Development of Wet-etch Chemistries for Selective Silicon Nitride Removal in 3D NAND Structure

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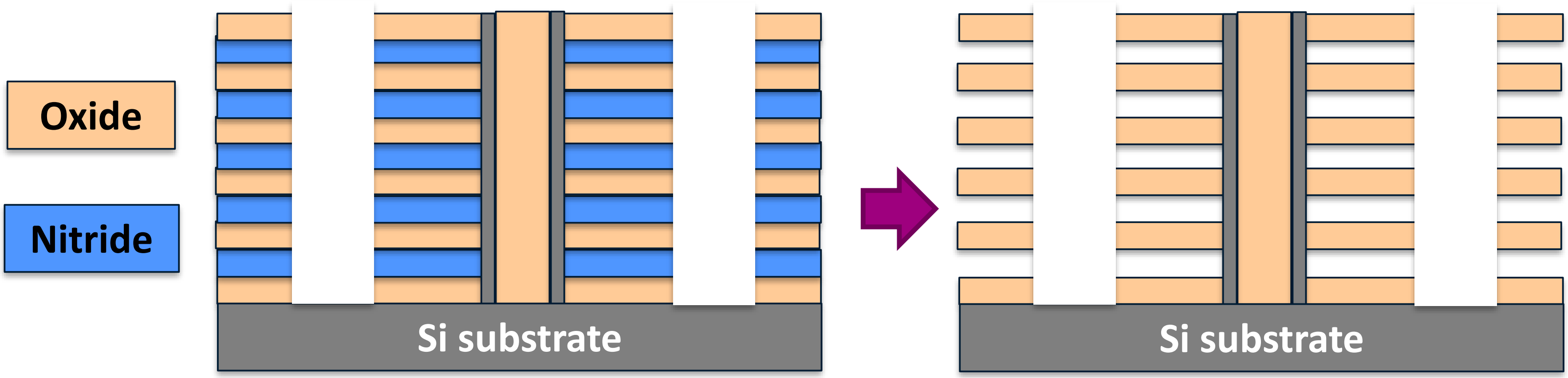
Technical Background

Sacrificial Nitride Strip for V-NAND

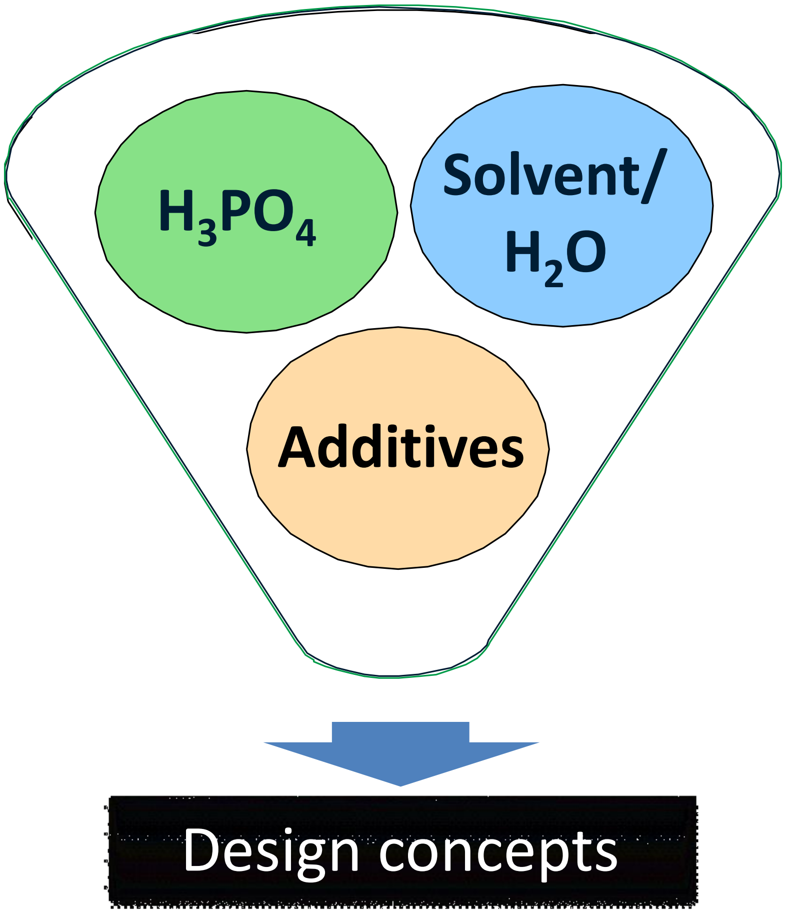


- To selectively remove the SiNx from the stack w/o damaging SiOx, high selective SiNx etch chemical is necessary.
- Hot phosphoric acid is a well-known wet etchant for SiNx removal, which can remove SiNx with minimal damage on SiOx.

$$3Si_3N_4 + 4H_3PO_4 + 27H_2O \rightarrow 4(NH_4)_3PO_4 + 9H_2SiO_3$$

- However, conventional H_3PO_4 chemistry faces challenges as the number of layers is >48. Therefore, the formulated H_3PO_4 chemistry is developed to further improve SiNx to SiOx selectivity.

Design Concepts



H_3PO_4

Solvent/ H_2O

Additives

Design concepts

H_3PO_4

Etchant for SiNx

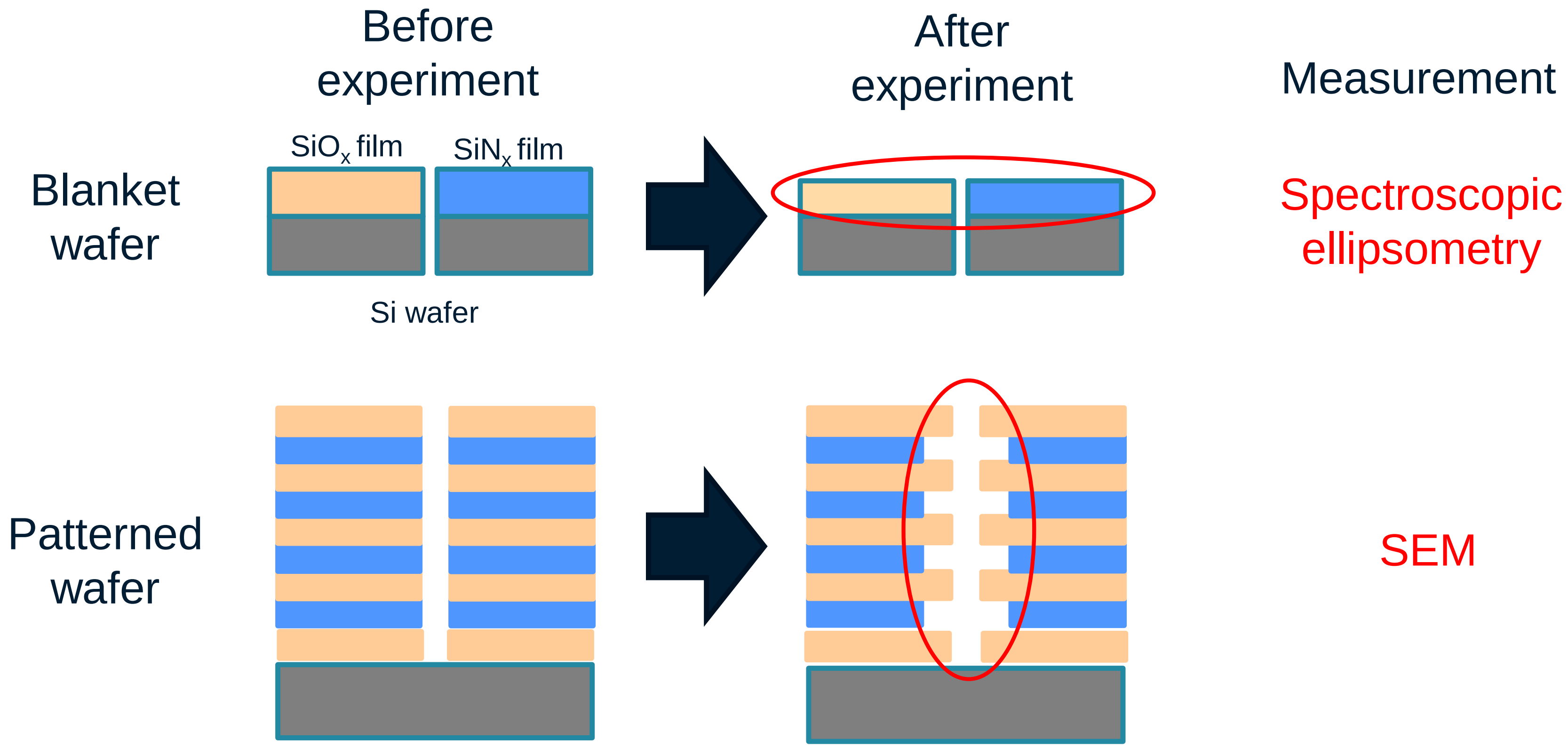
Solvents/H_2O

1. Improve SiNx to SiOx selectivity
2. Enhance the miscibility between H_3PO_4 and additives

Additives

1. Improve SiNx to SiOx selectivity
2. Oxide regrowth can be eliminated by adding proper additives

Experimental Process & Measurement



Before experiment

After experiment

Measurement

Blanket wafer

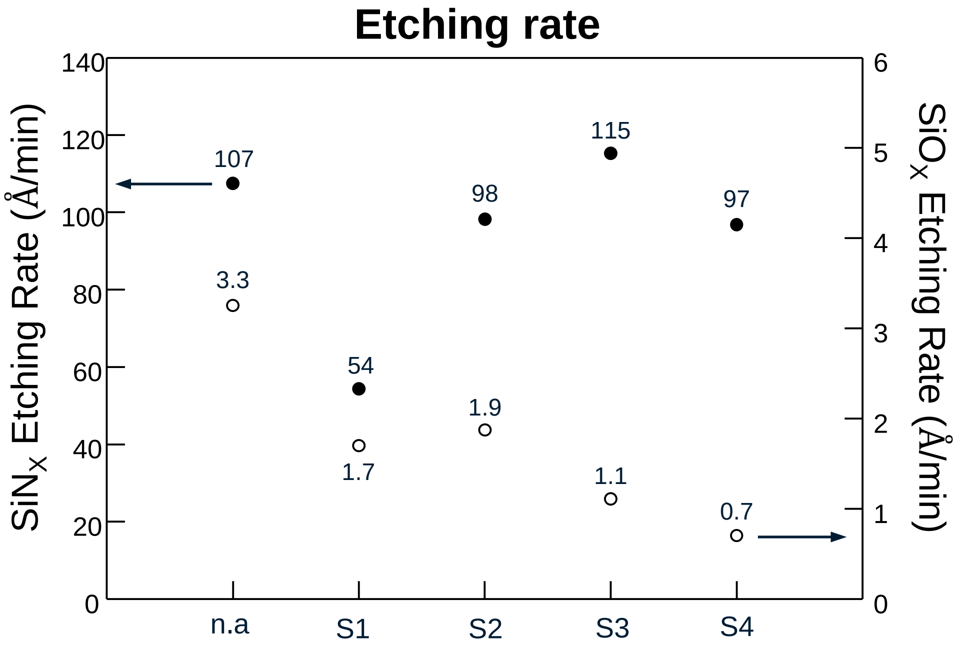
Spectroscopic ellipsometry

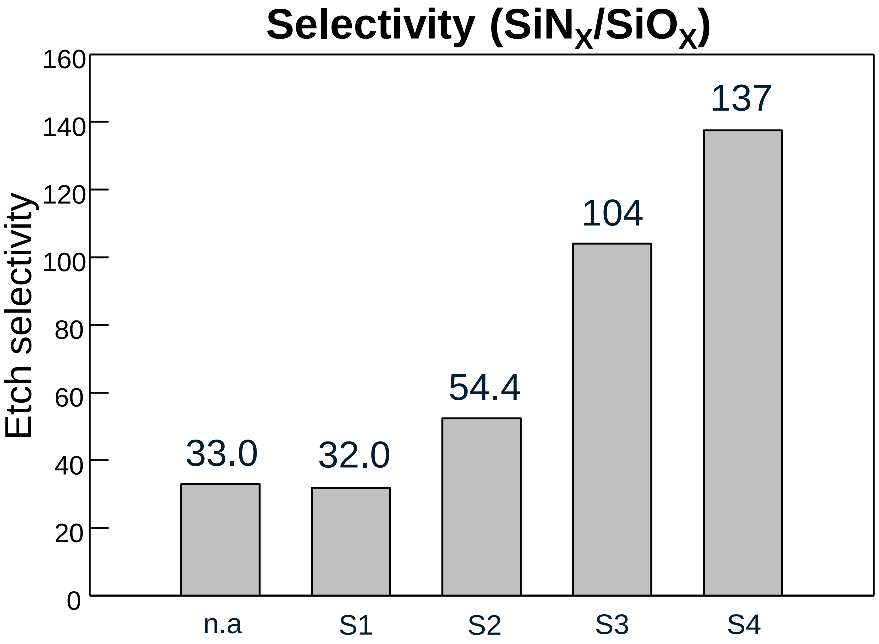
Patterned wafer

SEM

DHF(H_2O:HF=100:1) pretreatment was performed for 3mins on SiN_x blanket wafer and patterned wafer before etching experiments were performed.

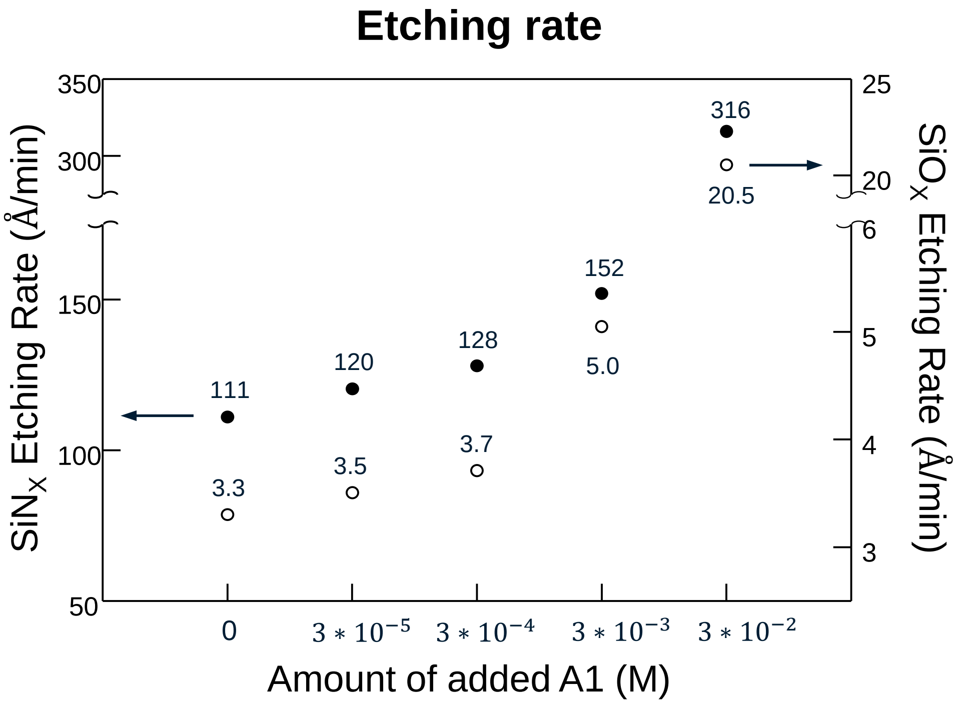
Effect from Solvent Addition

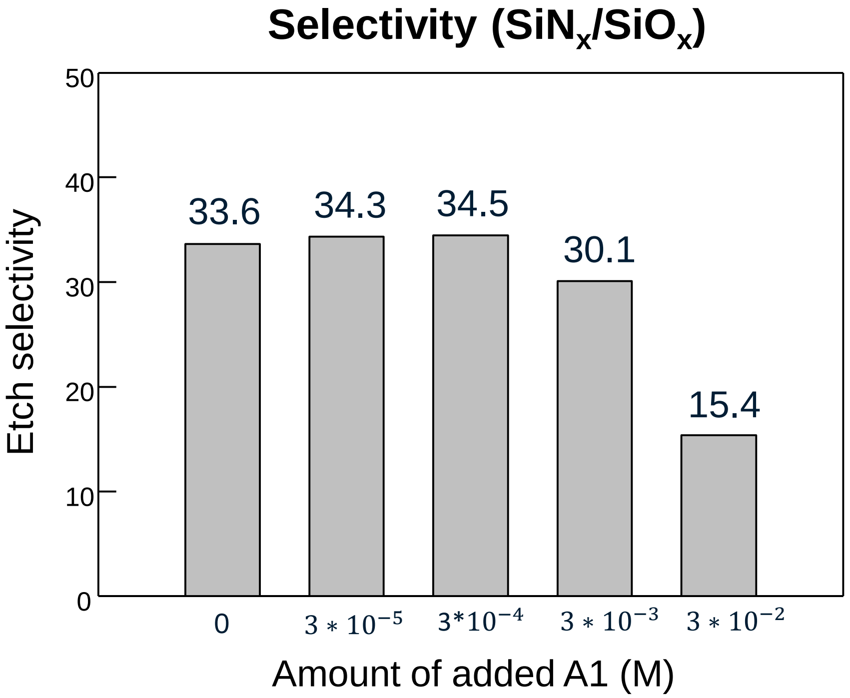

Etching rate


Selectivity (SiN$_X$/SiO$_X$)

- **With the addition of various solvents, etching of SiO$_X$ was suppressed.**
- **Addition of S1 decreased etch rates of both SiN$_X$ and SiO$_X$ without change of selectivity.**
- **Addition of S2 more decreased etch rate of SiO$_x$ with a selectivity increase to 54.**
- **Addition of S3 and S4 which have a specific functional group greatly suppressed the etching rate of SiO$_x$ with huge increases of selectivity to 104 and 137, respectively.**

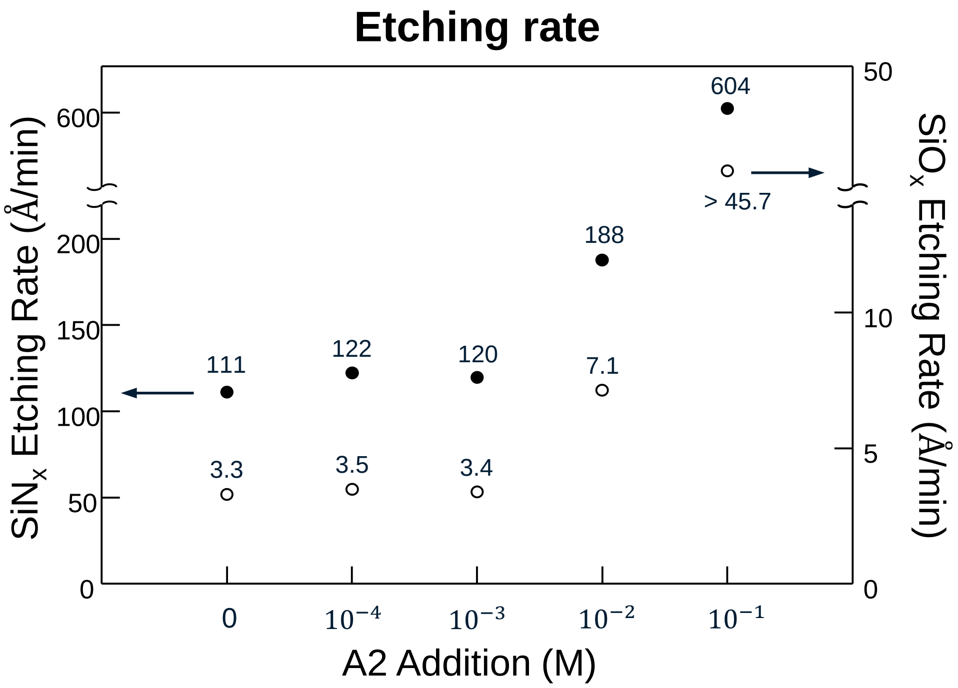
Effect from Additive(Type A) Addition – A1

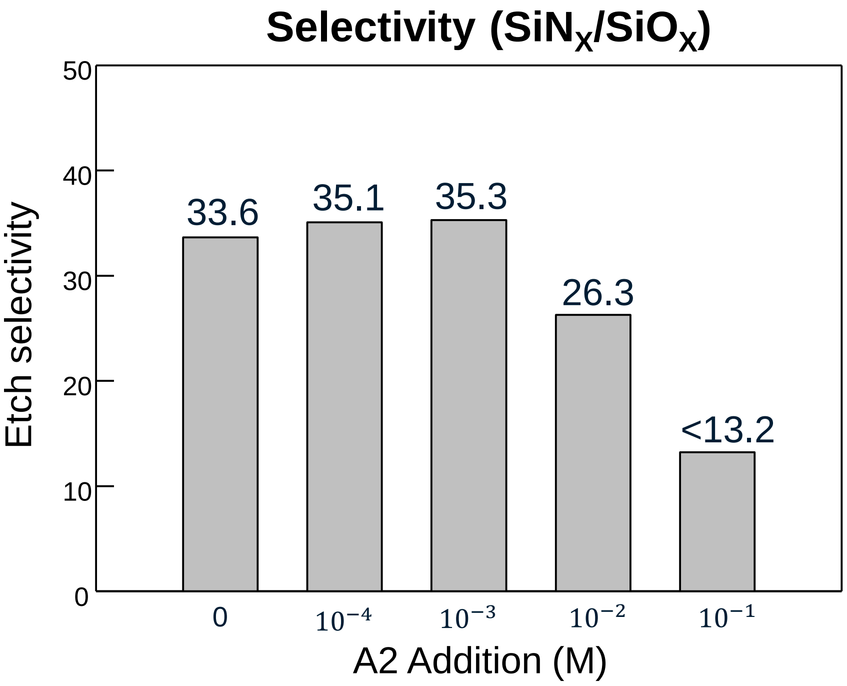




- **As the amount of added A1 increases, the etching rates of SiN_X and SiO_X increase.**
- **When $3*10^{-2}$M of A1 is added, the etching rate of SiN_x increases 2.8 times and that of SiO_x increases 6.2 times.**
- **With the addition of A1, etching rate of SiN_X increases but etching rate of SiO_X increases more, thus selectivity decreases.**

Effect from Additive(Type A) Addition – A2


Etching rate


Selectivity (SiN_X/SiO_X)

- **Etching rates of SiN_X and SiO_X remarkably increased with addition of A2 over 0.01 M. With 0.1 M addition, etching rates increased by 5.4 and 13.8 times for SiN_X and SiO_X, respectively.**
- **With the addition of A2, etching rate of SiN_X increases but etching rate of SiO_X increases more, thus selectivity decreases.**

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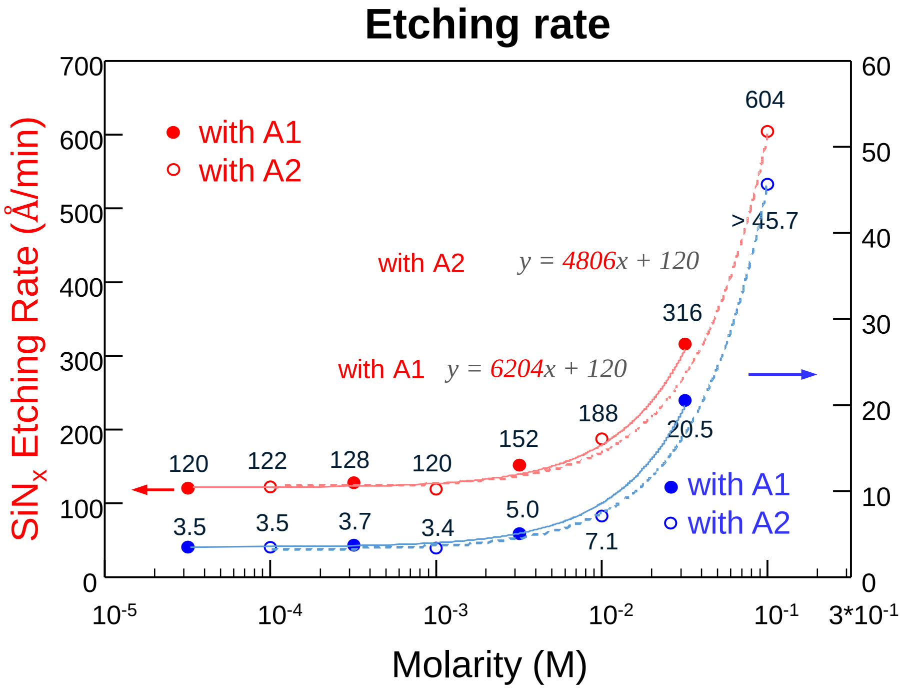
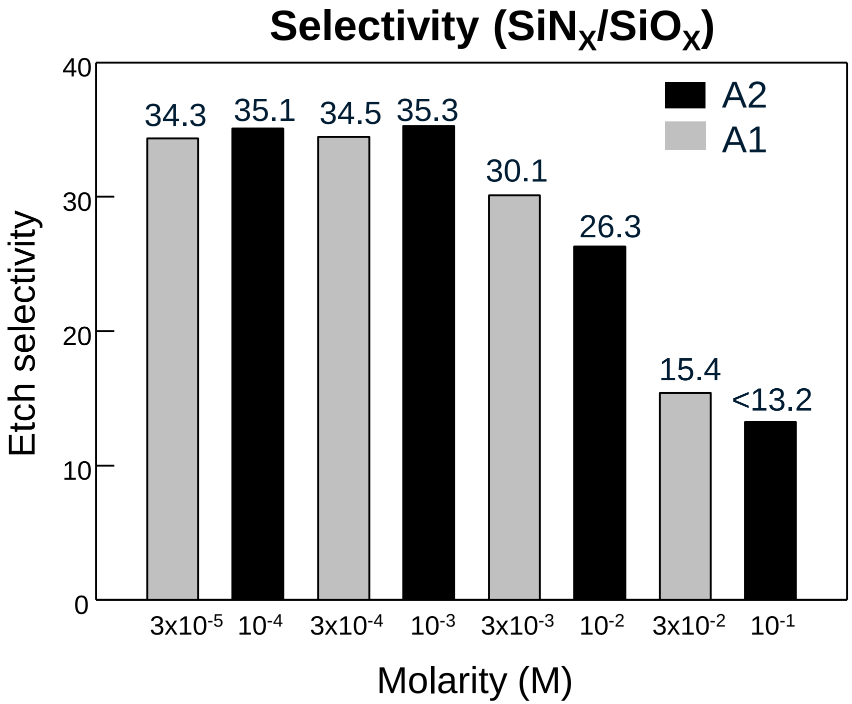
Comparison of the Effects from A1 & A2


Etching rate


Selectivity (SiN$_X$/SiO$_X$)

- **A1 and A2 are composed of the same anion, but different cations.**
- **Etching rates of SiN$_x$ and SiO$_x$ were fitted by linear function of additive's molarity. At a given ER$_0$ (intercept) of 120 Å/min, the coefficient (slope) of the molarity function for the etching rate of SiN$_x$ was larger with addition of A1 (~6200) than A2 (~4800), and the coefficient of the molarity function for the etching rate of SiO$_x$ was also larger with addition of A1 (542) than A2 (425).**
- **Etching rates of SiN$_x$ and SiO$_x$ with addition of A1 were observed to be as high as 1.3 times of those with addition of A2. No significant effect from the cation on the increase in the etching rate is observed.**

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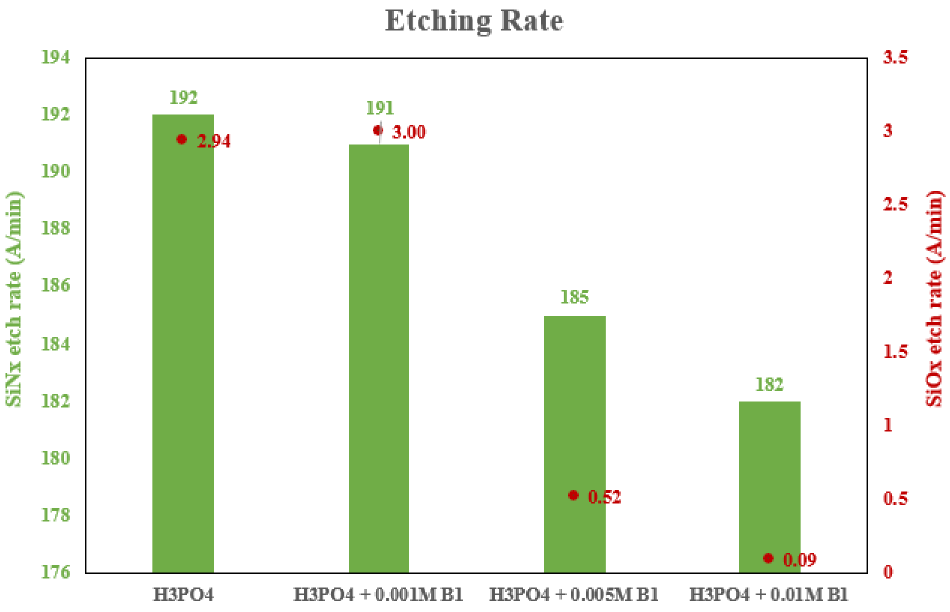
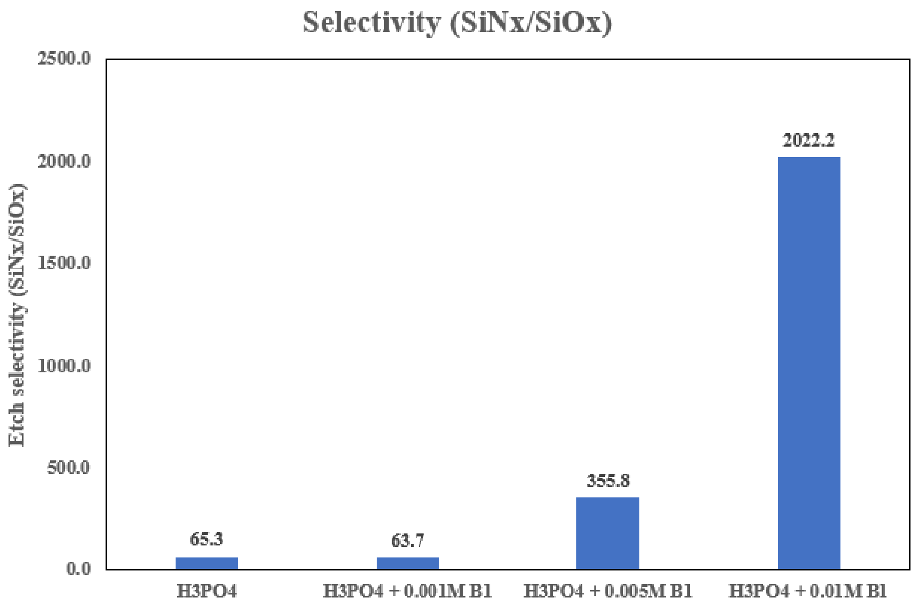
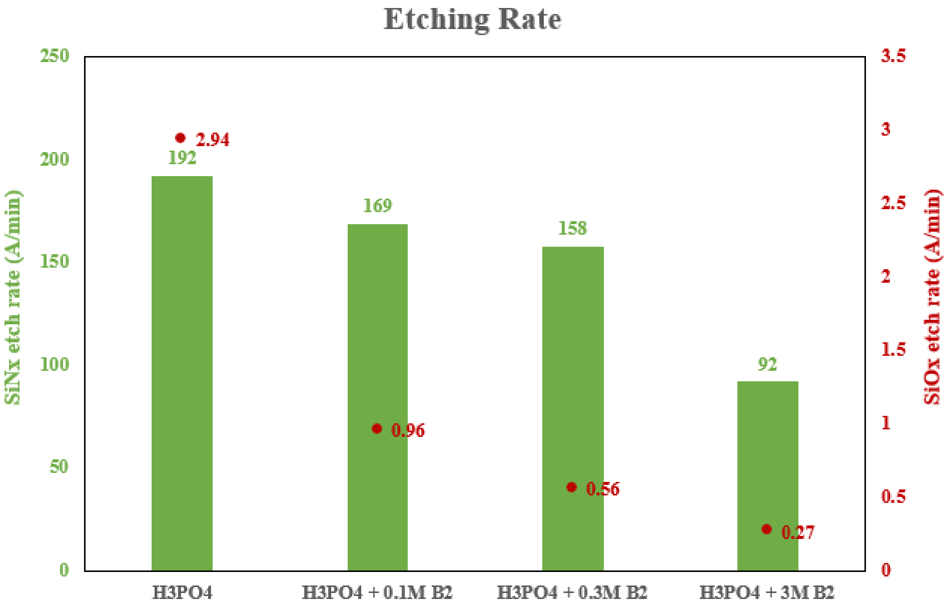
Effect from Additive(Type B) Addition – B1

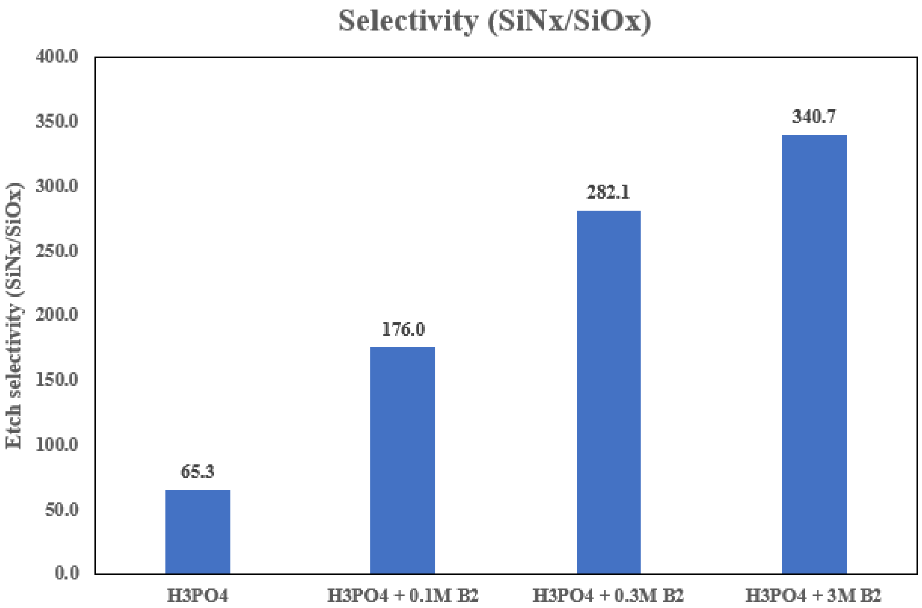




- **With the decrease in B1 concentration from 0.01M to 0.001M, SiNx etch rate increased, but SiOx etch rate increase more, thus SiNx/SiOx selectivity decreased.**
- **The concentration of B1 at around 0.01M can achieve 2000:1 etch selectivity.**
- **However, it showed oxide regrowth and clogging problem on pattern structure by processing with B1 contained chemicals.**

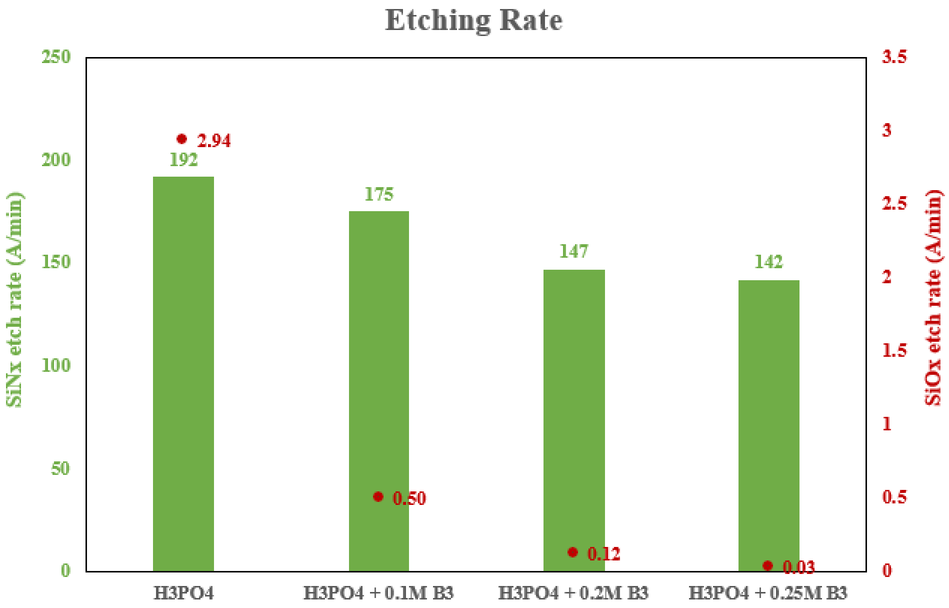
Effect from Additive(Type B) Addition – B2

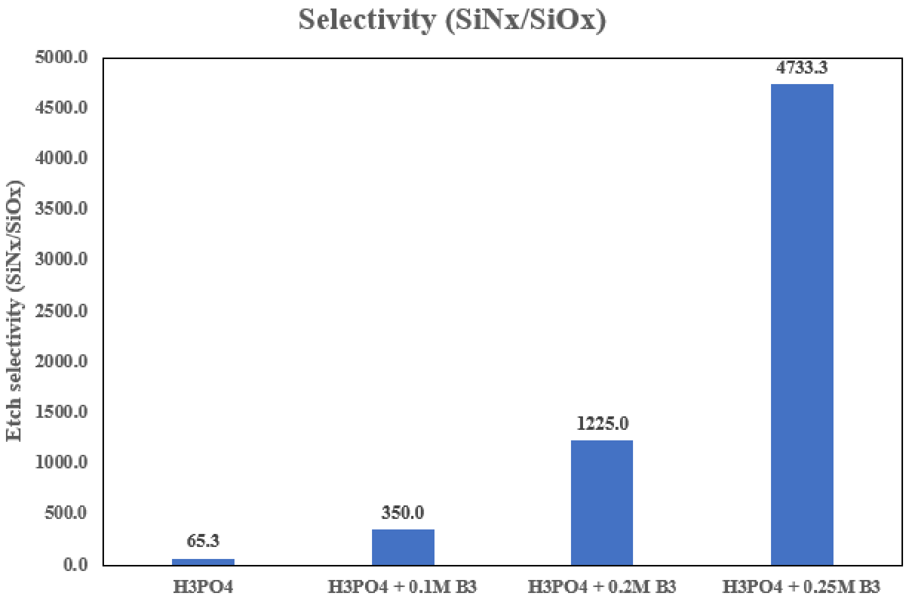




- **With the increase in B2 concentration from 0.1M to 3M, both SiNx and SiOx etch rates decreased, and SiOx etch rate decrease more, thus SiNx/SiOx selectivity increased.**
- **However, with such high concentration(3M) of B2 addition, it still can't achieve 2000:1 etch selectivity, and SiNx etch rate became too low that would lead to long process time.**
- **By processing with B2 contained chemicals on pattern structure, it showed uniform etching from top to bottom. In addition, no clogging and no thinning of SiOx trench layer were observed.**

Effect from Additive(Type B) Addition – B3





- **With the increase in B3 concentration from 0.1M to 0.25M, both SiNx and SiOx etch rates decreased, and SiOx etch rate decrease more, thus SiNx/SiOx selectivity increased.**
- **The concentration of B3 at 0.25M can achieve the etch selectivity higher than 2000:1.**
- **By processing with B3 contained chemicals on pattern structure, it showed uniform etching from top to bottom. In addition, no clogging and no thinning of SiOx trench layer were observed.**
- **However, the miscibility between H_3PO_4 and B3 is not good, and it needs to add other components to improve miscibility.**

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Comparison of B1, B2 & B3

Chemical	SiN_X E/R (A/min)	SiO_X E/R (A/min)	Selectivity (SiN_x/SiO_x)	Miscibility	Pattern Performance
H_3PO_4	192	2.94	65.3	-	-
H_3PO_4 + 0.01 M B1	182	0.09	2022.2	Bad	Clogging
H_3PO_4 + 3.0 M B2	92	0.27	340.7	Good	Uniform etching No clogging No thinning
H_3PO_4 + 0.25 M B3	142	0.03	4733.3	Not good	Uniform etching No clogging No thinning

Miscibility Improvement by Solvent Addition

Chemical	SiN_X E/R (A/min)	SiO_X E/R (A/min)	Selectivity (SiN_x/SiO_x)	Miscibility
H_3PO_4 + 0.25 M B3	142	0.03	4733.3	Cloudy
H_3PO_4 + 0.25 M B3 + 3wt% S6	148	0.10	1480.0	Cloudy
H_3PO_4 + 0.25 M B3 + 3wt% S7	146	0.05	2920.0	Opaque
H_3PO_4 + 0.25 M B3 + 3wt% S8	145	0.07	2071.4	Slightly Opaque

- S6, S7 and S8 are solvents with the same carbon number but different functional groups.
- Polarity: S6 > S7 > S8
- By adding S8, the solvent with lower polarity, in H_3PO_4 + 0.25 M B3, the miscibility is improved most.
- S7 contains the same functional group as S3, and it showed the best SiNx/SiOx selectivity.

Miscibility Improvement by Solvent Addition

Chemical	SiN_X E/R (A/min)	SiO_X E/R (A/min)	Selectivity (SiN_x/SiO_x)	Miscibility
H_3PO_4 + 0.25 M B3	142	0.03	4733.3	Cloudy
H_3PO_4 + 0.25 M B3 + 3wt% S7	146	0.05	2920.0	Opaque
H_3PO_4 + 0.25 M B3 + 3wt% S9	148	0.07	2114.3	Slightly Opaque
H_3PO_4 + 0.25 M B3 + 3wt% S10	153	0.06	2550.0	Transparent
H_3PO_4 + 0.25 M B3 + 3wt% S11	158	0.14	1128.6	Slightly Opaque

- S7, S9, S10 and S11 are solvents with the same functional group but different carbon numbers.
- Carbon number: S11 > S10 > S9 > S7; Polarity: S7 > S9 > S10 > S11
- By adding S10, the solvent with proper polarity, in H_3PO_4 + 0.25 M B3, the miscibility is improved most and the appearance is transparent. Meanwhile, SiNx/SiOx selectivity is still kept higher than 2000:1.

Effect from S10 Addition

Chemical	SiN_X E/R (A/min)	SiO_X E/R (A/min)	Selectivity (SiN_x/SiO_x)	Miscibility
H_3PO_4 + 0.25 M B3	142	0.03	4733.3	Cloudy
H_3PO_4 + 0.25 M B3 + 1wt% S10	149	0.05	2980.0	Slightly Opaque
H_3PO_4 + 0.25 M B3 + 3wt% S10	153	0.06	2550.0	Transparent
H_3PO_4 + 0.25 M B3 + 5wt% S10	162	0.10	1620.0	Transparent

- With higher concentration of S10 addition, the miscibility of the mixtures became better.
- With the increase in S10 concentration from 1wt% to 5wt%, SiNx etch rate increased, but SiOx etch rate increase more, thus SiNx/SiOx selectivity decreased.
- From both miscibility and selectivity aspects, H_3PO_4 + 0.25 M B3 + 3wt% S10 is the best combination.

Performance of H_3PO_4+0.25M B3+3wt% S10

Chemical	SiN_X E/R (A/min)	SiO_X E/R (A/min)	Selectivity (SiN_x/SiO_x)	Miscibility	Pattern Performance
H_3PO_4 + 0.25 M B3 + 3wt% S10	153	0.06	2550.0	Transparent	Uniform etching No clogging No thinning

- **By combination of H_3PO_4 with 0.25M B3 and 3wt% S10, it showed good miscibility and the appearance is transparent.**
- **H_3PO_4 + 0.25 M B3 + 3wt% S10 can achieve the SiNx/SiOx selectivity higher than 2000:1**
- **Additionally, it also performs uniform etching on patterned structure. Besides, no thinning of SiOx layer and no oxide regrowth while SiNx layer is totally removed.**

Summary

- Conventional H_3PO_4 chemistry faces challenges as the number of layers is >48. Therefore, we are developing the formulated H_3PO_4 chemistry to further improve SiNx/SiOx selectivity.
- Addition of the solvents with a specific functional group can greatly increase SiNx/SiOx selectivity.
- Addition of type A additives can promote SiN_X etch rate, but SiO_X etch rate would increase more at the same time, thus SiNx/SiOx selectivity decreases.
- By adding 0.25M B3 in H_3PO_4 can achieve the etch selectivity higher than 2000:1. In addition, it showed uniform etching from top to bottom on pattern structure, meanwhile no clogging and no thinning of SiOx trench layer were observed. However, the miscibility between H_3PO_4 and B3 is not good, and it needs to add other components to improve miscibility.
- By combination of H_3PO_4 with 0.25M B3 and 3wt% S10, it showed good miscibility and can achieve the SiNx/SiOx selectivity higher than 2000:1. Additionally, it also performs uniform etching on patterned structure. Besides, no thinning of SiOx layer and no oxide regrowth while SiNx layer is totally removed.

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THANK YOU

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