Task ID: 425.021
Task Title: Low Water and Low-Energy Rinsing and Drying of Patterned Wafers, Nano-Structures, and New Materials Surfaces
Deliverable: Report on the Rinse Model for Data Analysis and Process Developments

Summary/Abstract:

The primary objective of this work is to determine ways in which DI water usage in rinse processes can be reduced without sacrificing overall wafer cleanliness. In order to meet that objective, a study of the fundamental mechanisms involved in contaminant removal during rinse is being undertaken. The goals of this study are:

- Investigate the fundamental mechanisms governing the removal of chemical contaminants from the surface of both smooth and patterned wafers.
- Conduct experiments, which measure the temporal and spatial variations of the contaminant concentrations in the water near the wafer surface as the rinse process proceeds.
- Conduct experiments, which measure the temporal variations of the contaminant concentrations within a trench as the rinse process proceeds.
- Using the in-situ trench device as a prototype, develop robust industrial device that could become a benchmark for standard rinse evaluations.

Technical Results and Data:

Increasing environmental and economic concerns have brought attention to the need for efficient and effective rinse processes to clean residue from wafer surfaces. In particular, optimized rinsing processes can yield better device performance, reduced water consumption, shorter cycle times, higher tool utilization, and higher throughputs, which can lead to reduced cost of ownership [Helms (1994), Rosato et al. (1994), Kempka et al. (1994), Hall et al., (1995), Tonti (1995), Chiarello et al. (1997,2000)]. Cost of ownership models indicates that the relative cost of DI water will nearly triple compared to other cost. Unfortunately, process optimization is limited by the lack of suitable diagnostic techniques to non-intrusively monitor the chemical carryover removal during wafer rinse.

There is a desire for reliable methods to measure the temporal variation of the concentration of acid in high purity water in the vicinity of the silicon wafer surface. Two approaches are taken: an ion-selective probe, used successfully to study various biological systems (Kuhtreiber and Jaffe, 1987; Schiefelbein et al, 1992; Marcus and Shipley, 1994) with a spatial resolution of 2 to 5 microns; and second, a method for measuring contaminant concentration in the water trapped within the structure of a patterned wafer.

On rinsing of high aspect ratio surface features such as trenches and vias, relatively little published work exists. Most of the limited previous work focuses on the dominating effect of diffusion over fluid velocity (Nakao et al., 1990). Under normal post-HF rinse conditions the bottom of a typical DRAM trench (4 x 0.5 x 0.5 μm) decreases in concentration by seven orders of magnitude in roughly 10 seconds. Recent modeling and experimental work on post-piranha rinse (Aoki et al. 1999) found much longer rinse times, >1000 sec, due to the strong adsorption of SOx species on the SiO_2 sidewalls. All previous experimental techniques relied upon ex-situ measurements (Nakao et al. 1990, Aoki et al. 1999). This project incorporates in-situ, real-time measurements.

A novel Electrochemical Residue Sensor (ECRS) is designed, fabricated, and utilized to monitor the process of cleaning and rinsing in patterned wafers and well-characterized micro- and nano-structures. ECRS is capable of sensing the cleanliness of the small structures by monitoring the changes in the impedance of the fluid between two electrodes embedded in the microstructure. The unique features of this sensor include:

- Sensitivity of about 5 ppb (measured for sulfate ion contamination in water) during rinse; this cannot be achieved with conventional metrology methods, such as conductivity probes, used in rinse tanks
- Fast response time needed for rinse that is typically a highly transient process
- Real-time, and in-situ capability; currently no other metrology method is available to provide this for cleaning and rinsing tools.

Last year's work focused on a new ECRS design for improving the signal to noise ratio as well as methods for packaging and integration of the sensor into a full wafer that can be used in conventional rinse tanks. To replicate industrial rinse conditions, a full flow experimental setup was designed. Tests were also conducted at Freescale Semiconductor Inc as a part of joint effort with the Freescale team of co-investigators. A part of the work also focused on fabricating a version of the sensor, which is compatible with the chemical environment actually present in processing patterned wafers. In addition to rinsing experiments for various chemicals, a process model was developed to interpret the experimental results for better understanding of the cleaning mechanisms and revealing the bottlenecks of rinse.

A version of the ECRS was fabricated on a monitoring wafer and exposed to the chemicals environment present during the cleaning and rinsing processes. This allowed monitoring the actual concentration in the sensor trench representing the features of a patterned wafer. The results show that the concentration in the trench is quite different from that read by the resistivity probe which is typically located at the outlet of the tank. Figure 1 shows the difference in reading of a resistivity probe and that of the ECRS for a single wafer application. ECRS also shows that there is a delay for chemicals to move out from the wafer gap in the case of multi-wafer cassette rinse. This is due the laminar flow between the wafers, leading to a lack of adequate mixing. The results clearly indicate that using resistivity probe to monitor the rinse is ineffective and unreliable.

As shown in Figure 2, the ECRS monitoring results revealed the significant difference in the rinse dynamics among various chemicals. This indicates significant differences in the fundamental chemistry of transport processes and contaminants interactions with the fluid and the walls of the small structures. For example, the results show that the cleaning of HCl is much faster than that of H_2SO_4 and NH_4OH. Results also show the ECRS measuring the effect of wafer spacing on the surface cleanup during rinse in situ and in real time. A wafer exposed to the full turbulence of the rinse tank, such as the wafer in the front of a carrier, is more rapidly rinsed than one where water flow is forced into a narrow spacing. The ECRS shows a dramatic difference in reading on the two wafers, while the standard resistivity probe in the tank only gives a single average weighted measurement. Clearly the ECRS is more useful in developing rinse recipes.

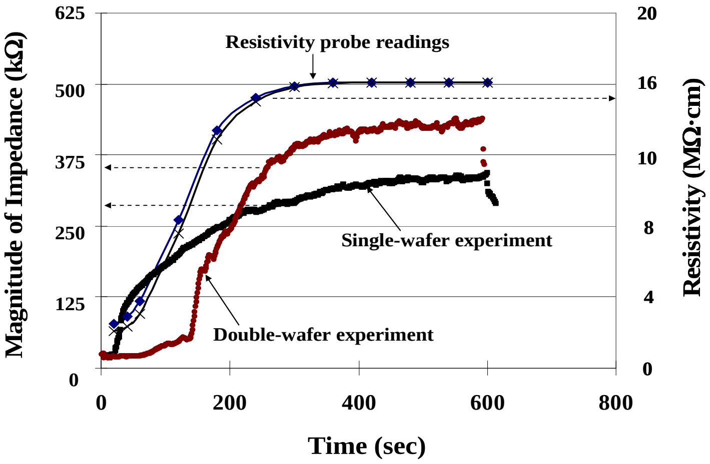
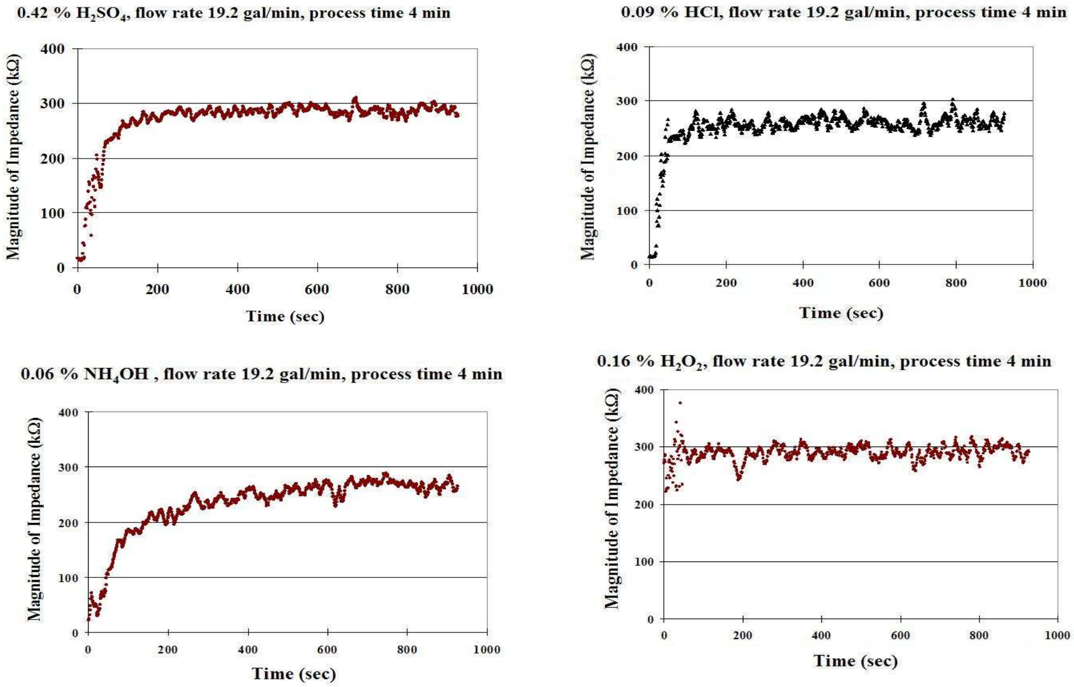


Figure 1: Comparison of resistivity probe reading vs the Electrochemical Residue Sensor reading.



0.42 % H_2SO_4, flow rate 19.2 gal/min, process time 4 min

0.09 % HCl, flow rate 19.2 gal/min, process time 4 min

0.06 % NH_4OH , flow rate 19.2 gal/min, process time 4 min

0.16 % H_2O_2, flow rate 19.2 gal/min, process time 4 min

Figure 2: Response of the Electrochemical Residue Sensor to various chemicals.

A comprehensive model was developed to determine the fundamentals of rinsing procedure for the purpose of data analysis and process parametric studies. The model consists of equations describing diffusion and migration for all the ionic species present during a typical rinse. In addition to the transport in the fluid phase, residual surface contaminants undergo adsorption and desorption. Moreover, the ionic species in a high aspect ratio feature experience electrostatic interaction with the surface. At low ionic strength, the potential resulting from the surface charge penetrates a few tenths of a micron into the liquid and significantly impacts the ion motion. In narrow pores, this can impact the rinsing time. Electrostatics are described by Poisson equation and included in the model. Lastly, concentration is related to the impedance measured by the ECRS, following Ohm's law. Following is a list of the key model equations:

$$\frac{\partial C_i}{\partial t} = \nabla \cdot (D_i \nabla C_i + z_i \mu_i F C_i \nabla \varphi) \qquad ---(1)$$

$$\frac{\partial C_{s2}}{\partial t} = k_{a2} C_2 \left(S_{02} - C_{s2}\right) - k_{d2} C_{s2} \qquad ---(2)$$

$$\nabla^2 \varphi = -\frac{\rho}{\varepsilon} \qquad ---(3)$$

$$\rho = F \sum_i z_i C_i \qquad ---(4)$$

$$\sigma \cdot \nabla V = J \qquad ---(5)$$

$$\sigma = \sum_i \lambda_i C_i \qquad ---(6)$$

Figure 3 shows typical model prediction and agreement with the experimental results. Using the parameters obtained by the process simulation, parametric studies were conducted. Sample results are shown in Figure 4, which shows the significant effect of feature size on the cleaning time. This indicated the potential challenges in cleaning and the increase in resource utilization as we move form micro to nano-scale processing. The cleaning time is also strongly dependent on the charge of the species. This may explain why NH_4OH is difficult to rinse.

Figure 3: Simulation vs experimental data for sulfuric acid.

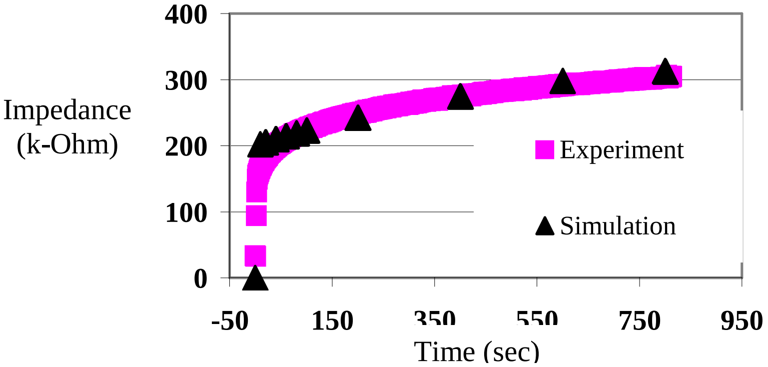


Figure 4: Effect of width of the trench on 99.99% cleanup of NH_4^+ for aspect ratio of 10.