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Study of Cu Contamination Removal Using Electrolytic Ionized Water

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This paper reports that electrolytic ionized anode water with Oxidation Reduction Potential (ORP) of 1000～1400mV and pH of 2～5 successfully removes Cu contamination from Si surface. Cu atoms on a Si surface are ionized to Cu^{2+} due to high ORP and dissolved into Electrolytic Ionized Water (EIW). It is confirmed that the key species for removing Cu contamination is ClO^- which is produced by electrolytic ionization. EIW is potentially useful for examining the mechanism of metallic contamination removal.

1. INTRODUCTION

We have reported that the Electrolytic Ionized Water (EIW) cleaning technique is effective for removing metallic contamination and particles.[1,2] Another characteristic of this technique is that the pH and ORP (Oxidation Reduction Potential) of solutions can be easily controlled by adjusting electrolytic conditions. This technique is thus potentially useful for examining the phenomena of wet processes. In the present study, we examined the mechanism of Cu removal from Si surfaces by using the EIW technique in order to control pH and ORP.

2. EXPERIMENTAL

The EIW production apparatus is shown schematically in Fig. 1. The apparatus, which is composed of three separated frames: anode, cathode, and middle frames, can produce EIW with a wide range of pH and ORP.[3] The anode water was produced by adding HCl to with a concentration of ～10 mmol/l in the anode chamber. The ORP was measured against the normal hydrogen electrode (NHE). In order to simulate the cleaning effect by each component dissolved in the EIW, standard solutions of the component were adjusted and applied for cleaning. Si substrate surfaces were intentionally contaminated by them dipping them in a diluted HF solution containing Cu (1 ppm) at room temperature before treatments. The surface Cu concentration was analyzed before and after the treatments by total reflection x-ray fluorescence spectroscopy (TREXRF). The dissolved ions in the solutions were analyzed by ion chromatography.

3. RESULTS

Figure 2 shows the ORP variance of an anode water and a diluted HCl solution as a function of pH, as well as the Cu ionization properties reported by Pourbaix.[4] The Cu ionization property diagram indicates that free Cu atoms are ionized to Cu^{2+} in a solution with a lower pH than 6 and a higher ORP than 350 mV. By comparing the Cu ionization properties and the ORP-pH characteristics of the solutions, it is found that both the anode water and the diluted HCl solution have enough ORP values to ionize Cu to Cu^{2+} at the pH lower than 7.

Figure 3 shows Cu removing abilities of HCl and anode water with a pH of 2. By rinsing Cu contaminated Si surfaces with anode water with a pH of 2.0 and an ORP of 1370 mV at room temperature, surface Cu atoms were reduced to less than $1x10^{10}$atoms/cm^2. In contrast, Cu contamination cannot be removed by rinsing in a diluted HCl solution with the same pH value, although the diluted HCl has an higher ORP than 350 mV as shown in Fig. 2. This is consistent with the results reported by Ohmi et al. that Cu atoms positively deposit on the Si surfaces in solutions with ORP below 750 mV at pH=0～5.[5] Namely a higher ORP than 750mV is necessary for removing Cu atoms adsorbed on Si surfaces. Therefore, the anode water which has an ORP of 1000～1400 mV at pH=2～5 is effective for Cu removal.

Oxidizing species contained in the anode water of ORP=1370 mV and pH=2.06 were analyzed as shown in Table 1. It is supposed that the high oxidation potential of the anode water is induced by $ClOx^-$ oxidizing species and O_3, because O_2 does not induce a high oxidation potential. To identify which component is essential for efficient Cu removal, the Cu removing effect was examined with

standard solution of NaClO, $NaClO_3$ which produce ClO^- and ClO_3^- ions and with O_3 water. The Cu removing effect of each species is shown in Fig.4. The Cu removing effect is obtained only by the solution including ClO^-. Therefore, ClO^- is the key species which is effective for Cu removal.

The Cu removing effect as a function of ClO^- concentration in the standard solution is shown in Fig.5. The Cu contamination on Si surfaces decreased to below the detection limit when the surfaces were rinsed in standard solution containing ClO^- at a concentration higher than 10 ppm. The Cu removing effect by ClO^- was also examined by using the anode water which causes no Na contaminations. The ClO^- concentration in the anode water was controlled by adjusting the electrolytic condition. Cu contamination on the Si surfaces was removed with anode water containing ClO^- at a concentration higher than 10 ppm (Fig.6). The dependence of Cu removal efficiency on ClO^- concentration in the anode water is quite similar to that for the solution. Therefore it is suggested that ClO^- is the species in the anode water which removes Cu contamination from Si surfaces.

4. CONCLUSIONS

We studied the Cu removal from Si surfaces by using EIW. It was confirmed that the species which is effective for removing Cu contamination from Si surfaces is ClO^-, which causes high oxidation potential of the solution. Electrolytic Ionization is an excellent technique to control the pH and ORP of solutions easily by adjusting electrolytic conditions. Such EIW is useful for examining wet chemical processes as well as removing Cu contamination.

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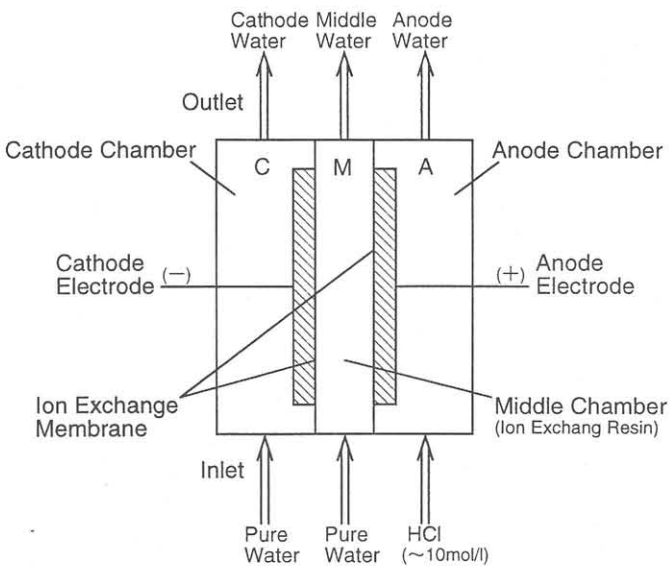

Fig. 1 A diagram of our electrolytic ionized water (EIW) production apparatus.

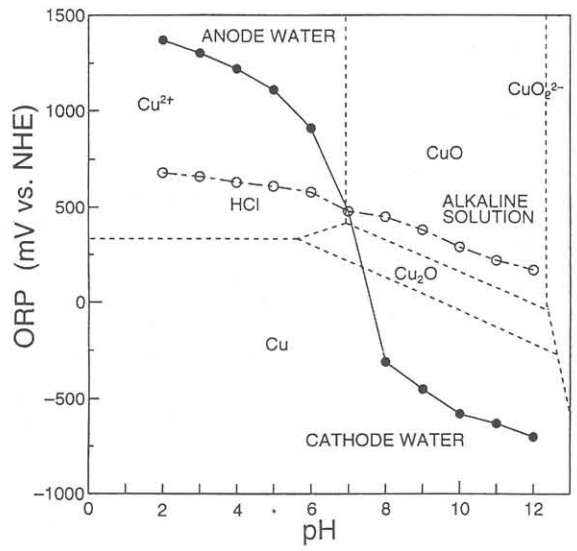

Fig. 2 Cu ionization properties as functions of pH and ORP.

Table I The oxidizing species included in the anode water.

pH	ORP	ClO^-	ClO_2^-	ClO_3^-	O_2	O_3
2.06	1370 (mV)	25 (ppm)	0 (ppm)	27.8 (ppm)	>20 (ppm)	1.35 (ppm)

(cf) O_3 concentration includs Cl_2 concentration.

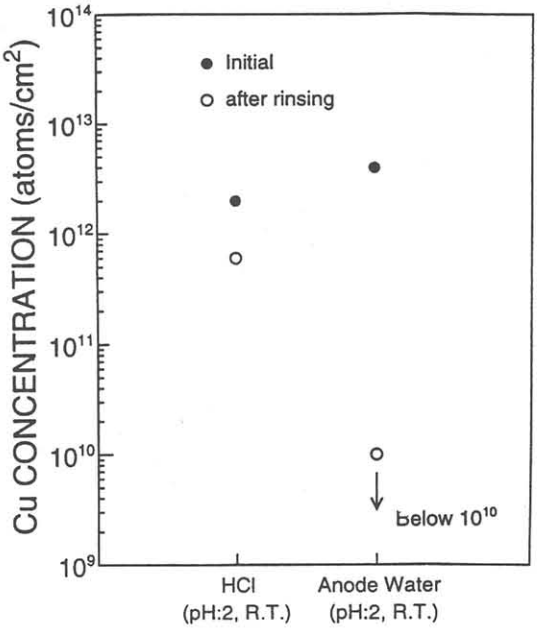

Fig. 3 Cu removing abilities of HCl and anode water with pH of 2.

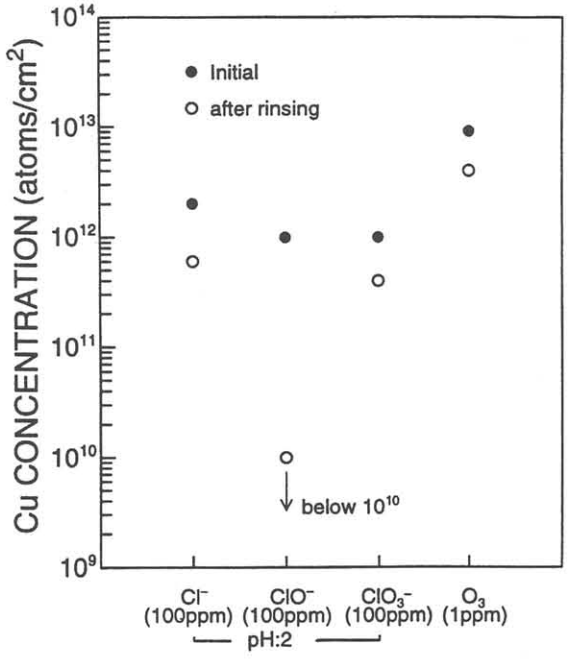

Fig. 4 Cu removing effect of the various oxidizing species

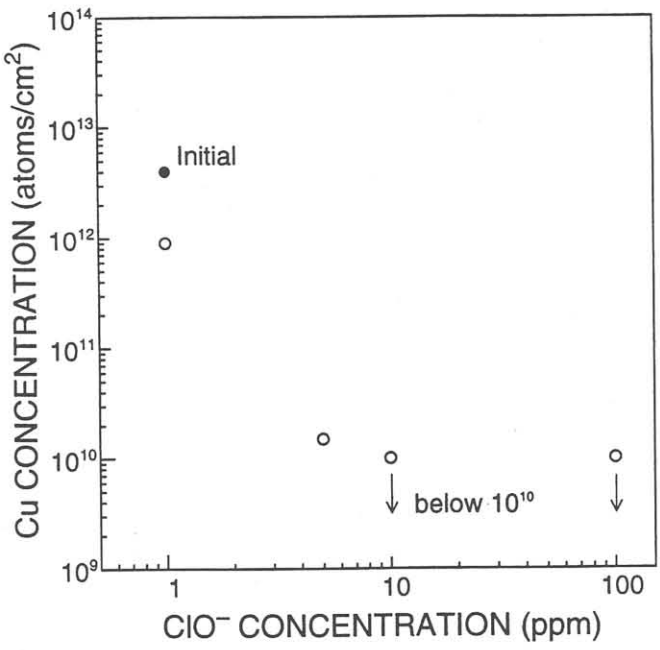

Fig. 5 Cu removing efficiency as a function of ClO^- concentration in standard solutions.

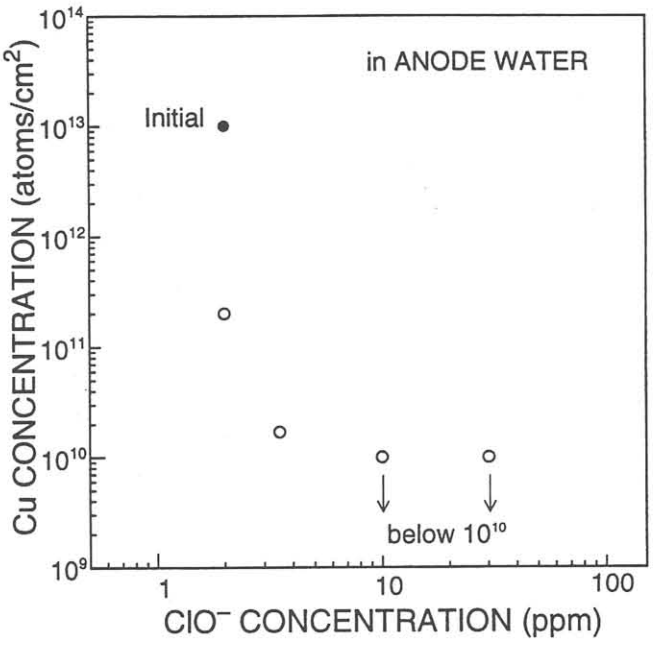

Fig. 6 Cu removing efficiency as a function of ClO^- concentration in the anode water controlled by the electrolytic condition.