전해 양극수를 이용한 디스플레이 신 세정 공정

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A new cleaning concept for display process with electrolyzed anode water

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Abstract

Display process has adopted RCA clean, being applied to large area and coped with environmental issue for last ten years. However, the approaching concept of ozonized, hydrogenised, or electrolyzed water cleaning technologies is within RCA clean paradigm. In this work, only electrolyzed anode water was applied to clean particles and organics as well as metals based on Pourbaix concept, and as a test vehicle, MgO particles were introduced to prove the new concept. The electrolyzed anode water is very oxidative with high oxidation reduction potential(ORP) and low in pH of more than 900mV and 3.1, respectively. MgO particles were immerged in the anode water and its weight losses due to dissolution were measured with time. Weight losses were in the ranges of 100 to 500 micrograms in 250ml anode waters depending on their ORP and pH. Therefore it was concluded that the cleaning radicals in the anode water was at least in the range of 1 to 5E20 ea per 250 ml anode water equivalent to 1E18 ea/cm3. Hence it can be assumed that the anode water be applied to display cleaning since 1E10 to 1E15 ea/cm3 ranges of contaminants are being treated. In addition, it was observed that anode water does not develop micro-roughness on hydrophobic surface while it does on the native silicon oxide.

I. INTRODUCTION

The cleaning process covers one third of total number of semiconductor processes and a significant portion of production costs, and hence takes an important role technically, economically, environmentally and ecologically. Also ultraclean wafer surface must be achieved, being particle free, metallic impurity free, organic free, moisture free, native oxide free, surface micro-roughness free, charge-up free, and hydrogen- terminated.[1-3] The major contaminants such as particles, metallic impurities and organics must be controlled precisely and uniformly so that high integration of semiconductor manufacturing can be realized economically. Many wet cleaning processes that aim to eliminate contaminants have been developed based on RCA cleaning. RCA cleaning is basically two step process which consists of highly concentrated NH_4OH /H_2O_2/H_2O (called SC1 or APM) and HCl/H_2O_2/H_2O (called SC2 or HPM)

treatments at relatively high temperature.[4-5] As the diameter of Si wafers increases and the semiconductor devices shrinks, the number of cleaning process units increases so that the amount of chemicals and ultra pure water(UPW) consumed in RCA cleaning process increases drastically and production cost and environmental burden increase as well. In order to resolve these issues, several candidates have been studied applying functional water such as hydrogenated ultra pure water(H_2-UPW)[6], ozonized water(O_3-UPW)[7-8], and electrolyzed water.[9-12] However their applications have not not overcome two step RCA concept as mentioned above. Pourbaix diagram however gives a clue that a strong oxidative agent could remove particle contaminations as well as metals. Anodic water shows very typical properties in ORP and pH, and could fit to Pourbaix diagrams of many metals maintaining them in ionized conditions.

Hence it is expected that submicron metal oxide particles can be easily and rapidly dissolved by anodic water. Anodic water cleaning is studied in this work, since it is assumed to provide the optimum conditions for requirements of the beyond Giga-DRAM semiconductor technology.

II. EXPERIMENTAL

The schematic of electrolyzing system used is shown in Fig. 1. The system consists of five chambers which are two anode, two cathode, and one middle chambers, electrolyzing water two times increasing ORP and decreasing pH more. Applied currents and voltages at fully steady state electrolysis were 10 amperes and 11 volts. NH$_4$Cl solution as an electrolyte was supplied to the middle chamber, providing Cl ions to generate strong oxidative radicals such as hydroxyle. Flow rates of water in anode and cathode chambers while electrolysis were 0.5l/min.

MgO particles of about 0.5um sizes were applied on the glass surface, soaked in UPW, dried on the hot plate for two minutes, immediately followed by weight measurements. Then that specimen was soaked in 250 ml anode water up to 30 minutes and dried, followed by immediate weight measurement. The weight decreases were observed and analyzed.

Silicon wafer surfaces were investigated with AFM(Atomic Force Microscope) to observe the micro-roughness changes. RCA cleaned silicon wafers having native silicon oxide were separated in two groups. One group were treated with anode water and the other group were treated with HF to remove the native oxide, followed by immediate anode water treatment.
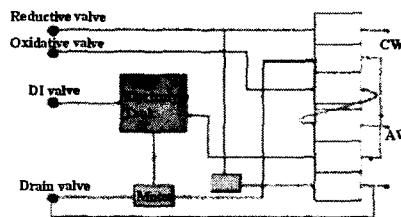

Figure 1. Schematic of electrolyzing system

III. RESULTS AND DISCUSSION

pH/ORP of anode and cathode waters were measured to be 3.1/+900 mV and 10.6/-750 mV, respectively. The electrolysis reaction could be postulated as follows. Cations such as NH4$^+$ and H$^+$ seems to migrate to the negative cathode electrode, while anions such as OH- and Cl$^-$ to the positive anode electrode. Then electrolysis takes place generating several new oxidation and reduction radicals at anode and cathode, respectively.

Then anode water was applied to remove MgO particles. It was observed that anode water resulted in MgO particle dissolution as shown in Fig. 2. As pH increases, dissolution of MgO decreases. Also it was observed that after 10 minutes, MgO dissolution no longer takes place. Dissolution saturation after 10 minutes was re-drawn as shown in Fig3. It was clear that anode water dissolved MgO particle while deionized water did not.
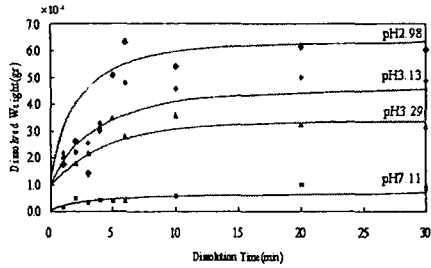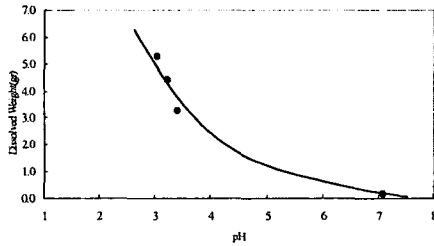
Figure 2. MgO dissolution by anode water

Figure 3. Saturated dissolution changes after 10
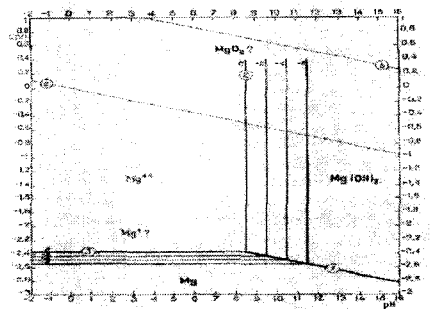minutes according to pH changes

Figure 4. Pourbaix diagram of Mg

These results could be reviewed with Fig. 4 of Pourbaix diagram.13   In anode water of pH 3-4 and ORP 800-1,000mV, Mg should exist as a form of Mg ion.   Hence MgO should be dissolved and MgO particle could be removed, which is very different from SC1 RCA cleaning concept.   It is known from Pourbaix diagrams that many elements such as Al, Mg, Ni, K, Na, Rb, Sr, Cd, Fe, Cu or Co behavior more or less like Mg.   Therefore many metal oxides can be removed with anode water.   However, oxide particles of Si and Sn and metal particles of precious metals can not be removed with anode water since those metals are very stable in anode water of pH 3-4 and ORP 800-1,000mV as shown in Fig. 5

Fig. 6 showed AFM data after treating silicon

wafers with anode water.   It was clearly shown that roughness increased as etch time increased for hydrophilic surface, but that it did not for hydrophobic surface in short etch time.   From Fig. 5, it was realized that silicon or silicon oxide could not be etched with anode water .   Hydrophobic surface seemed to follow this expectation while hydrophilic native silicon oxide surface did not.   It could be due to the chemical unstability of extreme thin thickness of native silicon oxide.   It could be conclusively said that anode water could be applied to clean the hydrophobic silicon surface.

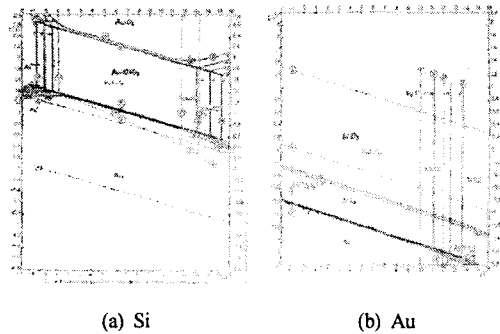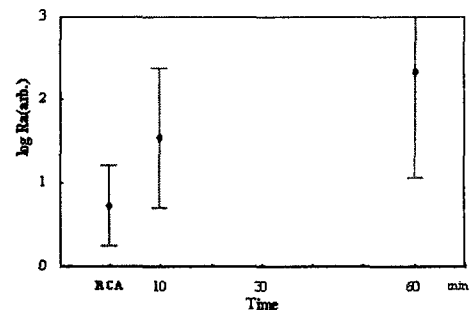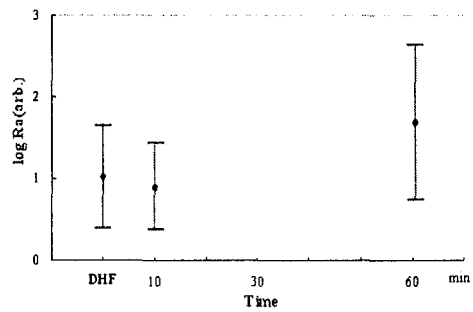(a) Si   (b) Au

Figure 5. Pourbaix diagrams of special elements

(a) on hydrophilic native silicon oxide

(b) on hydrophobic bare silicon substrate
Figure 6. Roughness changes of silicon wafer
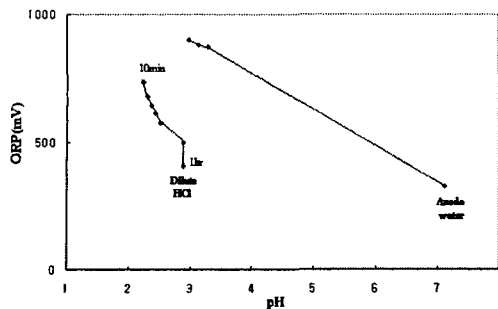surfaces after anode water treatment

Figure 7. comparison of anode water with HCl solution

Fig. 7 showed the merit of anode water application for cleaning instead of strongacidic solution. First, it is clear that ORP value of anode water is much higher than HCl solution at around pH 3.0. Hence anode water can be a strong candidate for cleaning, conforming to environmental issue. Secondly, pH values of anode water can be extended to wide range in accordance with significant ORP values, which enhances the capability of anode water for various conditions of device processes.

IV. CONCLUSION

Anode water was applied to clean particles and organics as well as metals. MgO particles were introduced to prove this new concept. MgO particles were immerged in the anode water and its weight losses due to dissolution were measured with time. Weight losses were in the ranges of 100 to 500 micrograms in 250 ml anode water. Therefore it was concluded that the cleaning radicals in the anodic water was at least in the range of 1 to 5E20 ea per 250 ml anode water equivalent to 1E18 ea/cm3 which is applicable to display cleaning. In addition, anode water does not develop micro-roughness on hydrophobic surface while it does on the native silicon oxide.

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