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Functionalized Water Production Methods using Membrane Contactors and its effect on Particle Removal Efficiency post CMP

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Abstract:

A variety of new processes for semiconductor wafer cleaning have been developed since the introduction of the RCA (SC1 & SC2) clean process in 1965. As the node size decreases, the particles approaching the node size present a cleaning challenge. In addition, the adhesion forces between the nanoparticles, the substrate, and the nano features become more difficult to overcome [1]. Chemical methods are effective at removing particle contamination; however, several repeated cleaning cycles are needed to remove the nanoparticles. The increase in chemical use poses increased materials and disposal costs affecting sustainability and environmental impacts. The use of dissolved gas-functionalized water presents a sustainable and effective alternative to enhance cleaning efficiency post-chemical mechanical polishing (CMP). This study explores the production of functionalized ultra-pure water (UPW) utilizing Liqui-Cel Membrane Contactor Technology operating under various conditions for chemically functionalizing UPW streams only using a dissolved gas. The research further explores the impact of functionalized water as an environmentally friendly method to enhance the removal efficiency of ceria nanoparticles which are commonly contained in CMP slurries.

1 Introduction:

As semiconductor process nodes have continued to miniaturize into the single nanometer scale, the removal of particles continues to be an ever-critical step in the fabrication of microelectronics. Innovation and development of environmentally friendly, high efficiency, substrate cleaning techniques are key to high yields and cost-effective fabrication. The concentrations of certain dissolved gases in ultra-pure water (UPW) combined with high frequency acoustic energy have a direct impact on nano-particle cleaning efficiency of megasonic baths [2]. UPW containing precisely controlled dissolved gas concentrations is commonly known as “functional or functionalized water.” Functionalized water production plays a critical role in enhancing the particle removal efficiency (PRE) of ultrapure water (UPW) at key post etching and chemical mechanical polishing (CMP) steps. Planarization is essential for microelectronics fabrication, and CMP is key to providing simultaneous local and global planarization [3]. However, removal of contaminants and nanoparticles generated by the CMP operation is an important necessary step to preserve high manufacturing yields.

2 Methods:

2.1 Large scale functional N_2-water production

Functional water production was performed in a recirculation loop with continuous replenishment supply of DI water. Dissolved gas measurements utilized Dual-channel Hach’s Orbisphere 510 controller, two K1100 LDO sensors, and Orbisphere Nitrogen (Thermal Conductivity) sensors with two, 6 mm sample flow chambers. A liquid ring vacuum pump was used to control pressure on the gas chamber of the membrane contactor module.

A membrane contactor (Liqui-Cel™, 8”x80” EXF, X40 hollow fiber, 3M Co., USA), operated with sweep plus vacuum, was utilized to significantly reduce dissolved O_2 and N_2 from the DI water stream to simulate post polishing gas concentrations. Another membrane contactor (3M™ Liqui-Cel™, 10”x28” EXF, X40 hollow fiber, 3M Co., USA) downstream of the polished DI water served to produce functionalized N_2-DIW by dissolving nitrogen gas into the effluent stream. The concentration of dissolved N_2 was controlled by two operation methods: mass flow and pressure control of the gas into the membrane contactor lumen ports.

2.1.1 Mass Flow Control for Functional N_2-UPW Production

Typical dissolved gas requirements post polishing is less than 1 ppb for dissolved O_2. The typical combination of high purity nitrogen gas and vacuum pressure utilized during the membrane contactor polishing steps yields UPW with dissolved N_2 concentrations ranging between 2-5 ppm. Given the degassed nature of the UPW produced post polishing, there is a natural tendency to absorb gases up to saturation, without pressure control.

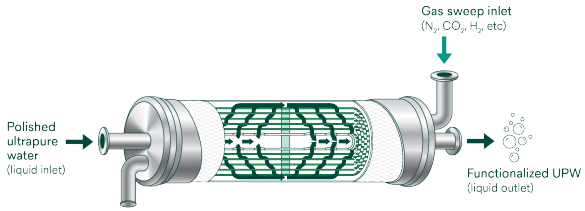

Figure 1: Membrane Contactor Flow Path

A mass flow control unit was utilized to introduce N_2 gas to the post polished DI water stream, counter current to the liquid flow **(Figure 1)**. No pressure control was applied to the gas side of the membrane contactor. The flow of nitrogen gas was limited to the stoichiometric quantity needed to increase the concentration of the polished water stream, from 1.5 to 10.3 mg/L. To model this operation mode, degassed DI water was introduced into the shell side of a Liqui-Cel EXF 10"x28", X40 membrane contactor. High purity nitrogen gas was introduced into the lumen port counter current to the water inlet. The opposite lumen side port contained a pressure gauge and a valve that was in the closed position to prevent the nitrogen gas from exiting the membrane contactor **(Figure 2)**.

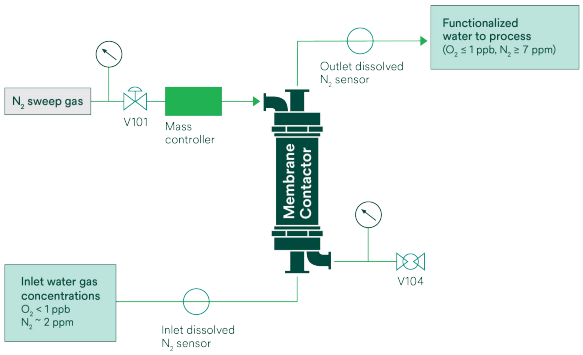

Figure 2: Mass Flow Control of Gas Concentration (N2)

2.1.2 Pressure Control for Functional N2-UPW Production

To contrast the mass flow setup operation mode, nitrogen addition was conducted by gas pressure control of the nitrogen gas introduced within the lumen chamber of the membrane contactor **(Figure 3)**.

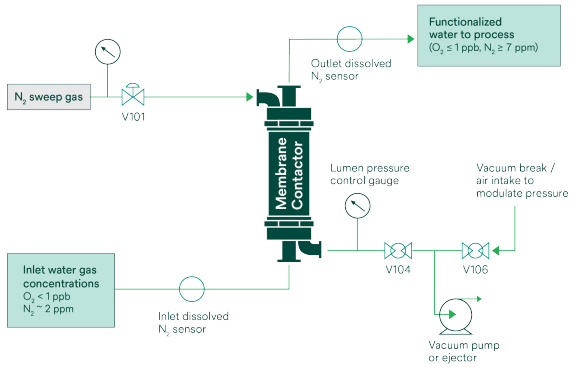

Figure 3: Pressure Control of Gas Concentration (N2)

2.2 Contamination of Wafers and Buff Cleaning

A 300 mm wafer was cut into 40 mm x 40 mm squares. Polishing was utilized to contaminate the SiO_2 film deposited on the silicon wafer. A 100 mm wafer polisher (Poli-400; GnP Technology, Korea) with a chuck was used. Two Colloidal slurries, A and B (Zenus, Solvay, Belgium) were used. The secondary particle size for Slurry A is 155 nm while slurry B is 90 nm. The wafer squares were chucked onto the polisher head with a vertical pressure of 21 kPa. The colloidal slurry was diluted to 0.5 wt% and dispensed at a rate of 120 mL/min. The polisher rotation speed was set to 93 rpm while the platen speed was kept at 87 rpm, and the polishing step was conducted for 60 seconds. Before buff cleaning, the polisher was cleaned with DIW and a sponge brush. The ceria contaminated pad was replaced with a new pad for the buff cleaning step. Each contaminated wafer was buff cleaned for 10 seconds with a vertical pressure of 11 kPa. The pads were conditioned with DIW followed by cleaning solutions composed of functionalized water. The three buff step cleaning solutions tested were DIW, N_2-DIW and CO_2-DIW.

The N_2 and CO_2 functionalized water cleaning solutions were produced by recirculating DIW through a membrane contactor (Liqui-Cel™, 2.5"x8", X50 hollow fiber, 3M Co., USA) for a limited time. Pressure of high purity gas (N_2 or CO_2) was set to 0.15 MPa while the water pressure was kept at 0.17 MPa.

3 Results and Findings:

3.1 Characterizing Functional UPW Large Scale Production Techniques

The production of functionalized N_2 DI water was achieved by dissolving nitrogen gas utilizing Liqui-Cel membrane contactor technology. The membrane contactor provides a large surface area for contact between the gas phase being dissolved and the liquid water phase, without dispersion of the gas through the liquid. The precise metering of the quantity of gas needed to reach the concentration setpoint of 10.3 mg/L was contrasted against the use of gas pressure to achieve an equal nitrogen concentration in the water effluent. Both methods produced the desired dissolved nitrogen concentrations, albeit the mass flow control method produced a stable and less variable result **(Figure 4)**.

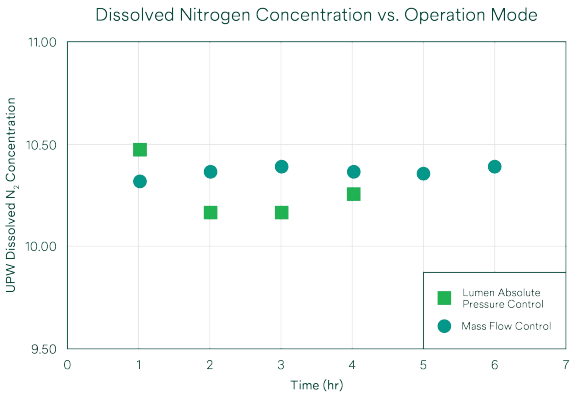

Figure 4: Gas Concentration Stability over Time

Experimental data demonstrated a very small difference between the nitrogen flow setpoint and the calculated stoichiometric mass flow to reach the dissolved nitrogen concentration within the water effluent. Effectively demonstrating the gas mass flow operation an effective method to provide accurate process control while minimizing excess consumption of the sweep gas for large scale functionalized water production **(Figure 5)**.

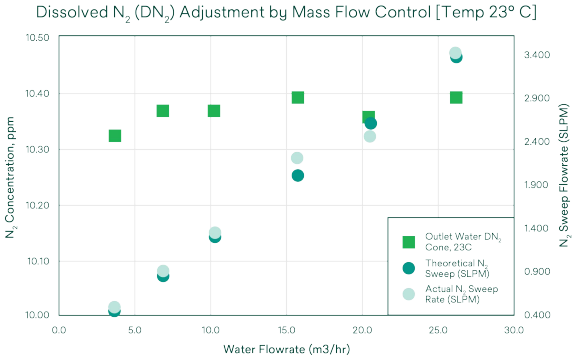

Figure 5: Comparison of actual vs. stoichiometric N2 sweep rate to reach target setpoint

Pressure control for production of functionalized UPW also demonstrated to be a viable method for large scale production. Pressure control does require the aid of a vacuum device for subsaturated dissolved N_2 setpoints. This method can be employed for scenarios where supersaturated dissolved gas levels are desired within a unit operation.

3.2: Relationship of functional water and particle removal efficiency

The relevance of functionalized water production comes into play, as the effectiveness of particle removal efficiency is characterized in buff cleaning post CMP process steps.

Membrane contactor technology was utilized to illustrate and contrast the particle removal efficiency (PRE) of deionized water and functionalized DIW with dissolved N_2 (N_2-DIW) and CO_2 (CO_2-DIW) respectively. Both N_2-DIW and CO_2-DIW demonstrated enhanced particle removal efficiency compared to DIW. CO_2-DIW showed improved PRE compared to N_2-DIW (**Figure 6a)**. The PRE for CO_2-DIW was also contrasted between saturated CO_2-DIW, twice diluted CO_2 water (CO_2 50%-DIW) and five times diluted CO_2 DIW (CO_2 20%-DIW) (**Figure 6b**).

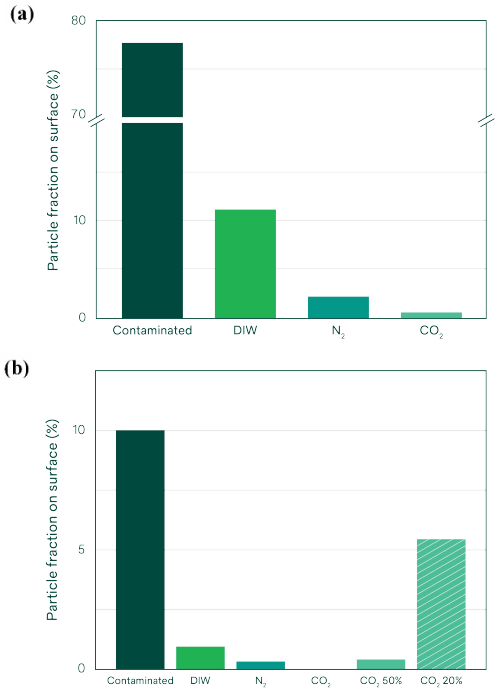

Figure 6: Surface coverage fraction of remaining ceria nanoparticles on an oxide film surface pre and post buff cleaning for (a) colloidal ceria slurry A and (b) colloidal ceria slurry B

Gas-dissolved water also demonstrated a supplementary function of particle dispersion. Insufficient particle dispersion has a significant influence on trajectory within the water flow, leading to agglomeration and redeposition onto the wafer surface [4]. This is characterized by the larger characteristic time (t_0) of agglomerated particles in the stokes flow equations:

$Stk = \frac{t_0 v_0}{l_0}$, $t_0 = \frac{\rho_p d_p^2}{18\mu_g}$, where t_0 is the characteristic time, v_0 is the fluid velocity, l_0 is the characteristic length of the flow, ρ_p is particle density, d_p is particle diameter, and μ_g is the dynamic fluid viscosity.

To further verify the role of functionalized gas dissolved DIW, oxide films were polished with DIW, N_2-DIW, CO_2-DIW, and a HNO_3 solution with the same pH as the CO_2-DIW to eliminate the effect of pH. Colloidal dispersion of both slurries (A and B), is indicated by the average particle size.

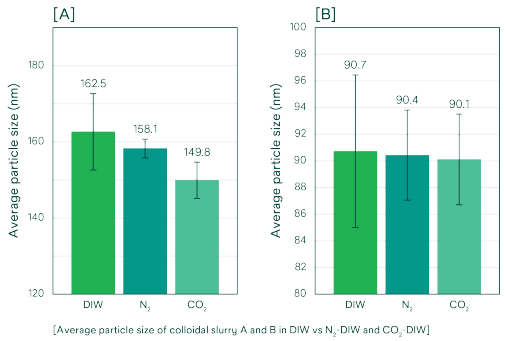

Figure 7: Mean Particle size of colloidal slurry A and B in DIW and Functionalized DIW

As indicated, solutions of slurries and functionalized DIW showed a reduced average particle size compared to solutions of DIW only **(Figure 7)**.

SEM imaging of polished oxide films was evaluated for particle size distribution for the slurry solutions with DIW and functionalized DIW. Dispersion was further supported by decreased concentration of large diameter particles ($d_p > 250$nm) within the gas-dissolved DIW (**Figure 8).** By also comparing particle size distribution with a slurry solution of dilute HNO_3 to match the CO_2-DIW pH, the effect of pH impact was deconvoluted.

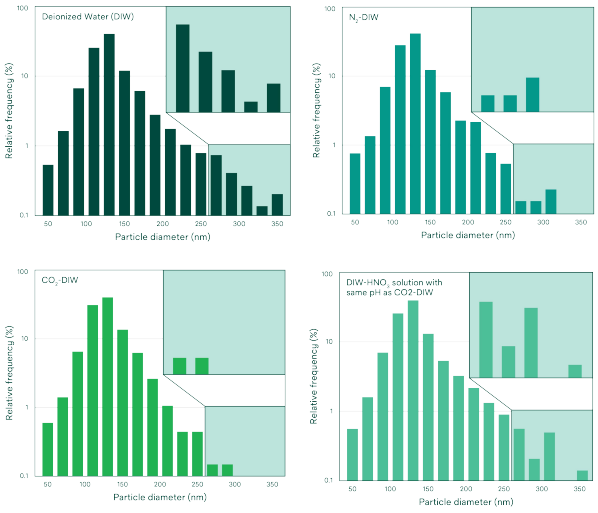

Figure 8: Particle size distribution on polished oxide film for DIW, N_2-DIW, CO_2-DIW, and DIW with same pH as CO_2-DIW modulated with HNO_3

Chemical mechanical polishing has the undesirable effect of introducing a higher quantity of contaminant particles onto the wafer surface. Buff cleaning with functionalized water is viable, effective and environmentally low impact cleaning method to improve the efficiency of removing these introduced particles. The particle removal mechanism within the buff polishing process is illustrated and contrasted between DIW and CO_2-DIW slurry solutions in **Figure 9**. By replacing DIW with CO_2-DIW, electrostatically charged CO_2 bubbles attract positively charged ceria particles. The attraction forces prevent accumulation and agglomeration within the polishing pad, promote flushing of the particles away from the pad surface and prevent redeposition of agglomerated ceria particles onto the wafer surface.

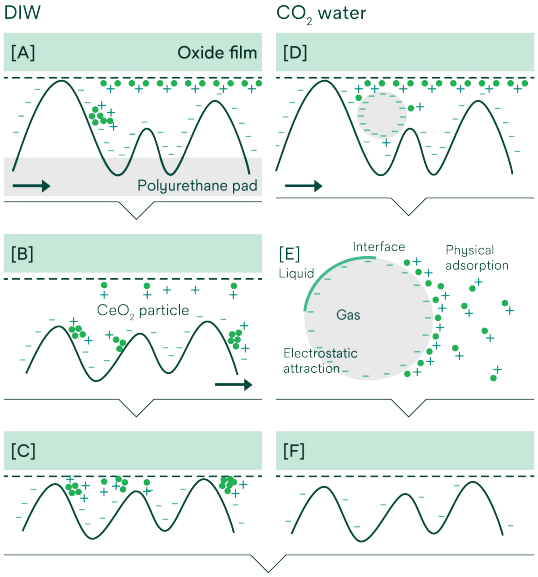

Figure 9: Mechanism comparison of DIW and CO2-DIW water buff cleaning

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