → Less dissociation in low pH ⇔ Lower metal removal efficiency
- Al removal : Showing over **90%** of MRE supported by both chelating agent and HF

AFM images after metal contamination removal

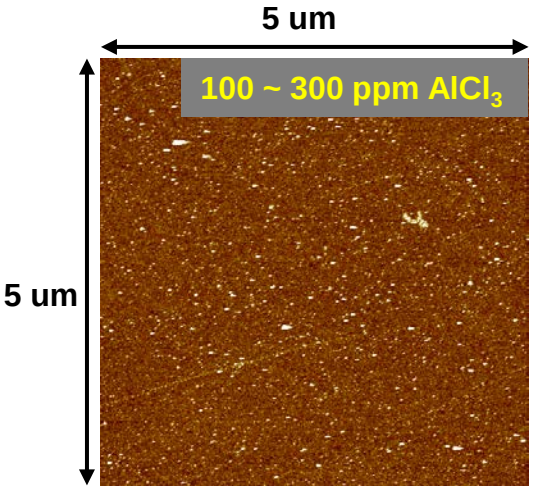
Cu contamination cleaning (in 0.05 wt% HF)

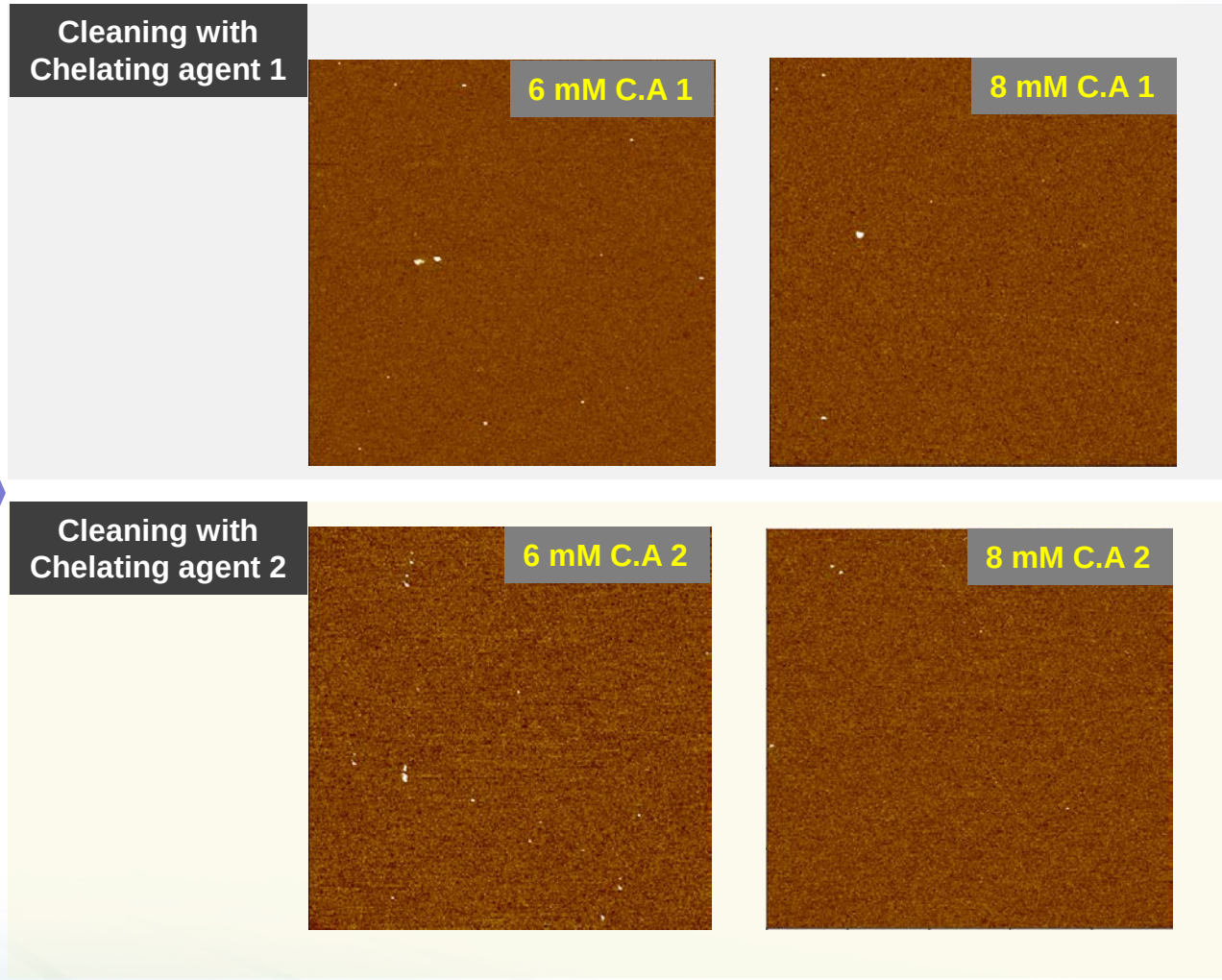




AFM images after metal contamination removal

Al contamination cleaning (in 0.05 wt% HF)



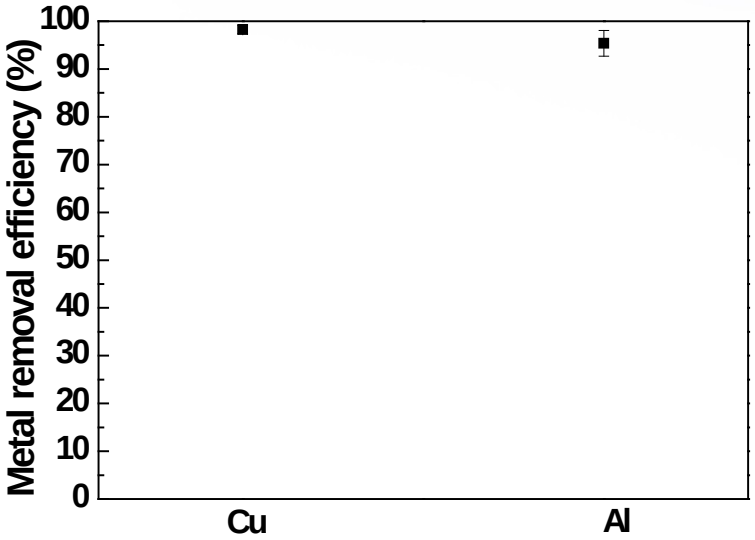


Metal removal by HF/DIO_3

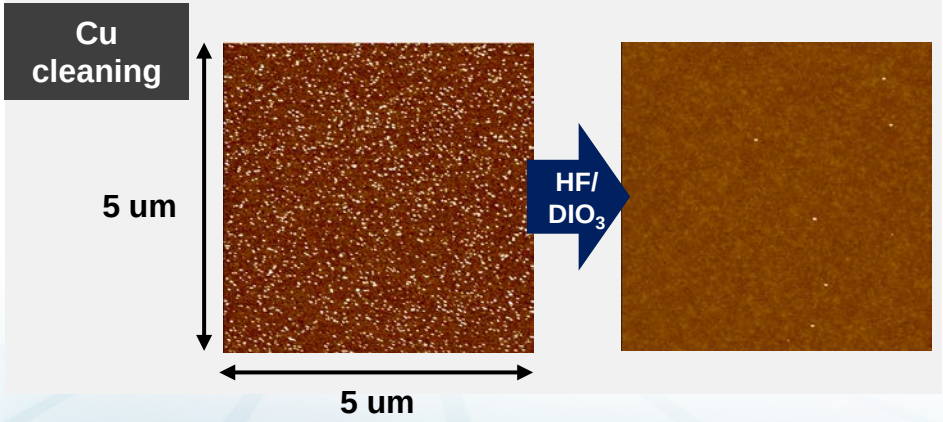
Metal removal efficiency evaluation

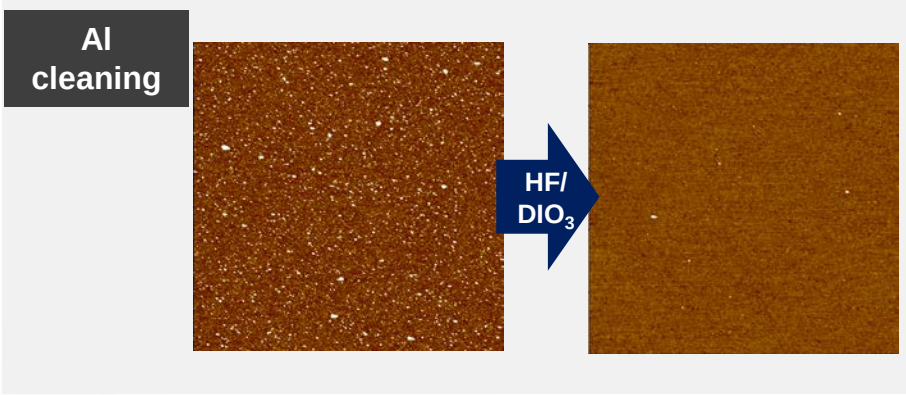
- Showing over **90%** of MRE for Cu and Al both
- Much higher MRE compared to chelating agent

➔ Expected to show **higher MRE than any conditions** of HF/DIO_3



AFM images after HF/DIO_3 cleaning





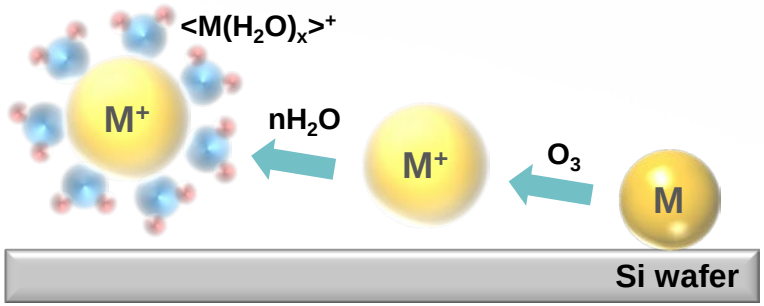
HF/Ozone solution

Metal removal by ozone

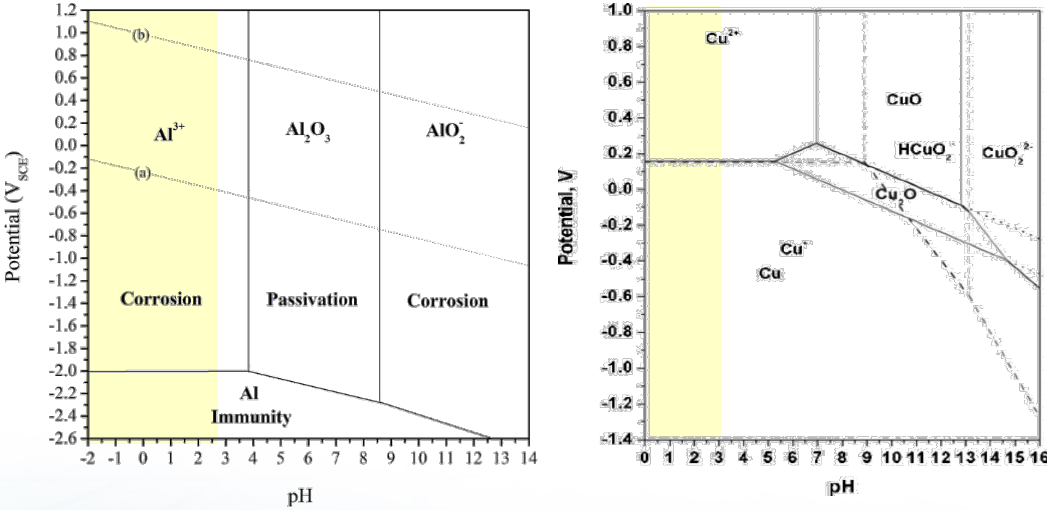
- Metal oxidation by O_3

1) Metallic impurity can be removed by oxidation by O_3
2) Ionization ↑ in **acidic** region :

   Complex formation of **$[M(H_2O)_x]^+$ ↑**



< Metal oxidation & removal mechanism by O_3 >



< Pourbaix diagram for Al and Cu >

HF	DIO_3	pH
0.05 wt%	0 ppm	3.18
	10 ppm	3.03
	20 ppm	2.96
	30 ppm	3.03
0.1 wt%	0 ppm	3.07
	30 ppm	3.08
Red-ox potential	$Cu^{2+} + 2e^- \rightleftarrows Cu$ / 0.34V	
	$Al_2(OH)_3 + 3e^- \rightleftarrows 2Al + 3OH^-$ / -1.66V	

Hyoseob Y, Kunkul R. A study of Si-wafer cleaning by electrolyzed water. Korea journal of materials research. Vol. 11, No.4 (2001)
Oh, Y. J., Park, G. S., & Chung, C. H. (2006). Journal of the Electrochemical Society, 153(7), G617-G621.
Sukiman, N. L., Hughes, A. E., Thompson, G. E., Mol, J. M. C., Birbilis, N., Garcia, S. J., & Zhou, X. (2012), techniques and developments. INTECH Open Access Publisher.

HF/Ozone solution

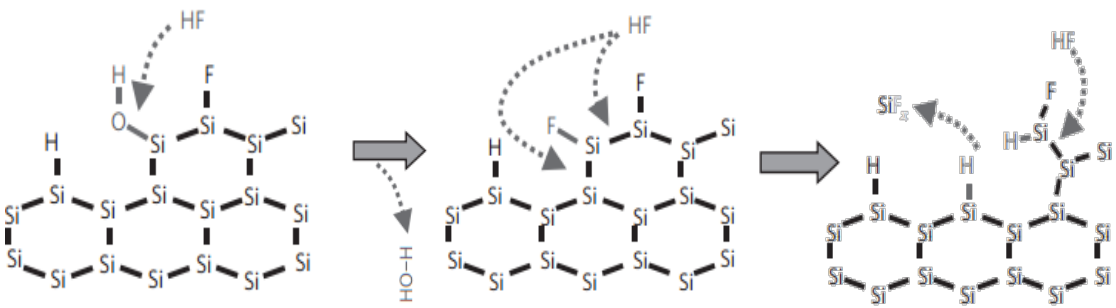
SiO_2 growth in DIO_3

- SiO_2 formation by higher red-ox potential of O_3

$$Si + 2O_3 \rightarrow SiO_2 + 2O_2$$
$$Si + O_2 \rightarrow SiO_2$$

Standard reduction potential (V vs. NHE)	
$O_3 + 2H^+ + 2e^- \rightleftarrows O_2 + H_2O$	2.076
$SiO_2 + 4H^+ + 4e \rightleftarrows Si + 2H_2O$	– 0.84

SiO_2 removal by HF



$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$$
$$H_2SiF_6 \rightarrow 2HF + SiF_4$$

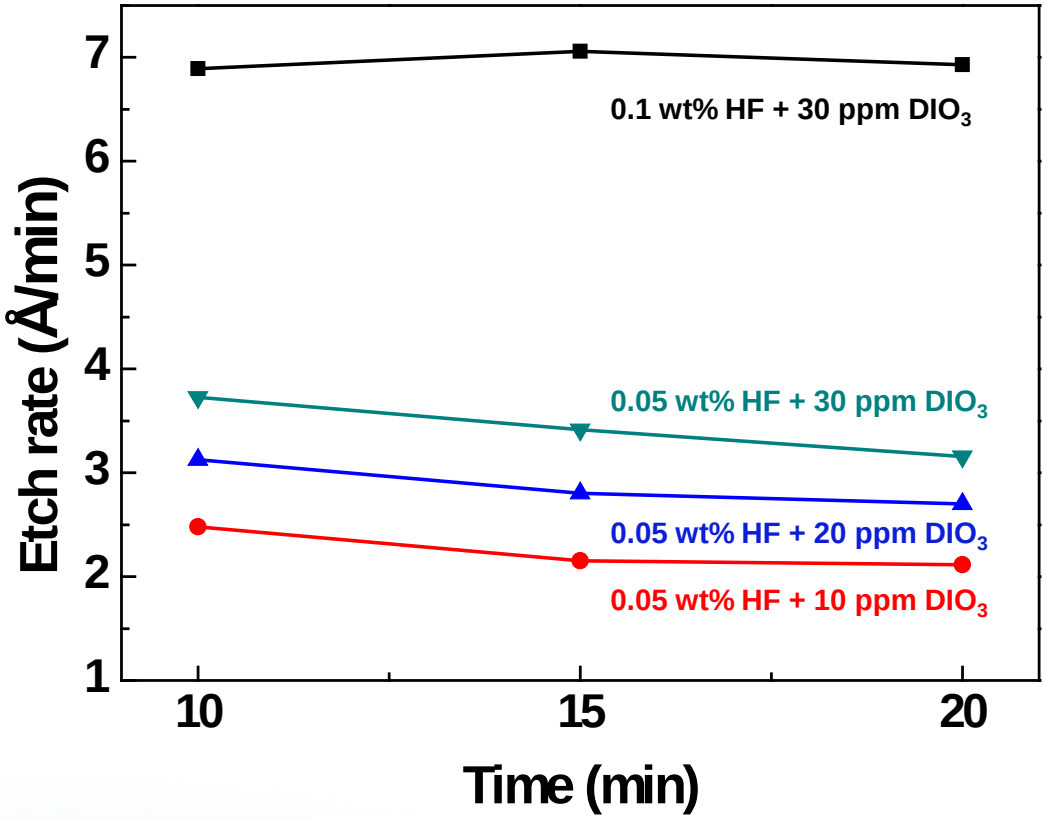
< SiO_2 etching mechanism by hydrofluoric acid >

- Stable Si-F bond formation breaking Si-O bond
- Volatile SiF_x formation by high electronegativity of fluorine ion(F^-) → **SiO_2 / Contaminant removal**

Yokota, Y. et al. (2011). U.S. Patent No. 7,972,441. Washington, DC: U.S. Patent and Trademark Office.
Knotter, D. M. (2000).Journal of the American Chemical Society, 122(18), 4345-4351.
Michalak, D. J. et al. (2010).. Nature materials, 9(3), 266-271.

HF/Ozone solution

Si etch rate change by HF/DIO_3 concentration



Cleaning conditions		
DHF	DIO_3	Etch rate (Å/min)
0.05 wt%	10 ppm	2.249
	20 ppm	2.877
	30 ppm	3.434
0.1 wt%	30 ppm	6.96

Summary

Metal removal using chelating agents

- **Cu removal**

  1) Chelating agent 1 : More ligands but less dissociation in acidic region

  → Proper for high pH or less chelating agent concentration for metal removal

  2) Chelating agent 2 : Less ligands but better dissociation in acidic region

  → Proper for low pH or high chelating agent concentration for metal removal

- **Al removal**

  1) High MRE supported by HF in addition to the chelating agents

	6mM		8mM	
	Chelating agent 1	Chelating agent 2	Chelating agent 1	Chelating agent 2
Cu MRE	57%	44%	59%	70%
Al MRE	Over 90%			

Metal removal using HF/DIO_3

- > 90% of MRE for Cu and Al by repeating the oxide film formation and removal

"Higher metal contamination removal efficiency in HF/O_3 Chemistry"

THANK YOU

NEMPL