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MECHANISM OF SILICON ETCHING IN $HF-KMnO_4-H_2O$ SOLUTION

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Abstract – The etching reaction of silicon in $HF-KMnO_4-H_2O$ mixed solution has been studied under various experimental conditions. The etch rates were measured as a function of agitation speed, HF and $KMnO_4$ concentrations, and etching temperature and time. A comprehensive mechanism for the silicon etching and insoluble solid-phase film (K_2SiF_6) 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_2SiF_6. With the increase of hole concentration at lower HF concentrations the etch rates decreased because of the deposition of K_2SiF_6 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 $HF-KMnO_4-H_2O$ solution. High HF concentration enough for dissolving K_2SiF_6 was apparently essential to obtain high etch rate in the silicon etching reaction.

Key words: Silicon Surface, Etch Rate, Etching Reaction Mechanism, $HF-KMnO_4-H_2O$ Solution, Insoluble Solid Phase K_2SiF_6, 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'Commor et al., 1988; Huo et al., 1989]. $HF-KMnO_4-H_2O$ 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_2O 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 $HF-KMnO_4-H_2O$ 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 $HF-KMnO_4-H_2O$ mixed solution. The etch rates were measured as a function of agitation speed, HF and $KMnO_4$ 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. $KMnO_4$ 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^3 was added into the reactor and the reaction started. The etching solutions of 40 cm^3, which is mixed solution of 20 cm^3 $KMnO_4$ and 20 cm^3 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^{-8} 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^2) and Si density (2.33 g/cm^3), 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-

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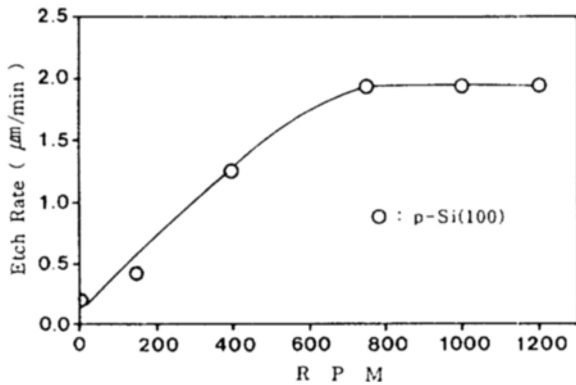


Fig. 1. The effect of agitation speed on etch rate in 12 M HF-0.05 M KMnO$_4$-H$_2$O solution at 293 K.

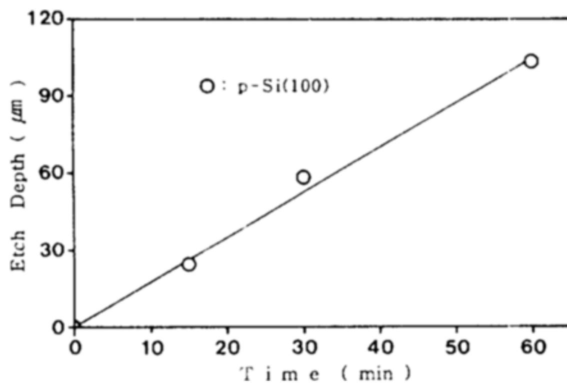


Fig. 2. The effect of reaction time on etch depth in 12 M HF-0.05 M KMnO$_4$-H$_2$O solution at 293 K and 800 RPM.

ined in the etching solution of 12 M HF-0.05 M KMnO$_4$-H$_2$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$_4$-H$_2$O mixed solution of 40 cm^3 was prepared by mixing 20 cm^3 of 0.1 M KMnO$_4$ and 20 cm^3 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$_4$-H$_2$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$_4$ Concentration

To investigate the effect of KMnO$_4$ concentration on the etch rate, silicon was etched at 293 K in 12 M HF-KMnO$_4$-H$_2$O solution with the variation of KMnO$_4$ concentration. Fig. 3 presents the

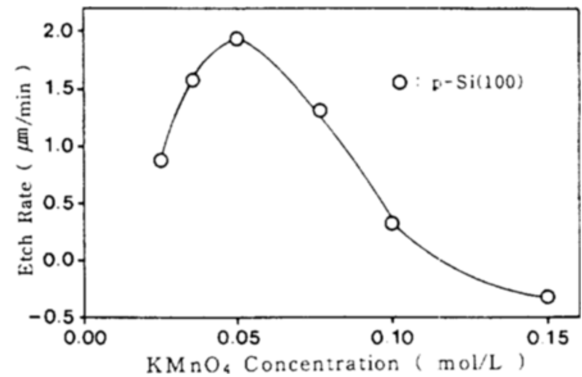
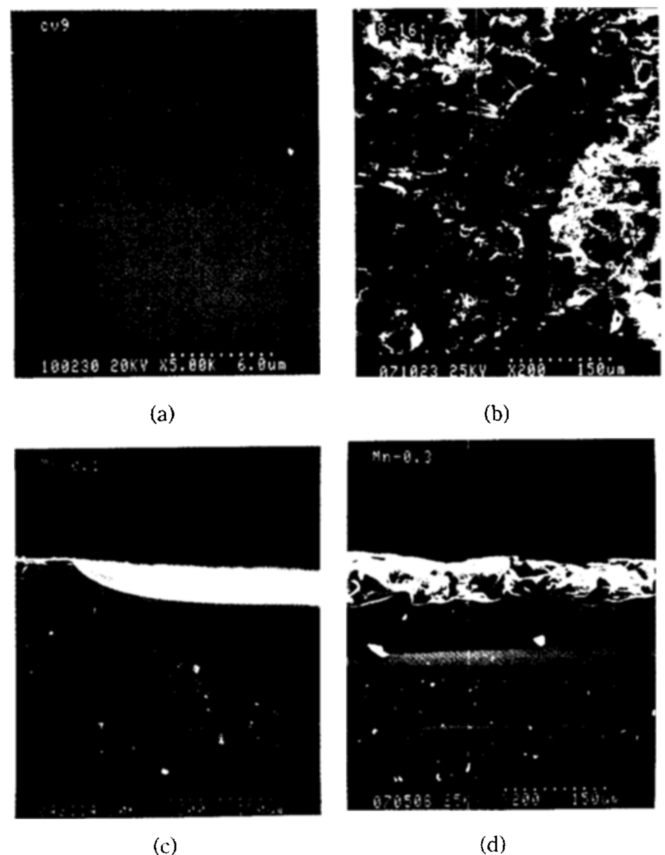


Fig. 3. The effect of KMnO$_4$ concentration on the etch rate in 12 M HF-KMnO$_4$-H$_2$O solution at 293 K and 800 RPM.



(a) (b)

(c) (d)

Fig. 4. The SEM photographs of the surfaces: (a) 0.05 M KMnO$_4$ and (b) 0.15 M KMnO$_4$ and cross sections: (c) 0.05 M KMnO$_4$ and (d) 0.15 M KMnO$_4$ of Si(100) etched in 12 M HF-KMnO$_4$-H$_2$O solution with varying KMnO$_4$ concentration at 293 K and 800 RPM.

measured etch rates. As the KMnO$_4$ 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$_4$ 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

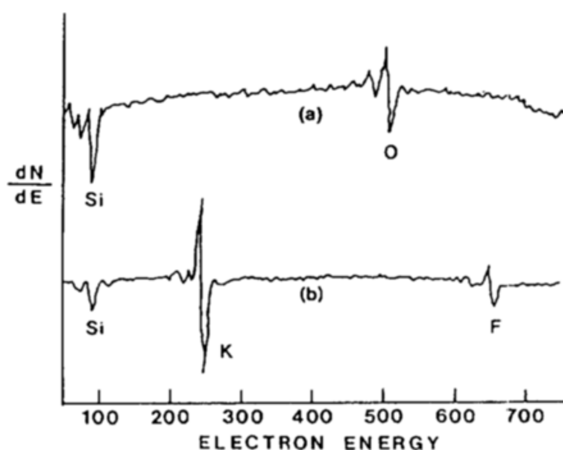


Fig. 5. Auger spectrums of the silicon surface etched in 12 M HF-$KMnO_4$-H_2O solution at 293 K and 800 RPM.: (a) 0.05 M $KMnO_4$ and (b) 0.15 M $KMnO_4$.

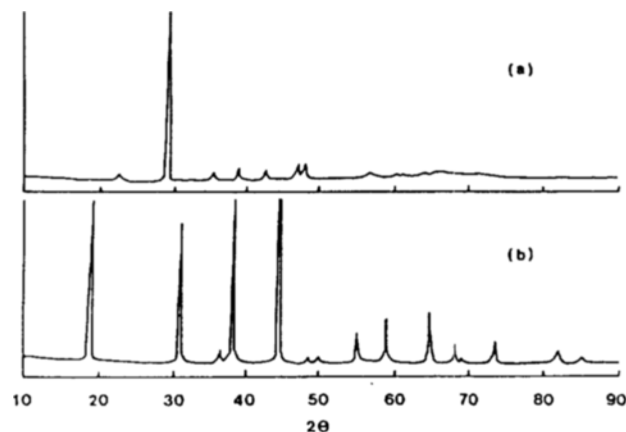


Fig. 6. The XRD patterns of the silicon surface etched in 12 M HF-$KMnO_4$-H_2O solution at 293 K and 800 RPM.: (a) 0.05 M $KMnO_4$ and (b) 0.15 M $KMnO_4$.

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 $KMnO_4$ concentrations. Fig. 4 shows SEM photographs of the surfaces and cross-sections of silicon wafers etched at the $KMnO_4$ concentrations of 0.05 and 0.15 M. It is clearly seen that the morphology of silicon surface etched at 0.15 M $KMnO_4$ is different from that at 0.05 M $KMnO_4$. A layer of visually white particles covers the surface etched at 0.15 M $KMnO_4$. Similar layer was also observed on the surface etched at 0.1 M $KMnO_4$. 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 $KMnO_4$, while the layer is not seen on the surface in 0.05 M $KMnO_4$. It can be concluded from the results that at high $KMnO_4$ 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 spectrums of the etched surfaces in 0.05 M and 0.15 M $KMnO_4$. Fig. 5(a) states that silicon was the chemical component of the surface etched in 0.05 M $KMnO_4$, whereas the surface components of the layer formed on the silicon surface in 0.15 M $KMnO_4$ are potassium (K), fluorine (F) and small amount of Si. The deposited layers at 0.1 M and 0.15 M $KMnO_4$ 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 $KMnO_4$ concentration increased. XRD was also used to analyze the bulk chemistry of the layer deposited in 0.15 M $KMnO_4$. Fig. 6 shows XRD spectra for silicon surfaces etched at 0.05 M and 0.15 M $KMnO_4$. The main peaks of diffraction angle (2θ, Cu-$K_{\alpha 1}$) are observed at 2θ values of 18.8°, 31.2°, 38.8°, and 45.5°, which are in agreement with the characteristic peaks of K_2SiF_6 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; Kikyuama et al., 1991].

4. Solubility of K_2SiF_6 in HF

The solubility of K_2SiF_6 in various compositions of aqueous HF solution was measured as a function of reaction time. Fig. 7 shows the solubility in terms of weight fraction of K_2SiF_6 owing to the dissolution. The amount of K_2SiF_6 deposited during the etching was obtained from the difference in weights of silicon wafer after the etching and after the complete removal of K_2SiF_6 in 48% HF solution. The K_2SiF_6 samples were prepared by reacting silicon

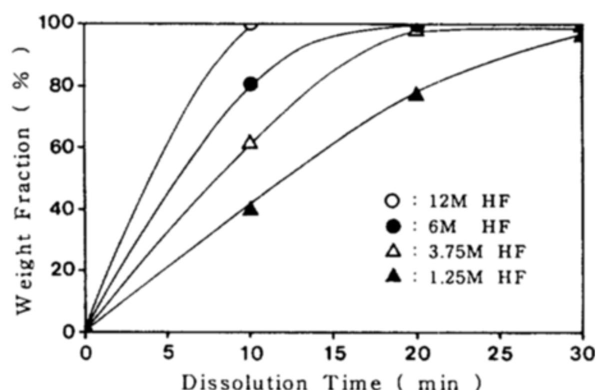


Fig. 7. The solubility of K_2SiF_6 in HF aqueous solutions at 293 K and 800 RPM.

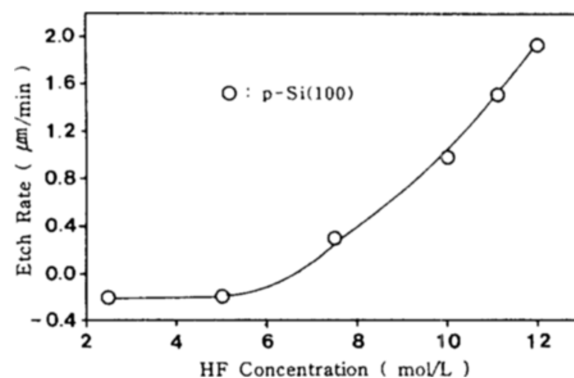


Fig. 8. The effect of HF concentration on the etch rate of silicon in HF-0.05 M $KMnO_4$-H_2O solution with varying HF concentration at 293 K and 800 RPM.

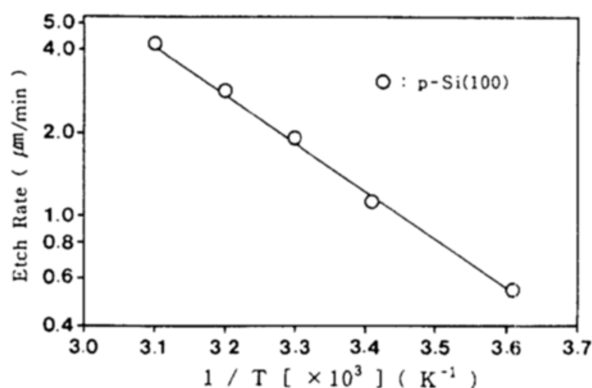


Fig. 9. The Arrhenius plot for Si(100) etching reaction in 12 M HF-0.05 M $KMnO_4$-H_2O solution at 800 RPM.

with 12 M HF-0.15 M $KMnO_4$-H_2O solution for 30 min. The deposited samples are almost soluble within 30 min even at 1.25 M HF aqueous solution. K_2SiF_6 was insoluble in water and aqueous $KMnO_4$ solution, but soluble in HF. This result draws a conclusion that K_2SiF_6 is dissolved easily in HF, but observed on the surface because the formation rate of K_2SiF_6 is greater than the dissolution rate of K_2SiF_6 by HF.

5. Effect of HF Concentration

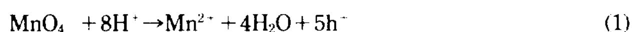
To see the effect of HF concentration on etch rate, silicon was etched at 293 K in HF-0.05 M $KMnO_4$-H_2O solution with the variation of HF concentration. Fig. 8 shows that the etch rates are negative values at concentrations lower than 5 M HF, but thereafter they increase rapidly with the increase 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

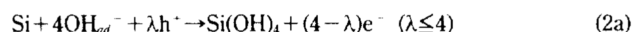
In a HF-oxidizing agent-H_2O solution, the silicon etching is carried out through a two step reaction, i.e., the oxidation of silicon atom by holes injected with the reduction of oxidizing agent and the dissolution of the oxidized silicon surface by HF [Seidel et al., 1990; Kelly et al., 1984]. $KMnO_4$, the oxidizing agent in this etching solution, generates MnO_4^- ion in the aqueous solution, which reacts with H^+ to produce holes on silicon surface by Eq. (1)



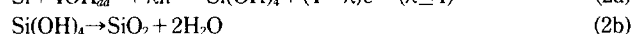
$$MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O + 5h^+ \quad (1)$$

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,



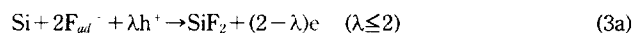
$$Si + 4OH_{ad}^- + \lambda h^+ \rightarrow Si(OH)_4 + (4-\lambda)e^- \quad (\lambda \leq 4) \quad (2a)$$



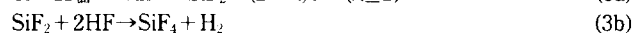
$$Si(OH)_4 \rightarrow SiO_2 + 2H_2O \quad (2b)$$

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O \quad (2c)$$

For high concentration of HF,



$$Si + 2F_{ad}^- + \lambda h^+ \rightarrow SiF_2 + (2-\lambda)e \quad (\lambda \leq 2) \quad (3a)$$



$$SiF_2 + 2HF \rightarrow SiF_4 + H_2 \quad (3b)$$

$$SiF_4 + 2HF \rightarrow H_2SiF_6 \quad (3c)$$

where the subscript ad denotes the adsorbed state, and h^+ and e^- represent hole and electron, respectively.

According to Eq. (1), the hole concentration increases with the increase of $KMnO_4$ concentration in the etching solution. Hence, the increase of $KMnO_4$ concentration should raise etch rates because holes accelerate the etching reaction. Fig. 3 shows that the etch rate increases with the increase of $KMnO_4$ concentration at low $KMnO_4$ concentration. At high $KMnO_4$ concentration, however, the increase of $KMnO_4$ concentration reduces the etch rate, but increases the formation rate of K_2SiF_6. 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_6^{-2} was formed as an intermediate product on the silicon surface during the etching reaction. SiF_6^{-2} may react with protons or potassium ions in the etching solution. The reaction of SiF_6^{-2} with protons produces the H_2SiF_6 which is dissolved immediately from the surface in aqueous environment, whereas that with potassium ions forms the K_2SiF_6 which is not soluble well in the etching solution consisted of low HF concentration. For large amounts of $KMnO_4$, the rate of forming SiF_6^{-2} may be so fast that all the SiF_6^{-2} adsorbed on the surface is not removed completely in the form of H_2SiF_6 from the surface and may be left in the form of insoluble K_2SiF_6 on the surface by the reaction of SiF_6^{-2} with K ion. The deposited K_2SiF_6 layer decreases the etch rate. The liquid etchants diffuse into the silicon surface through the interface of K_2SiF_6 particles and react with silicon to increase the thickness of K_2SiF_6 layer. On the other hand, the surface of K_2SiF_6 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_2SiF_6 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_2SiF_6 peaks at low HF concentration. In our previous report, we observed that the formation rate of K_2SiF_6 increased with the increase of the redox potential of etching solution [Seo et al., 1993, 1994]. $KMnO_4$ has higher value of redox potential enough to increase the hole concentration on the silicon surface, resulting in the acceleration of K_2SiF_6 formation at low HF concentrations. The formation rate of K_2SiF_6 increases at low HF concentrations because the formation rate of K_2SiF_6 is greater than the dissolution rate of K_2SiF_6 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_2SiF_6 is deficient.

The roles of H^+ was examined by adding HCl for H^+ to 5 M HF-0.05 M $KMnO_4$-H_2O and 12 M HF-0.05 M $KMnO_4$-H_2O solutions, respectively. Silicon was not etched in HCl-$KMnO_4$-H_2O so-

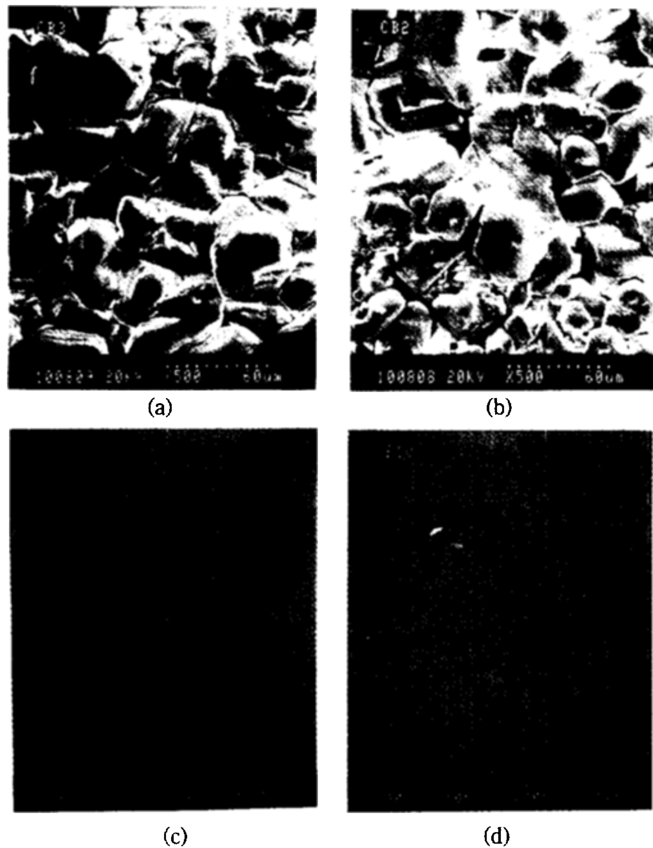


Fig. 10. The SEM photographs of the surface of Si(100) etched in HF-0.05 M $KMnO_4$-H_2O solution with varying HF concentration at 293 K and 800 RPM: (a) 2.5 M HF, (b) 5 M HF, (c) 7.5 M HF and (d) 12 M HF.

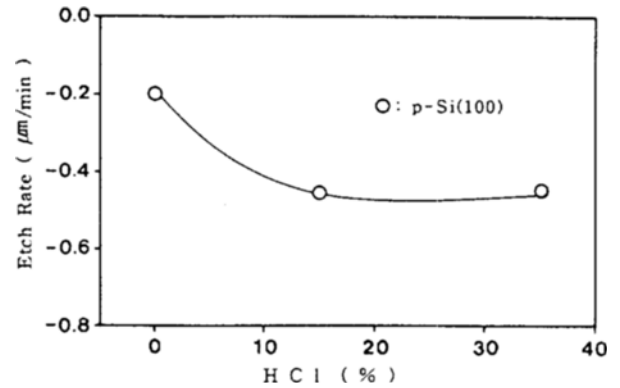


Fig. 11. The effect of the concentration of hydrogen ion on the etch rate in 5 M HF-0.05 M $KMnO_4$-H_2O solution at 293 K and 800 RPM.

lution. Fig. 11 shows the measured etch rates as a function of HCl concentration. 1 cm^3 HCl of 15 and 35% was added to the etching solutions. The etch rate decreases as H^+ concentration increases in 5 M HF-0.05 M $KMnO_4$-H_2O solution, which indicates the formation of K_2SiF_6. In order to observe the formation of K_2SiF_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 K_2SiF_6 on the surfaces. The cross-sectional SEM photographs for the wafers also showed the increase of K_2SiF_6 thickness and etch depth as H^+ concentration increases in the solution, as in Fig. 4 shown for the case of high $KMnO_4$ concentration. In 12 M HF-0.05 M $KMnO_4$-H_2O solution, however, the K_2SiF_6 layer was not observed on the etched surface. From these observations, it is clearly seen that 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 H^+ concentration accelerates the formation of K_2SiF_6 by the same mechanism as suggested for the case of high $KMnO_4$ concentration. At higher HF concentrations, the etch rate increases rapidly since the amount of H^+ needed for accelerating the hole formation and HF needed for dissolving K_2SiF_6 are sufficient.

The effect of F^- on the etching reaction was examined by increasing the amount of F^- in the solution by adding NH_4F to 5 M HF-0.05 M $KMnO_4$-H_2O and 12 M HF-0.05 M $KMnO_4$-H_2O solutions. The etch rates were almost the same for the solutions with or without the addition of NH_4F, which indicates that the etching reaction is not influenced by 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 $KMnO_4$ and H^+ concentrations. The holes not only accelerated the etch rate but also the formation rate of K_2SiF_6. The etch rate increases with the hole concentration at higher HF concentration, but decreases at lower HF concentration because of the formation of K_2SiF_6 by the reaction between potassium ions in the solution and SiF_6^{-2} formed in the course of etching process.

CONCLUSION

The etching reaction of silicon has been investigated experimentally in HF-$KMnO_4$-H_2O mixed solution. The etch rate increased with the agitation speed and the etch depth increased almost linearly with etching time. As the $KMnO_4$ concentration increased the rate increased to reach a maximum at 0.05 M $KMnO_4$, but decreased to have a negative value at high $KMnO_4$ concentration due to the formation of K_2SiF_6 by the reaction of 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 K_2SiF_6 was deficient, but thereafter they increased linearly with the increase of HF concentration at high HF concentration because H^+ needed for forming holes and HF needed for dissolving K_2SiF_6 were sufficient. The holes were indispensible for increasing the etch rate. For higher concentration of holes, however, the rate of forming SiF_6^{-2} may be so fast that all the SiF_6^{-2} adsorbed on the surface are not removed completely in the form of H_2SiF_6 from the surface and may be left in the form of insoluble K_2SiF_6 on the surface by the reaction of 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_2SiF_6, 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_2SiF_6 was apparently essential to obtain high etch rate in the silicon etching reaction.

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