Sensors and Materials, Vol. 15, No. 1 (2003) 043–051
MYU Tokyo

S & M 0508

Effects of ppb-Level Metal Impurities in Aqueous Potassium Hydroxide Solution on the Etching of Si{110} and {100}

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(Received October 1, 2002, accepted January 30, 2003)

Key words: silicon, wet etching, KOH solution, metal impurities, etch rate, surface roughness

We investigated the etching characteristics of Si{110} and Si{100} planes in KOH solutions containing ppb-levels of the metal impurities, Ag, Al, Cr, Cu, Pb, Fe, Ni and Zn. It is found that the ppb-level of Cu in aqueous potassium hydroxide solution roughens both the Si{110} and {100} surfaces and the etch rate of Si{110} and {100} planes is affected by the ppb-level of Cu and Pb in KOH solutions. One can recognize no particular changes of etching characteristics in KOH solution containing ppb-levels of Ag, Al, Cr, Fe, Ni and Zn. The effects of Cu and Pb can be qualitatively explained by the interaction between metal ions and hydrogen gas generated during etching on the basis of oxidation-reduction potentials.

1. Introduction

The anisotropic etching of Si in alkaline solutions is a key technology for the fabrication of Si microstructures. A smooth Si surface after etching and a constant etch rate lead to precise and reproducible production. However, the etching characteristics are unstable under certain conditions.[1] Campbell *et al.* observed the change of {100} silicon surface roughness in KOH solutions with a variety of chemical reagent makers from which the purity differed.[2] Hein *et al.* investigated the effects of the ppm ~ % level of metal impurities on the etching of Si {100}.[3]

We reported that the ppb-level of Cu in KOH solution roughens the Si{110} surface and the etching rate of Si{110} is affected by the ppb-level of Cu and Pb.[4] In this work, we investigated and compared the etching characteristics of Si{110} and {100} planes in KOH solution containing ppb-levels of the metal impurities Ag, Al, Cr, Cu, Pb, Fe, Ni and Zn.

2. Experimental Methods

The experiments were performed using p-type {110} and {100} CZ-silicon wafers. Plasma-CVD silicon nitride (500 nm) was deposited on the polished wafer (the surface roughness was below 0.01 μm) and served as an etching mask. Test structures were etched by 32wt% KOH. The etching treatments were performed at 80~115°C (±1°C) in a polypropylene vessel with a heater. The etch depth was 200 ~ 300 μm. In order to prevent concentration changes in the KOH solution due to evaporation, the vessel was covered with a polypropylene plate.

The concentrations of original impurities in 32wt% KOH solution were determined by inductively coupled plasma mass spectrometry (Yokogawa PMS-200) and are shown in Table 1.

Reagents for atomic absorption analysis (Wako Pure Chemical) were adopted as the additives; Ag, Al, Cr, Cu, Pb, Fe, Ni and Zn. They were added to the etching solution by means of a pipette. The concentrations used in this work were the amounts of the original and additive values.

The etch depth and the surface roughness were measured with a surface profilometer (Tokyo Seimitsu Surfcom 600). The etched surface was analyzed by SEM (JEOL T-300) and AES (JEOL JAMP-7800F).

3. Experimental Results

3.1 *Etch rate*

Figures 1 and 2 show the dependences of the etch rates of Si{110} and {100} planes on the concentration of metal impurities in the solution at 110°C, respectively. The etch rates changed with the ppb-levels of Cu and Pb in the solution. In the KOH solution containing

Table 1
Concentrations of original impurities in 32wt% KOH solution by ICP-MS.

Impurities	Concentration (ppb)
Al	41
Cr	82
Cu	21
Fe	890
Mg	31
Ni	<10
Pb	21
Zn	37

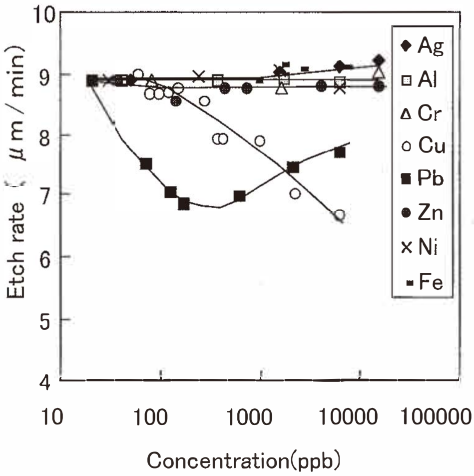

Fig. 1. Dependence of the etch rate of Si{110} plane on concentration of impurities (32wt% KOH, 110°C).

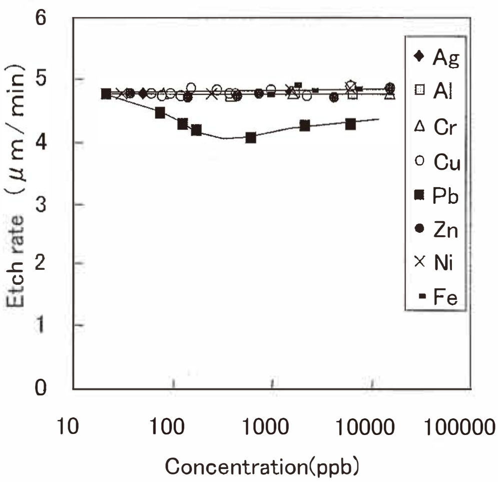

Fig. 2. Dependence of the etch rate of Si{100} plane on concentration of impurities (32wt% KOH, 110°C).

Cu, the Si{110} etch rate decreased gradually above 100 ppb of Cu in the solution. However, the Si{100} etch rate was constant below 20000 ppb of Cu. In the KOH solution containing the ppb-level of Pb, the etch rate of both Si{110} and {100} decreased to a minimum value at levels from 100 to 300 ppb, while above 300 ppb the etch rate increased. In the KOH solution containing ppb-levels of Ag, Al, Cr, Fe, Ni and Zn, one can recognize that there are no particular changes of etch rates.

3.2 *Activation energy*

Figures 3 and 4 show the dependences of the etch rates of Si{110} and {100} planes on temperature in the solution containing ppb-levels of Cu and Pb (Arrhenius diagram). The

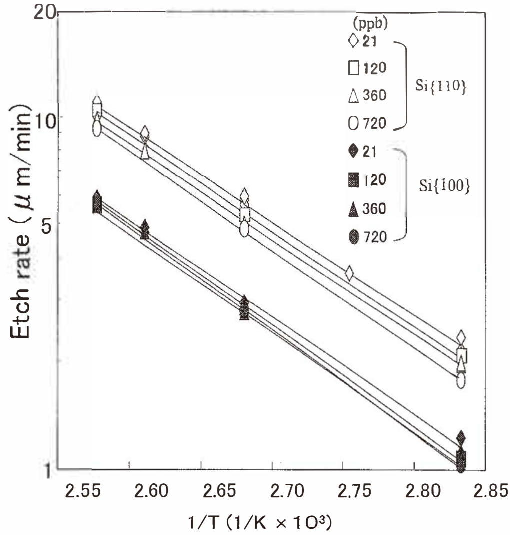

Fig. 3. Dependence of the Si{110} and {100} etch rates in KOH solution containing ppb-level of Cu on temperature (32wt% KOH).

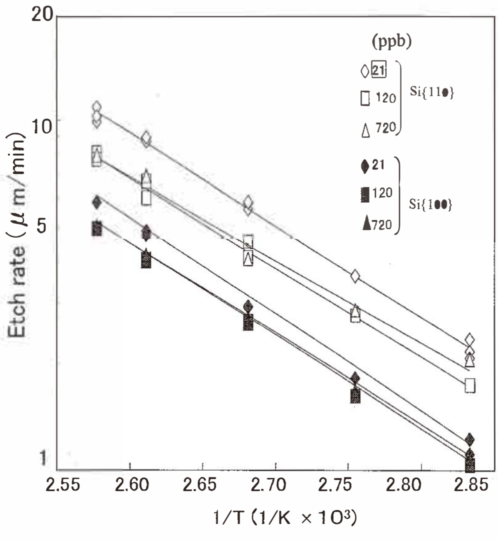

Fig. 4. Dependence of the Si{110} and {100} etch rates in KOH solution containing ppb-level of Pb on temperature (32wt% KOH).

Arrhenius plots were nearly linear. We calculated the activation energies for the Si{110} and {100} planes, and those in the solution containing the ppb-level of Cu are shown in Fig. 5 and those in the solution containing the ppb-level of Pb are shown in Fig. 6. The energies increased gradually with increasing concentration of Cu. On the other hand, the energies decreased with increasing concentration of Pb. It can be considered that the effects of Cu and Pb in the solution are expressed by the change of activation energy.

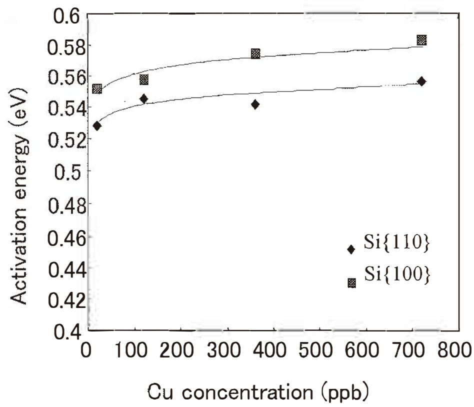

Fig. 5. Activation energies calculated for Si{110} and {100} in the solution containing ppb-level of Cu.

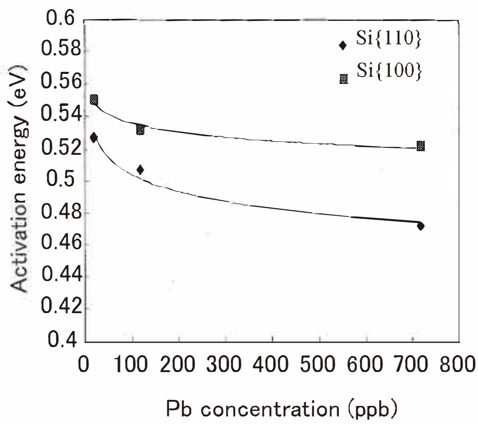

Fig. 6. Activation energies calculated for Si{110} and {100} in the solution containing ppb-level of Pb.

3.3 *Surface roughness*

Figures 7 and 8 show the dependences of the surface roughness of Si{110} and {100} planes on the concentration of impurities, respectively. The surface roughness after etching of both Si{110} and {100} remarkably increased above 100 ppb of Cu in the solution. The roughness of Si{110} and {100} reached their maxima of 4~5 μm and 0.4 μm above 300 ppb of Cu, respectively. However, ppb-levels of Pb, Ag, Al, Cr, Fe, Ni and Zn in the solution did not roughen the Si surface.

Figures 9 and 10 show SEM micrographs of the Si{110} and Si{100} etched surfaces at 360 ppb of Cu, respectively. Numerous hillocks were observed on the Si{110} etched surface. We reported that Cu particles were observed on the surface in detailed observation

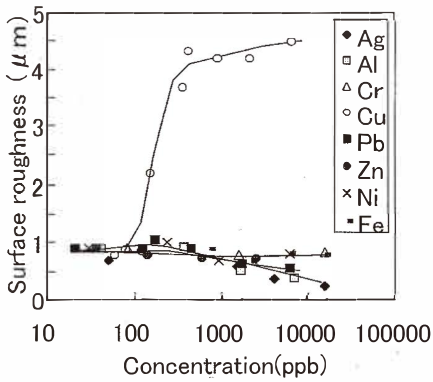

Fig. 7. Dependence of the surface roughness of Si{110} plane on concentration of impurities (32wt% KOH, 110°C).

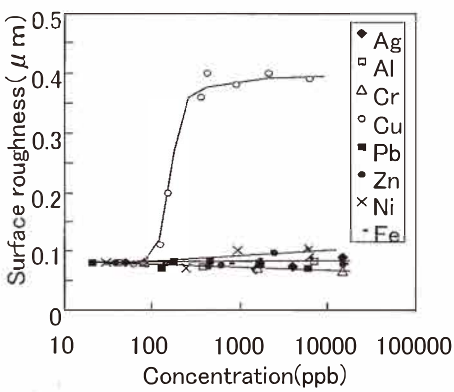

Fig. 8. Dependence of the surface roughness of Si{100} plane on concentration of impurities (32wt% KOH, 110°C).

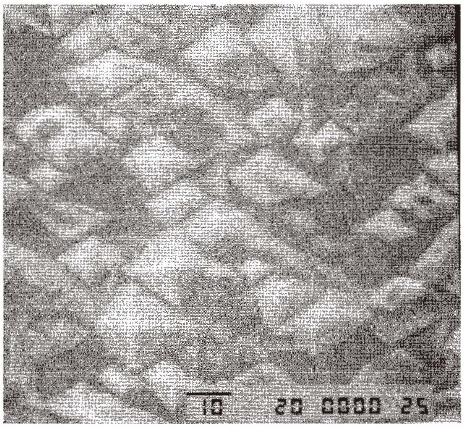

Fig. 9. SEM micrographs of the Si{110} etched surface at 360 ppb of Cu (32wt% KOH, 110°C).

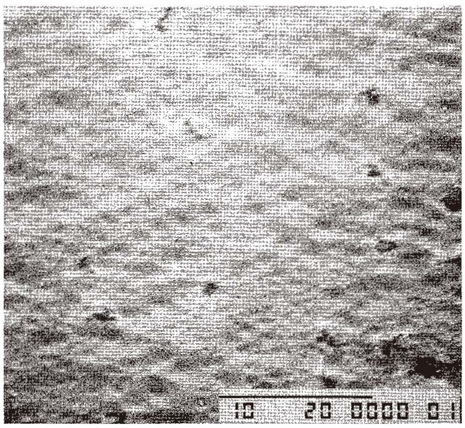

Fig. 10. SEM micrographs of the Si{100} etched surface at 360 ppb of Cu (32wt% KOH, 110°C).

and analysis with SEM and AES.[4] However, hillocks were not observed on the Si{100} etched surface.

4. Discussion

According to the results, the effect of impurities, particularly Cu or Pb in the solution, can be qualitatively explained by considering the oxidation-reduction potential. The values are shown in Table 2.[5] Cu or Pb in alkaline solutions at high pH become the Cu ion

Table 2
Reduction-oxidation potential values.

Element	Al	Zn	Cr	Fe	Ni	Pb	H	Cu	Ag
Potential (V vs SHE)	−2.55	−1.45	−1.42	−1.05	−1.00	−0.91	−0,85	−0.401	+0.25

(CuO_2^{2-}) or the Pb ion ($HPbO_2^-$).

Hydrogen gas is generated by the following etching reaction in alkaline solution.[6]

$$Si + 4\,OH^- \rightarrow Si(OH)_4 + 4\,e^- \tag{1}$$

$$4\,H_2O + 4\,e^- \rightarrow 4\,OH^- + 2\,H_2 \tag{2}$$

The potentials of Cu and Pb, which remarkably change the etching characteristics, are close to that of hydrogen generated during etching.

It is considered that Cu ion is reduced to Cu metal by hydrogen and that the Cu particles on the Si surface can act as an etching mask because the potential of Cu is higher than that of H. As a result, the Si surface is roughened.

On the other hand, because the oxidation-reduction potential value of Pb is equivalent to that of H, it is assumed that the reaction of Pb reduction-ionization can oppose the etching reaction, and thus the etching rate is changed. Therefore, because the Pb reduction-ionization is in an equilibrium, it is considered that the amount of Pb deposited on the Si surface is limited and does not affect the Si surface roughness.

Furthermore, the oxidation-reduction potential value of Ag is also higher than that of hydrogen. The potential of Ag is more positive than that of Cu. We consider that Ag ions reduce directly due to hydrogen gas during etching and become Ag metal particles in the solution because the potential of Ag is too high. It seems that effect of Ag does not appear on etching properties. And it also seems that the Si wafer and Cu ion can interact with each other.[7,8] However, further investigation for the interaction in detail between impurities and hydrogen or Si is required to understand the effect of impurities.

5. Conclusion

We investigated the etching characteristics of Si{110} and {100} planes in 32wt% KOH solution containing ppb-level metal impurities and obtained the following results.

(1) The etch rates were changed with ppb-levels of Cu and Pb in the solution.

(2) The activation energies of both Si planes increased gradually with increasing concentration of Cu. On the other hand, the energies decreased with increasing concentration of Pb.

(3) The surface roughnesses after etching of both Si{110} and {100} remarkably increased above 100 ppb of Cu in the solution. However, ppb-levels of Pb, Ag, Al, Cr, Fe, Ni and Zn in the solution did not roughen the Si surface.

(4) Numerous hillocks were observed on the Si{110} etched surface. However, hillocks

were not observed on the Si{100} etched surface. In the case of Si{110} surface after etching, Cu particles were observed by SEM and AES.

(5) The effects of Pb and Cu were explained by the interaction between metal ions and hydrogen generated during etching on the basis of reduction-oxidation potentials.

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