Ultra-pure Water for deep sub-micron Semiconductor fabrication

Polar Spring Corporation’s patented Crystallix™ process is a quantum leap in the production of UltraPure Water (UPW) for semiconductor fabrication. This innovative process combines extraordinary purification capability with energy savings and reliability. The Crystallix™ process removes 100% of sub-micron particles and 99% of dissolved contaminants. It is versatile, rugged, reliable and energy efficient, and can be applied to recovery of used wafer rinse water as well as production of the highest quality UPW.

Background

State of the art semiconductor fabrication plants consume as much as 10 million liters per day of water — roughly 10,000 liters per wafer [8]. Ultrapure water is prepared from raw water using a series of water treatment technologies including reverse osmosis, ion exchange, and ultrafiltration. Water costs are in excess of $1 per thousand liters [9] or $10 per wafer.

Semiconductor fabrication requires the utmost in cleanliness, so ultrapure water is essential to obtaining high yields. As device density increases, and linewidth decreases, water quality requirements become increasingly stringent. Semiconductor UPW generally requires removal of particles with sizes greater than 10 to 20% of the line width. Figure 1 shows the trend in water quality guidelines for increasing circuit density and the currently attainable water quality. Next generation circuits will be at the limit of currently attainable water quality, and subsequent generations of ICs will exceed current capabilities.

	Particles per Liter			
Particle Size	1M DRAM	4M DRAM	16M DRAM	Attainable
≤ 0.2 µm	< 2000	< 1000	< 500	< 200
0.2 - 0.5 µm	< 500	< 200	< 100	< 100
≥ 0.5 µm	< 50	< 50	< 25	< 1

Figure 1. Water Quality guidelines become increasingly stringent in both particle size and allowable number of particles, as circuit density increases. [2]

In the near future, line widths are expected to approach 0.12 micron [1], requiring removal of particles larger than 0.012 µ. Anticipating future requirements, Pate and Hollister [3] examined the ability of a variety of ultrafilters to remove 0.005 µm particles. None of the available filters had acceptable performance (99+% removal), and the best filter only removed 93% of particles. Substantial performance improvements are needed to support future generations of semiconductors.

Membrane filtration techniques (reverse osmosis and ultrafiltration) now in use will be impractical because of higher capital costs, replacement costs, and in-process qualification costs. A novel approach proposed by Ackerman [4] using electrostatic separation in a laminar flow water column removed 92% of particles larger than 0.05µm. Even if separation performance of this process were improved, this process could not supply sufficient UPW due to the low flow rates required to maintain laminar flow.

Another problem with existing technologies is that the filtration medium can contaminate the UPW. Chemical or biological degradation of the media induce shedding of small particles or debris. High shear stresses from fluid flow can cause tearing of a membrane or filter, allowing contaminants to cross a boundary. These stresses will become larger as the filter pore size is decreased to screen out small particles. Also, small pores are more prone to becoming plugged, increasing energy consumption, shear stresses, and the need for cleaning.

Verification of water quality is increasingly difficult as IC fabrication approaches optical limits. Since the allowable particles are smaller than the IC feature size, current process monitoring techniques, such as on-line laser particle counters, will have limited utility. New means will be needed to assure that water quality is adequate.

To provide ultra-pure water for forthcoming semiconductors a quantum leap in technology is needed. The ideal new technology would provide:

- Improved cost-effectiveness.
- Absolute removal of all sub-micron particles.
- Simplified performance verification.
- Reliable operation without degradation.

Polar Spring Corporation’s Crystallix™ process can meet the UPW needs of future IC manufacturing processes. Based on a patented, highly energy efficient, freeze crystallization technique, energy costs are less than existing UPW technologies. The Crystallix™ process can remove 100% of all sub-micron particles. Reliable operation is assured since all water contact surfaces are stainless steel, which is not subject to chemical, biological or shear stress degradation. Because the equipment does not degrade, it can be prequalified to verify absolute particle separation. Moreover, the Crystallix™ process further enhances water quality by removing virtually all (99%) of trace organic and inorganic contaminants. This process will produce UPW of a quality not achievable by current means.

Technical Approach

The Crystallix™ process is a Directional Freeze Crystallization method, similar in principle to the zone refinement method developed to purify silicon and germanium ores for semiconductor use. Freeze crystallization separates contaminants using the solubility difference between liquid and vapor phases. In the Crystallix™ process, particles are swept by the directional freezing front, providing absolute separation.

The Crystallix™ process works in a multi-step batch process as shown schematically in Figure 2, and described below.

- Raw water is transferred into a vessel containing a heat exchanger.
- Refrigerant flows through the heat exchanger, cooling the water and causing ice crystals to grow outward from the heat exchanger walls. Because contaminants are orders of magnitude more soluble in the liquid, the impurities are concentrated in the unfrozen water fraction.
- When the desired quantity of ice has been formed, the cooling system is turned off. The unfrozen liquid, containing the concentrated impurities, is drained from the vessel.
- The purified crystalline phase is melted to become UPW and is drained from the vessel.

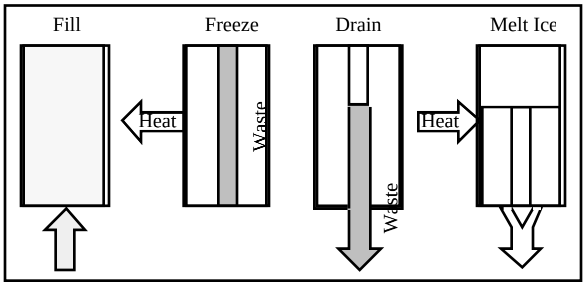

Figure 2. The Crystallix™ process removes impurities in a four step sequence.

Purification using crystallization methods, such as zone refinement or the Crystallix™ process, is well understood. Impurity separation occurs because contaminants are one to two orders of magnitude more soluble in the liquid phase than in the solid phase. Crystallization is insensitive to the type of contaminant, so all types of dissolved contaminants can be removed. Critically important for semiconductor UPW applications is the ability of the Crystallix™ process to remove **all** sub-micron particles.

Particles smaller than a certain size are swept in front of the directional freezing front used in the Crystallix™ process. The relationship between the ice front velocity and the particle size is shown in Figure 3. The critical velocity is inversely proportional to particle size, so smaller particles are more easily removed, the opposite of filtration methods.

The relationship between particle size and critical velocity is not known with certainty. Uhlmann et al. [5] experimentally and analytically investigated particle separation at an ice-water interface. They predicted a critical ice front velocity of about 200 μ/sec for a 4μ diameter particle and an inverse square dependence on the particle diameter for particles less than 100 μ. Corte [6] investigated particles ranging from about 0.1 to 1 mm in diameter at various freezing rates. His data showed that a moving ice front rejected particles, with the critical velocity inversely related to particle size. For particles with diameters of 0.1 mm, the critical velocity was in the range of 27 to 83 μ/sec. These data indicated an asymptotic behavior with rapidly increasing critical velocities for particles smaller than 0.1 mm. Kuo and Wilcox [7] investigated particle motion in the zone refining of organic compounds. Critical velocities of 200 to 1,000 μ/sec were observed for carbon and copper particles of 0.5 to 55μ diameter.

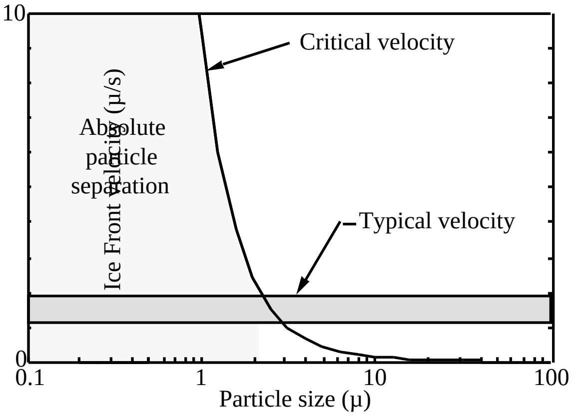

Figure 3. Particles with sizes to the left of the critical velocity curve will be removed by the directional freezing front. Typical ice front velocities used in the Crystallix™ process are capable of removing all sub-micron particles of concern to semiconductor manufacturers.

These results have important implications.

- The Crystallix™ process is an enabling technology for deep sub-micron semiconductor fabrication.
- Smaller particles are more effectively removed than larger particles, complementing existing filtration technologies.
- The critical velocities for sub-micron particles are large enough to make high volume UPW production practical.
- Analytical models of the phenomenon allow performance extrapolations from known size particles to particle sizes too small to observe, making calibration and verification practical.

Implementation

A Crystallix™ based UPW system would consist of a patented dual heat pump refrigeration system and parallel trains of crystallizers. The dual heat pump system is a dramatic improvement in batch crystallization systems. It consists of heat exchangers to alternately freeze and melt the treated water, conserving energy. Operating costs are estimated at less than $0.25 per thousand liters, a 75% cost savings over existing technology. Additionally, there are no degradable filters or membranes, so the system will be highly reliable.

Applications

The Crystallix™ process is exceptionally versatile for semiconductor UPW applications. We expect it will be applied for production of process water and recycling and recovery of rinse water used in wafer fabrication. In the production of UPW, the key benefits will be its unequaled ability to remove sub-micron particles. Just as important, its ability to remove all kinds of contaminants, coupled with the ruggedness of the crystallization equipment, make it ideal for recovery and recycling of rinse water. The low energy consumption and low maintenance requirements will be benefits for both applications. The long service life of this rugged system, together with its ability to meet all future needs for particle removal, make this an ideal capital investment for semiconductor manufacturers.

References

1. R. K. Wallace. *Editorial — Step up boldly*, Electronic Engineering Times, Sept. 20, 1993, p. 34.
2. Balazs Analytical Laboratory. 1993 Pure Water Guidelines.
3. K. Pate and L. Hollister, *Colloidal Silica—Filtration Performance of Deionized Water Filters when Challenged with Colloidal Silica Solutions*, Ultrapure Water, December 1993, pp 40-45.
4. A. Ackerman, *A New Particle Separation Technology for High-Purity Water*, Proc. Ultrapure Water Expo '94.
5. D. R. Uhlmann, B. Chalmers and K.A. Jackson, *Interaction between particles and a solid/liquid interface*, Journal of Applied Physics, **35**(10):2986-2992, (1964).
6. A. E. Corte, *Vertical migration of particles in front of a moving freezing plane*, Journal of Geophysical Research, **67**(3): 1085-1090, (1962).
7. V. H. S. Kuo and W. R. Wilcox, *Removal of particles by solidification*, Industrial and Engineering Chemistry Process Design and Development, **12**(3): 376-379, (1973).
8. V. Chase, *Distilled Wisdom on Ultrapure Water Recycling*, R&D Magazine, June 1995, pp61-62.
9. SWAG. need reference — estimated based on experience and energy consumption for RO.