Introduction

Many wet etch and clean processes for wafer surface cleaning require temperature conditioning of the cleaning chemicals. The cleaning processes are broadly grouped into two categories: Front End of the Line (FEOL) and Back End of the Line (BEOL). FEOL processes are primarily wafer cleaning, etching and photore sist stripping steps leading up to the first metal deposition. BEOL processes start after the first metallization step. The FEOL clean (also known as RCA clean) primarily focuses on the removal of wafer surface contaminants—particles, organics and metallics and prepares the clean wafer surface for further processing steps.

RCA FEOL processes involve the use of above-ambient temperature cleaning with aggressive, oxidizing chemicals. Typically, these cleaning steps start with a $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ treatment at high temperature, followed by dilute HF, SC1 ($\text{NH}_4\text{OH}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$) and SC2 ($\text{HCl}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$) steps, with water rinses between each step. The BEOL cleaning involves less harsh chemicals to prevent damage to the deposited metal layers. Solvents such as N-methylpyrrolidone and hydroxylamine are used, commonly at temperatures about 70°C (148°F).

Other cleaning applications where heating chemicals/liquids is required include hot phosphoric acid for silicon nitride and aluminum metal etching, hot deionized water rinses, and heated organic amine-based photore sist strippers. Electrochemical plating baths are also maintained at sub-ambient temperatures. Heating chemical mechanical planarization (CMP) liquids and abrasive slurries can also be critical to control removal rates. In many semiconductor manufacturing processes liquids with accurately controlled temperature are dispensed onto substrates to form thin films. In these applications, the liquid temperature has an effect on the uniformity and thickness of the final film. Accurate and repeatable temperature conditioning requires heating or cooling liquids such as spin on dielectrics, photoresists, antireflective coatings and developers prior to dispense onto a wafer. The recent shift toward higher processing temperatures in single wafer cleaning also creates a need for drain cooling, as hot chemical waste must be cooled before it can be safely discharged to the fab drainage system.

Heat exchangers are generally used for temperature conditioning of semiconductor liquids. Fluoropolymer material based heat exchangers are preferred because of their chemical inertness and corrosion resistance. In this paper we discuss the design and performance of a new, all-fluoropolymer Phasor® X heat exchanger (HEX) that has a high-heat transfer area (about 1.20 sq. m. per liter volume), enhanced flow distribution and small hold up volume. Also described are examples of temperature control systems incorporating the HEX device for precise temperature control.
High-performance pHasor X Heat Exchanger Design

The HEX is configured as a shell and tube type device constructed using a perfluorinated thermoplastic material. Thermoplastic tubes are fusion bonded into a thermoplastic shell/housing. The tubes in the device are uniquely braided, twisted, or plaited to form strands, which are thermally annealed to set the plait of the strand in place prior to fusion bonding. Such strands provide a high-packing density, enhanced liquid flow distribution in the device without the need for heat transfer enhancing baffles.

The HEX’s compact design provides a high-heat transfer surface area in a small volume; its chemically inert materials can withstand operation at elevated temperatures with organic as well as corrosive and oxidizing liquids. Its high surface-to-volume design produces more efficient performance than devices made with flat sheet materials of similar composition.

The device can be operated in a tube side flow or a shell side flow configuration. In the tube side flow a process fluid flows through the lumen of the tubes, and is separated by the fusion potted ends from a second working fluid, which flows through the shell (as shown in Figure 1a and 1b). In the shell side contacting, flows are switched.

The pHasor X heat exchanger is available in two configurations and sizes:

**U-style**

![Figure 1a. Counter flow configuration in pHasor X U-style (PHX03U and PHX08U series)](image)

**S-style**

![Figure 1b. Counter flow configuration in pHasor X S-style (PHX08S series)](image)
Temperature Management with HEX System and Process Control

Temperature Control for Recirculation Bath System

Controlling and conditioning the liquid temperature in wet cleaning recirculating systems improves process yield. Its fast response to temperature changes, chemically inert heating surface, high-heat transfer area and low volume are key advantages of the heat exchanger in this application. Other key components installed in the fluid circuit are temperature and flow sensors, flow control valves, cooling fluid reservoir and a microprocessor to control the temperature.

Figure 2 shows the flow diagram of such a recirculation test system. The objective of the system is to control the bath liquid temperature to within a narrow range of pre-set process temperatures by flowing and conditioning liquids through the heat exchanger. As seen from the test results in Figure 3, the 45-liter bath liquid temperature is maintained within setpoint range of 38°C (100°F) and 39.5°C (103.1°F) using two 1000W immersion heaters. The recirculating bath liquid flows at 7.2 L/min. through the heat exchanger and is conditioned with a second liquid maintained at 25°C (77°F), flowing at 6.2 L/min. through the shell side.
**Controlled Volume Dispense with Precise Temperature Control**

Another application is for dispensing a controlled liquid volume heated to a pre-set temperature. In a typical system the heat exchanger is coupled with a flow sensor, temperature sensor and control valves to enable controlled volume dispense of precisely temperature-controlled liquids.

Figure 4 shows the flow schematics of such a system dispensing a precise volume of liquid with controlled temperature. In this test the working liquid contained in a 60-liter reservoir is heated to 70°C (158°F) with three 1000W heaters. Process liquid at a temperature of 23°C (73.4°F) is flowed through the heat exchanger and contacted with the hot working liquid. A dispense consisting of 330 milliliter (mL) volume of liquid is delivered at a flow rate of about 22 mL/sec. for 15 seconds. The process liquid was dispensed through a flow control valve into the heat exchanger for energy exchange with the 70°C (158°F) working liquid (900 mL/min.). The test results in Figure 5 show the system can heat the volume of liquid from 23°C (73.4°F) to about 65.7°C (150.3°F) and dispense in a repeatable manner.
**Figure 4.** Flow schematics dispense with precise temperature control.

**Figure 5.** Controlled dispense with precise temperature control results.
Temperature Stability in Response to Fluctuations in Inlet Temperature

To extend the utility of 193 nm illumination beyond 65 nm technology, the industry is gearing up for a radical move to switch from “193 nm dry lithography” to the “193 nm immersion lithography” using ultrapure water (UPW). In immersion lithography, a higher refractive index liquid (e.g., DI water, index = 1.44) is placed between the final lens and the wafer (replacing the lower index air, index = 1). The liquid’s refractive properties are used to create higher resolution images than a “dry” lens system will allow. The higher refractive index of the DI water delivers two benefits: improved resolution and increased depth-of-focus of up to 50% for printing the finer circuit lines onto wafers.

To maintain stable optical (refractive index) and physical properties (surface tension, density), it is critical to precisely and accurately control the process water temperature in the immersion lithography process. Figure 6 shows a flow schematic of a temperature control system that is designed to maintain the outlet UPW temperature to an immersion tool constant despite fluctuations in the incoming UPW flow rate and temperature. The system uses two heat exchangers with associated sensors and controllers. The incoming water to the heat exchangers was intentionally subjected to temperature fluctuations for the varying amounts of time at several flow rates. The inlet process water temperature variation is at least 8 times the variation of the inlet cooling water temperature. The results (see Figures 7 and 8) show the dual HEX phasor X heat exchanger configuration is able to maintain the UPW temperatures within ±0.1°C (0.18°F) in a single pass process, handling repeated fluctuations in the inlet temperature of up to ±0.4°C (0.72°F) and flow rates up to 3 L/min. for prolonged periods of time. Temperature controllability improves significantly as the process flow rates decrease due to smaller heat loads. The device responds efficiently with minimal delays to changes in the inlet water temperature.

**Figure 6. Temperature control testing setup.**
2-Minute Period
Shell Inlet: 22°C (71°F) ±0.013°C (0.02°F)
HEX Outlet: 22°C (71°F) ±0.050°C (0.09°F)
HEX Inlet: 22°C (71°F) ±0.216°C (0.39°F)

Figure 7. Process DI water flow rate = 0.5 L/min.; Tube side = process fluid; Shell side = working fluid.

2-Minute Period
Shell Inlet: 22°C (71°F) ±0.003°C (0.00°F)
HEX Outlet: 22°C (71°F) ±0.002°C (0.00°F)
HEX Inlet: 22°C (71°F) ±0.158°C (0.28°F)

Figure 8. Process DI water flow rate = 3 L/min.; Tube side = process fluid; Shell side = working fluid.
Conclusions

Design of temperature control subsystems and components for liquid chemicals used in wet cleaning applications are demonstrated. A key component of the subsystem is the perfluorinated material-based, compact pHasor X heat exchanger. It provides a high-heat transfer surface area in a small volume; its chemically inert materials can withstand operations at elevated temperatures with corrosive and oxidizing liquids as well as organics. And its high surface-to-volume design produces more efficient performance than devices made with flat sheet materials of similar composition. The pHasor X-based temperature control systems have demonstrated ability to precisely control liquid temperatures in applications for recirculation bath systems, dispense of controlled volume and immersion lithography.

For Additional Information

For more information on controlling liquid temperature in wet cleaning process systems using the high-performance perfluorinated pHasor X heat exchanger, contact Entegris, Inc.