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A New Cleaning Concept for Display Manufacturing Process with Electrolyzed Anode Water

Kunkul Ryoo*

전해 양극수를 이용한 새로운 디스플레이 세정

류 근 걸*

Abstract Display manufacturing process has adopted RCA cleaning, applying to larger area and coping 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 900 mV 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 250 ml anode water 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 5×10^{20} ea per 250 ml anode water equivalent to 1×10^{18} ea/cm^2. Hence it can be assumed that the anode water applied to display cleaning from now on 1×10^{10} to 1×10^{15} ea/cm^2 ranges of contaminants are being treated. In addition, it was observed that anode water did not develop micro-roughness on hydrophobic surface while it did on the native silicon oxide.

요 약 디스플레이 세정의 개념은 기존의 반도체 세정인 RCA세정을 근간으로 하고 있으며, 대면적화와 환경친화적인 관점으로 발전하여 왔다. 본 연구에서는 프베이 도표에 근거하여 전리수를 이용하여 입자를 제거할 수 있음을 예측하고 이를 확인하였다. 이 때 연구 대상으로 MgO 분말을 사용하였다. 사용된 전리수는 산화전위가 800 mV 이상이고 pH가 3.1으로 산화상이 강하였다. 전리수에 용해되는 MgO 분말의 무게를 pH에 조사하였으며, 250 ml의 전리수에 100-500 microgram 범위로 용해됨을 알 수 있었다. 이는 1E18 ea/cm^3 정도의 용해 물질을 내포하고 있음을 의미하며, 따라서 1E15 ea/cm^3 정도 수준의 불순물을 다루는 디스플레이 세정에 적용할 수 있음을 알 수 있었다. 특기할 것은 전리수는 반도체의 기판인 실리콘 웨이퍼의 자연산화막을 식각하여 표면거칠기를 증가시킴을 처음으로 관찰하였다.

Key Words : Electrolyzed water, electrolyzed anode, cleaning, dispaly, semiconductor, surface roughness

1. 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 [1-2] 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 (RCA corp., U.S.A.) 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/

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Soonchunhyang University, Shinchang, Asan, Chungnam, Korea
*Corresponding author: Kunkul Ryoo(kraten@sch.ac.kr)

H_2O_2/H_2O(called SC_2 or HPM) treatments at relatively high temperature [3-4]. 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)[5], ozonized water (O_3-UPW)[6-7], and electrolyzed water [8-10]. 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 Oxidation Reductive Potential (ORP) and pH, and could fit to Pourbaix diagrams of many metals maintaining them in ionized conditions [11]. Hence it is expected that submicron metal oxide particles can be easily and rapidly dissolved by anodic water. Anodic water cleaning was studied in this work, since it is assumed to provide the optimum conditions for requirements of the beyond Giga-DRAM semiconductor technology.

2. 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, to electrolyze water two times to increase ORP and to decrease pH more. Applied current and voltage at fully steady state electrolysis were 10 ampere and 11 volt. NH_4Cl solution as an electrolyte was supplied to the middle chamber, providing Cl ions to generate strong oxidative radicals such as hydroxyle. Flow rate of water in anode and cathode chambers during electrolysis were 0.5 l/min.

MgO particles of about 0.5 μm 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 another group were treated with HF to remove the native oxide, followed by immediate anode water treatment.

3. 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 NH_4^+ 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 dissolved MgO particles as shown in Fig. 2. As pH increases,

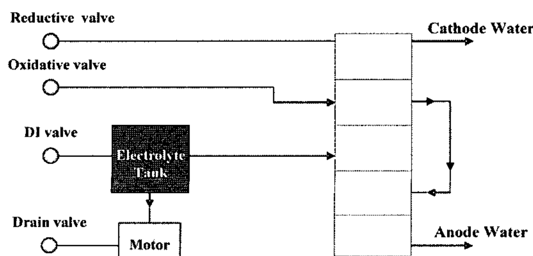


Fig. 1. Schematic diagram of electrolyzing system.

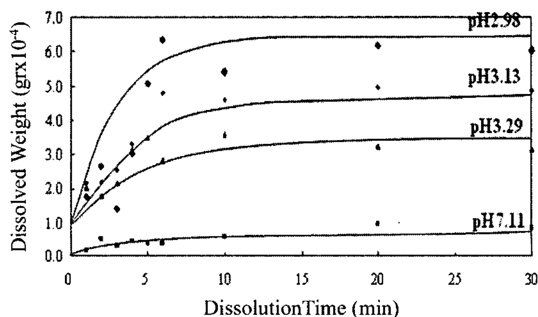


Fig. 2. MgO dissolution by anode water.

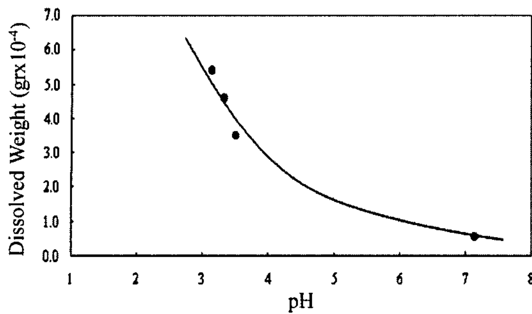


Fig. 3. Saturated dissolution changes after 10 minutes according to pH changes.

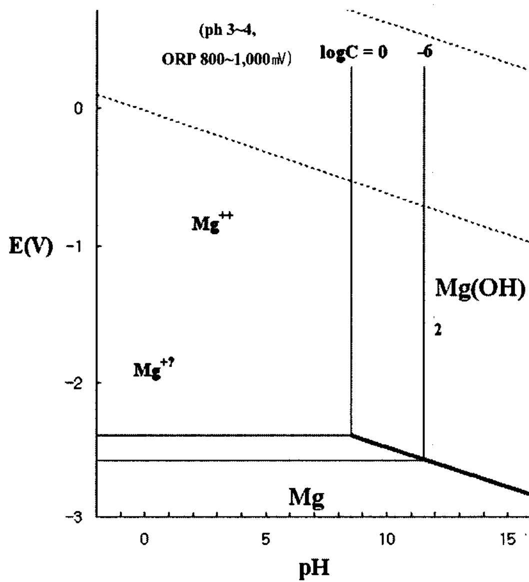
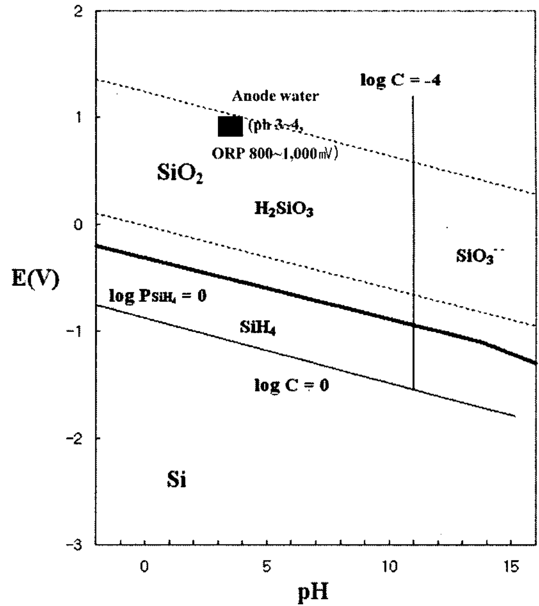


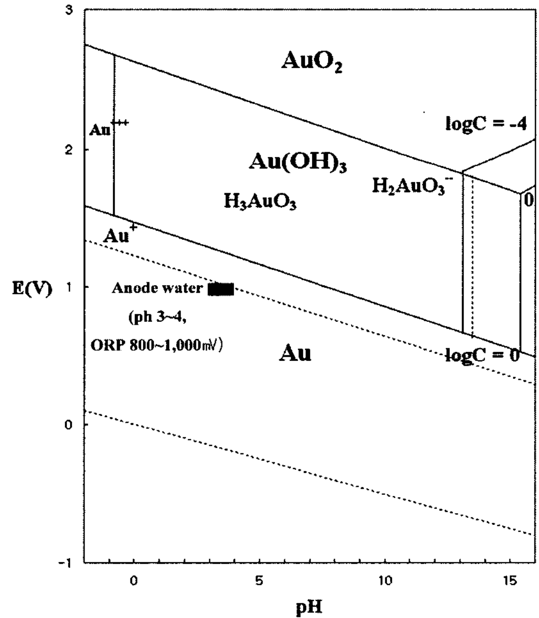
Fig. 4. Pourbaix diagram of Mg.

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 Fig. 3. It was clear that anode water dissolved MgO particle while deionized water did not.

These results could be reviewed with Fig. 4 of Pourbaix diagram [11]. In the range of anode water of pH 3-4 and ORP 800-1,000 mV, Mg should exist as a form of Mg ion, which means that, 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, Sn and metal particles of precious metals can not be removed with anode water since those metals are very stable in the range of anode water of pH 3-4 and ORP 800-1,000 mV as shown in Fig. 5 .

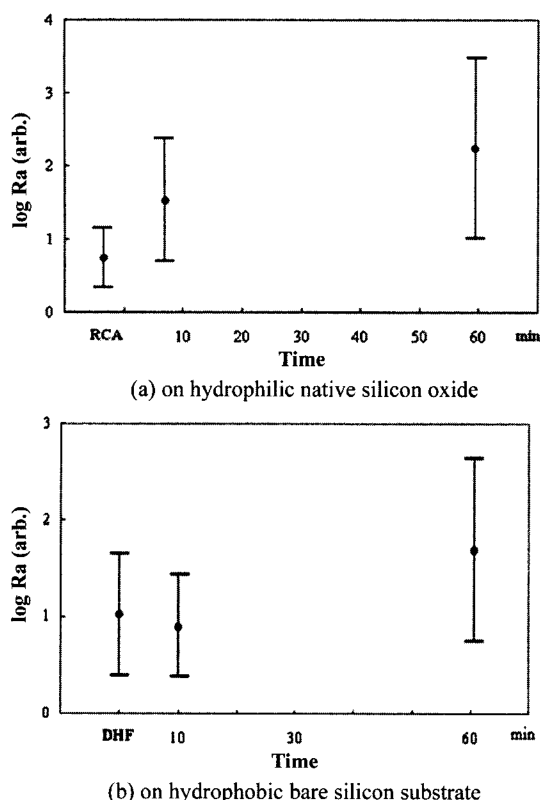


(a) Si



(b) Au

Fig. 5. Pourbaix diagrams of special elements.



(a) on hydrophilic native silicon oxide

(b) on hydrophobic bare silicon substrate

Fig. 6. Roughness changes of silicon wafer surfaces after anode water treatment.

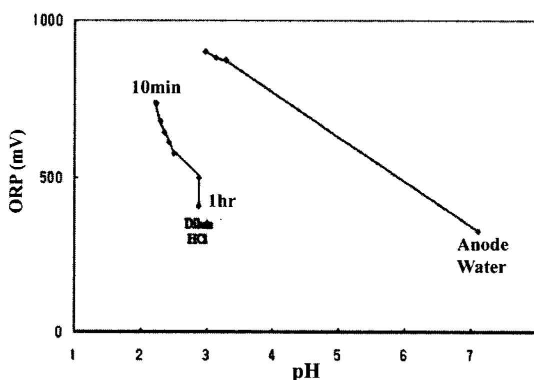


Fig. 7. Comparison of ORP/pH changes of anode water with HCl solution.

Fig. 6 showed AFM data after treating silicon wafers with anode water. It was clearly shown that roughness increased as etching time increased for hydrophilic surface, but that it decreased for hydrophobic surface in short etching time. Fig. 5 showed that silicon or silicon oxide could not be etched with anode water. Namely, 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.

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

4. CONCLUSION

Anode water was applied on silicon wafers with or without native silicon oxide to clean particles and organics as well as meta s on silicon wafer. 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, which can be converted to 5×10^{18} ea per 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 5×10^{18} ea per 250 ml anode water equivalent to 1×10^{18} ea/cm^3 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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류 근 걸(Kun-Kul Ryoo) **[정회원]**

- 1976년 2월 : 서울대학교 금속공학과 (공학사)
- 1978년 2월 : 한국과학원 재료공학과 (공학석사)
- 1986년 8월 : 오레곤 과학기술대학원 재료공학과(공학박사)
- 1998년 3월~현재 : 순천향대학교 신소재공학과 부교수

<관심분야>
디스플레이, 반도체, MEMS, 전리수 응용