

## MECHANISM OF SILICON ETCHING IN HF-KMnO<sub>4</sub>-H<sub>2</sub>O SOLUTION

Kee Suk Nahm<sup>†</sup> and Young Hun Seo

Department of Chemical Engineering and Technology, Chonbuk National University, Chonju 560-756, Rep. of Korea

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**Abstract**—The etching reaction of silicon in HF-KMnO<sub>4</sub>-H<sub>2</sub>O mixed solution has been studied under various experimental conditions. The etch rates were measured as a function of agitation speed, HF and KMnO<sub>4</sub> concentrations, and etching temperature and time. A comprehensive mechanism for the silicon etching and insoluble solid-phase film (K<sub>2</sub>SiF<sub>6</sub>) formation has been proposed. The holes formed at silicon surface accelerated not only the etch rate of silicon but also the formation rate of K<sub>2</sub>SiF<sub>6</sub>. With the increase of hole concentration at lower HF concentrations the etch rates decreased because of the deposition of K<sub>2</sub>SiF<sub>6</sub> on etched silicon surface. Under the condition of sufficiently high HF concentration, the rate increased with the increase of hole formation and the formation of holes at silicon surface was the rate limiting step of the silicon etching reaction in HF-KMnO<sub>4</sub>-H<sub>2</sub>O solution. High HF concentration enough for dissolving K<sub>2</sub>SiF<sub>6</sub> was apparently essential to obtain high etch rate in the silicon etching reaction.

**Key words:** Silicon Surface, Etch Rate, Etching Reaction Mechanism, HF-KMnO<sub>4</sub>-H<sub>2</sub>O Solution, Insoluble Solid Phase K<sub>2</sub>SiF<sub>6</sub>, Dissolution, Intermediate Species, Oxidizing Agent, Redox Potential, Hole Formation

### INTRODUCTION

The wet chemical etching technology has been widely used for wafer polishing and cleaning, and for delineation of the required patterns on the thin films in semiconductor fabrication processes [O'Connor et al., 1988; Huo et al., 1989]. HF-KMnO<sub>4</sub>-H<sub>2</sub>O mixed solution has long been used for the etching of silicon, but most studies for this etching system merely described the observed etch rate and morphology with the variation of etching condition [Theunissen et al., 1970; Schimmel and Elkind, 1978]. The previous reported data for the etching process in HF-oxidizing agent-H<sub>2</sub>O based etchants reveal that at low HF concentration a solid-phase film that is usually soluble in HF solution is formed on the silicon surface and inhibits the etching reaction [Ohmi et al., 1992; Matsumura and Morrison, 1983]. This film usually has a strong influence on the characteristics and mechanism of the silicon etching. Therefore the study on the etching mechanism of silicon in HF-KMnO<sub>4</sub>-H<sub>2</sub>O solution is apparently significant to explain explicitly the effects of etchants on the etch rate and morphology, and the cause of the formation of the insoluble film.

The etching reaction of silicon was examined under various etching conditions to investigate the mechanism of silicon etching reaction in HF-KMnO<sub>4</sub>-H<sub>2</sub>O mixed solution. The etch rates were measured as a function of agitation speed, HF and KMnO<sub>4</sub> concentrations, and etching temperature and time. The formation mechanism of the surface species during etching process was also discussed intensely. Various analytic techniques were used to study the chemical species of etched wafer surfaces.

### EXPERIMENT

p-type Si (100) single crystal wafers manufactured by Siltron, Inc. with Czochralski technique were used in this experiment. The p-Si (100) was doped with boron and had the resistivity of

7-9 ohm-cm. KMnO<sub>4</sub> and 48% (24M) HF of reagent grade, and deionized water were used to make etching solutions of various compositions.

Silicon specimens of 10 mm × 10 mm was etched in a cylindrical polypropylene reactor. The experimental apparatus used in this work are described elsewhere [Seo et al., 1993, 1994].

Prior to the etching reaction silicon sample was cleaned with acetone and treated with 48% HF solution to remove organic impurities and native oxide films of the silicon surface. It was then rinsed with DI water and dried with a nitrogen.

With the exception of reacting surface all the specimen surfaces were covered with photoresist, and the test sample was mounted on the center of the reactor bottom. After placing the reactor in the water bath at a fixed temperature, etching solution of 40 cm<sup>3</sup> was added into the reactor and the reaction started. The etching solutions of 40 cm<sup>3</sup>, which is mixed solution of 20 cm<sup>3</sup> KMnO<sub>4</sub> and 20 cm<sup>3</sup> HF, was used in each run. The experimental data were taken in the etching solution of various compositions over temperature ranges from 273 K to 323 K. The etching solution was stirred sufficiently enough to exclude the effect of mass transfer on the liquid-solid reaction.

A microbalance Mettler 3M of capacity up to 10<sup>-8</sup> g was used to weigh the sample before and after etching reaction. The etch rate was obtained by dividing the amount of etched Si by reaction time, exposed wafer area (0.196 cm<sup>2</sup>) and Si density (2.33 g/cm<sup>3</sup>), and was compared with that measured by a scanning electron microscope (SEM). The morphologies of the surfaces and cross-sections of the etched Si wafer were observed with SEM. The surface chemistry after etching was analyzed by Auger electron spectroscopy (AES), inductively coupled plasma-atomic emission spectroscopy (ICP) and X-ray diffraction (XRD).

### RESULTS

#### 1. Effect of Agitation and Etching Time

The effect of agitation speed on etch rate of silicon was exam-

<sup>†</sup>The author to whom all correspondences should be addressed.

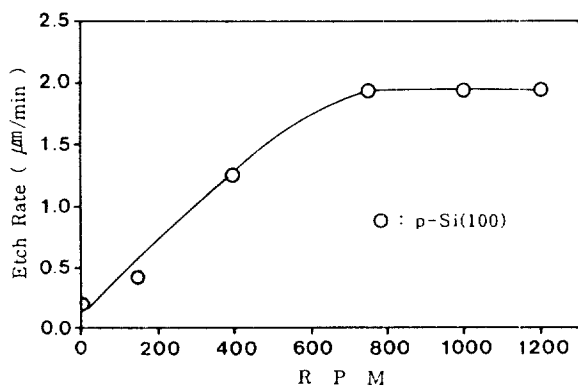


Fig. 1. The effect of agitation speed on etch rate in 12 M HF-0.05 M KMnO<sub>4</sub>-H<sub>2</sub>O solution at 293 K.

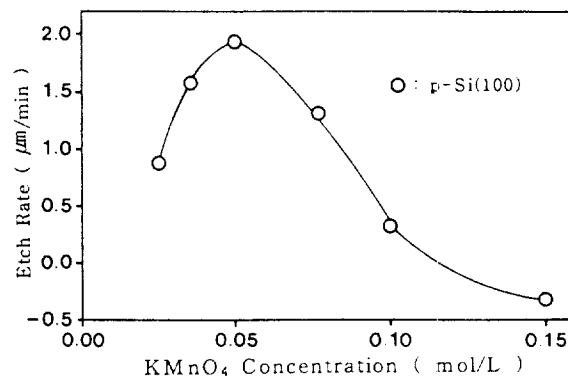


Fig. 3. The effect of KMnO<sub>4</sub> concentration on the etch rate in 12 M HF-KMnO<sub>4</sub>-H<sub>2</sub>O solution at 293 K and 800 RPM.

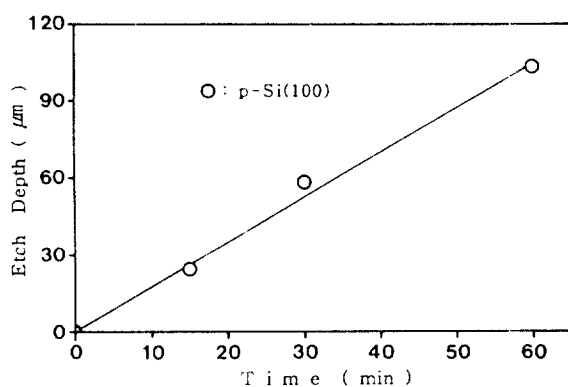


Fig. 2. The effect of reaction time on etch depth in 12 M HF-0.05 M KMnO<sub>4</sub>-H<sub>2</sub>O solution at 293 K and 800 RPM.

ined in the etching solution of 12 M HF-0.05 M KMnO<sub>4</sub>-H<sub>2</sub>O with the variation of the speed. The reaction time and temperature were 30 min and 293 K, respectively. 12 M HF-0.05 M KMnO<sub>4</sub>-H<sub>2</sub>O mixed solution of 40 cm<sup>3</sup> was prepared by mixing 20 cm<sup>3</sup> of 0.1 M KMnO<sub>4</sub> and 20 cm<sup>3</sup> of 24 M HF aqueous solutions. It is seen from Fig. 1 that the etch rate increases with the agitation speed up to 800 RPM and then reaches a saturated value. The observed linear variation in the etch rate at low speeds is due mainly to ineffective mass transfer of the reaction species near the silicon surface. At higher agitation speeds the mass-transfer rate of the species through the liquid-solid interface is greatly increased thereby favoring silicon etching. The saturation in the etch rate is the expected maximum in the reaction for a given etchant concentration. Therefore, all the experiments were performed at 800 RPM to exclude the mass transfer effect.

The etch depth of silicon was measured as a function of etching time to investigate the effect of the time on the etch rate. Silicon was etched in 12 M HF-0.05 M KMnO<sub>4</sub>-H<sub>2</sub>O solution at 293 K and 800 RPM. Fig. 2 shows that the etch depth increases linearly with time. The observed linear dependency of the etch depth implies that the etch rate maintains a constant value during the etching reaction. Hence, all silicon specimens were subjected to etching for 30 minutes throughout the experiment.

## 2. Effect of KMnO<sub>4</sub> Concentration

To investigate the effect of KMnO<sub>4</sub> concentration on the etch rate, silicon was etched at 293 K in 12 M HF-KMnO<sub>4</sub>-H<sub>2</sub>O solution with the variation of KMnO<sub>4</sub> concentration. Fig. 3 presents the

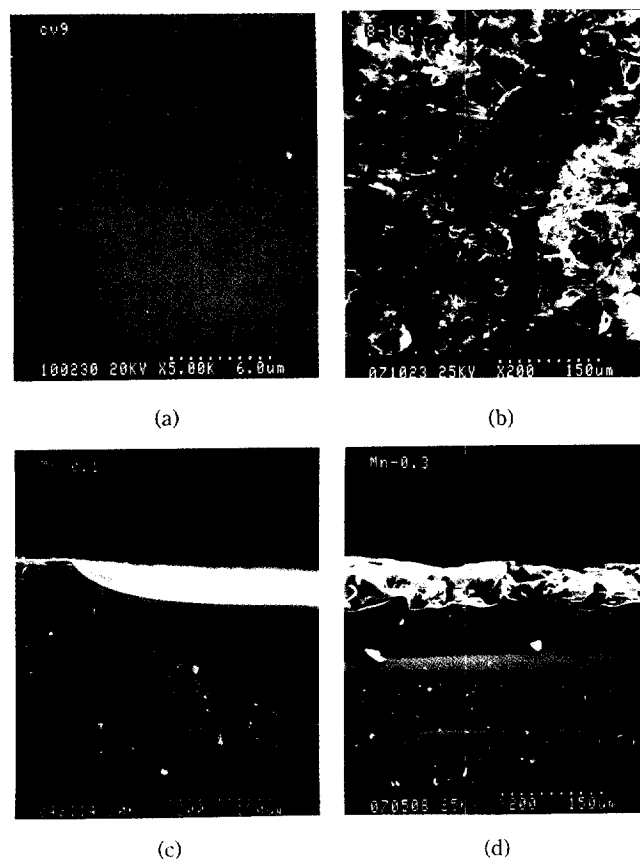


Fig. 4. The SEM photographs of the surfaces: (a) 0.05 M KMnO<sub>4</sub> and (b) 0.15 M KMnO<sub>4</sub> and cross sections: (c) 0.05 M KMnO<sub>4</sub> and (d) 0.15 M KMnO<sub>4</sub> of Si(100) etched in 12 M HF-KMnO<sub>4</sub>-H<sub>2</sub>O solution with varying KMnO<sub>4</sub> concentration at 293 K and 800 RPM.

measured etch rates. As the KMnO<sub>4</sub> concentration increases the etch rate increases to become a maximum value at 0.05 M and then decreases to have negative values. It is considered from this result that a deposition process takes place at higher KMnO<sub>4</sub> concentrations. The analysis of the solution compositions before and after the etching by ICP showed negligible change in etchant concentrations. No accumulation of particulate matter was also observed at the bottom of the reactor. These results state that

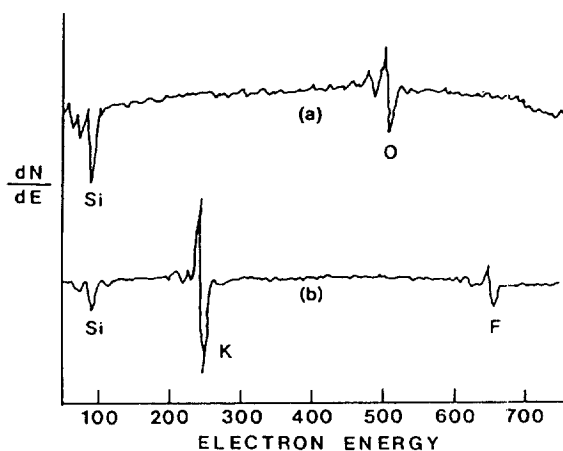


Fig. 5. Auger spectra of the silicon surface etched in 12 M HF-KMnO<sub>4</sub>-H<sub>2</sub>O solution at 293 K and 800 RPM.: (a) 0.05 M KMnO<sub>4</sub> and (b) 0.15 M KMnO<sub>4</sub>.

the etchants exist sufficiently in the etching solutions and deposition process takes place only on the silicon surface by surface reaction and not in etching solution by liquid-phase reaction.

### 3. Chemical Analyses of Etched Silicon Surface

The etched silicon surfaces were analyzed to explain the decrease of the etch rates at high KMnO<sub>4</sub> concentrations. Fig. 4 shows SEM photographs of the surfaces and cross-sections of silicon wafers etched at the KMnO<sub>4</sub> concentrations of 0.05 and 0.15 M. It is clearly seen that the morphology of silicon surface etched at 0.15 M KMnO<sub>4</sub> is different from that at 0.05 M KMnO<sub>4</sub>. A layer of visually white particles covers the surface etched at 0.15 M KMnO<sub>4</sub>. Similar layer was also observed on the surface etched at 0.1 M KMnO<sub>4</sub>. As shown in Fig. 4(c) and (d), the cross-sectional SEM photographs of the wafers show that the deposited layer is observed at 0.15 M KMnO<sub>4</sub>, while the layer is not seen on the surface in 0.05 M KMnO<sub>4</sub>. It can be concluded from the results that at high KMnO<sub>4</sub> concentrations the etch rates are retarded due mainly to the formation of a layered film.

The surface chemistry of the layer was investigated using AES. Fig. 5 presents Auger spectra of the etched surfaces in 0.05 M and 0.15 M KMnO<sub>4</sub>. Fig. 5(a) states that silicon was the chemical component of the surface etched in 0.05 M KMnO<sub>4</sub>, whereas the surface components of the layer formed on the silicon surface in 0.15 M KMnO<sub>4</sub> are potassium (K), fluorine (F) and small amount of Si. The deposited layers at 0.1 M and 0.15 M KMnO<sub>4</sub> concentrations were completely dissolved in 48% HF solution and analyzed with ICP. The analyzed result showed that Si and K were main components of the layer and the amounts of them increased as KMnO<sub>4</sub> concentration increased. XRD was also used to analyze the bulk chemistry of the layer deposited in 0.15 M KMnO<sub>4</sub>. Fig. 6 shows XRD spectra for silicon surfaces etched at 0.05 M and 0.15 M KMnO<sub>4</sub>. The main peaks of diffraction angle ( $2\theta$ , Cu-K $\alpha_1$ ) are observed at  $2\theta$  values of 18.8°, 31.2°, 38.8°, and 45.5°, which are in agreement with the characteristic peaks of K<sub>2</sub>SiF<sub>6</sub> reported in the JCPDS card [JCPDS, 1977]. Similar result was observed by many workers who have etched silicon in the etching solution containing cations [van der Meerakker and van Vegchel, 1989; Kikyuma et al., 1991].

### 4. Solubility of K<sub>2</sub>SiF<sub>6</sub> in HF

The solubility of K<sub>2</sub>SiF<sub>6</sub> in various compositions of aqueous HF

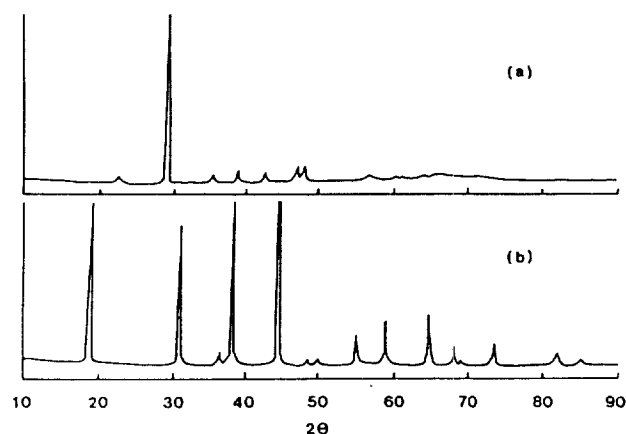


Fig. 6. The XRD patterns of the silicon surface etched in 12 M HF-KMnO<sub>4</sub>-H<sub>2</sub>O solution at 293 K and 800 RPM.: (a) 0.05 M KMnO<sub>4</sub> and (b) 0.15 M KMnO<sub>4</sub>.

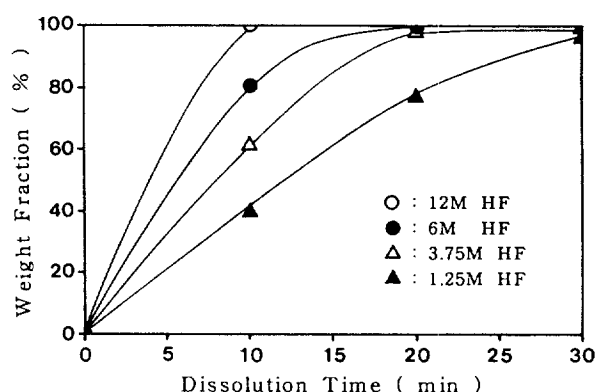


Fig. 7. The solubility of K<sub>2</sub>SiF<sub>6</sub> in HF aqueous solutions at 293 K and 800 RPM.

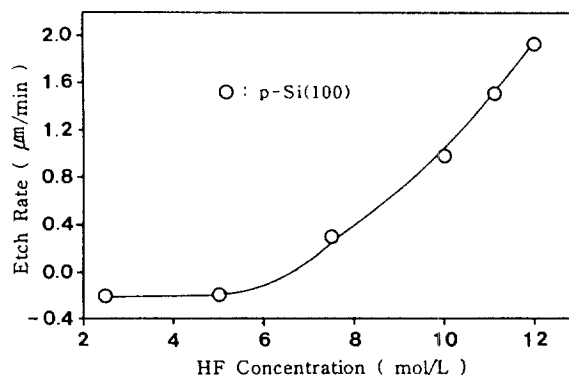


Fig. 8. The effect of HF concentration on the etch rate of silicon in HF-0.05 M KMnO<sub>4</sub>-H<sub>2</sub>O solution with varying HF concentration at 293 K and 800 RPM.

solution was measured as a function of reaction time. Fig. 7 shows the solubility in terms of weight fraction of K<sub>2</sub>SiF<sub>6</sub> owing to the dissolution. The amount of K<sub>2</sub>SiF<sub>6</sub> deposited during the etching was obtained from the difference in weights of silicon wafer after the etching and after the complete removal of K<sub>2</sub>SiF<sub>6</sub> in 48% HF solution. The K<sub>2</sub>SiF<sub>6</sub> samples were prepared by reacting silicon

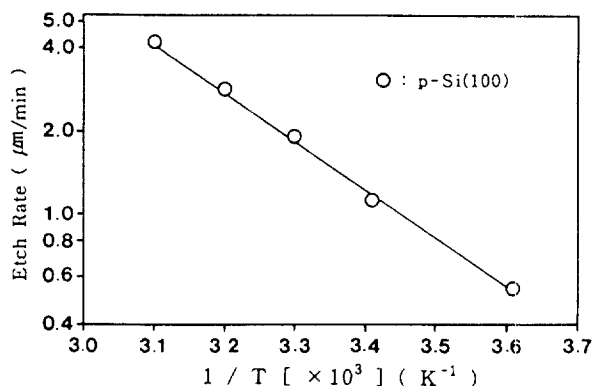


Fig. 9. The Arrhenius plot for Si(100) etching reaction in 12 M HF-0.05 M KMnO<sub>4</sub>-H<sub>2</sub>O solution at 800 RPM.

with 12 M HF-0.15 M KMnO<sub>4</sub>-H<sub>2</sub>O solution for 30 min. The deposited samples are almost soluble within 30 min even at 1.25 M HF aqueous solution. K<sub>2</sub>SiF<sub>6</sub> was insoluble in water and aqueous KMnO<sub>4</sub> solution, but soluble in HF. This result draws a conclusion that K<sub>2</sub>SiF<sub>6</sub> is dissolved easily in HF, but observed on the surface because the formation rate of K<sub>2</sub>SiF<sub>6</sub> is greater than the dissolution rate of K<sub>2</sub>SiF<sub>6</sub> by HF.

##### 5. Effect of HF Concentration

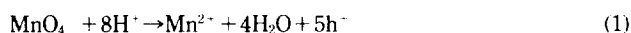
To see the effect of HF concentration on etch rate, silicon was etched at 293 K in HF-0.05 M KMnO<sub>4</sub>-H<sub>2</sub>O solution with the variation of HF concentration. Fig. 8 shows that the etch rates are negative values at concentrations lower than 5 M HF, but thereafter they increase rapidly with the increase of HF concentration. Similar experimental results were observed by many workers [Matsumura and Morrison, 1983; van der Meerakker and van Vegchel, 1989].

##### 6. Effect of Etching Temperature

Fig. 9 shows the Arrhenius plot for silicon etching reactions to see the temperature dependency of etch rate. The activation energy was obtained from the slope of the straight line of Fig. 9 and was about 6.8 K-cal/g-mol of Si.

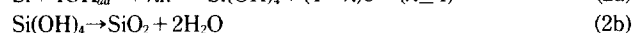
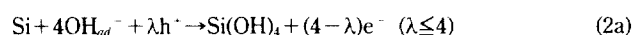
## DISCUSSION

In a HF-oxidizing agent-H<sub>2</sub>O solution, the silicon etching is carried out through a two step reaction, i.e., the oxidation of silicon atom by holes injected with the reduction of oxidizing agent and the dissolution of the oxidized silicon surface by HF [Seidel et al., 1990; Kelly et al., 1984]. KMnO<sub>4</sub>, the oxidizing agent in this etching solution, generates MnO<sub>4</sub><sup>-</sup> ion in the aqueous solution, which reacts with H<sup>+</sup> to produce holes on silicon surface by Eq. (1)

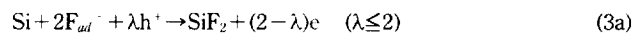


The dissolution of the oxidized silicon is reported to be carried out through one particular mechanism of the following two reaction mechanisms, depending on the HF concentration in etching solution. However, the holes accumulated on the silicon surface are apparently essential to both reactions [Matsumura and Morrison, 1983; Memming and Schwandt 1966; Zhang et al., 1989].

For low concentration of HF,



For high concentration of HF,



where the subscript ad denotes the adsorbed state, and h<sup>+</sup> and e<sup>-</sup> represent hole and electron, respectively.

According to Eq. (1), the hole concentration increases with the increase of KMnO<sub>4</sub> concentration in the etching solution. Hence, the increase of KMnO<sub>4</sub> concentration should raise etch rates because holes accelerate the etching reaction. Fig. 3 shows that the etch rate increases with the increase of KMnO<sub>4</sub> concentration at low KMnO<sub>4</sub> concentration. At high KMnO<sub>4</sub> concentration, however, the increase of KMnO<sub>4</sub> concentration reduces the etch rate, but increases the formation rate of K<sub>2</sub>SiF<sub>6</sub>. This results may be explained by the followings. Eddowes [Eddowes, 1990], Etman [Etman et al., 1991] and Gerischer [Gerischer and Lubke, 1987] reported that SiF<sub>6</sub><sup>2-</sup> was formed as an intermediate product on the silicon surface during the etching reaction. SiF<sub>6</sub><sup>2-</sup> may react with protons or potassium ions in the etching solution. The reaction of SiF<sub>6</sub><sup>2-</sup> with protons produces the H<sub>2</sub>SiF<sub>6</sub> which is dissolved immediately from the surface in aqueous environment, whereas that with potassium ions forms the K<sub>2</sub>SiF<sub>6</sub> which is not soluble well in the etching solution consisted of low HF concentration. For large amounts of KMnO<sub>4</sub>, the rate of forming SiF<sub>6</sub><sup>2-</sup> may be so fast that all the SiF<sub>6</sub><sup>2-</sup> adsorbed on the surface is not removed completely in the form of H<sub>2</sub>SiF<sub>6</sub> from the surface and may be left in the form of insoluble K<sub>2</sub>SiF<sub>6</sub> on the surface by the reaction of SiF<sub>6</sub><sup>2-</sup> with K ion. The deposited K<sub>2</sub>SiF<sub>6</sub> layer decreases the etch rate. The liquid etchants diffuse into the silicon surface through the interface of K<sub>2</sub>SiF<sub>6</sub> particles and react with silicon to increase the thickness of K<sub>2</sub>SiF<sub>6</sub> layer. On the other hand, the surface of K<sub>2</sub>SiF<sub>6</sub> layer reacts slowly with HF to form KF abundant surface, that is in good agreement with the result of AES analysis.

The result of Fig. 8 was observed by many workers [Matsumura and Morrison, 1983; van der Meerakker and van Vegchel, 1989]. They postulated that a surface layer is formed at low HF concentration and may inhibit further etching reaction. Fig. 10 shows SEM photographs for the silicon etched at various HF concentrations. It is clearly seen that at low HF concentration the etched surfaces are covered with the layer of K<sub>2</sub>SiF<sub>6</sub> particles, while a relatively smooth and planar surfaces are obtained at high HF concentration. AES and XRD spectra for the surfaces showed only Si peaks at high HF concentration, but K<sub>2</sub>SiF<sub>6</sub> peaks at low HF concentration. In our previous report, we observed that the formation rate of K<sub>2</sub>SiF<sub>6</sub> increased with the increase of the redox potential of etching solution [Seo et al., 1993, 1994]. KMnO<sub>4</sub> has higher value of redox potential enough to increase the hole concentration on the silicon surface, resulting in the acceleration of K<sub>2</sub>SiF<sub>6</sub> formation at low HF concentrations. The formation rate of K<sub>2</sub>SiF<sub>6</sub> increases at low HF concentrations because the formation rate of K<sub>2</sub>SiF<sub>6</sub> is greater than the dissolution rate of K<sub>2</sub>SiF<sub>6</sub> by HF. Hence, it is concluded that the rates are negative values at lower HF concentration because the amount of HF required for dissolving K<sub>2</sub>SiF<sub>6</sub> is deficient.

The roles of H<sup>+</sup> was examined by adding HCl for H<sup>+</sup> to 5 M HF-0.05 M KMnO<sub>4</sub>-H<sub>2</sub>O and 12 M HF-0.05 M KMnO<sub>4</sub>-H<sub>2</sub>O solutions, respectively. Silicon was not etched in HCl-KMnO<sub>4</sub>-H<sub>2</sub>O so-

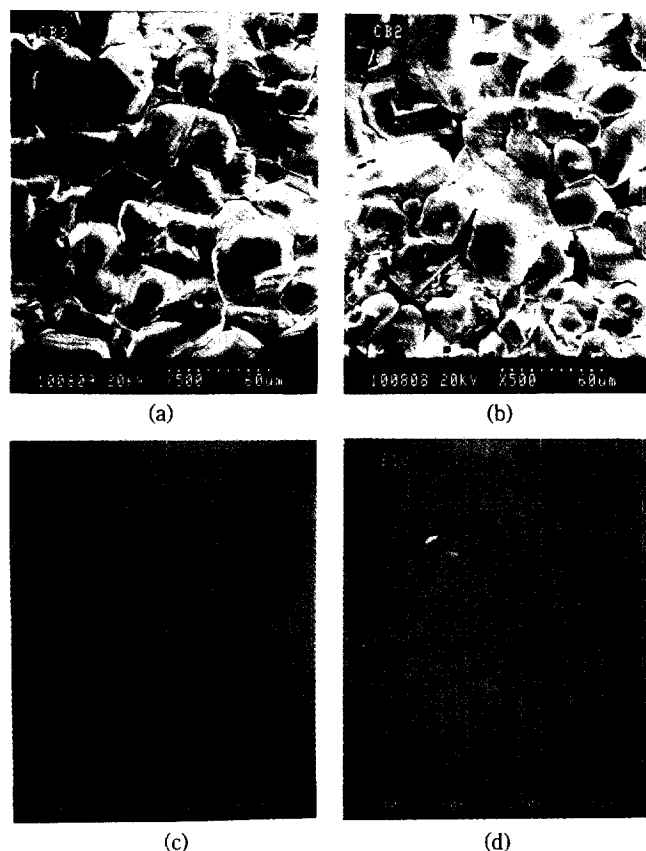


Fig. 10. The SEM photographs of the surface of Si(100) etched in HF-0.05 M  $\text{KMnO}_4$ - $\text{H}_2\text{O}$  solution with varying HF concentration at 293 K and 800 RPM: (a) 2.5 M HF, (b) 5 M HF, (c) 7.5 M HF and (d) 12 M HF.

lution. Fig. 11 shows the measured etch rates as a function of HCl concentration. 1 cm<sup>3</sup> HCl of 15 and 35% was added to the etching solutions. The etch rate decreases as  $\text{H}^+$  concentration increases in 5 M HF-0.05 M  $\text{KMnO}_4$ - $\text{H}_2\text{O}$  solution, which indicates the formation of  $\text{K}_2\text{SiF}_6$ . In order to observe the formation of  $\text{K}_2\text{SiF}_6$ , the silicon surfaces etched at the conditions used in Fig. 11 were analyzed by XRD and SEM. The analysis of XRD revealed the existence of  $\text{K}_2\text{SiF}_6$  on the surfaces. The cross-sectional SEM photographs for the wafers also showed the increase of  $\text{K}_2\text{SiF}_6$  thickness and etch depth as  $\text{H}^+$  concentration increases in the solution, as in Fig. 4 shown for the case of high  $\text{KMnO}_4$  concentration. In 12 M HF-0.05 M  $\text{KMnO}_4$ - $\text{H}_2\text{O}$  solution, however, the  $\text{K}_2\text{SiF}_6$  layer was not observed on the etched surface. From these observations, it is clearly seen that  $\text{H}^+$  concentration in the solution is of great importance for the hole formation by reaction 1, which increases the etch rate. At low HF concentrations, however, the etch rate decreases because high  $\text{H}^+$  concentration accelerates the formation of  $\text{K}_2\text{SiF}_6$  by the same mechanism as suggested for the case of high  $\text{KMnO}_4$  concentration. At higher HF concentrations, the etch rate increases rapidly since the amount of  $\text{H}^+$  needed for accelerating the hole formation and HF needed for dissolving  $\text{K}_2\text{SiF}_6$  are sufficient.

The effect of  $\text{F}^-$  on the etching reaction was examined by increasing the amount of  $\text{F}^-$  in the solution by adding  $\text{NH}_4\text{F}$  to 5 M HF-0.05 M  $\text{KMnO}_4$ - $\text{H}_2\text{O}$  and 12 M HF-0.05 M  $\text{KMnO}_4$ - $\text{H}_2\text{O}$  solutions. The etch rates were almost the same for the solutions

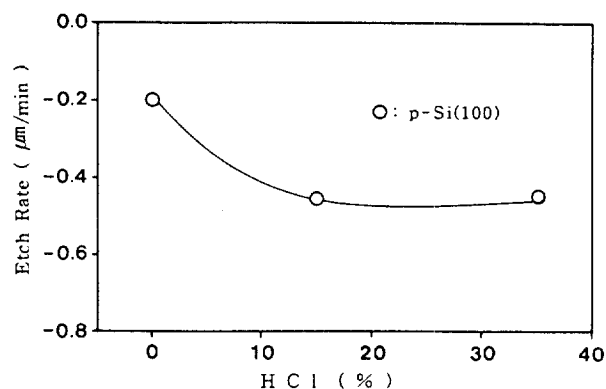


Fig. 11. The effect of the concentration of hydrogen ion on the etch rate in 5 M HF-0.05 M  $\text{KMnO}_4$ - $\text{H}_2\text{O}$  solution at 293 K and 800 RPM.

with or without the addition of  $\text{NH}_4\text{F}$ , which indicates that the etching reaction is not influenced by  $\text{F}^-$ . This is in good agreement with the observation by Schimmel and Elkind [Schimmel and Elkind, 1978], who insisted that only the undissociated HF was used for the dissolution of silicon.

In our previous work [Seo et al., 1993], we changed the concentration of holes on the silicon surface by applying the solution potential or illuminating laser light on the surface without changing the etchant composition. The experimental results showed that the etch rate increased with the concentration of hole formed at the silicon surface and the rate determining step of the silicon etching was the formation of holes at the surface.

Consequently, the concentration of holes on the silicon surface increases with the increase of  $\text{KMnO}_4$  and  $\text{H}^+$  concentrations. The holes not only accelerated the etch rate but also the formation rate of  $\text{K}_2\text{SiF}_6$ . The etch rate increases with the hole concentration at higher HF concentration, but decreases at lower HF concentration because of the formation of  $\text{K}_2\text{SiF}_6$  by the reaction between potassium ions in the solution and  $\text{SiF}_6^{2-}$  formed in the course of etching process.

## CONCLUSION

The etching reaction of silicon has been investigated experimentally in HF- $\text{KMnO}_4$ - $\text{H}_2\text{O}$  mixed solution. The etch rate increased with the agitation speed and the etch depth increased almost linearly with etching time. As the  $\text{KMnO}_4$  concentration increased the rate increased to reach a maximum at 0.05 M  $\text{KMnO}_4$ , but decreased to have a negative value at high  $\text{KMnO}_4$  concentration due to the formation of  $\text{K}_2\text{SiF}_6$  by the reaction of  $\text{SiF}_6^{2-}$  with potassium ions in the etching solution. The rates were negative values at low HF concentration because the amount of HF required for dissolving  $\text{K}_2\text{SiF}_6$  was deficient, but thereafter they increased linearly with the increase of HF concentration at high HF concentration because  $\text{H}^+$  needed for forming holes and HF needed for dissolving  $\text{K}_2\text{SiF}_6$  were sufficient. The holes were indispensable for increasing the etch rate. For higher concentration of holes, however, the rate of forming  $\text{SiF}_6^{2-}$  may be so fast that all the  $\text{SiF}_6^{2-}$  adsorbed on the surface are not removed completely in the form of  $\text{H}_2\text{SiF}_6$  from the surface and may be left in the form of insoluble  $\text{K}_2\text{SiF}_6$  on the surface by the reaction of  $\text{SiF}_6^{2-}$  with K ion. At low HF concentration the etching reaction was greatly influenced by both the formation of holes and the removal of

K<sub>2</sub>SiF<sub>6</sub>, but the formation of holes at silicon surface was the rate limiting step of the silicon etching reaction at high HF concentration. High HF concentration enough for dissolving K<sub>2</sub>SiF<sub>6</sub> was apparently essential to obtain high etch rate in the silicon etching reaction.

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