



# Selective wet etching of Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> in phosphoric acid with the addition of fluoride and silicic compounds<sup>☆</sup>



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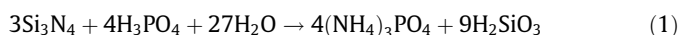
## ABSTRACT

Various additives were added to H<sub>3</sub>PO<sub>4</sub> in order to achieve a highly selective wet etching of Si<sub>3</sub>N<sub>4</sub> to SiO<sub>2</sub>. Fluoride compounds such as HF, NH<sub>4</sub>F, and NH<sub>4</sub>HF<sub>2</sub> were added to the H<sub>3</sub>PO<sub>4</sub> in order to increase the etch rate of the Si<sub>3</sub>N<sub>4</sub>. In addition, silicic compounds, including H<sub>2</sub>SiF<sub>6</sub>, TEOS, and Si(OH)<sub>4</sub>, were added to decrease the etch rate of SiO<sub>2</sub>. The addition of the fluoride compounds into the H<sub>3</sub>PO<sub>4</sub> increased the etch rate of the Si<sub>3</sub>N<sub>4</sub>, but the etch selectivity of the Si<sub>3</sub>N<sub>4</sub> to SiO<sub>2</sub> decreased due to the greater increase in the etch rate of the SiO<sub>2</sub>. Both the etch rate and the selectivity showed strong relationships with the amount of fluorine added in H<sub>3</sub>PO<sub>4</sub>. The addition of TEOS and Si(OH)<sub>4</sub> increased the etch selectivity by reducing the etch rate of the SiO<sub>2</sub>. In particular, the addition of Si(OH)<sub>4</sub> to H<sub>3</sub>PO<sub>4</sub> in the presence of NH<sub>4</sub>F and NH<sub>4</sub>HF<sub>2</sub> produced an etch selectivity greater than 10<sup>4</sup>.

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## 1. Introduction

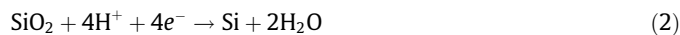
Silicon dioxide (SiO<sub>2</sub>) and silicon nitride (Si<sub>3</sub>N<sub>4</sub>) are dielectric materials that are used extensively in semiconductor devices such as logic and memory devices. They can be used as a passivation layer, an implantation barrier layer, an isolation layer and other applications. However, highly selective etching should be performed for the fabrication of large scale integrated circuits in the presence of both SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> on the wafer surface; for example, on the shallow trench isolation (STI) structure for submicron devices [1]. Generally, Si<sub>3</sub>N<sub>4</sub> is highly resistant to many chemicals, but it is etched in H<sub>3</sub>PO<sub>4</sub> by the following process [2]:



when focusing on the etching of Si<sub>3</sub>N<sub>4</sub>, the etch selectivity is defined as the etch rate of the Si<sub>3</sub>N<sub>4</sub> film over that of SiO<sub>2</sub>, since the Si<sub>3</sub>N<sub>4</sub> film is etched in boiling H<sub>3</sub>PO<sub>4</sub> at a much higher rate than SiO<sub>2</sub> [3]. A well-defined STI fabricated by highly selective etching produces smaller junction leakage current and junction capacitance [4] as well as better device performance [5]. On the contrary, low etch selectivity induces a variation in the effective field height [1]. Etch selectivity is critical; however, it is not desirable to lower the etch rates of both the Si<sub>3</sub>N<sub>4</sub> and SiO<sub>2</sub>, because slow etch rates reduce the process efficiency. Therefore, an etching process that produces

high etch selectivity of Si<sub>3</sub>N<sub>4</sub> to SiO<sub>2</sub> and has a high Si<sub>3</sub>N<sub>4</sub> etch rate is required.

It has been reported that the etching of Si<sub>3</sub>N<sub>4</sub> forms hydrated silica and ammonium phosphate in the etchant [2]. The hydrated silica slows down the etching of the Si<sub>3</sub>N<sub>4</sub> and SiO<sub>2</sub> thin films, because the reaction system tends to maintain equilibrium. Therefore, it was determined that both the etch rate and the selectivity are affected by the presence of dissolved silicic material in the etching bath. In addition, the water content in the bath affects the etch rate of Si<sub>3</sub>N<sub>4</sub> [6]. While the reaction equation of Si<sub>3</sub>N<sub>4</sub> etching is given as Eq. (1), the etching of SiO<sub>2</sub> is not described well by Eq. (1). Etching of SiO<sub>2</sub> is determined by the H<sup>+</sup> concentration decomposed from H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, and HPO<sub>4</sub><sup>2-</sup> as well as the water content [6]:



Taking into consideration the etching reaction mechanisms of Si<sub>3</sub>N<sub>4</sub> and SiO<sub>2</sub> shown in Eqs. (1) and (2), it has been shown that the addition of several additives can improve the etch selectivity of Si<sub>3</sub>N<sub>4</sub> to SiO<sub>2</sub> by controlling the reaction mechanism [1,6,7]. The most common method for improving etch selectivity in the past has been to suppress the etching of the SiO<sub>2</sub>.

For example, the addition of hydrofluorosilicic acid (H<sub>2</sub>SiF<sub>6</sub>) into H<sub>3</sub>PO<sub>4</sub> improved etch selectivity of Si<sub>3</sub>N<sub>4</sub> to SiO<sub>2</sub> by inhibiting the etching of the SiO<sub>2</sub> and accelerating the etching of the Si<sub>3</sub>N<sub>4</sub> within a certain temperature range [7]. It has also been reported that the addition of H<sub>2</sub>SO<sub>4</sub> significantly reduced the etch rate of SiO<sub>2</sub>, thereby increasing the etch selectivity [8]. However, the amount of added H<sub>2</sub>SO<sub>4</sub> in H<sub>3</sub>PO<sub>4</sub> was as high as 75 vol.% and only produce a few-fold higher etch selectivity [8].

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In this study, two kinds of additives were added to the  $\text{H}_3\text{PO}_4$ : fluoride compounds to increase the etching of  $\text{Si}_3\text{N}_4$  and silicic compounds to suppress the etching of  $\text{SiO}_2$ . The addition of fluoride compounds to the solution may produce  $\text{F}^-$ , which is known to primarily etch  $\text{Si}_3\text{N}_4$  [9]. Also, this addition may generate difluoride ( $\text{HF}_2^-$ ), which is a primary source of  $\text{SiO}_2$  etching [9–11]. However, in strong acidic solution such as  $\text{H}_3\text{PO}_4$ , it is unlikely for anionic fluoride species like  $\text{F}^-$  and ( $\text{HF}_2^-$ ) to exist. Therefore, the correlation of the fluoride compound concentration with the etch rate and selectivity was studied. In particular, the effects of the addition of two different kinds of additives on the etch rates of  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  and the wet etch selectivity of  $\text{Si}_3\text{N}_4$  to  $\text{SiO}_2$  were investigated.

## 2. Experiments

In order to study the selective etching of  $\text{Si}_3\text{N}_4$  to  $\text{SiO}_2$ , wafers with low pressure chemical-vapor-deposited (LPCVD)  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  were prepared. Then, the wafers were cut into  $2 \times 2$  cm. Phosphoric acid (85%  $\text{H}_3\text{PO}_4$ , OCI Co., Ltd.) was used as the primary etchant. For the purpose of increasing the etch rate of  $\text{Si}_3\text{N}_4$ , three types of fluoride compounds were added to the  $\text{H}_3\text{PO}_4$ : hydrofluoric acid (HF, 48 wt.% in water, Sigma–Aldrich), ammonium fluoride solution ( $\text{NH}_4\text{F}$ , 40% in water, Sigma–Aldrich), and ammonium hydrogen difluoride ( $\text{NH}_4\text{HF}_2$ , 99.999%, Aldrich). In order to inhibit the etching of  $\text{SiO}_2$ , three types of silicic compounds, hydrofluorosilicic acid ( $\text{H}_2\text{SiF}_6$ , 40%, DC Chemical Co., Ltd.), tetraethyl ortho-silicate (TEOS,  $\text{Si}(\text{OC}_2\text{H}_5)_4 \geq 99.9\%$ , Sigma–Aldrich), and monosilicic acid ( $\text{Si}(\text{OH})_4$ , 99.9%, Sigma–Aldrich), were added to the  $\text{H}_3\text{PO}_4$ . After the addition of the additives, a PFA-coated magnetic bar was put into the bath, and the etchant was stirred on a stirrer for 15 min. The etching bath was covered with a glass lid and sealed with parafilm in order to prevent the evaporation of the etchant. Then, the etchant was heated until the temperature reached  $165^\circ\text{C}$ . The  $\text{Si}_3\text{N}_4$  wafer was first immersed in the etchant for 15 min. After the  $\text{Si}_3\text{N}_4$  wafer was taken out of the etchant, the  $\text{SiO}_2$  wafer was immersed in the etchant and etched for 15 min. In STI layer processing, both  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  etching occurs simultaneously rather than sequentially. However, we discovered from our preliminary study that better reproducibility in etch results could be achieved in a sequential etch process, which is why, in the current study,  $\text{SiO}_2$  has been etched in a bath where products such as hydrated silica from the preceding  $\text{Si}_3\text{N}_4$  etch are pre-existing. Thus, we expected the effect of fluoride and other additives on the etching of  $\text{SiO}_2$  to be easily observed, with reduced impact of the hydrated silica in the solution due to a sequential etch process. In addition, fresh wafers were used for each run. On the other hand, in order to investigate the effects of the etching cycle on the etch rates and selectivity, five groups of each  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  were successively etched for 10 min in the same etchant. In that case,  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  films were etched simultaneously. A deionized (DI) water rinse was performed after each etching process. The etch rates of  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  were calculated by measuring their thicknesses before and after each etching process using a spectroscopic ellipsometry (MG-1000, Nano-View). An incident angle of  $69.48^\circ$  was used. The thicknesses at nine different locations were measured and averaged. The etch selectivity was calculated by dividing the etch rate of the  $\text{Si}_3\text{N}_4$  by that of  $\text{SiO}_2$ .

## 3. Results and discussion

In order to increase the etch rate of the  $\text{Si}_3\text{N}_4$ , the following fluoride compounds, HF,  $\text{NH}_4\text{F}$ , and  $\text{NH}_4\text{HF}_2$ , were added to the  $\text{H}_3\text{PO}_4$ . Fig. 1(a) shows the changes in the etch rates of  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  depending on the concentrations of HF,  $\text{NH}_4\text{F}$ , and  $\text{NH}_4\text{HF}_2$ . The etch rate of the  $\text{Si}_3\text{N}_4$  increased with the concentrations of all fluo-

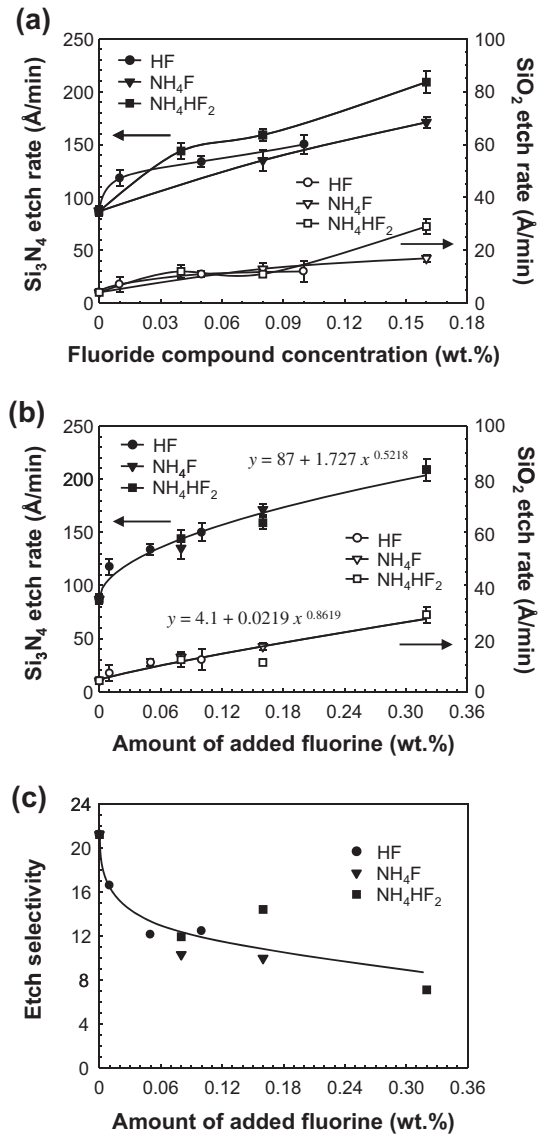


Fig. 1. (a) and (b) Etch rates of  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  films and (c) etch selectivity of  $\text{Si}_3\text{N}_4$  to  $\text{SiO}_2$  with the addition of HF,  $\text{NH}_4\text{F}$ , and  $\text{NH}_4\text{HF}_2$ .

ride compounds. However, the  $\text{SiO}_2$  etch rate also increased as the concentration of the fluoride compounds increased. Although  $\text{SiO}_2$  is etched primarily by difluoride ( $\text{HF}_2^-$ ) and  $\text{Si}_3\text{N}_4$  is etched by monofluoride ( $\text{F}^-$ ) when they are present in dilute aqueous solution [9–11], those anionic species may not exist in 85%  $\text{H}_3\text{PO}_4$  even after the addition of HF,  $\text{NH}_4\text{F}$ , and  $\text{NH}_4\text{HF}_2$ . Instead, the addition of fluoride compounds such as HF,  $\text{NH}_4\text{F}$ , and  $\text{NH}_4\text{HF}_2$  can produce volatile  $\text{SiF}_4$  and  $\text{H}_2\text{SiF}_6$  by reaction with the hydrated silica dissolved in aqueous solution [12]. As a result, the etch rate of  $\text{SiO}_2$  as well as that of  $\text{Si}_3\text{N}_4$  increases due to the reduced concentration of hydrated silica in the bath,  $[\text{SiO}_2]_{\text{aq}}$ .

On the other hand, it is reported that  $\text{NH}_4\text{F}$  can be dissolved and ionized into  $\text{NH}_4^+$  and  $\text{F}^-$ , and  $\text{NH}_4\text{HF}_2$  can be ionized into  $\text{NH}_4^+$  and  $\text{HF}_2^-$  [13]. In this case, the concentration of  $\text{HF}_2^-$  would be higher with the addition of  $\text{NH}_4\text{HF}_2$  than with  $\text{NH}_4\text{F}$ , and a higher etch rate of  $\text{SiO}_2$  and a lower etch rate of  $\text{Si}_3\text{N}_4$  would be observed with the addition of  $\text{NH}_4\text{HF}_2$ , as compared with the addition of HF and  $\text{NH}_4\text{F}$ . However, an increase was observed in both the etch rates of  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  with the addition of  $\text{NH}_4\text{HF}_2$ , as shown in Fig. 1a, which implies that the etching of  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  was not driven by  $\text{F}^-$  and  $\text{HF}_2^-$ . Therefore, the etch rate of  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  is thought

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