Supercritical Fluids for Single Wafer Cleaning

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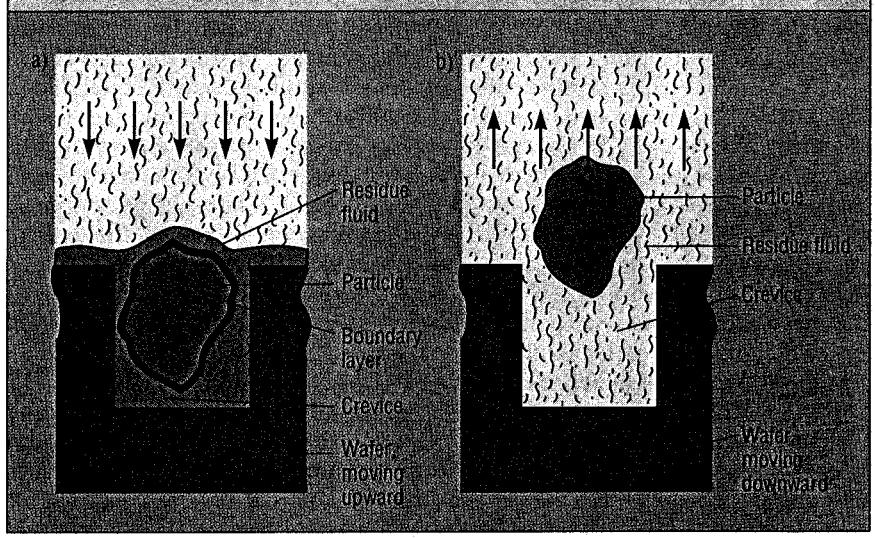
Supercritical fluid extraction is the name given to a cleaning process that removes contaminants using a supercritical fluid, that is, a gas-like substance above its critical temperature and pressure. Supercritical fluids possess liquid-like solvating properties and gas-like diffusion and viscosity that enables rapid penetration into crevices and boundary layer films with complete removal of organic and inorganic contaminants contained therein. Moreover, by cycling pressure between supercritical and subcritical values, particles can be very effectively dislodged during the expansion phase of the pulsation (Fig. 1).

The definition of a supercritical fluid can be fully appreciated by examining a phase diagram such as the one for CO_2 in Fig. 2. The key property is that above the critical temperature (T_c) condensation cannot occur at any pressure. The region to the right of T_c and above P_c defines the supercritical state. A supercritical fluid can have very high density.

FIGURE 1



Dislodging of a particle by supercritical fluid pressure pulsation. (a) 1200 psi, and (b) 800 psi.

CO_2 as the Cleaning Fluid

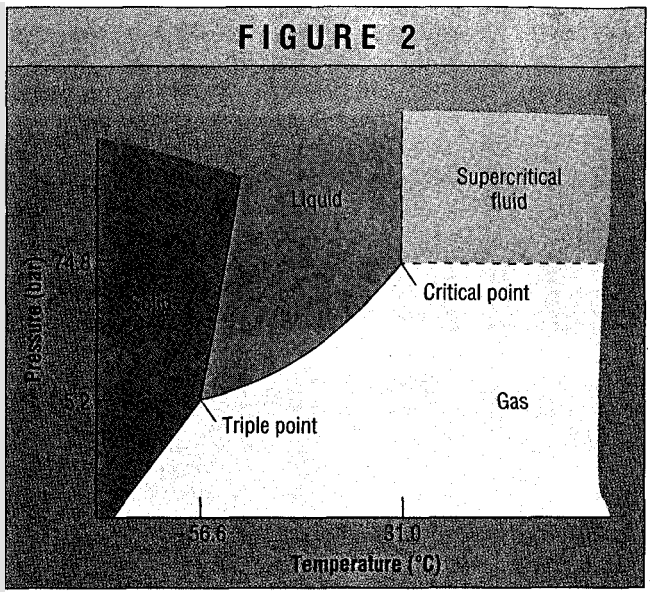
Supercritical CO_2 was chosen as a primary cleaning fluid for its low viscosity (0.05 centipoise), high diffusivity, and very low surface tension, as well as other environmental, safety, and cost considerations (Table I). For CO_2, the critical temperature, T_c, is 31 °C and the critical pressure is also in a practical range (P_C = 73 bar = 1050 psi).

Figure 3 shows density versus pressure for an isotherm just above the critical temperature. Density changes dramatically with pressure near the critical point. At 31 °C, for example, the density is only 0.002 g/cm^3 at ambient pressure, compared to 0.468 g/cm^3 at P_C (a 234-fold increase!).

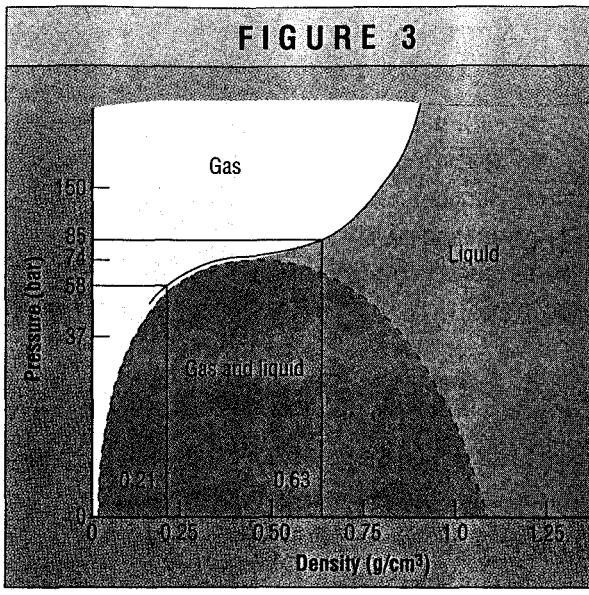
CO_2 above P_C has a density and solvating capabilities comparable to organic liquids. The solvent strength of CO_2 varies with pressure for a constant temperature. Physicochemical properties can be exploited both above and below P_C, i.e., supercritical and subcritical properties are *both* important in a well-designed cleaning process. In such a process, the fluid is cycled between two pressures as indicated in Fig. 3.

Wafer Cleaning Process

A wafer cleaning system that uses CO_2 in the critical region has recently been introduced. As shown in Fig. 4, the wafer is loaded between the upper and lower blocks of the cleaning chamber. The chamber height is about 5 mm during loading, and the wafer is held therein by vacuum grips in the top block. The lower block is then raised until the chamber is sealed, at which point the chamber



CO_2 phase diagram, including values for critical pressure (P_c) and critical temperature (T_c). (The *critical* point is distinct from the *triple* point for solid-liquid-gas equilibrium.)



Density vs. Pressure for 31 °C isotherm. For comparison, the density of solid CO_2 at – 79 °C is 1.56 gm/cm².

height is only slightly larger than the wafer thickness (~ 1 mm). CO_2 pressurized at ~ 800 psi is then supplied through centrally positioned orifices.

During the cleaning cycle, the supercritical fluid is pulsated by a hydraulic mechanism. The lower chamber block is actually a thin-walled, stainless steel membrane, i.e., a diaphragm. The hydraulic fluid pressure changes the chamber height via elastic deformation of the diaphragm, i.e., the supercritical fluid pressure is varied according to the volume of the cleaning chamber. Pressure is typically cycled between 800 and 1200 psi at a frequency of 25 to 50 Hz.

A separate expulsion cycle is used less frequently (every 1 to 3 sec) to replenish the cleaning fluid with fresh fluid. The expulsion cycle is effected by dropping the lower chamber block so a 2 µm gap is opened to atmospheric pressure around the outer circumference of the cleaning chamber. Contaminant-carrying fluid then rushes outward through passages into the exhaust system. The seal is then reclosed and fresh fluid is admitted through the inlet valves, which are centrally positioned above and below the wafer chamber.

The "stored energy" of the supercritical fluid is the main factor contributing to cleaning effectiveness. Residues are ejected during expansion, and supercritical fluid is forced into crevices during compression. A 40 sec process usually removes all contaminants in this manner. Nonetheless, additives may be included to modify the chemical properties, polarity, or solvating power of the fluid. For example, O_2, O_3, or H_2O_2 may be used to oxidize the wafer surface or organic contaminants. Through the use of such additives, the technology can be optimized for specific applications.

Microscopic Cleaning Dynamics

The compression cycle mixes and whirls the fluid in the upper and lower cleaning gaps. Density increases threefold (from 0.21 to 0.63 g/cm³). The cleaning fluid penetrates molecular layers and micrometer-sized crevices. Substantial fluid movement contributes to mechanical scrubbing, particle dislodging, and dissolving of organic material.

During the expansion stroke, the CO_2 changes from a supercritical fluid to a subcritical gas. Density decreases threefold, causing rapid mixing actions and outflow of fluid from the wafer surfaces. The fluid, moving at high velocities, quickly relocates suspended particles and dissolved contaminants. These are flushed out of the chamber by makeup cleaning fluid during the expulsion step. Redeposition is prevented by the rapidity of fluid flow throughout the process.

Suspended contaminants are removed from the cleaning chamber during the expulsion cycle whic curs every 1 to 3 sec. At this t nearly all of the fluid is expelled the center in a lateral outward d tion. The seal is then closed and n up CO_2 is centrally injected into upper and lower cleaning gaps, rounding the wafer.

Cleaning Unit

A double floating (DF), pulsa wafer cleaning unit is shown in F The "DF" designation refers to fact that the wafer floats freely i percritical fluid, not touching ei the top or bottom of the chan This is accomplished by properly ing the inflow of fluid through lower input valve, so that the waf always floating on a cushion of f Early designs allowed for cleanin only one side of the wafer. The unit is an advanced design whic lows both sides of the wafer t cleaned simultaneously.

The wafer cleaning chamber i signed for an 8 in. wafer. The entr and exit portals for robotic w transfer into and out of the clea module are only 5 mm high. Du loading and unloading, the l chamber drops several millimete accommodate the robotic tran arm. When the wafer is first load the chamber, it is held against th per chamber by a vacuum grip. lower chamber block is then ra

TABLE I

Desirable Features of CO_2 as a Cleaning Fluid

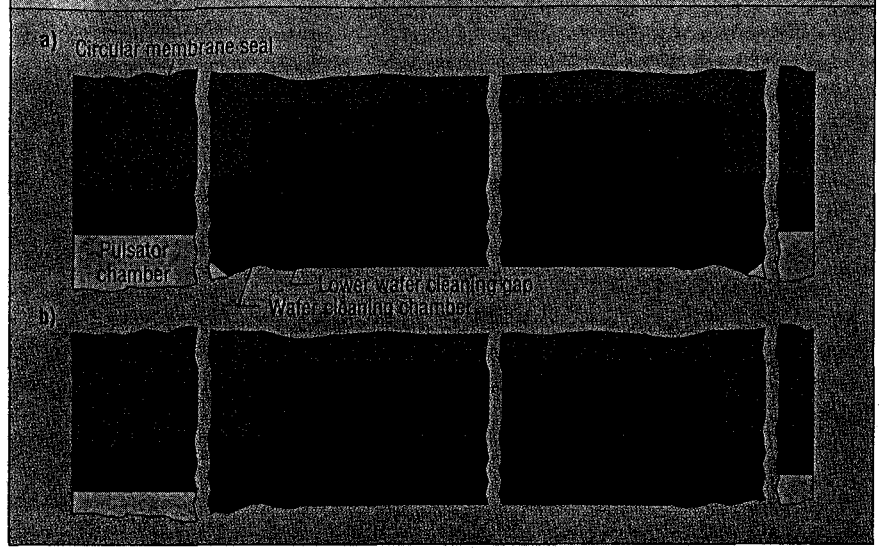
- Environmentally nonhazardous
- Noncorrosive
- Nonflammable
- Readily available
- Inexpensive
- High purity grades

TABLE II

Summary of the Supercritical Fluid Extraction Process

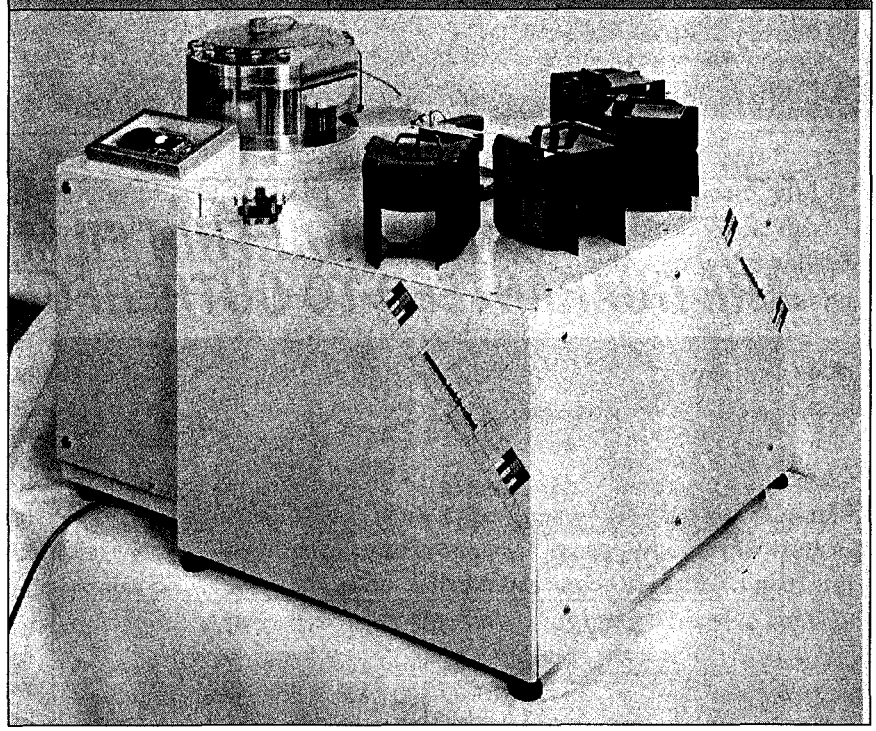
- High rate of dislodging / extraction / removal
- Complete dislodging / extraction / removal
- Simple processing
- Readily available system components
- Low fluid usage

FIGURE 4



Pulsating wafer cleaning within the sealed-off wafer cleaning chamber: (a) expansion stroke, and (b) compression stroke.

FIGURE 5



Wafer cleaning unit.

until the unoccupied volume within the chamber is extremely small.

The lower cleaning gap is very small (< 30 μm). As a result, the wafer follows the reciprocating movement of the lower chamber block. A hydraulically actuated pulsator in the central section drives the lower chamber block. This provides an optimal wafer cleaning action in both the upper and lower wafer clean gaps. The total fluid volume surrounding all sides of the wafer is only about 5 cm^3 ($\approx \pi r^2 h \approx \pi$ $20 \times 20 \times 0.0125$ cm^3) in the uncompressed (800 psi) position. This low cleaning fluid requirement simplifies control of fluid purity.

The fluid properties and chamber design are such that the pressure varies little from the top to bottom surfaces of the wafers. At any given time, even during the strokes, an essentially uniform pressure distribution exists in the chamber. The wafer is totally surrounded by the cleaning fluid during the cleaning process. Thus the wafer is not physically stressed by the thrusts or pressure changes of the cleaning fluid.

The diaphragm was a key element of the equipment design. The diaphragm needed to be thin enough to undergo significant elastic deformation, yet strong enough to withstand the high operating pressures of the process requirement. The chamber is presently designed to withstand continuous operating pressures up to 1500 psi.

Chemical treatments such as HF etching (wet or anhydrous) are notorious for leaving an electrostatically active wafer surface which attracts particle and chemical contaminants. Such oxide removal or cleaning processes are usually followed by further processing to clean and passivate the wafer surface. Cleaning with supercritical CO_2 alleviates the electrostatic problem because the volume of fluid between the wafer and the cleaning chamber's metal walls has been minimized. Also, the high pressure cleaning agent can include additives to passivate the surface.

Successful removal of organic contaminants, metal ions, and particles has been demonstrated on a DF 4000 module in our Class 100 cleanroom. For example, 98 to 99.5 percent of all particles > 0.3 μm have been removed from a wafer, using a process time under one minute. As this new technology continues to develop, further results will be forthcoming from customer beta sites.

The module typically would be used after the HF process and/or during the clean cycle. The system is ideally suited for single wafer, cluster-tool configurations where supercritical fluid cleaning can provide a contaminant-free, passivated surface between various processing steps.

Summary

Along with equipment design features, various fluid properties of sub- and supercritical CO_2 contribute to the workabililty of this new "dry cleaning" process (Table II). Initial work promises increased yield for densely patterned, large diameter, ULSI/VLSI wafers. ■