Electrolyzed water cleaning for semiconductor manufacturing

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A semiconductor cleaning technology has been based upon RCA cleaning which consumes vast amounts of chemicals and ultra pure water. This technology hence gives rise to many environmental issues, and some alternatives such as electrolyzed water are being studied. In this work, intentionally contaminated Si wafers were cleaned using the electrolyzed water. The electrolyzed waters were obtained in anode and cathode with oxidation reduction potentials and pH of −1050mV and 4.8, and -750mV and 10.0, respectively. The electrolyzed water deterioration was correlated with CO_2 concentration changes dissolved from air. Overflowing of electrolyzed water during cleaning particles resulted in the same cleanness as could be obtained with RCA clean. The roughness of patterned wafer surfaces after EW clean maintained that of as-received wafers. RCA clean consumed about 9ℓ chemicals, while electrolyzed water clean did only 400mℓ HCl or 600mℓ NH_4Cl to clean 8" wafers in this study. It was hence concluded that electrolyzed water cleaning technology would be very effective for releasing environment, safety, and health(ESH) issues in the next generation semiconductor manufacturing.

I. INTRODUCTION

Ultraclean wafer surface must be achieved for the next generation semiconductor processes.[1-3] 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 chemical 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. In order to resolve these issues, advanced cleaning methods 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(EW).[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 diversely and accurately than those of other functional waters such as hydrogenated UPW or ozonized UPW. Hence, silicon wafer cleaning is studied introducing EW in this work.

II. EXPERIMENTAL

The electrolyzing apparatus consists of three chambers which are anode, cathode, and middle chambers. EW was generated by electrolysis of UPW or diluted electrolytes of NH_4OH, HCl, or NH_4Cl, with electrolyzing current of 9A and voltage of 10.5V. Properties of EW such as ORP, pH, and lifetime were measured. The pH and ORP were measured by Denver-225 and AgCl/Ag electrodes, respectively. Contact angles of differently treated surfaces of wafers were measured with *SEO 300A*. Inlet of UPW was degassed with a DOR-2000AJ before electrolyzing, and oxygen concentrations in UPW and EW were quantified with an ORION 850 DO meter. Finally CO_2

concentrations in EW were measured with FT-IR/ATR of Perkin Elmer 1730x.

In this study, p-type, (100), Czochralski (CZ) wafers of 200 mm diameter with a resistivity range of 5~20 Ω-㎝ were used. 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 such as Al, Ni, Cu, and Fe.

Cleaning time was 5 minutes and the number of rinse was five in all cases. 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. After cleaning, patterned wafers were observed with Transmission Electron Microscope(TEM). Particle counts on all Si wafer surfaces were evaluated using Tencor-6220.

Si wafers were oxidized and nitrided, followed by patterning. The patterned wafers were shallow -trenched for isolation(STI). After STI process, one group wafers were oxidized, and the other was not oxidized. Patterned wafers were cleaned with EW to verify the surface micro-roughness to compare with that of RCA cleaning.

III. RESULTS AND DISCUSSION

In case of NH_4OH 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. It was observed that reductive alkaline solution was generated in cathode chamber with the NH_4OH 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, and it was observed that oxidative acid solution was generated in anode chamber. In case of NH_4Cl electrolyte, the pH/ORP of AW and CW were measured to be 4.8/+1050 mV and 10.0/-750 mV, respectively. 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, while CW with low ORP for particle removal.

CO_2 concentration changes dissolved in EW were measured with FT-IR/ATR. CO_2 concentrations in EW increased as exposured time to air increased after EW generation. After 2-3 hour exposure to air CO_2 concentration decreased gradually to the level that the normal water could take. It seemed that ORP deterioration could be correlated with temporal oversaturation of CO_2. Cleaning was carried out to evaluate metallic impurity removal capability of EW generated with NH_4Cl electrolyte RCA cleaning was compared with EW cleaning, and it was realized that RCA cleaning showed the best results so far. Metallic removal efficiency of AW was nearly as much as RCA cleaning, and therefore possible application of AW for metallic removal was confirmed. These results could be reviewed with Pourbaix diagram.[12]

In this experiment, RCA and HPM cleaning were applied at 65℃ and comsumed about 9ℓ and 6ℓ chemicals, respectively, while EW was applied at room temperature and included only 400㎖ HCl electrolyte or 600㎖ NH_4Cl electrolyte uses. The consumption of chemicals with 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.

Patterned wafers were cleaned to compare the micro roughness changes of wafer surfaces with that of RCA cleaning. It was observed that surface roughness changes due to EW cleaning were as low as the conventional RCA cleaning. Hence, EW cleaning could substitute the conventional RCA cleaning for patterned wafer cleaning, but EW cleaning should be optimized for Giga DRAM.

IV. Conclusions

Ultrapure water was electrolyzed as a cleaning medium for the next generation device fabrication. The obtained ORP/pH for anode water and cathode water with NH_4Cl electrolyte were +1050 mV/4.7 and –750 mV/9.8, respectively. AW was deteriorated after electrolyzed, which seemed to be due to CO_2 oversaturation in electrolyzed water. However their lifetimes maintained for more than 40 minutes sufficiently enough for cleaning. Electrolyzed water(EW) which was generated with NH_4Cl electrolyte was very effective in removing metallic impurities from Si wafer surfaces. Micro-roughness changes of wafer surfaces due to CW cleaning were as low as those of the RCA cleaning. The concentration of chemicals in EW is 1/22~1/10 times less than those of RCA or HPM cleaning processes. Hence it was concluded that EW clean could be applied for the future wafer cleaning.

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