REACTION KINETICS OF SILICON ETCHING IN $HF\text{-}K_2Cr_2O_7\text{-}H_2O$ SOLUTION

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Abstract—The reaction kinetics of silicon etching in $HF\text{-}K_2Cr_2O_7\text{-}H_2O$ solution was studied experimentally. The etch rates were measured with varying HF and $K_2Cr_2O_7$ concentrations, agitation speed, reaction temperature and time. The etch rates of n- and p-Si (100) were both similar. The etched surfaces consisted mainly of silicon and showed a relatively smooth and planar morphology. At sufficiently high HF concentration, the etch rate was increased with increasing $K_2Cr_2O_7$ concentration due to the increase of hole formation on the silicon surface. However, at low HF concentration, the etch rate maintains low value and increases very slowly because of insufficient hole concentration for etching reaction. The apparent activation energy was about 7.8 kcal/g-mole, and the rate equation for the silicon etching reaction in $HF\text{-}K_2Cr_2O_7\text{-}H_2O$ solution was obtained as

$$-r_{Si}=600\ \exp(-3900/T)\ C_{K_2Cr_2O_7}^{0.5}\ C_{HF}^{3}$$

at HF concentrations greater than 8 M.

INTRODUCTION

Wet chemical etching technology has been widely used in semiconductor fabricating processes, i.e., wafer polishing, cleaning, and delineating the required patterns on thin films [1, 2]. In spite of emerging new technologies such as plasma etching process [3], the chemical etching process still plays an important role in semiconductor industry. $HF\text{-}K_2Cr_2O_7\text{-}H_2O$ solution has long been used as one of HF-oxidizing agent-H_2O solutions, and reported as a good etching solution because of no formation of stains on the silicon surface after etching [4-7].

In this work, the reaction kinetics of silicon etching in $HF\text{-}K_2Cr_2O_7\text{-}H_2O$ solution was studied under various reaction conditions. In order to elucidate the etching mechanism and reaction rate parameters, the etch rates were examined with varying HF and $K_2Cr_2O_7$ concentrations, temperature, reaction time and agitation speed. The surfaces of etched wafers were analyzed using SEM (scanning electron microscope), AES (Auger electron spectroscopy) and XRD (X-ray diffraction).

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EXPERIMENT

The wafers used in this work were n- and p-Si (100) single crystals grown by Siltron Co. with Czochralski technique. The resistivities of the n-Si (100) doped with phosphorus and the p-Si (100) doped with boron were 7-8 and 7-9 ohm-cm, respectively. The reagent-grade chemicals and deionized water were used to make etching solutions.

The etching reactions were carried out in a cylindrical polyethylene reactor of 60 mmφ×85 mm H. The reactor was maintained at isothermal conditions in a constant-temperature water bath controlled within ±0.1C accuracy using Margon thermometer. The schematic diagram of the experimental unit is shown in Fig. 1.

Silicon specimens were pretreated with acetone to remove organic impurities, and with 48% HF solution to eliminate native oxide films formed on the silicon surface. The Si samples were then rinsed with DI water and dried with nitrogen flow. The surface except the reacting area was covered with a photoresist, and the test specimen was mounted on the center of the reactor bottom. The etching solution was prepared by mixing 20 ml HF and 20 ml $K_2Cr_2O_7$ aqueous solutions of preset concentration. The etching reaction started

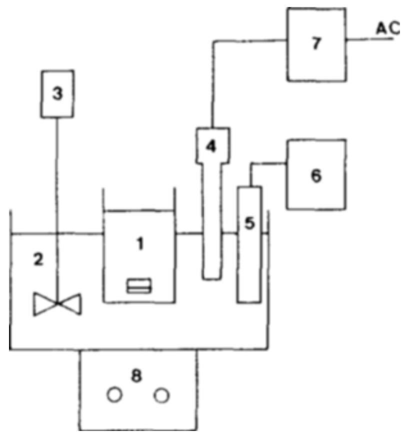

Fig. 1. Schematic diagram of experimental unit for the etching reaction of silicon.

1. Reactor	2. Water bath
3. Agitator	4. Margon thermometer
5. Heater	6. Slidax
7. Sensitive relay	8. Magnetic stirrer

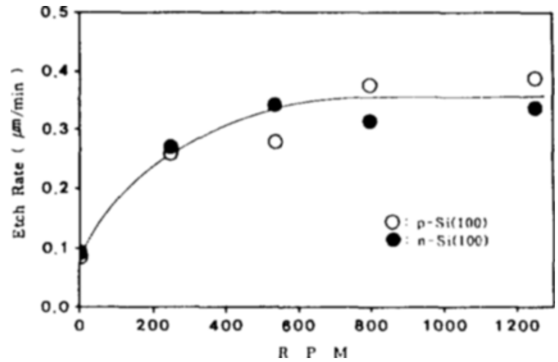

Fig. 2. The effect of agitation speed on etch rate in 12 M HF-0.05 M $K_2Cr_2O_7$-H_2O solution at 293 K.

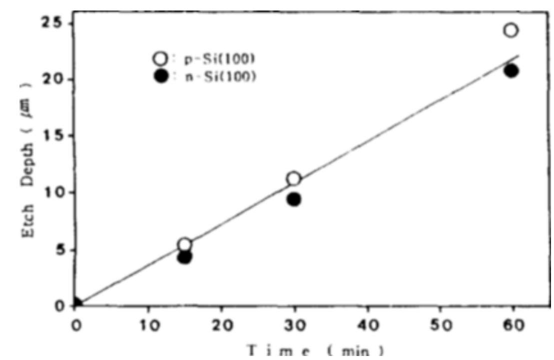

Fig. 3. The effect of reaction time on etch depth in 12 M HF-0.05 M $K_2Cr_2O_7$-H_2O solution at 293 K and 800 RPM.

as soon as the etching solution of 40 ml was added into the stirred reactor.

A microbalance Mettler M3 that has minimum weighing capacity of 10^{-8} g was used to weigh the sample before and after etching. The etch depth was obtained by dividing the etched amount of silicon, i.e., weight difference of Si before and after etching, by surface area exposed to etching solution (0.196 cm^2) and silicon density (2.33 g/cm^3). The obtained etch depth was also compared with that measured with SEM, and the etch rate was obtained by dividing the obtained etch depth by reaction time. The chemical components of the etched Si surface were analyzed using SEM, AES and XRD.

RESULTS AND DISCUSSION

1. Effect of Agitation and Etching Time

The Si etching is a solid-liquid reaction. The overall etching reaction may involve the following steps: (1) diffusion of etchant to Si surface, (2) chemical reaction at the surface, and (3) diffusion of reaction product out of the surface. These steps are affected by reaction time and agitation speed in terms of resistance to mass transfer of etchant.

To study the effect of agitation speed on etch rate, Si (100) was etched at 293 K in the etching solution of 12 M HF-0.05 M $K_2Cr_2O_7$-H_2O with varying agitation speed from 0 to 1200 RPM. It is seen from Fig. 2 that the etch rate increased with agitation speed up to 800 RPM and thereafter leveled off. Hence, to exclude the external mass transfer effect, all experiments were performed at 800 RPM.

The effect of reaction time was also studied by measuring the etch depth as a function of time. The Si (100) was etched in 12 M HF-0.05 M $K_2Cr_2O_7$-H_2O solution at 293 K and 800 RPM. The etch depths were measured at 15, 30 and 60 min after etching reaction started, and the results are shown in Fig. 3. It is seen that the etch depth increased linearly with time. This result indicates that the etch rate of silicon is constant during the etching reaction. Hence, all Si specimens were subjected to etching for 30 minutes throughout.

2. Effect of $K_2Cr_2O_7$ Concentration

In order to study the effect of $K_2Cr_2O_7$ concentration on the etch rate, the etching of Si (100) was performed at 293 K with varying $K_2Cr_2O_7$ concentration from 0.025 to 0.15 M for constant HF concentration of 12 M. The measured etch rates are shown in Fig. 4. It is seen that the etch rate increased with increasing the K_2Cr_2-

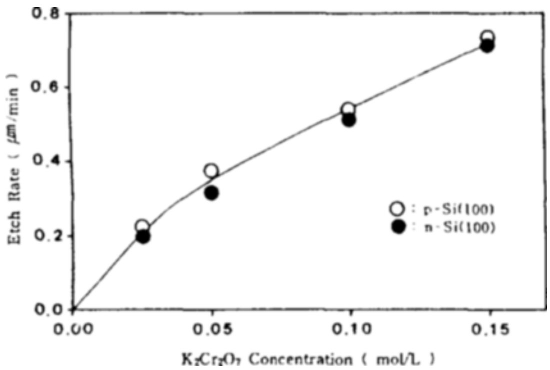

Fig. 4. The effect of $K_2Cr_2O_7$ concentration on the etch rate in 12 M HF-$K_2Cr_2O_7$-H_2O solution at 293 K and 800 RPM.

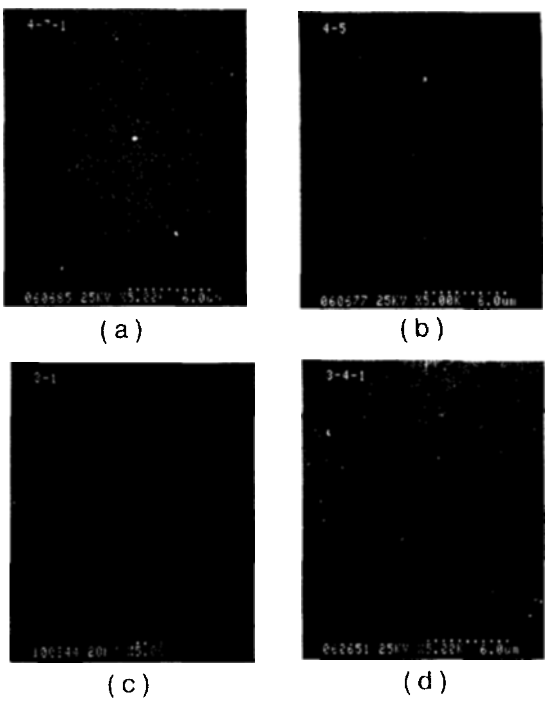

Fig. 5. The SEM photographs of the surface of Si (100) etched in 12 M HF-$K_2Cr_2O_7$-H_2O solution with varying $K_2Cr_2O_7$ concentration at 293 K and 800 RPM.

(a) 0.025 M $K_2Cr_2O_7$, (b) 0.05 M $K_2Cr_2O_7$, (c) 0.1 M $K_2Cr_2O_7$ and (d) 0.15 M $K_2Cr_2O_7$.

O_7 concentration. To analyze the morphology of the etched surface, the etched samples were observed with SEM. It is seen from the SEM photographs in Fig. 5 that the etched surface is smooth, but becoming

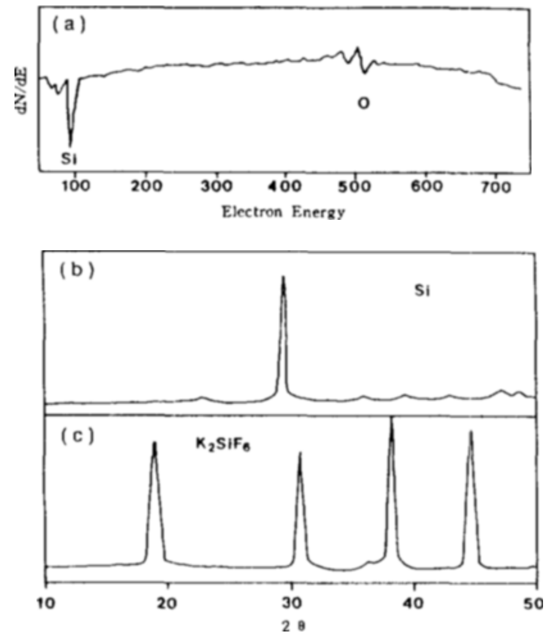

Fig. 6. Surface analysis of etched silicon surface.

(a) Auger spectrum of the silicon surface etched in 12 M HF-0.05 M $K_2Cr_2O_7$-H_2O solution, (b) XRD pattern of silicon etched in 12 M HF-0.05 M $K_2Cr_2O_7$-H_2O solution and (c) XRD pattern of K_2SiF_6 formed in 5 M HF-0.05 M $KMnO_4$-H_2O solution.

a little rough with increasing $K_2Cr_2O_7$ concentraion.

AES and XRD were used to analyze the chemical components of the silicon surface etched in 12 M HF-0.05 M $K_2Cr_2O_7$-H_2O and 12 M HF-0.15 M $K_2Cr_2O_7$-H_2O solutions. The analyzed results showed that the chemical components of the etched surface in both of the solutions were mainly silicon [Fig. 6 (a) and (b)] [8, 9].

It is known in general that the etching reaction of silicon in a HF-oxidizing agent-H_2O solution involves the reduction of oxidizing agent and the dissolution of silicon [10, 11]. For the case of $K_2Cr_2O_7$ as an oxidizing agent, $Cr_2O_7^{-2}$ ion reacts with H^+ ion to form holes on the silicon surface according to the following equation:

$$Cr_2O_7^{-2} + 14H^+ \rightarrow 2Cr^{+3} + 7H_2O + 6h^+ \quad (1)$$

The holes (h^+) formed in Eq. (1) play an important role in the following dissolving mechanism of silicon [12]:

For low concentration of HF,

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

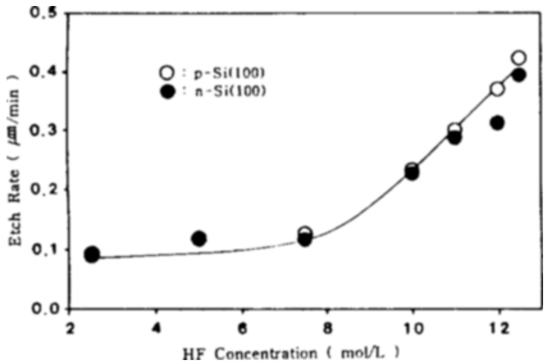

Fig. 7. The effect of HF concentration on the etch rate of silicon in HF-0.05 M $K_2Cr_2O_7$-H_2O solution with varying HF concentration at 293 K and 800 RPM.

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

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

For high concentration of HF,

$$Si + 2F^- + \lambda h^+ \rightarrow SiF_2 + (2-\lambda)e^- \ (\lambda \leq 2) \quad (3a)$$

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

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

It is known that the etching of silicon may occur through one of the above two reactions, depending on the HF concentration in the solution [13]. However, it is clear that the holes formed on surface are essential to both reactions of Eqs. (2) and (3). Furthermore, it is known that the etching reaction is initiated when the holes are injected into the valence band of semiconductor from an oxidizing agent [14]. Hence, Eq. (1) implies that since the oxidizng agent plays a role of producing holes, the generation rate of holes on the silicon surface increases with increasing concentration of the oxidizing agent. The increased rate of hole generation then enhances the production rate of SiF_6^{-2} on silicon surface. The produced SiF_6^{-2} reacts with H^+ to form H_2SiF_6 resulting in etching the silicon surface.

Hence, it may be concluded that the etching rate is increased with increasing $K_2Cr_2O_7$ concentraion due to the increase of hole generation on the silicon surface.

3. Effect of HF Concentration

The effect of HF concentration was studied with varying HF concentration from 2.5 to 12.5 M at 293 K for fixed $K_2Cr_2O_7$ concentration of 0.05 M. The measured etch rates are shown in Fig. 7. It is seen that the etch rate maintains low value and increases very slowly at concentrations lower than 8 M HF, but thereafter it increases drastically with increasing HF concentration. Similar experimental results have been observed by many workers [15, 16]. They postulated that a film that inhibits the etching reaction is formed at low HF concentration on the silicon surface resulting in low etch rate.

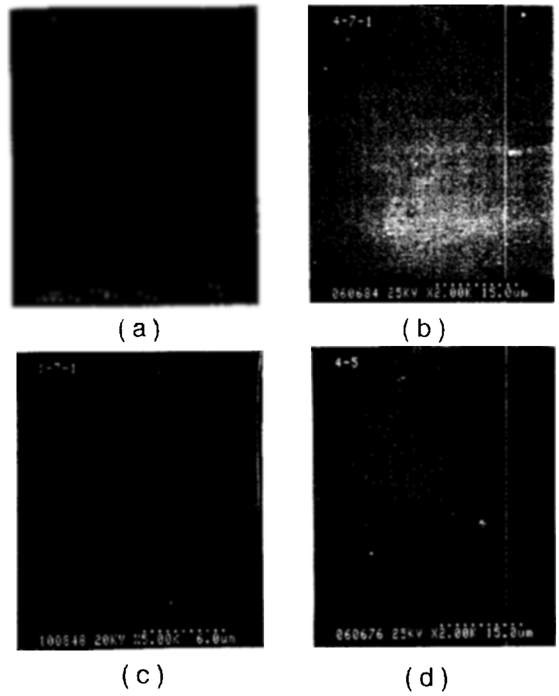

Fig. 8. The SEM photographs of the surface of Si (100) etched in HF-0.05 M $K_2Cr_2O_7$-H_2O solution with varying HF concentration at 293 K and 800 RPM. (a) 2.5 M HF, (b) 5 M HF, (c) 7.5 M HF and (d) 12 M HF.

SEM photographs of the silicon etched with varying HF concentration are shown in Fig. 8. The SEM analysis showed that the morphology of the etched silicon was independent of HF concentration. AES and XRD analyses were also carried out to analyze the etched silicon surface, and the results showed only Si peaks in spite of different HF concentrations.

According to our previous results [17-19], the holes on the valence band drift toward silicon surface due to the energy difference between the valence band of Si and the redox potential of etchant, resulting in the increase of hole concentration on the silicon surface. The increased hole concentration not only accelerates the etch rate but also the formation of K_2SiF_6 layer. However, since K_2SiF_6 is dissolved very slowly

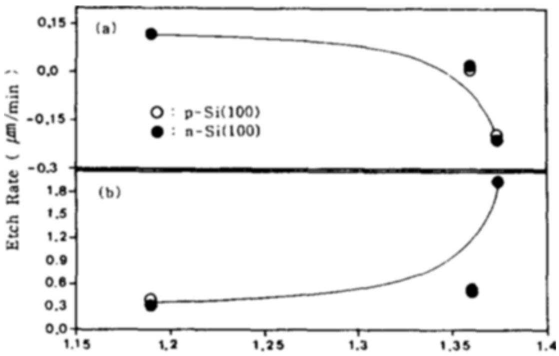

Fig. 9. The effect of the redox potential of oxidizing agent on the etch rate at 293 K and 800 RPM.
(a) 5 M HF-0.05 M oxidizing agent-H_2O and (b) 12 M HF-0.05 M oxidizing agent-H_2O.

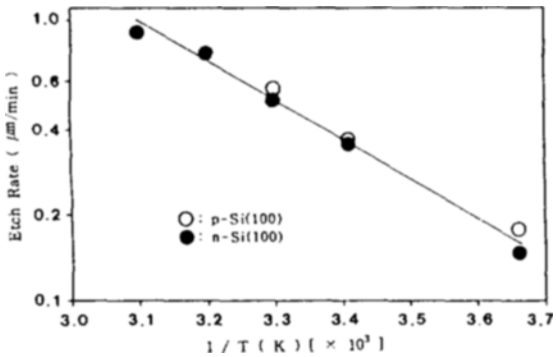

Fig. 10. The Arrhenius plot for Si (100) etching reaction in 12 M HF-0.05 M $K_2Cr_2O_7$-H_2O solution at 293 K and 800 RPM.

in low HF concentration, the increased hole concentration on silicon surface with higher redox potential causes the formation rate of K_2SiF_6 greater than the dissolution rate of it with HF. Hence, at low HF concentration, an K_2SiF_6 film is formed on the surface and retards the etch rate. The effects of hole concentration on the etch rate and film formation rate were examined at high and low HF concentrations of the HF-$K_2Cr_2O_7$-H_2O solution, respectively.

Fig. 4 showed that the etch rate increased in proportion to $K_2Cr_2O_7$ concentration, which means that the rate of forming holes increases with $K_2Cr_2O_7$ concentration. However, at 5 M HF concentration, the rate of forming holes was nearly independent of $K_2Cr_2O_7$ concentration.

Instead of $K_2Cr_2O_7$, $KMnO_4$ and $KBrO_3$ that have greater redox potential than $K_2Cr_2O_7$ were used in the etching solution. The order of redox potential strength is $KMnO_4$>$KBrO_3$>$K_2Cr_2O_7$ [19]. It is seen from Fig. 9 that the etch rate was increased at high HF concentration with the oxidizing agent of higher redox potential, but this trend was reversed at low HF concentration. Especially the use of $KMnO_4$ resulted in negative etch rate because of insoluble product deposited on the surface. The insoluble product was K_2SiF_6, which was reported in our previous reports [17] as shown in Fig. 6 (c). K_2SiF_6 was insoluble in water and aqueous $KBrO_3$ solution, but slightly soluble in HF.

According to Eq. (1), the reduction of oxidizing agent generates holes on silicon surface, and the hole concentration is increased with the increase of H^+ concentration. The concentration of hydrogen ion becomes low at lower HF concentration, and consequently the hole concentration on the silicon surface is low. This may explain why the etch rate is kept at low values at low HF concentrations.

All the above experimental results showed that the increase of hole formation rate increases the etch rate at high HF concentration, but decreases the etch rate at low HF concentration due to the formation of K_2SiF_6. Putting all the above results together, we can draw a conclusion that HF plays an important role in accelerating the formation rate of holes at the silicon surface and the removal rate of K_2SiF_6 formed on the wafer surface during the reaction. At low HF concentrations, the formation rate of K_2SiF_6 is very slow and all K_2SiF_6 formed are effectively removed by HF, but the rate of hole formation is too slow for the etch rate to be increased. At sufficiently high concentrations of HF, the rate increases substantially since HF accelerates the formation rate of holes as well as the removal rate of K_2SiF_6.

4. Effect of Temperature

The effect of temperature on etch rate is shown in Fig. 10 by the Arrhenius plot for varying reaction temperature. The activation energy obtained from the slope was about 7.8 kcal/g-mol.

5. Analysis of Reaction Rate Data

It was figured out from the experimental results that the etch rate depends on temperature and concentrations of $K_2Cr_2O_7$ and HF. Hence, the rate of etching silicon can be expressed as

$$-r_{Si} = k\, C_{K_2Cr_2O_7}{}^{n}\, C_{HF}{}^{m} \tag{4}$$

where n, m and k are, respectively, reaction orders and rate constant that are determined from the experimental results.

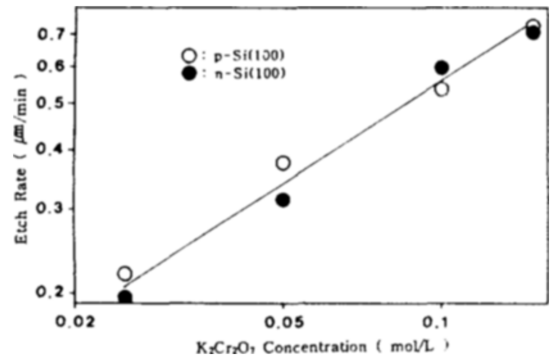

Fig. 11. Logarithmic plot of etch rate vs. $K_2Cr_2O_7$ concentration at 293 K and 800 RPM.

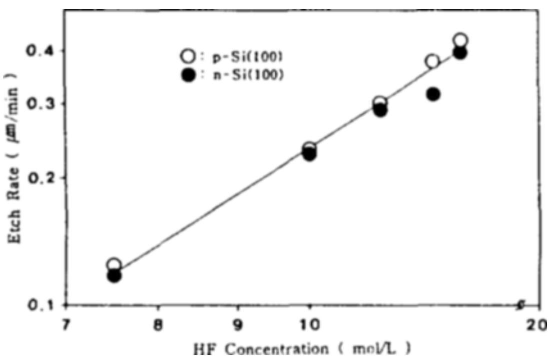

Fig. 12. Logarithmic plot of etch rate vs. HF concentration at 293 K and 800 RPM.

To determine the dependency of the etch rate on $K_2Cr_2O_7$ concentration, for constant HF concentration, Eq. (4) can be rewritten as

$$-r_{Si}=k'C_{K_2Cr_2O_7}{}^{n} \quad (5)$$

where $k'=k\ C_{HF}{}^{m}$.

The reaction order of $K_2Cr_2O_7$ is then obtained by taking logarithm of both sides of Eq. (5), that is

$$\ln(-r_{Si})=\ln(k')+n\ \ln(C_{K_2Cr_2O_7}) \quad (6)$$

The experimental data from Fig. 4 were plotted according to Eq. (5), and shown in Fig. 11. The reaction order n of $K_2Cr_2O_7$ was 0.5 from the slope of the straight line.

Similarly, for constant concentration of $K_2Cr_2O_7$, Eq. (4) can be rewritten as

$$-r_{Si}=k''C_{HF}{}^{m} \quad (7)$$

where $k''=kC_{K_2Cr_2O_7}{}^{n}$. Taking logarithm of Eq. (7) yields

$$\ln(-r_{Si})=\ln(k'')+m\ \ln(C_{HF}) \quad (8)$$

According to Eq. (8), the experimental data of Fig. 7 are plotted in Fig. 12. It was determined from the slope that the reaction order m of HF is 3.

Hence, the etch rate of silicon in HF-$K_2Cr_2O_7$-H_2O solution can be expressed as

$$-r_{Si}=600\ \exp(-3900/T)\ C_{K_2Cr_2O_7}{}^{0.5}\ C_{HF}{}^{3} \quad (9)$$

CONCLUSIONS

The etching reaction of silicon in HF-$K_2Cr_2O_7$-H_2O solution was carried out under various reaction conditions. The etch rates were similar for both of n- and p-Si (100). The etch rate increased with agitation speed of etching solution up to 800 RPM and thereafter leveled off. The etch depth increased linearly with reaction time. The etch rate at high HF concentration increased with increasing the $K_2Cr_2O_7$ concentration since $K_2Cr_2O_7$ plays a role of accelerating the formation rate of holes on the silicon surface. The etch rate maintains low value and increases very slowly at HF concentrations lower than 8 M because the rate of forming hole is low, but increases at HF concentrations greater than 8 M because HF accelerates the formation rate of hole at the silicon surface and removal rate of insoluble product. The etched surfaces consisted mainly of silicon and showed a relatively smooth and planar morphology. The apparent activation energy was 7.8 kcal/g-mole. The reaction rate of silicon etching in HF-$K_2Cr_2O_7$-H_2O solution was obtained as

$$-r_{Si}=600\ \exp(-3900/T)\ C_{K_2Cr_2O_7}{}^{0.5}\ C_{HF}{}^{3}$$

at HF concentrations greater than 8 M.

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