Electrolyzed water as an alternative for environmentally-benign semiconductor cleaning chemicals

Kunkul Ryoo and Byeongdoo Kang

Advanced Materials Engineering Department,
Soonchunhyang University, Eupnae-ri, Shinchang-myun,
Asan-si, Korea

ABSTRACT

A present semiconductor cleaning technology is based upon RCA cleaning technology which consumes vast amounts of chemicals and ultra pure water(UPW) and is the high temperature process. Therefore, this technology gives rise to the many environmental issues, and some alternatives such as electrolyzed water(EW) are being studied. In this work, intentionally contaminated Si wafers were cleaned using the electrolyzed water. The electrolyzed water was generated by an electrolysis system which consists of three anode, cathode, and middle chambers. Oxidative water and reductive water were obtained in anode and cathode chambers, respectively. In case of NH4Cl electrolyte, the oxidation-reduction potential and pH for anode water(AW) and cathode water(CW) were measured to be +1050mV and 4.8, and -750mV and 10.0, respectively. AW and CW were deteriorated after electrolyzed, but maintained their characteristics for more than 40 minutes sufficiently enough for cleaning. Their deterioration was correlated with CO2 concentration changes dissolved from air. Contact angles of UPW, AW, and CW on DHF treated Si wafer surfaces were measured to be 65.9° , 66.5° and 56.8° , respectively, which characterizes clearly the electrolyzed water. To analyze the amount of metallic impurities on Si wafer surface, ICP-MS was introduced. It was known that AW was effective for Cu removal, while CW was more effective for Fe removal. To analyze the number of particles on Si wafer surfaces, Tencor 6220 were introduced. The particle distributions after various particle removal processes maintained the same pattern. In this work, RCA consumed about 9 ℓ chemicals, while EW did only 400㎖ HCl electrolyte or 600㎖ NH4Cl electrolyte. It was hence concluded that EW cleaning technology would be very effective for promoting environment, safety, and health(ESH) issues in the next generation semiconductor manufacturing.

1. INTRODUCTION

The cleaning process takes an important role technically and economically in semiconductor manufacturing processes. Ultraclean wafer surface must be achieved in terms of 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 on Si wafer surface is categorized into three groups, which are particles, metallic impurities and organics. Many wet cleaning processes that aim to eliminate contaminants have been developed based on RCA cleaning. RCA cleaning is the several 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 SC_2 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 increases as well. Therefore RCA cleaning technology gives the economic and environmental issues, which would be expected to be considered mandatorily in near future. In order to resolve these issues, advanced cleaning methods have been studied applying functional water such as the hydrogenated ultra pure water(H_2-UPW)[6], ozonized water(O_3-UPW)[7-8], and electrolyzed water. [9-11]

It is expected that application of EW would increase in semiconductor manufacturing because the characteristics of EW are able to be controlled more easily and accurately than other functional waters such as hydrogenated UPW or ozonized UPW. Hence, silicon wafer cleaning is studied introducing EW in this work, since EW is the controllable water by electrolysis in terms of pH and oxidation-reduction potential (ORP) variations.

2. EXPERIMENTAL DETAILS

The EW generation apparatus used in this study is shown schematically in Fig. 1. The apparatus consists of three chambers which are anode, cathode, and middle chambers. The block flow diagram of EW generation is shown in Fig. 2. During UPW was supplied to each chamber, the electrolyte was supplied to the middle chambers via middle tank. EW was generated by electrolysis of UPW or diluted electrolytes such as NH_4OH, HCl, and NH_4Cl, with electrolyzing current of 9A and voltage of 10.5V. The electrolytes such as NH_4OH, HCl and NH_4Cl were supplied in the middle tank. The capacity of middle tank was 1.5 ℓ and the concentration of each chemical varied from 20mℓ/1.5 ℓ, 400mℓ/1.5 ℓ, to 600mℓ/1.5 ℓ, respectively. Properties of EW such as ORP, pH, and lifetime were measured. The pH and ORP were measured by Denver-225 and AgCl/Ag electrode, respectively. In order to compare characteristics of AW with those of CW on dilute HF(~2%) treated Si wafer surface, contact angles were measured with SEO 300A. As variables for affecting stabilities of EW, dissolved oxygen(DO) contents in EW and EW temperature were measured. Inlet UPW was degassed with a DOR-2000AJ, and oxygen concentration in UPW and EW was quantified with an ORION 850 DO meter. Finally CO_2 concentrations in EW were measured with FT-IR with ATR of Perkin Elmer 1730x.

In this study, p-type, (100) direction, Czochralski (CZ) wafers of 200 mm diameter with a resistivity range of 5~20 Ω-cm were used. For metal cleaning evaluation, Al-, Ni-, Cu-, and Fe-contaminated wafers were prepared. To prepare intentionally contaminated wafers(ICW), wafers were dipped in

dilute HF(~2%) solution. Then wafers were dipped in a contaminated APM solution with metallic impurities of 1ppb concentration such as Al, Ni, Cu, and Fe.

Wet bench used in this study was made by Poly Design Co. Ltd., and each bath capacity was 25 ℓ. Si wafer surfaces were measured before and after the cleaning. For comparison, ICWs were separated into three parts. A part of ICWs were cleaned with RCA cleaning and the second part were dipped HPM($HCl:H_2O_2:H_2O$ = 1:1:6) at 65℃, and the third part were cleaned with AW and CW at room temperature. EW cleaning time was 5 minutes and the number of rinse was five in all cases, as shown schematically in Fig. 3.

In order to analyze the amount of metallic impurities on Si wafer surface, ICP-MS (Inductively Coupled Plasma Mass Spectrometer) was introduced. For particle removal evaluation, contaminated wafers with CMP slurry, silica or polystyrene latex (PSL) were used. Particle removal processes were summarized in Table Ⅰ. Megasonic was applied directly in all processes, except for process steps with HF adding. Particle counts on all Si wafer surfaces were evaluated using Tencor-6220.

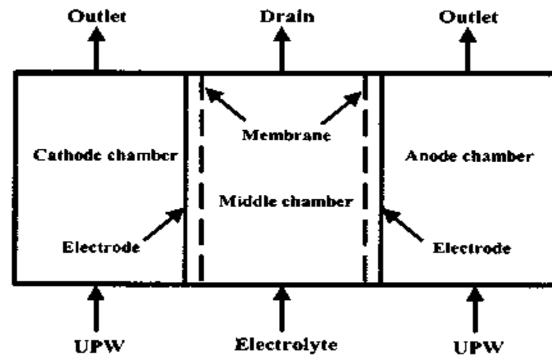


Fig. 1. The schematic of electrolytic apparatus.

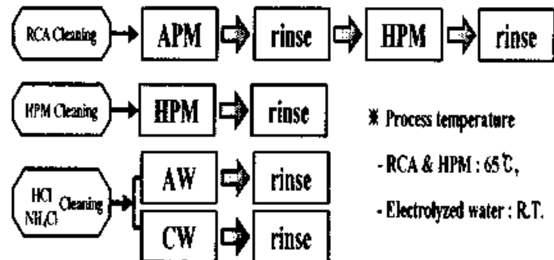
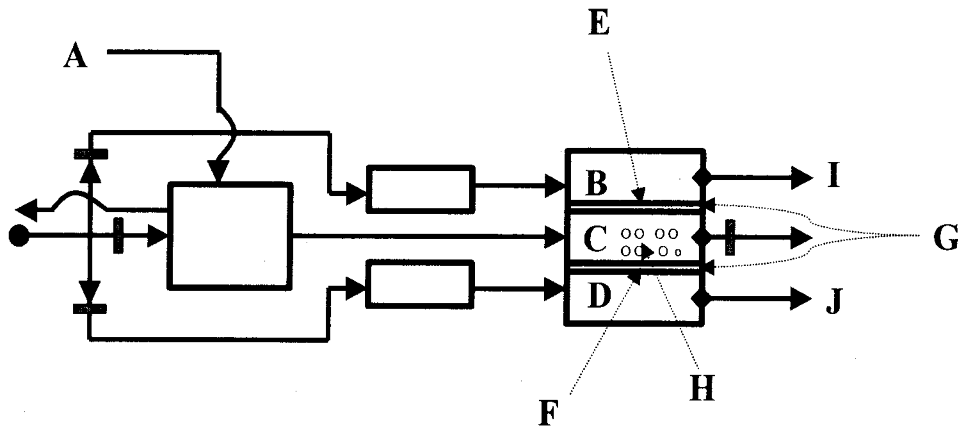


Fig. 3. Metallic impurities cleaning procedure.



A : Chemical supply, B : Cathode chamber, C : Middle chamber, D : Anode chamber,
E : Cathode electrode, F : Anode electrode, G : Membrane,
I : Anode water, J : Cathode water, H : Solid electrolyte

Fig. 2. The block flow diagram of electrolyzed water generation.

Table Ⅰ. Particle cleaning process with EW.

	Cleaning process	Remarks
Case 1	CW-CW, CW-CW-CW CW-AW-CW	Megasonic
Case 2	CW(10min)-CW(1min) CW(10min)-CW(1min, with HF*) CW(1 min, with HF*)-CW(10min)	〃
Case 3	LDO**_CW(silica contamination) LDO**_CW(PSL contamination)	〃
Case 4	LDO**_CW	〃

HF* ; dilute HF(HF:UPW=1:2000)
LDO** ; low dissolved oxygen

3. RESULT & DISCUSSION

The pH/ORP characteristics of EW were measured as shown in Fig. 4. By electrolyzing UPW with no added electrolyte in the middle chamber, the ORP of oxidative AW and reductive CW with about pH 6.3 were developed to be +450 mV and 550 mV, respectively, as shown in Fig. 4(a). In case of NH4OH addition as an alkaline electrolyte, the pH/ORP for AW and CW were measured to be 6.3/+450 mV, and 9.8~10.0/-750 mV, respectively, as in Fig. 4(b). It was observed that reductive alkaline solution was generated in cathode chamber with the NH4OH electrolyte. In case of HCl addition as acid electrolyte, the pH/ORP for AW and CW were 4.7/+1000 mV and 6.3/-550 mV, respectively, as in Fig. 4(c), and it was observed that oxidative acid solution was generated in anode chamber. In case of NH4Cl electrolyte, the pH/ORP of AW and CW were measured to be 4.8/+1050 mV and 10.0/-750 mV, respectively, as in Fig. 4(d). It was also observed that AW and CW were suddenly deteriorated after electrolyzed, but maintained their characteristics at least for more than 40 minutes. AW with high ORP was expected to be applied to remove metallic contaminations because of its oxidative characteristic.

The electrolyzing reactions in the chambers could be postulated as in Table II. For electrolyzing UPW without electrolyte, OH- and H+ ions in UPW in the middle chamber would be migrated to the positive(+) electrode and the negative(-) electrode, respectively. Ionic species generated in electrolyzed UPW would be OH- and H+ in anode chamber and cathode chamber, respectively, since there was no added electrolyte. For electrolytes such as HCl, NH_4OH and NH_4Cl in the middle chamber, cations such as NH_4^+ and H^+ were expected to migrate to the negative electrode, while anions such as OH- and Cl- were expected to migrate to the positive electrode. Hence, the electrochemical reactions in anode chamber using UPW and NH_4OH electrolyte, and the cathode chamber using UPW and HCl electrolyte could be expected to have similarity as in Table II. Therefore, AW electrolyzed without added electrolyte seemed to be similar to AW electrolyzed with NH_4OH electrolyte, and CW electrolyzed without added

Table 2. Expected electrochemical reactions in electrolysis cell.

Electrolyte	UPW	NH_4OH	HCl	NH_4Cl
Cathode chamber	$H_2O \rightarrow H^+ + OH^-$ $2e^- + 2H^+ \rightarrow H_2(g)$ $2H_2O + 2e^- \rightarrow$ $H_2(g) + 2OH^-$	← $NH^+ + e^- \rightarrow NH_3 + \frac{1}{2}H_2$ $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$	$H_2O \rightarrow H^+ + OH^-$ $2e^- + 2H^+ \rightarrow H_2(g)$ $2H_2O + 2e^- \rightarrow$ $H_2(g) + 2OH^-$	← $NH^+ + e^- \rightarrow NH_3 + \frac{1}{2}H_2$ $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$
Anode chamber	$H_2O \rightarrow H^+ + OH^-$ $4OH^- \rightarrow O_2(g) + 2H2O + 4e-$ $2H_2O \rightarrow O_2(g) + 4H^+ + 4e^-$	←	$H_2O \rightarrow H^+ + OH^-$ $4OH^- \rightarrow O_2(g) + 2H_2O + 4e^-$ $O_2(g) + H_2O \rightarrow$ $O_3(g) + 2H^+ + 2e^-$ $Cl^- + O_3 \rightarrow ClO^- + O_2$	←

electrolyte seemed to be similar to CW electrolyzed with HCl electrolyte. In case of NH_4Cl electrolyte, oxidative anode water and reductive cathode water could be generated simultaneously. This postulation explained the results shown in Fig. 4.

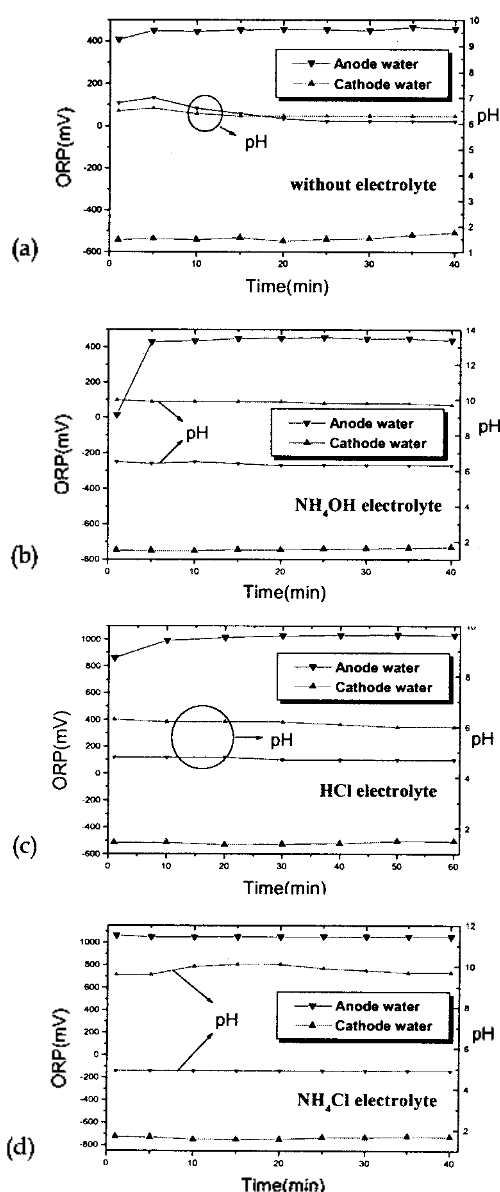


Fig. 4. pH and ORP characteristics of various electrolyzed waters.

Contact angles were measured after UPW, AW or CW had been dropped on Si wafer surface treated with dilute HF. Contacts of waters on Si wafer surface were photographed as shown in Fig. 5. Contact angles of UPW, AW, and CW on Si wafer surfaces were measured to be 65.88 °, 66.45 °, and 56.80 °, respectively. Therefore it was understood that CW was prone to wetting on hydrogen-terminated surface. It was assumed that this result was due to a plenty of OH^- ions dissolved in CW and that therefore H+ ion of hydrogen-terminated substrate surface could combine easily with OH- ion.

EW, which was generated artificially, seemed to be too unstable chemically to obtain the reliable cleaning results, satisfying requirements that ORP of EW should be maintained in a certain period of time. As variables for affecting stabilities of EW, dissolved oxygen(DO) contents in EW and EW temperature were considered. Dissolved oxygen contents of UPW, AW and CW before and after degassing were measured as in Fig. 6. Before and after degassing, concentrations of DO in UPW were about 1.6ppm and 0.1ppm, respectively. Concentration of DO in AW was larger than that in CW before and after degassing. It was regarded that concentrations of DO in AW seemed to increase by oxygen generated by electrolyzing in anode chamber, while concentration of DO in CW seemed to decrease by reaction with H^+ generated by electrolyzing in cathode chamber. Fig. 7 shows the influence of DO in CW on ORP changes. The values of ORP were reduced abruptly in CW when megasonic was applied directly to CW which was not degassed. However, for degassed CW, lifetimes of ORP were extended enough for cleaning. Therefore, dissolved oxygen in CW must be minimized for maintaining stabilities of CW.

Temperature effect was evaluated for EW stability. Water temperature was increased gradually. As shown in Fig. 8, in spite of temperature increase, ORP of AW was maintained from at

RT(Room Temperature) up to 40℃. On the other hand, ORP of CW was changed suddenly at 30℃ and 35℃ with and without megasonic application, respectively. Megasonic cleaning clearly reduced the temperature for ORP change. This could be due to the acceleration of transformation from unstable OH^- radicals to H_2O. Therefore, it could be said that megasonic application or process temperature might be carefully controlled. CO_2 concentration changes dissolved in EW were measured with FT-IR/ATR as shown in Fig. 9. CO_2 concentrations in EW increased to oversaturation as exposured time to air after EW generation increased. After 2-3 hour exposure to air CO_2 concentration decreased gradually to the level that the normal water could take. ORP changes also followed very similar pattern to CO_2 concentration changes while pH did not change significantly. Hence it was concluded that ORP deterioration could be correlated with temporal oversaturation of CO_2.[13]

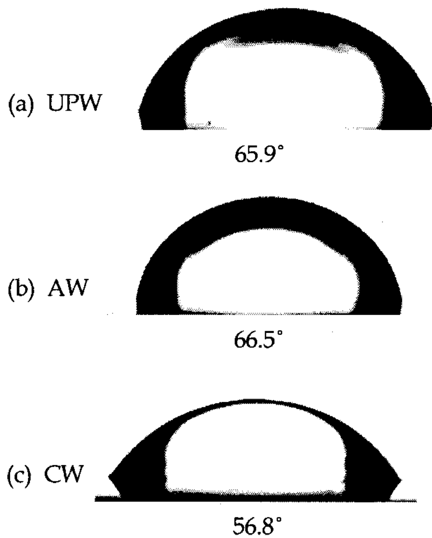


Fig. 5. Static contact angles of waters on the Si wafer surfaces. (measured after 30 seconds)

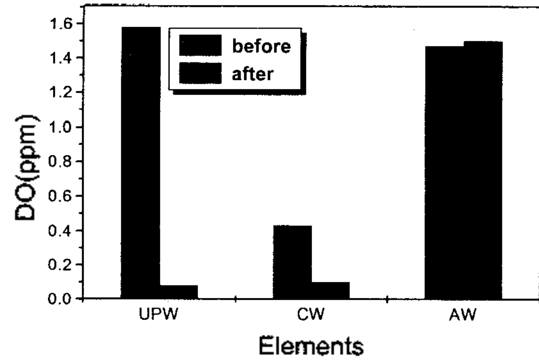


Fig. 6. Dissolved oxygen contents of UPW, AW and CW before and after degassing.

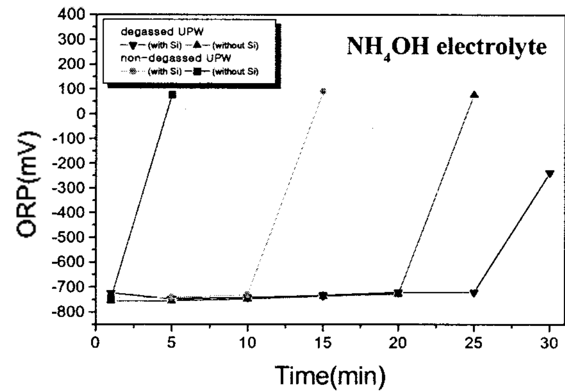


Fig. 7. Comparison of CW ORPs before and after degassing.

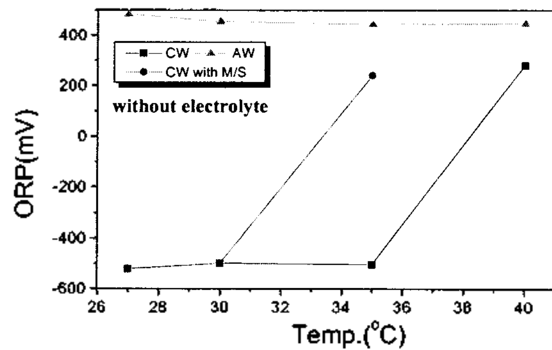


Fig. 8. Dependence of ORP on water temperature.

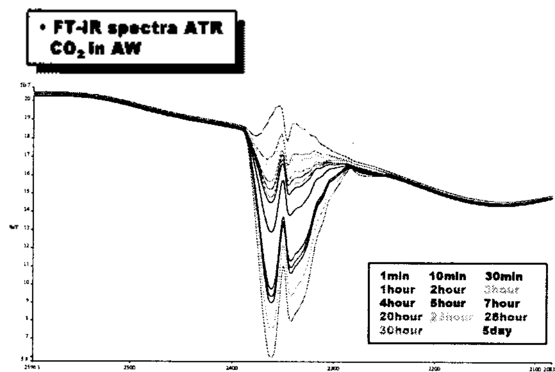


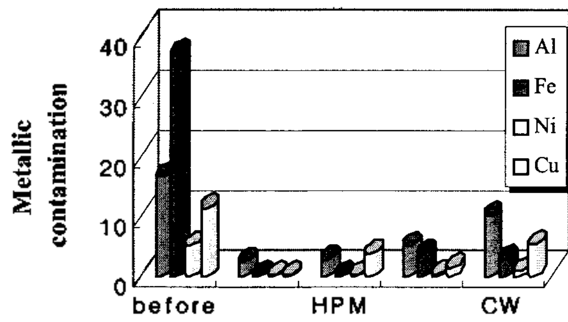
Fig. 9. FT-IR / ATR Spectroscopy of CO_2 in AW

Cleaning was carried out to evaluate metallic impurity removal capability of EW generated with HCl and NH4Cl electrolytes. AW was used for cleaning metallic impurities and the results are shown in Fig. 10. Cleaning capabilities of various solutions were compared before and after cleanings. RCA cleaning was compared with EW cleaning, and it was realized that RCA cleaning showed the best results. Metallic removal efficiency of AW was nearly as much as RCA cleaning, and therefore possible application of AW for metallic removal was confirmed. It was clear that cleaning efficiency of AW seemed to be better than that of CW as well as that of HPM solution. It was postulated in Table II that AW contained the oxidants such as oxoacid(ClOx-) or O_3 generated by electrolysis, which seemed to induce better cleaning efficiency. However, in case of Fe removal, CW seemed to be better than AW.

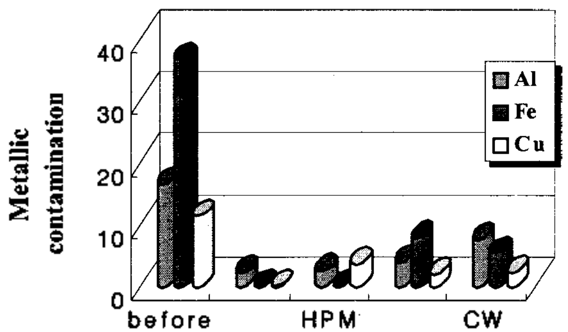
These results could be reviewed with Pourbaix diagram. Potential-pH (E-pH) diagrams, also called predominance or Pourbaix diagrams, have been adopted universally to explain the cleaning mechanism since their introduction in the 1950s. They have been repetitively proven as an elegant way to represent the thermodynamic stability of chemical species in given aqueous environments. E-pH diagrams are typically plotted for various equilibria on normal cartesian coordinates with potential (E) as the ordinate (Y axis) and pH as the abscissa (X axis).[12] Pourbaix diagrams of Cu and Fe metals in aqueous solution were shown in Fig. 11. Characteristics of EW generated by NH_4Cl electrolyte were marked on Pourbaix diagrams of Cu and Fe as AW and CW. In order for metallic impurities to be removed from Si wafer surface, metallic impurities or metallic complexes should be ionized in a cleaning solution. Fig. 11(a), which is Pourbaix diagram of Cu overlapped with AW and CW properties, is confirmed to be very typical for the general transition metals. It could be recognized from Fig. 11(a) that Cu existed as a state of ion in the generated AW. Consequently, Cu and other metallic contaminants were prone to be removed by AW cleaning. On the other hand, in case of Fe contaminant, there existed no state of ion in AW or CW. However CW was closer to Fe ion region than AW. Therefore, it could be said from the Fig. 11 that Fe contaminant removal by CW cleaning was easier than AW cleaning.

In this experiment, RCA and HPM cleaning were applied at 65℃ and contained about 9 ℓ and 6 ℓ chemicals, respectively, while EW was applied at room temperature and included only 400㎖ HCl electrolyte or 600㎖ NH_4Cl electrolyte uses. The concentration of chemicals in EW is 1/22~1/10 times less than that of RCA or HPM cleaning processes. By employing EW for metal removal in a cleaning process, it was expected that not only saving chemicals but also obtaining a drastic reduction in the amount of rinsing UPW could be achieved.

Fig. 12 shows the normalized particle distributions obtained with various EW removal processes. In spite of various removal processes with EW, the particle distributions maintained the same patterns. It was observed that 0.16㎛ particles were not removed sufficiently with EW. Particle size below 0.16㎛ is very crucial for the next generation device fabrication. Hence more careful application of EW for particle removal must be evaluated in the future work.

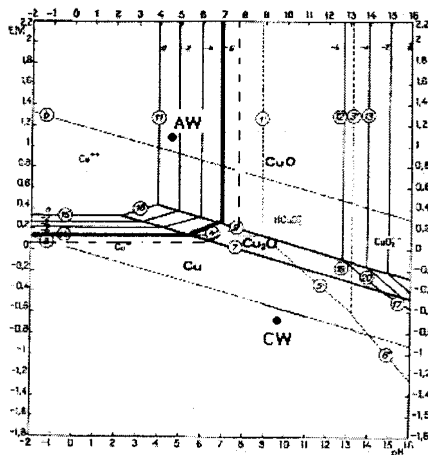


(a) AW with HCl electrolyte

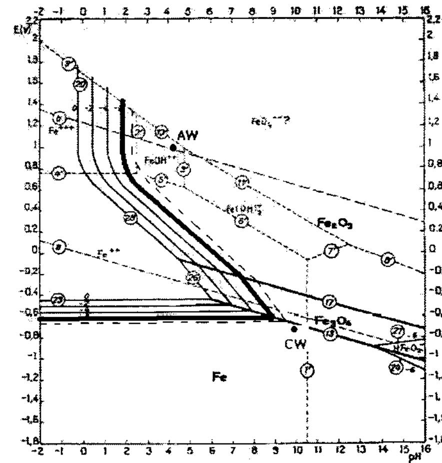


(b) AW with NH_4Cl electrolyte

Fig. 10. Metallic contamination on Si wafer surface before and after AW cleaning. [unit : 1×1010 atoms/cm2]



(a) Cu



(b) Fe

Fig. 11. Pourbaix diagram of (a) Cu and (b) Fe.

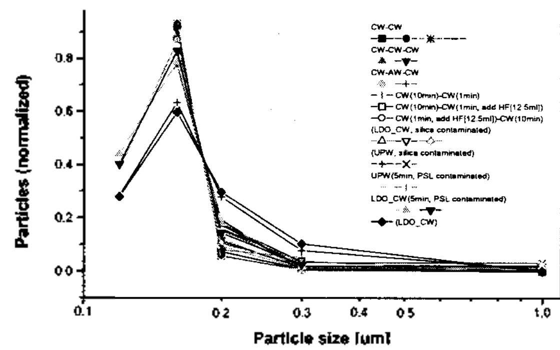


Fig. 12. Particle distribution after particle removal process.

4. CONCLUSIONS

Ultrapure water was electrolyzed as a cleaning medium for the next generation device fabrication. The obtained ORP/pH for anode water(AW) and cathode water(CW) with NH_4Cl electrolyte were +1050 mV/4.7 and 750 mV/9.8, respectively. Electrolyzed water(EW) which was generated with diluted HCl or NH_4Cl electrolyte was very effective in removing metallic impurities from Si wafer surfaces. In spite of various removal processes, the particle distribution maintained the same patterns. AW and CW were deteriorated after electrolyzed, which seemed to be due to CO_2

oversaturation in electrolyzed water, but maintained their characteristics for more than 40 minutes sufficiently enough for cleaning. Contact angles of UPW, AW, and CW on DHF treated Si wafer surfaces were measured to be 65.9° , 66.5° and 56.8° , respectively, which characterizes clearly electrolyzed water. The concentration of chemicals in EW is 1/22~1/10 times less than those of RCA or HPM cleaning processes. It was realized that EW cleaning had a great potential for ecologically safe and low cost semiconductor manufacturing.

ACKNOWLEDGMENTS

This work was supported by Soonchunhyang University under contract No. 20010097.

REFERENCE

1. Ohmi, T., 'Chemical-Vapor-Free Wet Cleaning process', Ultra Clean Technology, Vol. 9, supplement 1, pp. Ⅲ19-Ⅲ22(1997)
2. Futatsuki, T. et al., Behavior of Ultrafine Metallic Particles on Silicon Wafer Surface, J. Electrochem. Soc., Vol. 142, No. 3, pp. 966-970(1995)
3. Choi, B. et al., A Study on the Removal of Cu and Fe Impurities on Si Substrate, Korean Journal of Materials Research, Vol. 8, No. 9, pp. 837-842(1998)
4. Kern, W. and Puotinen, D. A., Cleaning Solutions Based on Hydrogen Peroxide for use in Silicon Semiconductor Technology, RCA Rev., pp. 187-206(1970)
5. Edited by Chang, C. Y. and Sze, S. M., 'ULSI Technology', Mc Graw-hill international editions, pp. 60-104(1996)
6. Morita, H. et al., Hydrogenated Ultrapure Water Production System for Future Wet Cleaning Process, Solid State Phenomena Vols. 65-66, pp. 7-10(1999)
7. Hattori, T. et al., Contamination Removal by Single-Wafer Spin Cleaning with Repetitive Use of Ozonized Water and Dilute HF, J. Electrochem. Soc., Vol. 145, No. 9, pp. 3278-3283(1998)
8. Ojima, S. et al., Megasonic Excited Ozonized Water for the Cleaning of Silicon Surfaces, J. Electrochem. Soc., Vol. 144, No. 4, pp. 1482-1487(1997)
9. Yamanaka, K. et al, Electrolyzed Water as the Novel Cleaning Media in Ultra-Large-Scale Integration and Liquid-Crystal Display Manufacturing, Langmuir, Vol. 15, No. 12, pp. 4165-4170(1999)
10. Aoki, H. et al., Cleaning Technologies using Electrolytic Ionized Water and Analysis Technology of Fine Structures for Next Generation Device Manufacturing, Mat. Res. Soc. Symp. Proc. Vol. 477, pp. 501-512(1997)
11. Shiramizu, Y. et al., Removal of Metal and Organic Contaminants from Silicon Substrates Using Electrolysis-Ionized Water Containing Ammonium Chloride, J. Electrochem. Soc., Vol. 143, No. 5, pp. 1632-1635(1996)
12. Pourbaix, M., 'Atlas of Electrochemical Equilibria in Aqueous Solutions', NACE Interantional Cebelcor, pp. 158-384(1974)
13. Yang, W. J., 'Water Chemistry', Shin Kwang, pp. 127-154(1991)