

2015 CMP Users Group Meeting on Apr 16th, 2015

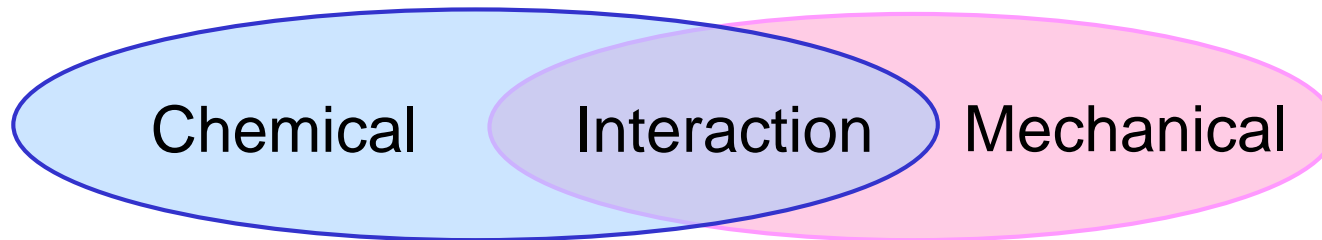
Development of a higher Si₃N₄ selectivity slurry

Hisashi Takeda¹, Koichi Sakabe², Yukinobu Yoshizaki², Tomohiko Akatsuka², and Kazumi Sugai²

¹ Fujimi Corporation, 11200 SW Leveton Drive, OR 97062 USA

² Fujimi Incorporated, 1-8, Techno Plaza, Kakamigahara, Gifu 509-0109 Japan

1. Introduction
2. Key challenge for Si_3N_4 CMP
3. Polishing mechanism
4. Approach for improvement
5. Results
6. Summary

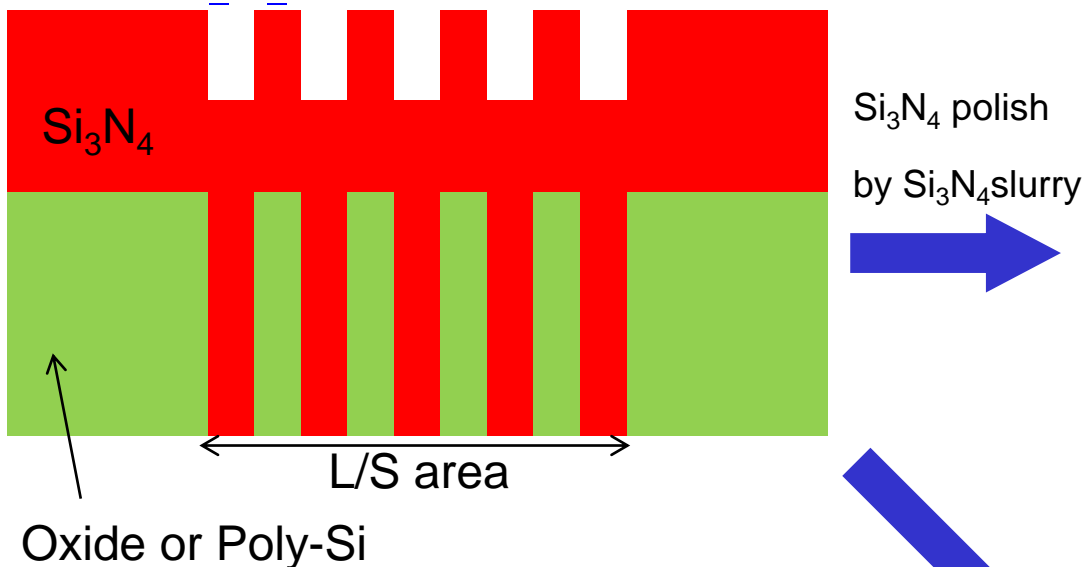


Category	Chemical	Interaction	Mechanical
Force	Chemical reaction (polished material-chemical)	Solid-Liquid Solid-Solid	Physical energy (friction)
Strength	Reaction potential	Hydrophobicity/ Hydrophilicity, electric charge	Size, Shape, and Material of abrasive
Frequency	Chemical concentration	Surface area	Number of abrasive (surface area)

The effects of chemical, mechanical, and those interactions are considered in design for CMP slurry.

Key challenge for Si_3N_4 CMP

Si_3N_4 patterned wafer

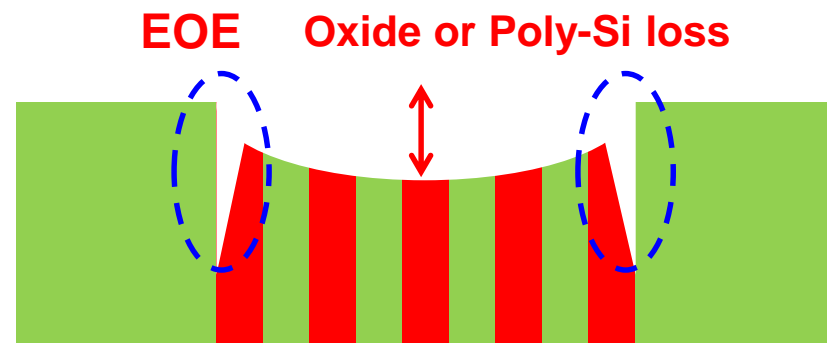


Ideal

- Planarization
- No loss of Oxide or Poly-Si



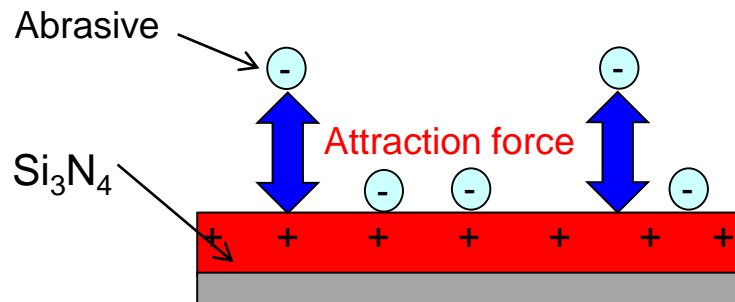
Issue



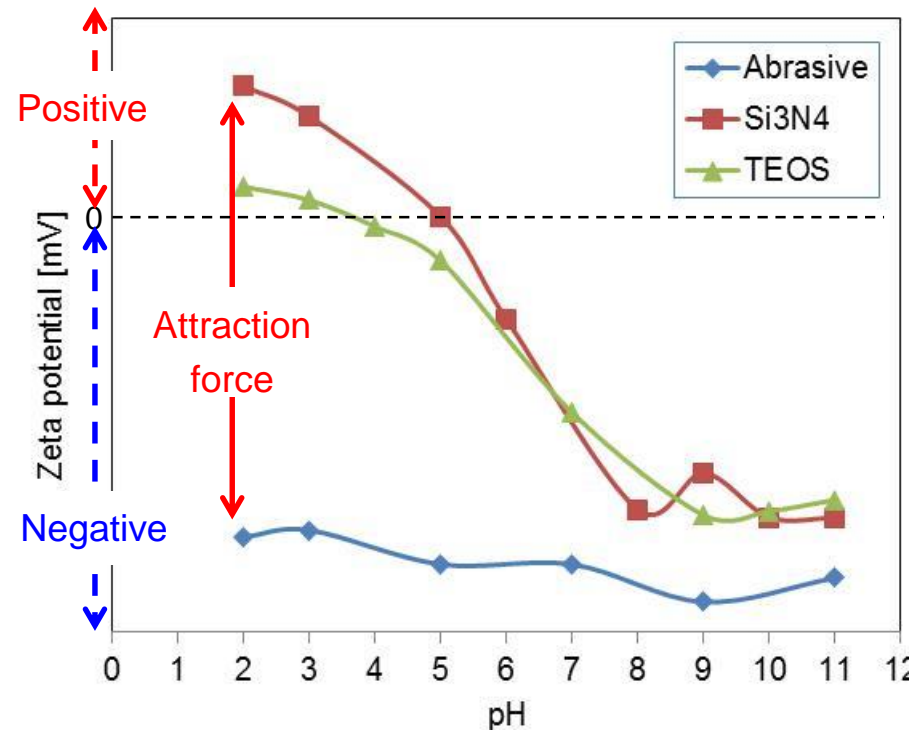
Loss of oxide or Poly-Si, known as erosion, is caused in finer L/S area after Si_3N_4 clearing. Oxide or Poly-Si removal rates have to be suppressed in a patterned wafer maintaining Si_3N_4 removal rate, and edge over erosion (EOE) needs improved as well.

Polishing mechanism for Si_3N_4

- Abrasive is negatively charged pH-independently while Si_3N_4 is positively charged in a solution below pH 5.
- Si_3N_4 removal rate can be enhanced by attraction force between Si_3N_4 and abrasive.



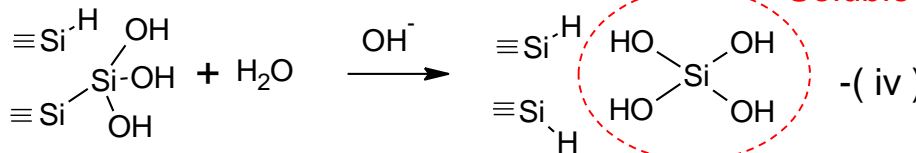
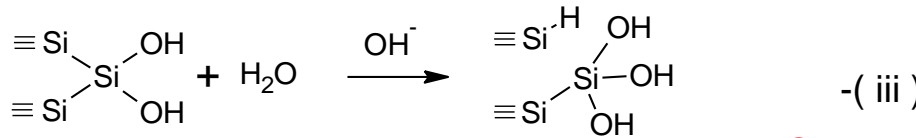
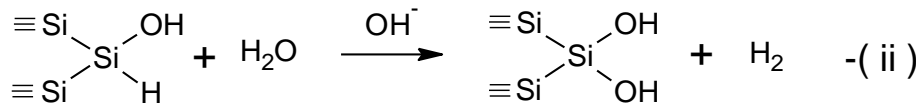
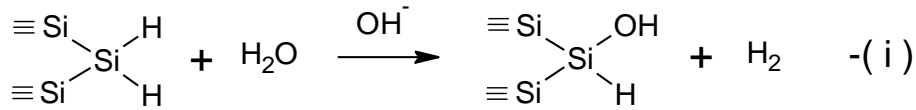
pH vs. zeta potential



FUJIMI Si_3N_4 slurry is designed in acidic pH to enhance Si_3N_4 removal rate.

Polishing mechanism for Si

Silicon wet etching can be described as following reactions.



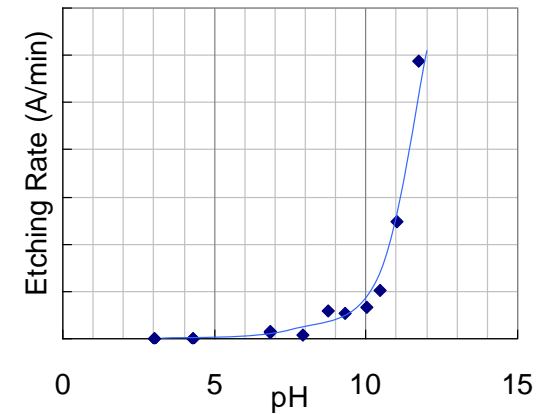
Soluble in water

Perhydroxylated silanol

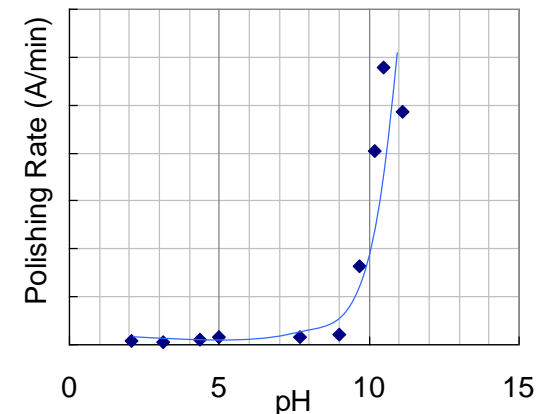
Silicon etching in wet system is driven by hydrolysis.

Since hydroxide ion (OH⁻) accelerates these reactions as a catalyst, higher pH (higher OH⁻ concentration) can enhance Si etching rate, resulting in higher Si removal rate.

pH vs. Si etching rate



pH vs. Si polishing rate



Ref) M. Elwenspoek, and H. V. Jansen. *Silicon Micromachining*. Cambridge University Press (2004)

Lower pH is better to reduce both Si etching and Si removal rate.

Influence of pH on the solubility of SiO₂ at 25°C

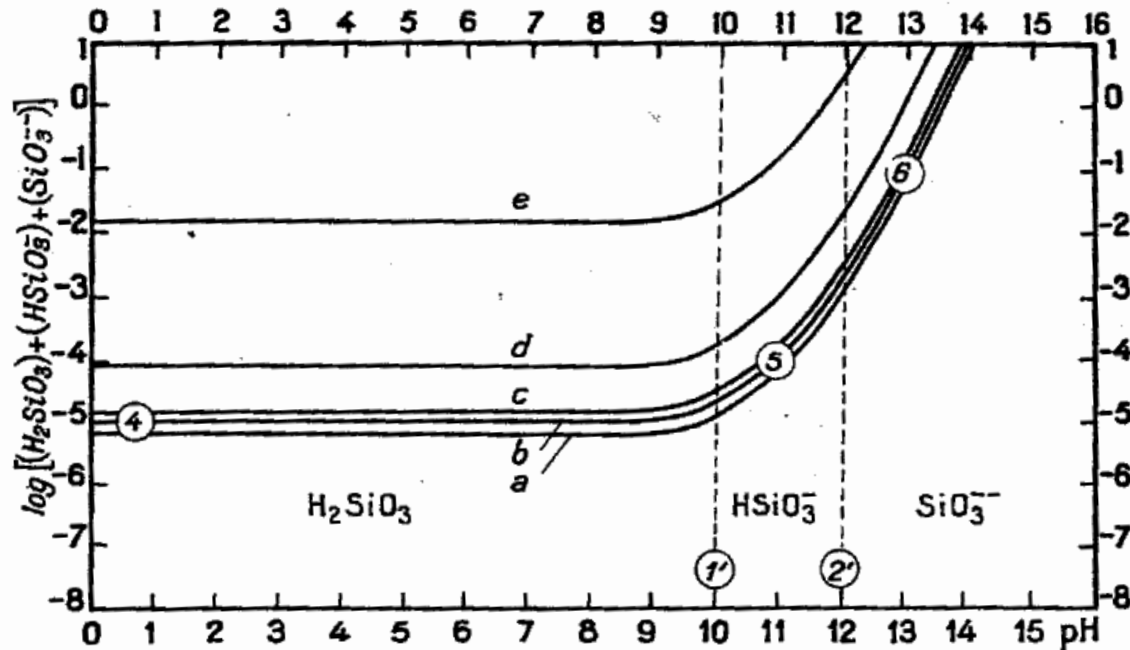


FIG. 2. Influence of pH on the solubility of silica SiO₂, at 25°C.
a, quartz; b, cristobalite; c, tridymite; d, vitreous silica; e, amorphous silica.

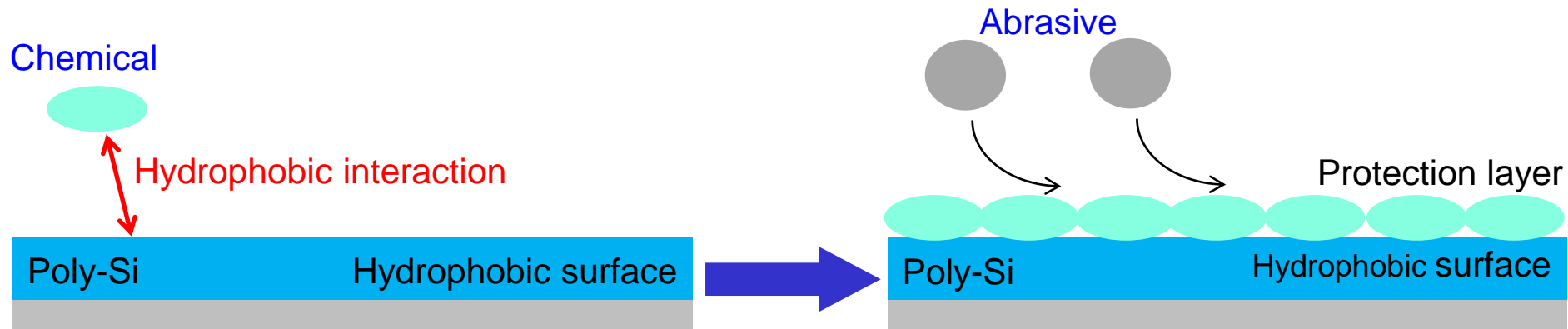
Ref) M. Pourbaix. *Atlas of Electrochemical Equilibria in Aqueous Solutions*.
National Association of Corrosion p462 (1974)

Higher solubility of SiO₂ is observed in a solution above pH 10, contributing to Oxide removal rate.

Lower pH helps minimize Oxide removal rate.

A model for Poly-Si removal rate reduction

- Poly-Si film has hydrophobic surface.
- Hydrophobic chemical adsorbs on surface of Poly-Si film via hydrophobic interaction to make a protection layer.

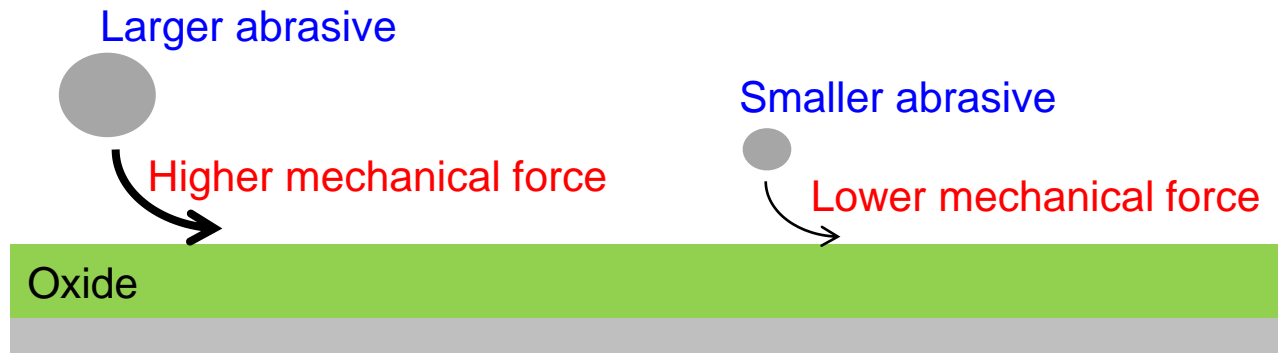


Design for Poly-Si removal rate reduction

- Acidic pH
- Poly-Si suppressor to make a protection layer on Poly-Si surface to decrease mechanical force

A model for Oxide removal rate reduction

- Oxide removal rate depends on mechanical force.
- Smaller size of abrasive with lower mechanical force can decrease Oxide removal rate.

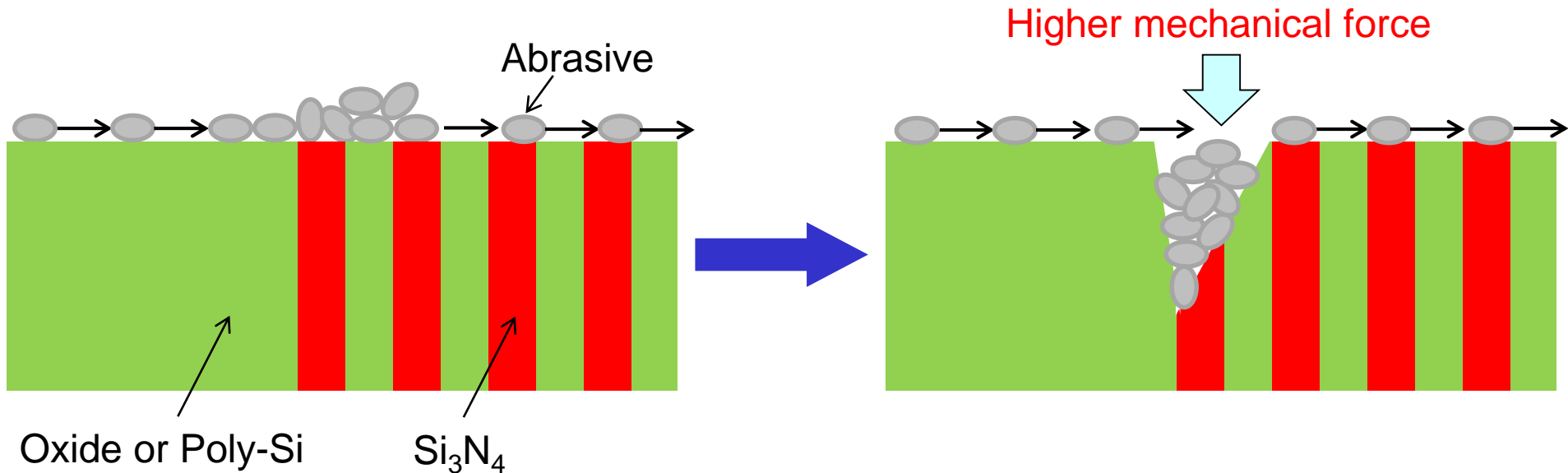


Design for Oxide removal rate reduction

- Acidic pH
- Smaller size of abrasive to decrease mechanical force

A model for EOE generation

- Abrasives stumbling in a boundary accumulate locally.
- Accumulating abrasives give higher mechanical force locally in a boundary, resulting in generating EOE.



Design for EOE improvement

- Smaller size of abrasive to decrease mechanical force

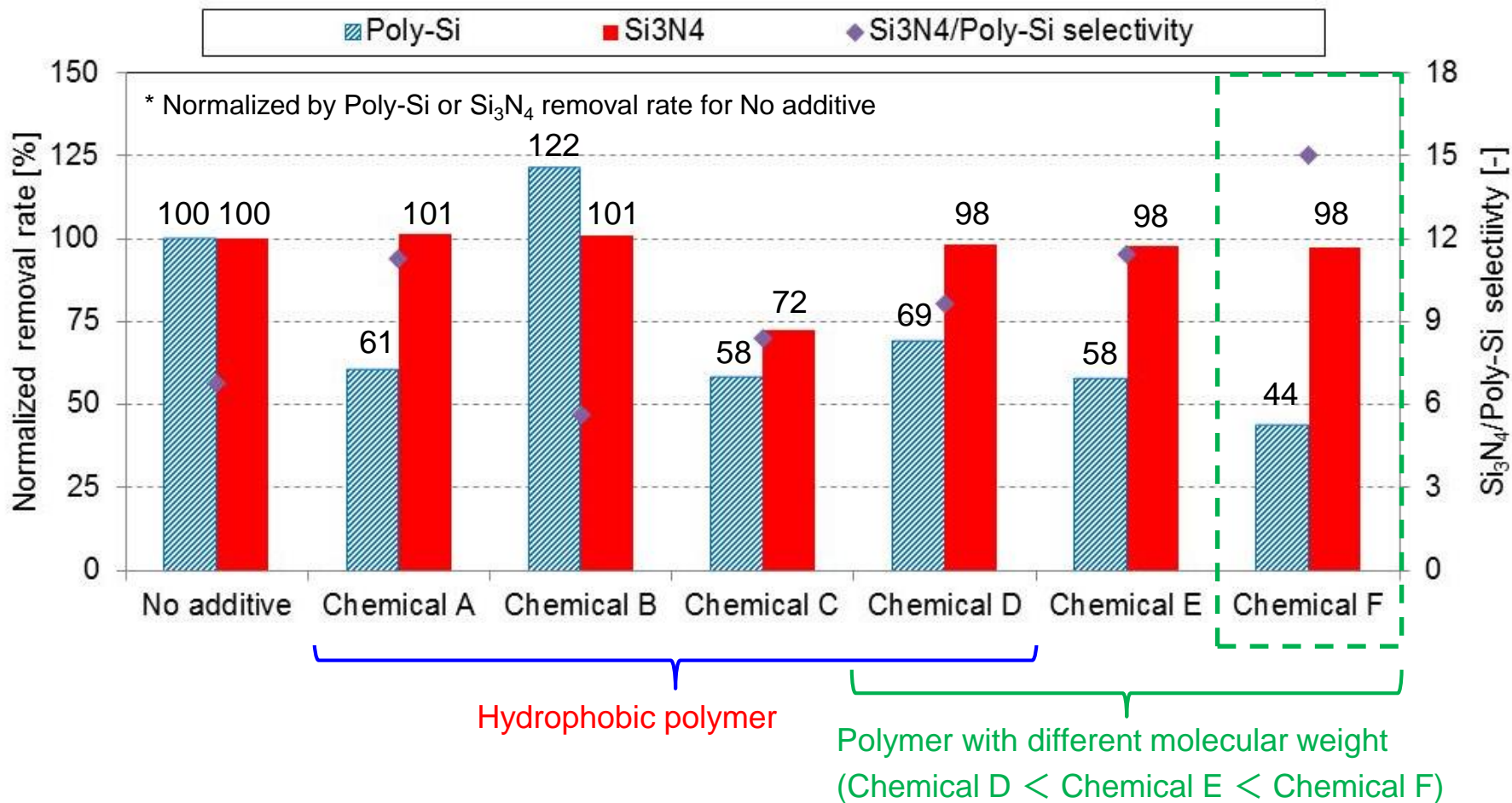
Summary for our approaches

Item		Approaches
Removal rate reduction	Poly-Si	<ul style="list-style-type: none">- Acidic pH- Poly-Si suppressor to make a protection layer on Poly-Si surface to decrease mechanical force
	Oxide	<ul style="list-style-type: none">- Acidic pH- Smaller size of abrasive to decrease mechanical force
EOE improvement		<ul style="list-style-type: none">- Smaller size of abrasive to decrease mechanical force

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Poly-Si suppressor screening

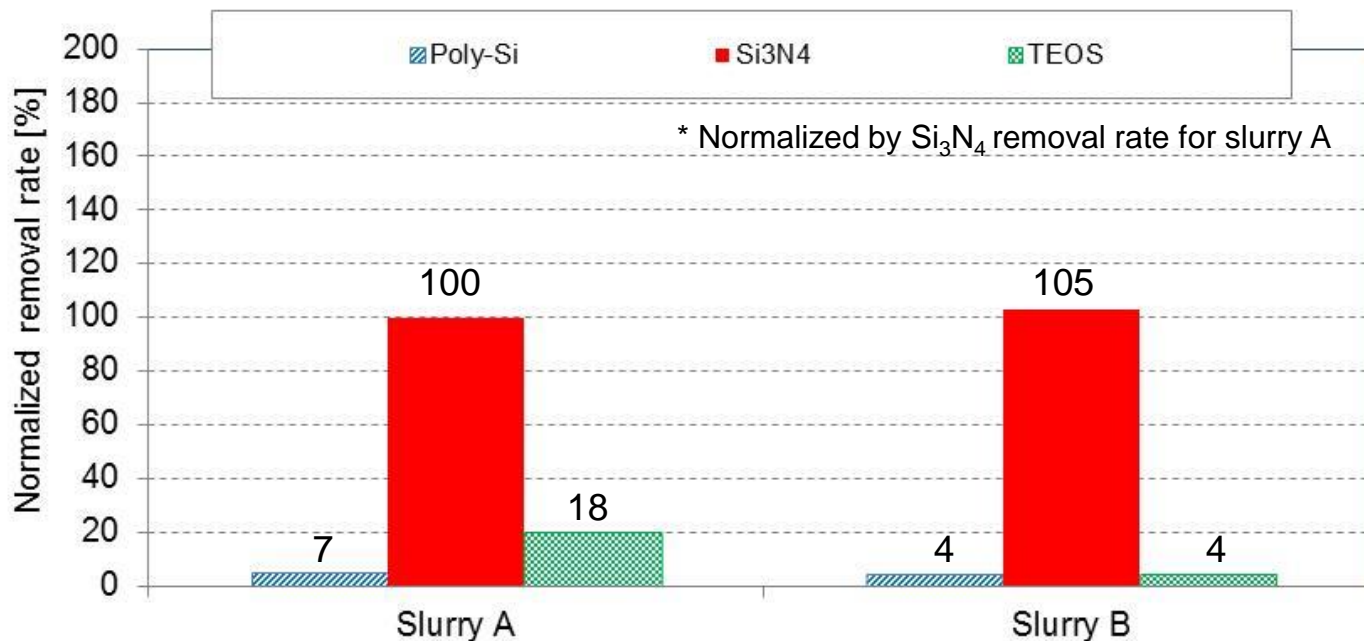


Chemical F suppressed Poly-Si removal rate keeping Si₃N₄ removal rate and gave the highest Si₃N₄/Poly-Si selectivity.

Summary for our approaches

Item		Approaches
Removal rate reduction	Poly-Si	<ul style="list-style-type: none">- Acidic pH- Poly-Si suppressor to make a protection layer on Poly-Si surface to decrease mechanical force
	Oxide	<ul style="list-style-type: none">- Acidic pH- Smaller size of abrasive to decrease mechanical force
EOE improvement		<ul style="list-style-type: none">- Smaller size of abrasive to decrease mechanical force

Abrasive size effect on removal rates



Item		Slurry A	Slurry B
Abrasive	Type	High purity colloidal silica	High purity colloidal silica
	Normalized secondary particle size	1.0	0.6
	Concentration	Same concentration	
pH		Acidic pH	
Poly-Si suppressor		Chemical F	
Selectivity	Si ₃ N ₄ /Poly-Si	23	24
	Si ₃ N ₄ /TEOS	5	25

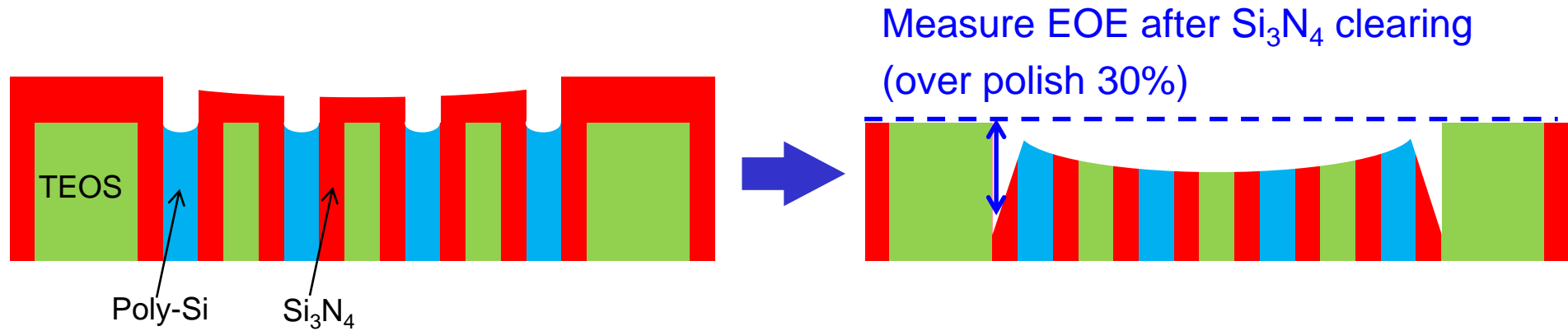
Slurry B gave higher Si₃N₄/TEOS selectivity than slurry A.
 ⇒ Smaller size of abrasive significantly reduced TEOS removal rate.

Summary for our approaches

Item		Approaches
Removal rate reduction	Poly-Si	<ul style="list-style-type: none">- Acidic pH- Poly-Si suppressor to make a protection layer on Poly-Si surface to decrease mechanical force
	Oxide	<ul style="list-style-type: none">- Acidic pH- Smaller size of abrasive to decrease mechanical force
EOE improvement		<ul style="list-style-type: none">- Smaller size of abrasive to decrease mechanical force

Abrasive size effect on EOE

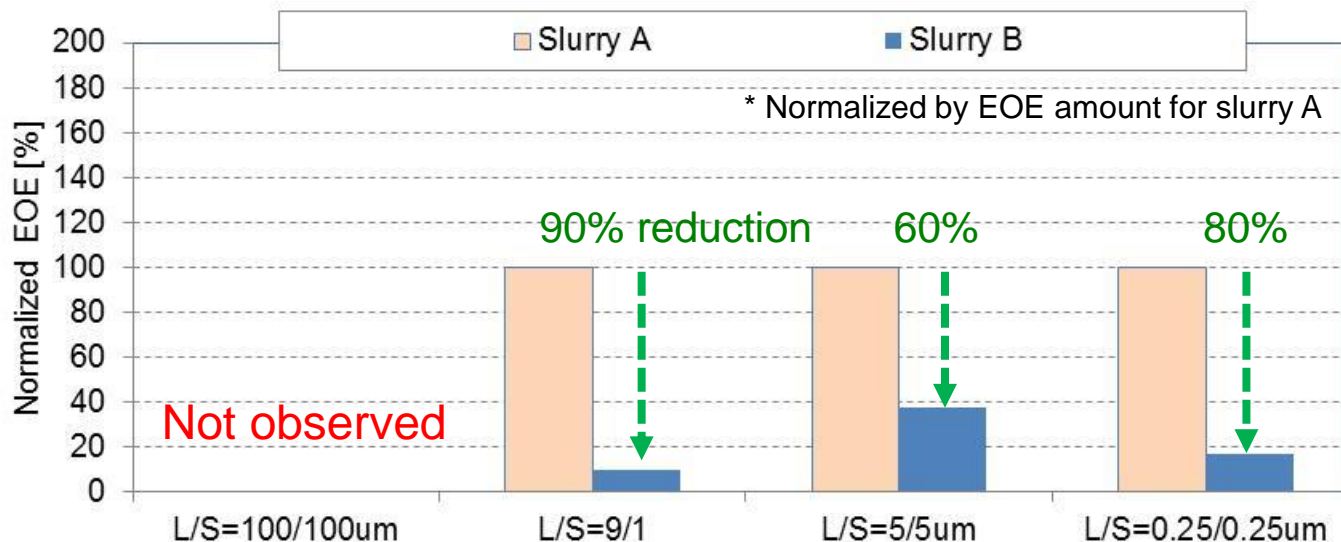
Evaluation procedure



Test samples

Item		Slurry A	Slurry B
Abrasive	Type	High purity colloidal silica	High purity colloidal silica
	Normalized secondary particle size	1.0	0.6
	Concentration	Same concentration	
pH		Acidic pH	
Poly-Si suppressor		Chemical F	

Abrasive size effect on EOE



Test samples

Item		Slurry A	Slurry B
Abrasive	Type	High purity colloidal silica	High purity colloidal silica
	Normalized secondary particle size	1.0	0.6
	Concentration	Same concentration	
pH		Acidic pH	
Poly-Si suppressor		Chemical F	

Slurry B significantly improved EOE (> 60%) compared to Slurry A.

⇒ Smaller size of abrasive reduced EOE, possibly due to lower mechanical force.

- ◆ A chemical with hydrophobic character, which can form a protection layer on Poly-Si surface via hydrophobic interaction, decreased Poly-Si removal rate maintaining Si_3N_4 removal rate.
- ◆ Smaller size of abrasive significantly decreased TEOS removal rate by reducing mechanical force while it maintained Si_3N_4 removal rate.
- ◆ Smaller size of abrasive significantly improved EOE in the patterned wafer, possibly due to lower mechanical force.