Development of PCMP Cleaner for both Tungsten and Cobalt Applications

Excellent Metal Compatibility and Si_3N_4 , Oxide Surface Clean

Ching-Hsun Chao, Chi Yen, Ting-Kai Huang, Chih-Chin Tsou, Cass Shang*

EKC Technology, DuPont Electronics and Communications

Chi.Yen@dupont.com

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- Mechanism of additive 2 to clean Si3N4 surface
- Additive 3 is optimized for the smallest contact angle due to surfactant property

Summary

Problem statement

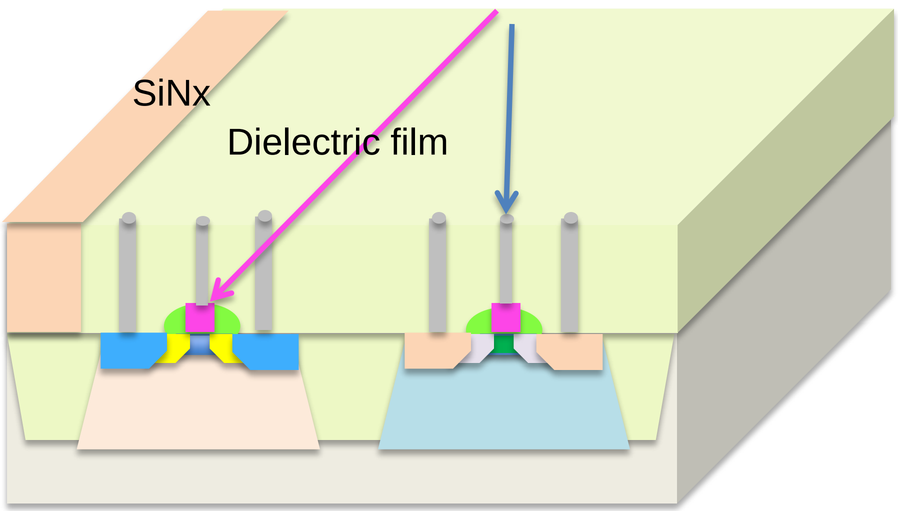
1. Metal Compatibility

a. **Metal Corrosion**
b. **Metal Plug Recess or Dishing**

2.Clean Efficiency on Dielectric film

a. **Particle**
b. **Slurry residue**

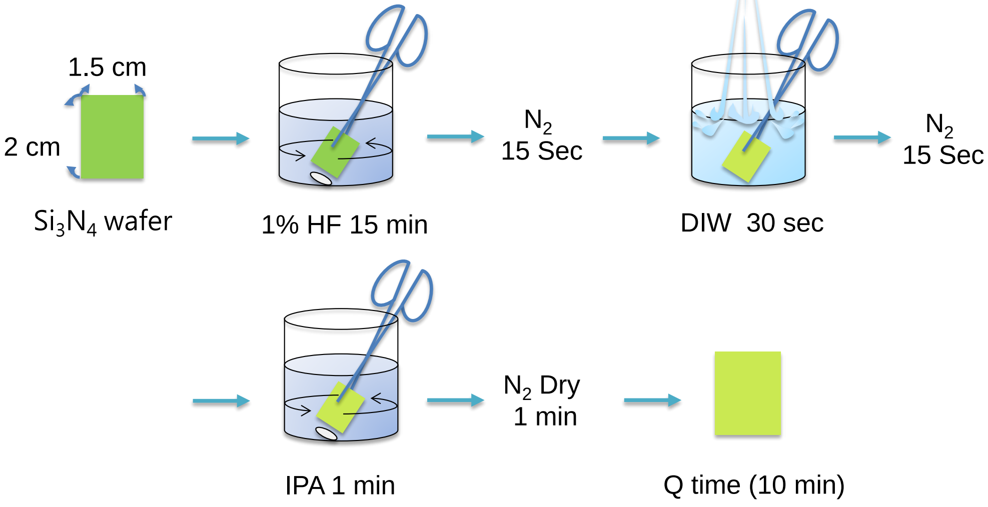
Post cleaner for Cobalt plug & Tungsten gate



n-MOS p-MOS

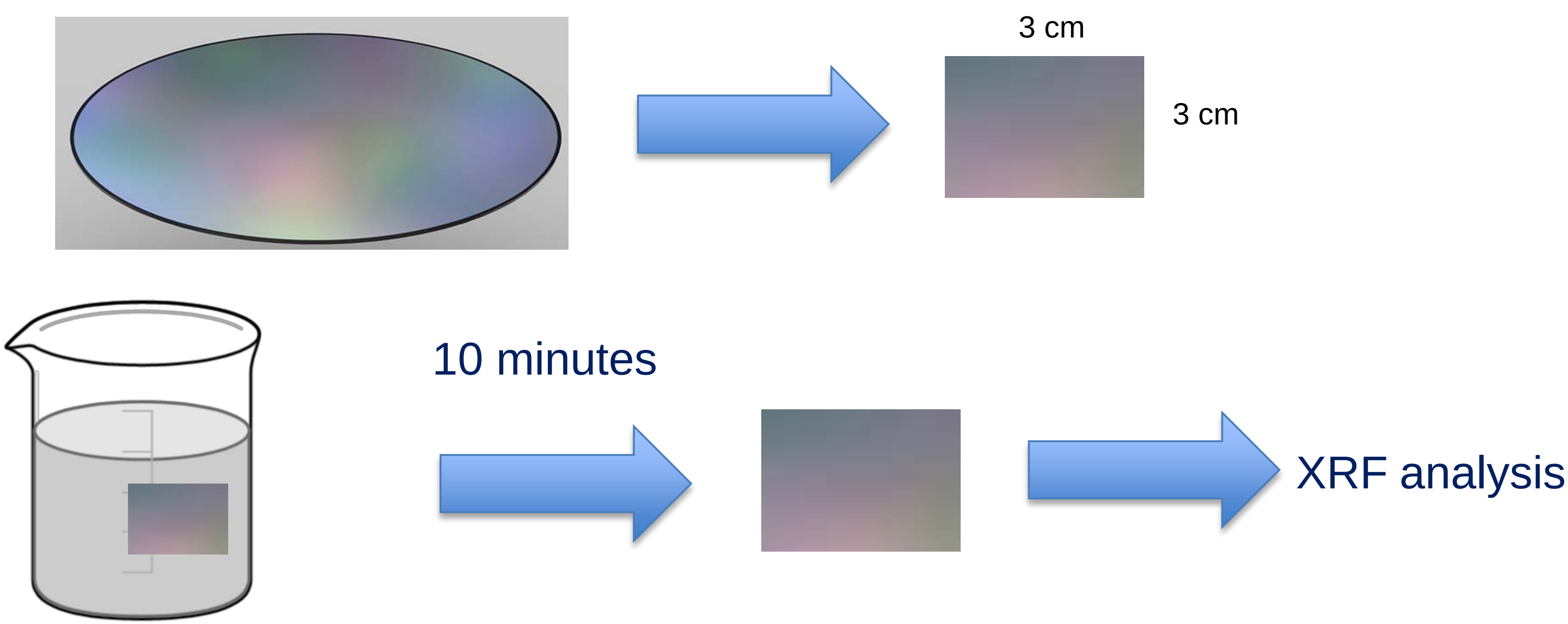
Si_3N_4 wettability evaluated by contact angle

- Pretreatment Si_3N_4 Wafers by 1% HF
- Cut 1.5x2 cm square cubic area
- Measure contact angle



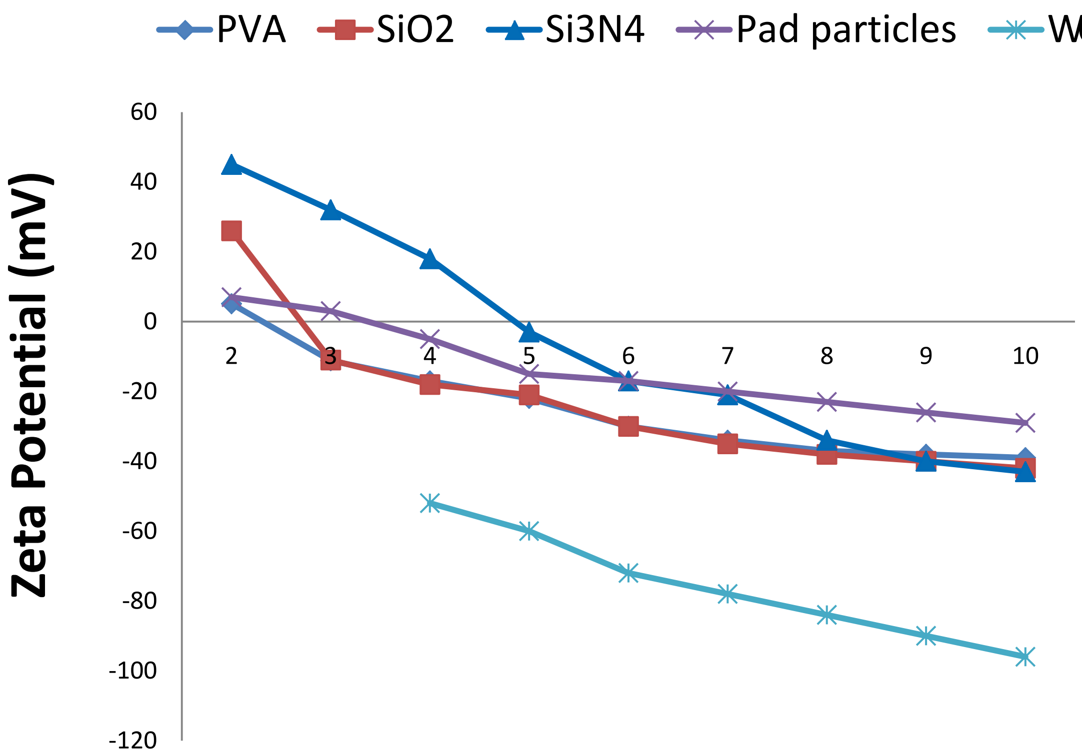
W and Co compatibility analysis by static etching rate measurement

- Pretreatment tungsten or cobalt Wafers
- Cut 3 cm square cubic area
- Put coupon chip on 100 mL formulation post clean beaker in 10 minutes.
- Measure thickness of tungsten or cobalt by XRF



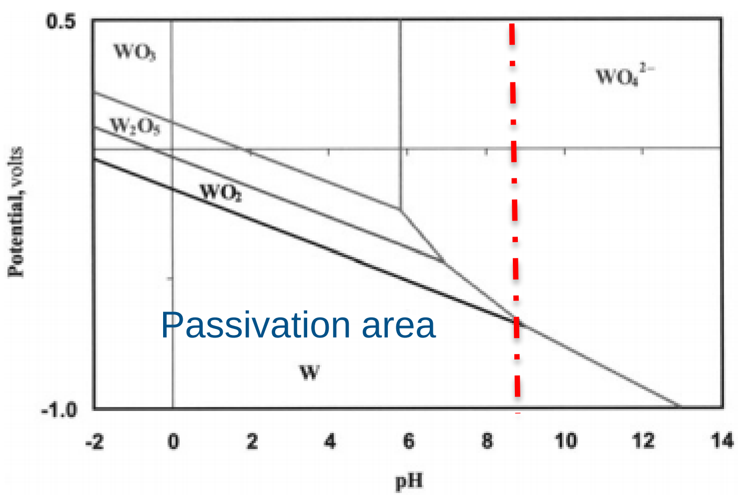
Si_3N_4 wettability evaluated by contact angle

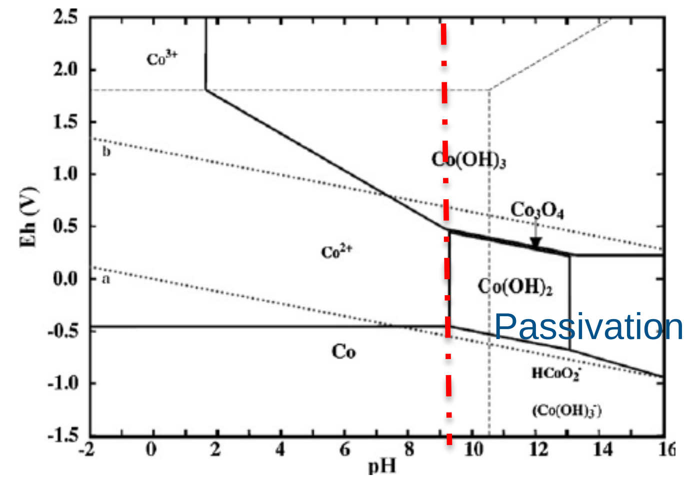
Zeta Potential Measurement



- Adjust formulation pH to measure zeta potential

Tungsten is easy to corrode by high pH region





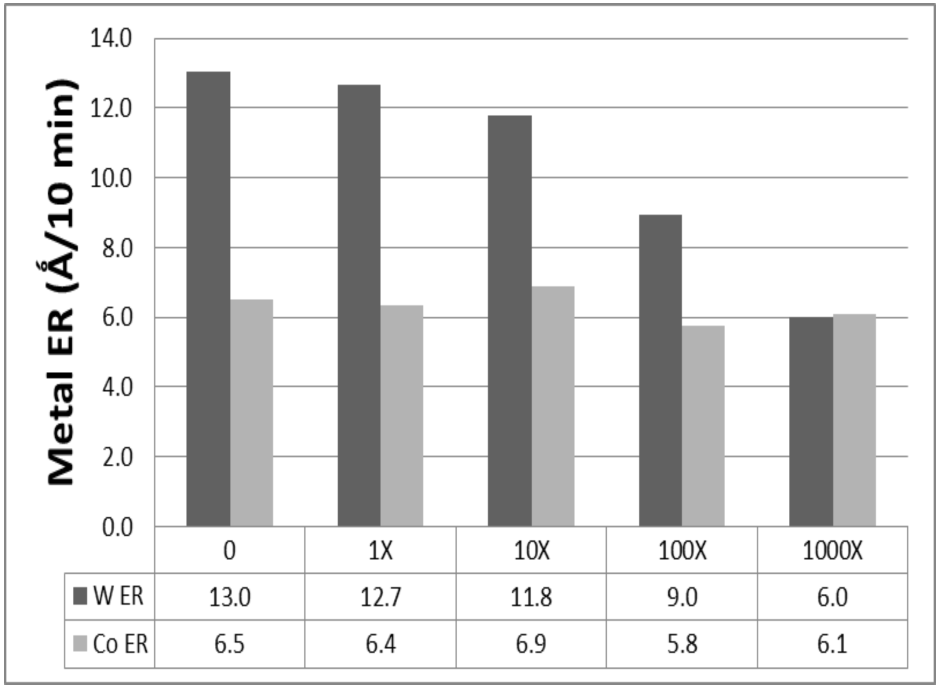
Chemical-Mechanical Planarization of Semiconductor Materials
Oliver, M. R. (Ed.)

Journal of Power Sources 185(1):549–553 · October 2008

- Co was observed to exhibit high corrosion in low pH region and dissolution rates as well as a strong possibility of galvanic corrosion due to the difference in the corrosion potentials between Co and other metal. However, W is easy to corrode by high pH region.

Improvement 1 showed better tungsten compatibility

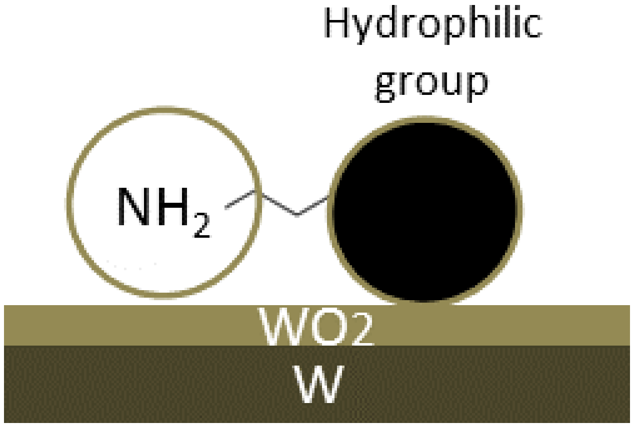
Formulation	Co ER	W ER	pH
POR	7 (Å/10 min)	80 (Å/10 min)	11
Improvement1	6 (Å/10 min)	6 (Å/10 min)	10



- The pH value of **POR** formulation is 11 and W will dissolve as WO_4^{-2}. W static etching ate is around 80 Å/min. Compared to **improvement 1** static etching rate is 6 Å/min. **Improvement 1** showed better tungsten compatibility.

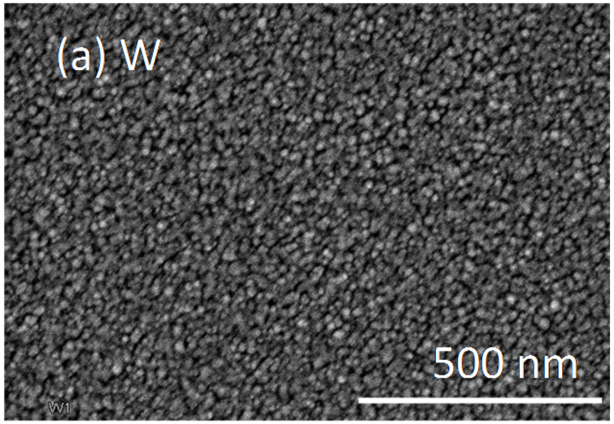
- The W etching rate would decrease with concentration of **additive 1**.

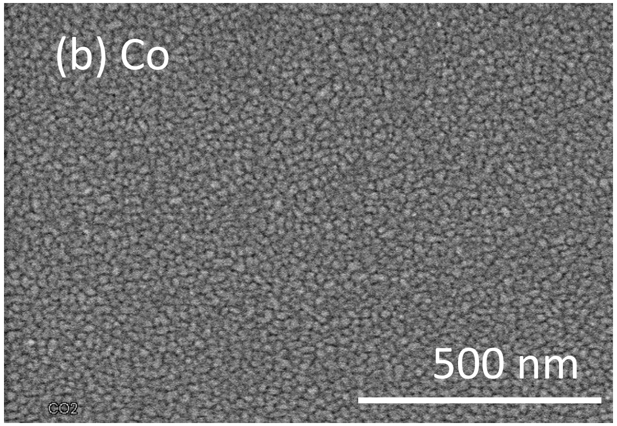
Additive1 is an effectively for W inhibitor in high pH region because additive 1 could adhere on W surface



- **Additive1** is an effectively for W inhibitor in high pH region because **additive 1** could adhere on W surface to prevent W to react with water to form as WO_4^{-2} in strong bases. **Additive 1** is to form by two major function groups. One is amine group and another is hydrophilic group. These two group could chelate on WO_2 to balance W surface to W (+VI).
- Co loss is no impact due to native passivation layer like $Co(OH)_2$ or CoO and additive could not provide more protection for Co.

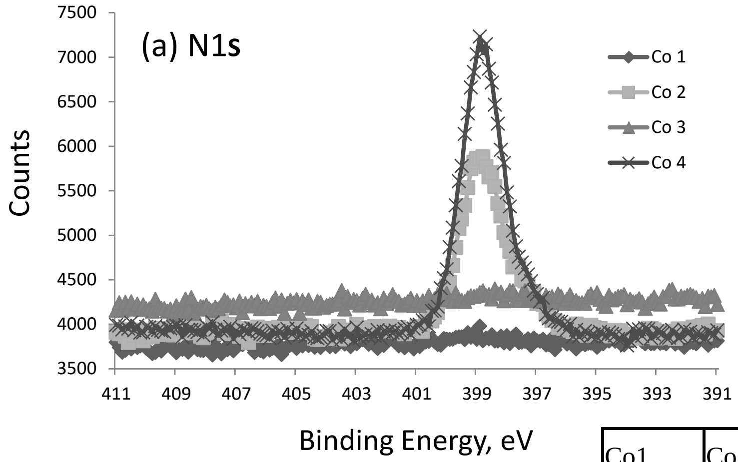
Additive1 is an effectively for W inhibitor in high pH region because additive 1 could adhere on W surface

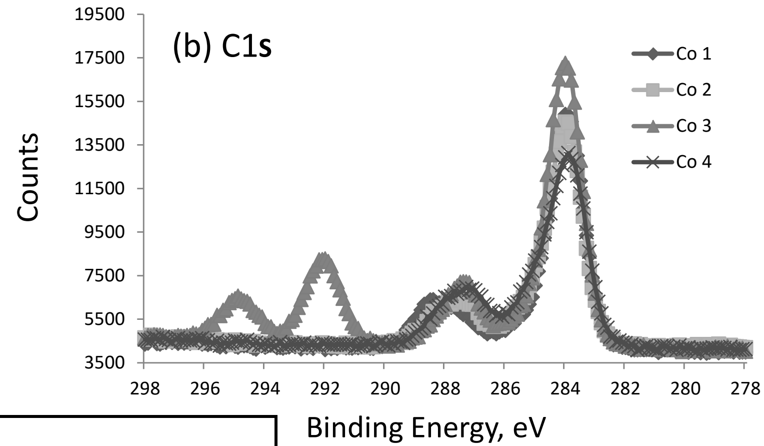




- **Improvement 1** showed effective clean performance and additive would not result in organic resdiue defect on Co and W wafers because of its highly hydrophilic property.

Additive 1 could help to clean Co surface

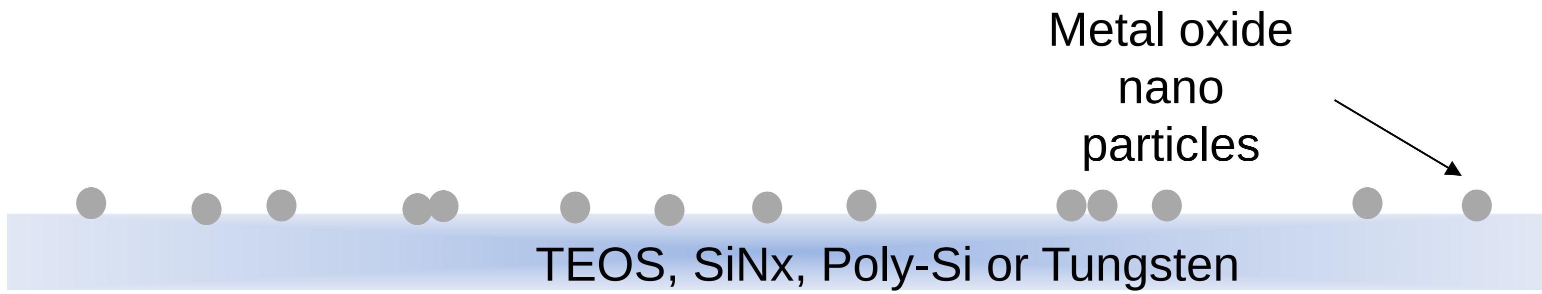




Co1	Co-blank
Co2	Additive 1
Co3	Additive 2
Co4	Improve1 (Additive 1+Additive 2)

- The N signal is existed on 399 eV and this peak is fitted by NH_2. It showed **additive 1** adhered on Co surface. The **improvement 1** showed the same peak because it includes **additive 1** and other components and pH didn't affect it chelate Co property. From N1s spectra, it described additive 1 provide protection for Co to prevent pitting defect on Co surface.
- Co 3 condition showed that **additive 2** could absorb on Co surface due to 295 and 292 eV for α and β carbon link with carbonyl group. **Additive 2** result in organic residue defect on Co surface but it could help to improve organic residue defect on Si_3N_4. Co 4 (**improvement 1** solution) condition show that **additive 1** adhere on Co surface to prevent **additive2** to adhere on Co surface because **additive 1** to change Co surface property. Therefore, **additive 1** could help to clean Co surface to prevent particle re-deposite.

Concept for break van der Waals attractive from wafer surface to form passivator by Additive 1

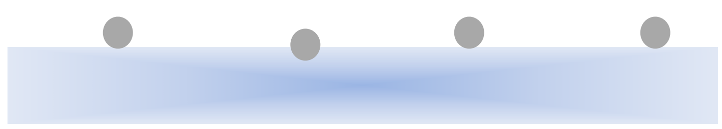


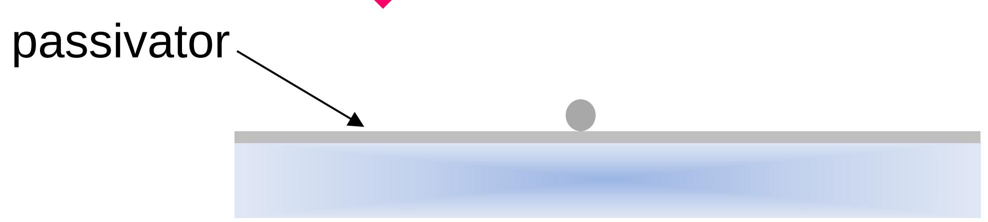
Cleaning step

Without passivator
1)Mechanical displacement
2)Particle undercut and bond cleavage

Cleaning step

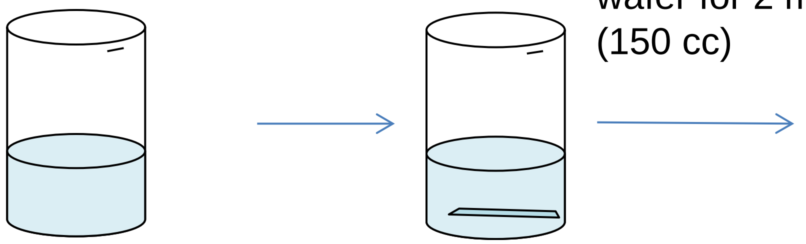
With passivator
1)Mechanical displacement
2)Particle undercut and bond cleavage
3)Small molecule or polymer layer prevents nano metal oxide re-deposition





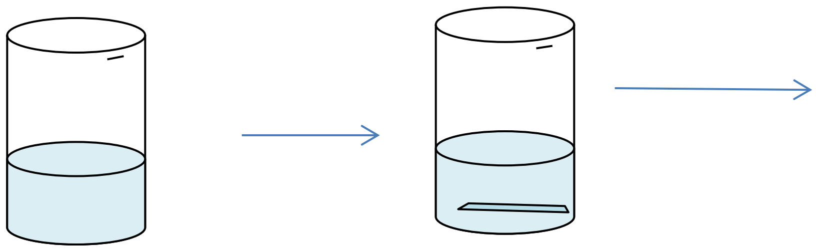
Particle re-deposition evaluation with Additive 1 on TEOS wafers

Immerse wafer for 2 min (150 cc)

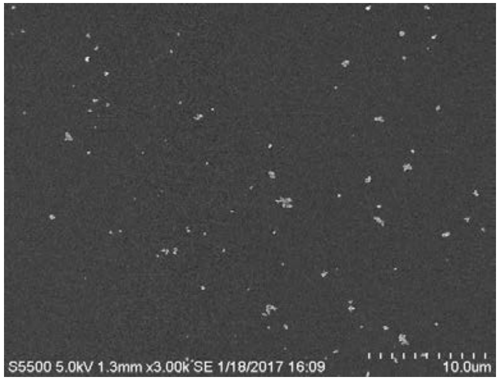


Sol A:
TiO_2 0.5g +
50X Formulation 100g

S3-3-2233
(with additive 1)

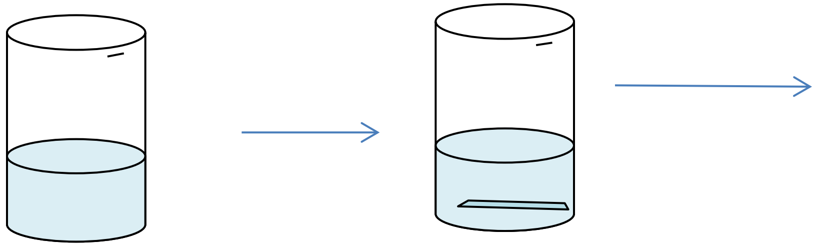


Sol B:
TiO_2 0.5g +
0.5% NH_4OH + 0.5% HF 100g

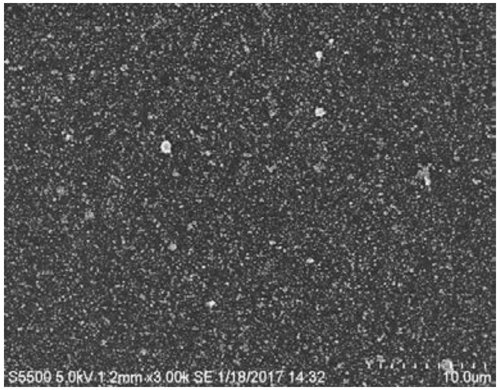


0.5% NH_4OH
+ 0.5% HF

Blank test



Sol B:
TiO_2 0.5g + D.I. Water (pH 3)

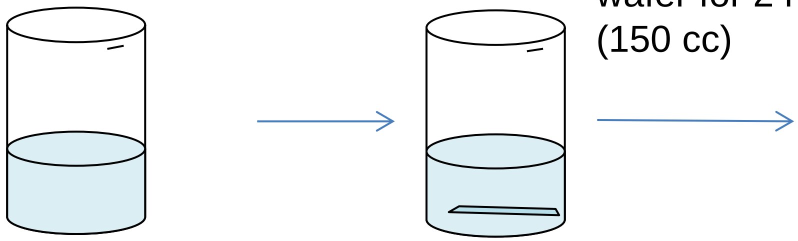


D. I. water
(pH 3)

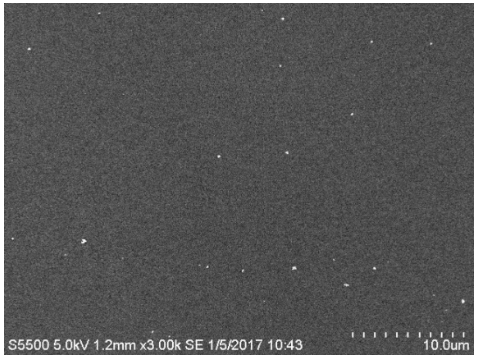
Particle re-deposition evaluation with Additive 1

On SiN wafers

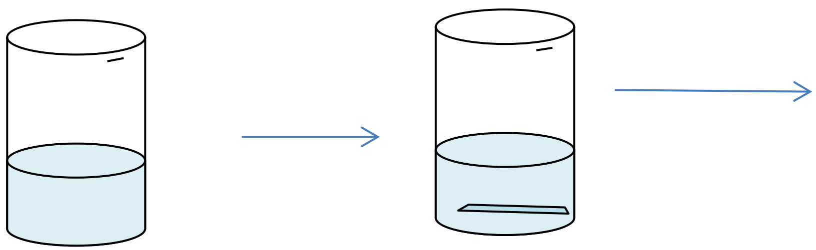
Immerse wafer for 2 min (150 cc)



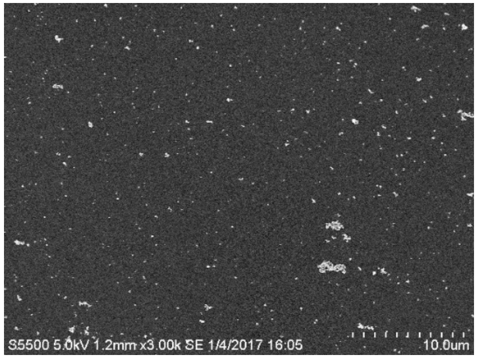
Sol A:
TiO_2 0.5g +
50X Formulation 100g



S3-3-2233
(with additive 1)

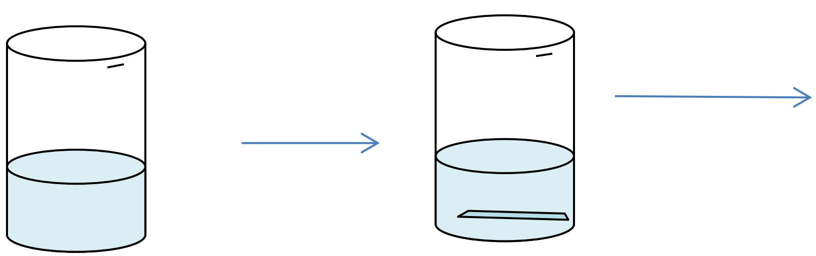


Sol B:
TiO_2 0.5g + 2% NH_4OH

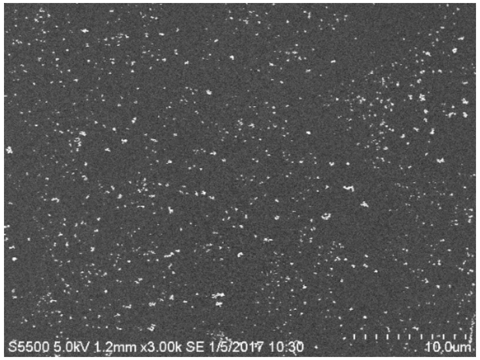


2% NH_4OH

Blank test

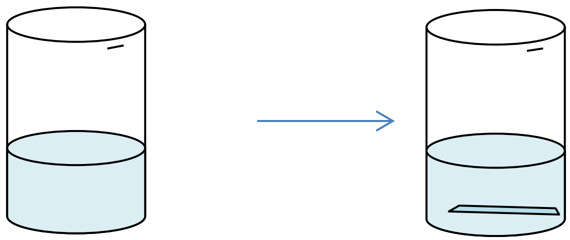


Sol B:
TiO_2 0.5g + D.I. Water (pH 3)



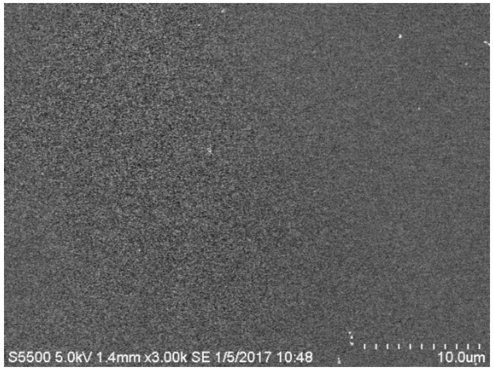
D. I. water
(pH 3)

Particle re-deposition evaluation with Additive 1 on W wafers

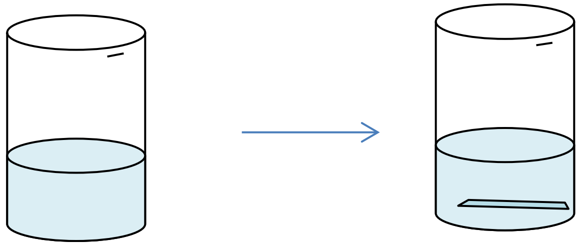


Sol A:
TiO_2 0.5g +
50X Formulation 100g

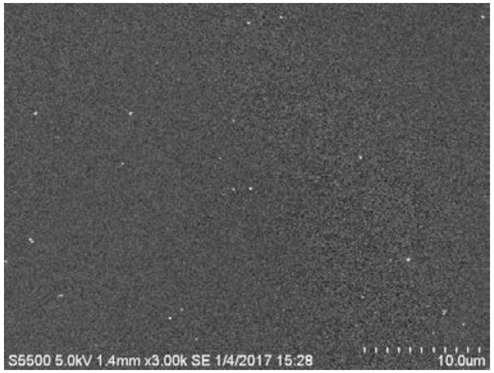
Immerse wafer for 2 min (150 cc)



S3-3-2233 (with additive 1)

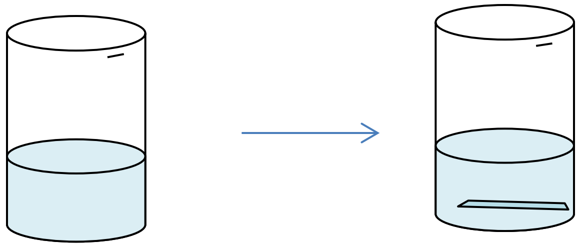


Sol B:
TiO_2 0.5g + 2% NH_4OH

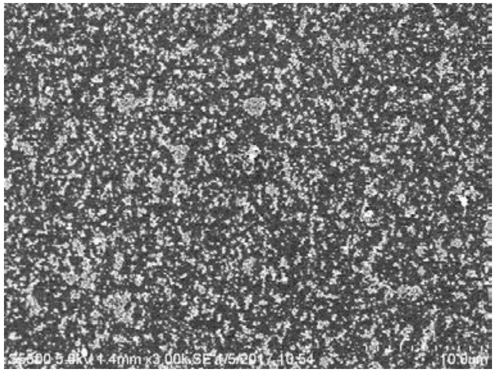


2% NH_4OH

Blank test

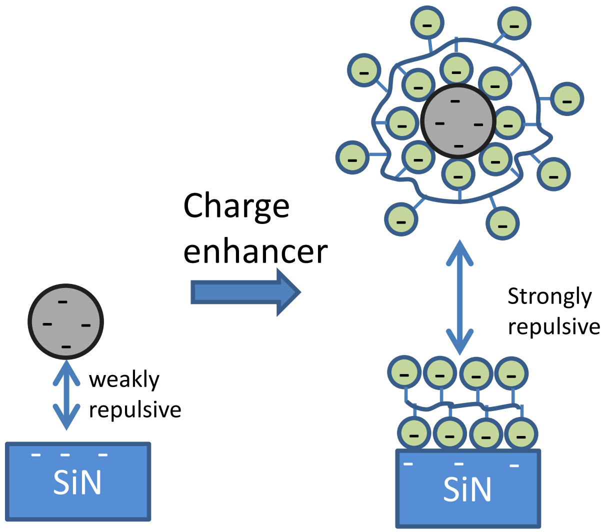


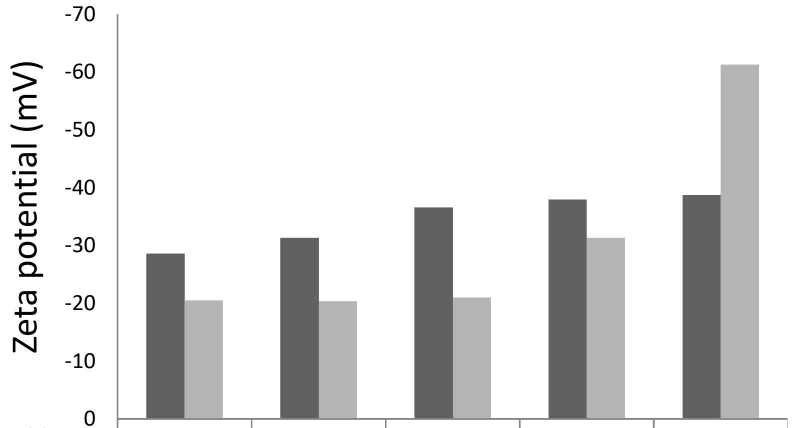
Sol B:
TiO_2 0.5g + D.I. Water



D. I. water

Mechanism of additive 2 to clean Si3N4 surface

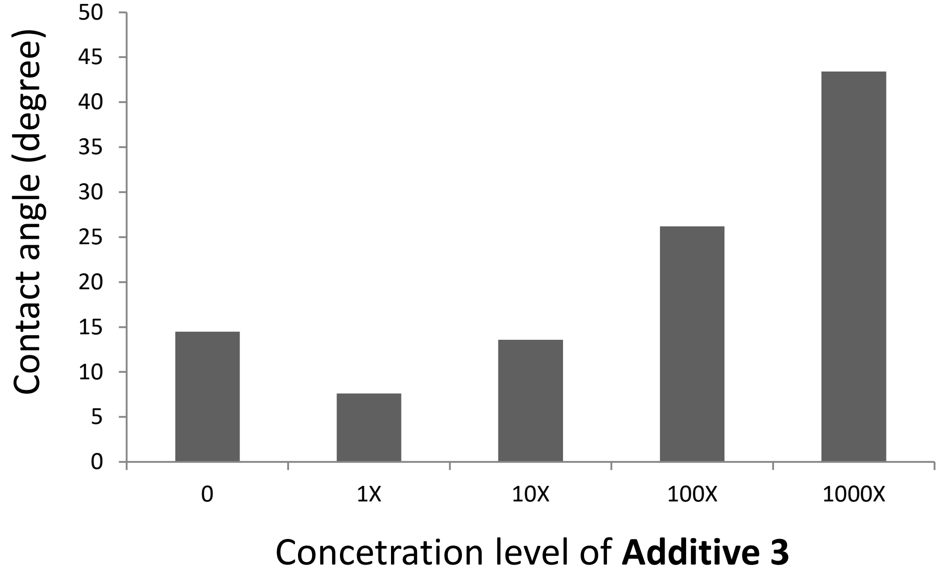




Additive 2	0	1X	10X	100X	1000X
Si3N4	-28.6	-31.31	-36.57	-37.92	-38.72
SiO2	-20.5	-20.33	-20.97	-31.33	-61.24

- Si_3N_4 clean is an another requirement for W or Co plug in MOL. We propose a mechanism to clean Si_3N_4 surface. We added **additive 2** into **improvement 1** to modify surface charge on Si_3N_4 film surface and SiO_2 particle surface to enhance electric repulsive force between Si_3N_4 film and SiO_2 particle.
- It could prevent to re-deposited SiO_2 particle on Si_3N_4 film and help SiO_2 particle remove from Si_3N_4 film surface.
- Zeta potential of Si_3N_4 and SiO_2 would be enhance by increaed **additive 2** concentration because of its negative charge function group. Strongly electric repulsive force would result in better clean efficiency.

Additive 3 is optimized for the smallest contact angle due to surfactant property



- Wettability sustain the water flow momentum on the interface of SiN film and particles. When wettability is enhanced, the clean performance of Si_3N_4 film could be improved. We added **additive 3** into **improvement 1** to change solution contact angle on Si_3N_4 film. The concentration of **additive 3** is optimized for the smallest contact angle due to surfactant property.
- Co loss is no impact due to native passivation layer like $Co(OH)_2$ or CoO and additive could not provide more protection for Co.

Summary

- The **additive 1** is a efficiency inhibitor for W and help to clean Co surface and suppress Co pitting.
- The **additive 1** is combined by amine and hydrophilic function group and is easy to remove by water and brush.
- Zeta potential of Si_3N_4 and SiO_2 would be enhance by added **additive 2** due to its negative charge function group.
- The wettability of improvement 1 is improved by optimized **additive 3** to enhance clean performance.

Thank you

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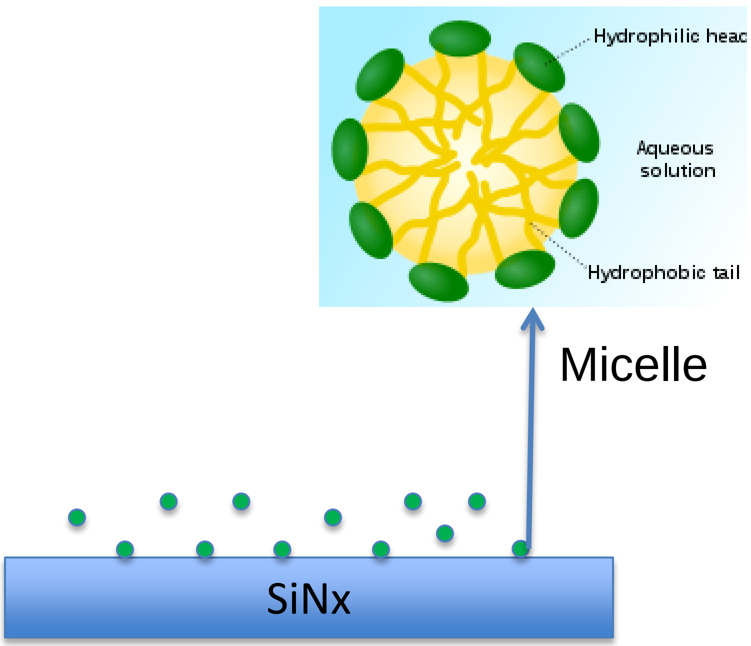
Fundamental mechanism of surfactant

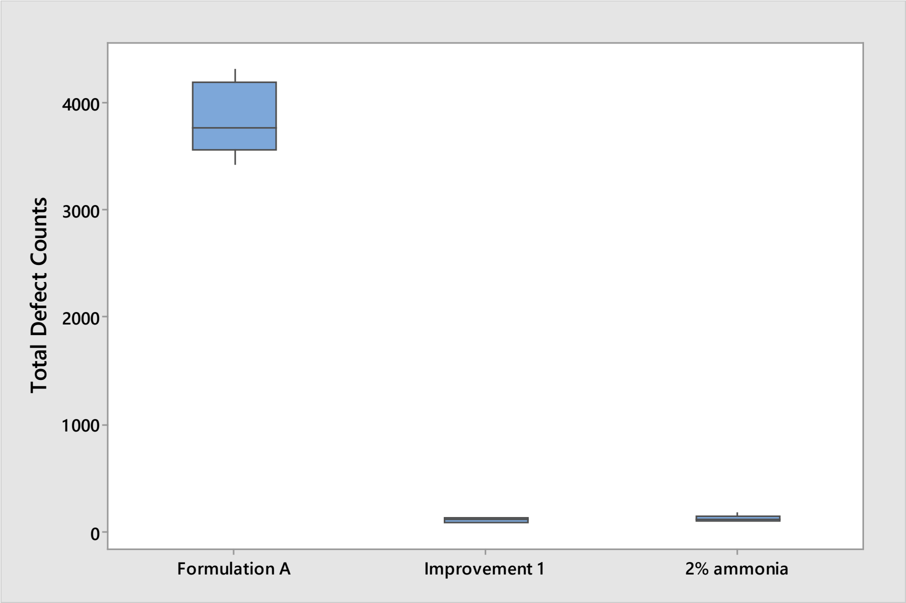
Too much surfactant



Suitable surfactant

Hydrophilic head to change SiNx surface property

improvement 1 (include chemical A) could provide better clean efficiency and tungsten compatibility than 2% ammonia



SiNx wafers

- The most commonly used chemical for the cleaning process is ammonia. Ammonia is very effective in neutralizing the polishing slurry and undercutting the substrate and lowering the adhesion between abrasive particles and oxide surface. However, a high pH solution sometimes does cause defects such as corrosion and pitting. Therefore, alternative cleaning solutions have been sought and evaluated.
- DuPont EKC improvement 1 could provide better clean efficiency and tungsten compatibility than 2% ammonia.