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CO₂-Based Supercritical Fluids as
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CO₂-Based Supercritical Fluids as Environmentally-Friendly Processing Solvents

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Abstract:

The production of integrated circuits involves a number of discrete steps that utilize hazardous or regulated solvents. Environmental, safety and health considerations associated with these chemicals have prompted a search for alternative, more environmentally benign, solvent systems. An emerging technology for conventional solvent replacement is the use of supercritical fluids based on carbon dioxide (CO₂). Supercritical CO₂ (SCCO₂) is an excellent choice for IC manufacturing processes since it is non-toxic, non-flammable, inexpensive, and is compatible with all substrate and metallizations systems. Also, conditions of temperature and pressure needed to achieve the supercritical state are easily achievable with existing process equipment.

We first describe the general properties of supercritical fluids, with particular emphasis on their application as alternative solvents. Next, we review some of the work which has been published involving the use of supercritical fluids, and particularly CO₂, as they may be applied to the various steps of IC manufacture, including wafer cleaning, thin film deposition, etching, photoresist stripping, and waste treatment. Next, we will describe the research work conducted at Los Alamos, on behalf of Hewlett-Packard, on the use of SCCO₂ in a specific step of the IC manufacturing process: the stripping of hard-baked photoresist.

As a replacement for current methods, which use highly acidic, highly alkaline or organic solvent systems, we have been testing a closed-loop CO₂-based supercritical fluid process, known as Supercritical CO₂ Resist Remover, or SCORR. The SCORR treatment process uses a non-flammable, non-hazardous, non-regulated compound, dissolved

in supercritical CO₂, to completely remove photoresists. The system has been successfully tested on metallized Si wafers coated with positive photoresists both before and after ion-implantation. This treatment process could not only replace conventional solvent systems, but also significantly reduce the amount of DI water for post-strip rinsing and drying steps.

1. INTRODUCTION

1.1. Supercritical fluids

The temperature at which the vapor pressure above a pure liquid reaches one atmosphere is known as the normal boiling point. For water, the normal boiling point at one atmosphere is 100°C. In an open container, Figure 1, the temperature of liquid water cannot be raised above 100°C since this would cause the vapor pressure of water to rise above one atmosphere, which would exceed the ambient pressure conditions. If we place a quantity of liquid water in a sealed container, however, then we may heat to higher temperatures, since the vapor pressure of the water can now exceed one atmosphere. As we uniformly heat the sealed container, the density of the liquid water decreases through thermal expansion. Simultaneously, the density of the water vapor increases. We can continue this heating process until the density of the liquid has been so reduced, and the density of the vapor phase has been so increased, that the two densities become equal. The temperature where the liquid and vapor densities become equal is called the critical temperature. Since the temperature inside the sealed container is everywhere equal, and the density is everywhere equal, thermodynamics dictates that the pressure inside the container be everywhere equal. This pressure is called the critical

Figure 1. Schematic illustration of supercritical fluid formation by heating of a liquid in a sealed vessel.

pressure. A fluid that has been brought to conditions above its critical temperature and pressure is known as a supercritical fluid.

This physical description of the formation of a supercritical fluid suggests that all simple fluids can be made supercritical by generating the appropriate conditions of temperature and pressure. This is indeed correct, and Table 1 gives the critical temperatures and pressures of some common fluids.

Supercritical fluids are used as solvents in many commercial applications, including the extraction of caffeine from coffee, fats from foods, and essential oils and spices from plants. The attractiveness of supercritical fluids as solvents stems from their unique combination of liquid-like and gas-like properties. Table 2 gives a comparison of some physico-chemical properties of a typical organic fluid in the liquid, supercritical, and gaseous states. To a first approximation, the solvent power of a fluid is

Table 1. Critical temperature and pressure for some common fluids.

Fluid	Critical temperature (°C)	Critical Pressure (psi)
Neon, Ne	-229	400
Nitrogen, N ₂	-147	492
Argon, Ar	-122	706
Xenon, Xe	17	858
carbon dioxide, CO ₂	31	1072
Sulfur hexafluoride, SF ₆	46	545
propane, C ₃ H ₈	97	617
ammonia, NH ₃	133	1654
water, H ₂ O	374	3209

Figure 2. Pressure-temperature-density surface for pure CO₂.

related to its density. The high, liquid-like density achievable in supercritical fluids therefore allows for substantial solubilities. Figure 2 shows the pressure-temperature-density surface for pure carbon dioxide. The critical point for pure CO₂ (31°C and 1072 psi) is shown in the figure by the large, solid circle. It can be seen that relatively small changes in temperature or pressure, near the critical point, result in large changes in density. It is this tunability of density, and therefore tunability of solvent power, which is the most attractive attribute of supercritical fluids. Also, the gas-like properties of low viscosity and high diffusivity, Table 2, and absence of surface tension provides for efficient penetration and mass transport into granular, micro-porous, and polymer matrices.

In order to make the best use of a supercritical fluid as a solvent, it is desirable to use a flowing, closed-loop system. Figure 3 shows a schematic pressure-temperature phase diagram for CO₂, which also incorporates a process flow diagram for a closed-loop supercritical fluid treatment system. The treatment cycle begins with a liquid-CO₂ storage reservoir. The liquid is brought to above its critical pressure during a pumping operation, which sends the pressurized liquid to a heating unit. The heating unit warms the pressurized CO₂ to above its critical

Table 2. Comparison of physico-chemical properties of a typical organic fluid in the liquid, gas, and supercritical fluid state.

	Diffusivity (cm ² /s)	Viscosity (mN·s/m ²)	Density (kg/m ³)
Liquid	10 ⁻⁵	1	1000
Supercritical Fluid	10 ⁻³	10 ⁻²	300
Gas	10 ⁻¹	10 ⁻²	1

temperature, so that a supercritical fluid is formed. The supercritical fluid enters the treatment vessel and is brought into contact with the substrate. It is during this time that the materials to be removed are solubilized in the CO₂. There is a constant flow of CO₂ through the treatment vessel, so that clean, dry CO₂ is continuously made available. On exiting the treatment vessel, the SCCO₂, containing the dissolved material, is sent to a separation vessel. In the separator, the SCCO₂ is de-pressurized to a gas, reducing the CO₂ density to a gas-like value. The solubility of the entrained materials in the low-density CO₂ gas is greatly reduced and they precipitate in the bottom of the separator. The clean CO₂ gas exits the top of the separator, where it is condensed into a liquid by a cooling unit before re-entering the storage vessel.

Such a closed-loop system means that there are no uncontrolled waste streams exiting the system. All of the extracted materials are retained in the separation vessel for subsequent analysis, recycle, treatment and/or disposal. Further, the extracted/removed materials are concentrated in the separator, greatly reducing the volume of waste.

Supercritical fluids based on CO₂ are gaining popularity as alternative, environmentally friendly process solvents as CO₂ is non-toxic, non-flammable, and inexpensive. Its critical conditions are easily achievable with existing process equipment. Also, there is already an extensive transportation infrastructure, as the food service industry relies on the use of solid and high-pressure gaseous CO₂ for food storage and carbonated drinks, respectively. This unique combination of physical, chemical and economic properties of SCCO₂ has

prompted an evaluation into its use as a replacement for process solvents currently used in the semiconductor manufacturing processes of wafer cleaning, film deposition, etching, photoresist stripping, and waste treatment.

1.2. Supercritical CO₂ as a surface-cleaning solvent

The Montreal Protocol and its subsequent modifications mandate a phase-out of the manufacture and use of chloro-fluorocarbons (CFC's). This has prompted an intensive search for alternative cleaning solvents. Hydro-fluorocarbons (HFC's), viewed as potential replacements, can generate corrosive compounds if subjected to high temperatures, and it is not clear that these compounds satisfy toxicity issues. Further, it is likely that these compounds, too, will eventually be subjected to strict environmental regulations. Aqueous-based systems have received wide attention, but these generate large waste streams, and the inherently high surface tension of these solutions limits their use in cleaning substrates containing fine-scale surface structures. Surfactants can be used to reduce surface tension, but this necessitates a subsequent rinsing and drying step, requiring large amounts of DI water

In the supercritical state, SCCO₂ behaves as a non-polar organic solvent, similar to hexane. Consequently, pure SCCO₂ is excellent for solubilizing other organics, such as greases, oils, lubricants and fingerprints. In addition, the low surface tension and low viscosity of SCCO₂ promote particulate removal by significantly reducing the thickness of the surface boundary flow layer. Table 3 illustrates the desirable physical and chemical properties of dense-phase (supercritical and liquid) CO₂ compared to some commonly used liquid cleaning solvents. There has been considerable work done in developing supercritical fluids, and SCCO₂ in particular, for the precision-cleaning of inorganic surfaces,[1,2,3] including metals,[4,5,6,7] optical elements,[8] Si wafers,[9] and micro-electromechanical devices fabricated on Si.[10,11,12]

The advantage of surface cleaning using pure SCCO₂ is that the process leaves no residues, since it evaporates completely when depressurized. As a result, subsequent rinsing and drying steps are not required. In addition to organic residues, however, semiconductor wafer cleaning may also involve the removal of inorganic particulates and trace metals. Pure CO₂ would require the use of specific modifiers, or co-solvents, for this purpose, and there are a number of surfactants [13] and metal chelating agents [14] which can be used. Even if such

Figure 3. Pressure-temperature phase diagram of pure CO₂ with a superimposed flow diagram for a closed-loop supercritical fluid treatment process.

Table 3. Physico-chemical properties of dense-phase carbon dioxide and some common cleaning fluids.
(Typical values at ambient conditions unless otherwise stated.)

Solvent	Viscosity (mPa·s)	Surface Tension (mN/m)	Relative Dielectric Constant	Dipole moment (Debye)	Density (kg/m ³)
Liquid CO ₂	0.02 (20°C, 59 atm)	1.5 (20°C, 58 atm)	1.5 (20°C, 59 atm)	0	792 (20°C, 60 atm)
Supercritical CO ₂	0.03 (35°C, 75 atm)	≅ 0 (T ≥ T _c and P ≥ P _c)	1.1 (35°C, 73 atm)	0	258 (35°C, 73 atm)
1,1,1-trichloroethane (methyl chloroform)	0.79	25.2	7.5	1.8	1339
1,1,2-trichloro 1,2,2-trifluoroethane (Freon-113)	0.66	17.8	2.4	0.9	1564
Methanol	0.54	22.1	32.7	1.7	791
Isopropyl alcohol	2.04	20.9	20.2	1.6	786
Acetone	0.31	23.5	21.0	2.9	790
hexane	0.30	17.9	1.9	0	655
Water	1.00	72.0	78.5	1.8	1000

modifiers were necessary, a final "rinse and dry" using pure CO₂ should eliminate their residues. There is a commercial system available for micro-electromechanical device fabrication that uses pure CO₂, [15] and large capacity systems for machine part cleaning are being installed in Europe.

1.3. Supercritical CO₂ as a media for thin film deposition

SCCO₂ has been used as a deposition media for the production of metallic powders and thin films. [16,17] A chemical pre-cursor, such as an organo-metallic compound, is dissolved in the supercritical fluid, which is then expanded through an orifice, producing a fine aerosol of the dissolved precursor. In the neighborhood of the substrate, the finely-divided precursor is made to deposit the metal by thermal decomposition, hydrolysis, or oxidation/reduction reaction. [18,19,20]

There are several advantages in using a supercritical fluid-based deposition technique, compared to conventional methods. First, any metal-bearing compound that can be made soluble in SCCO₂ can be used as a pre-cursor. CVD, on the other hand, requires the use of highly volatile source materials. Also, a single supercritical fluid can be made to simultaneously deposit a multi-component film, whereas CVD usually requires the use of multiple sources, with the attendant control systems for flow, temperature, etc. Supercritical fluid deposition, like CVD, can produce conformal depositions over complex shapes, in contrast to line-

of-sight methods, such as electron-beam and thermal evaporation and sputter deposition.

In addition to metals, other materials of interest to the microelectronics industry have been synthesized in supercritical fluids, including SiO₂ films in supercritical alcohol, [21] nitrides and sulfides in supercritical ammonia, [22,23,24] sulfides in supercritical amines, [25,26] transition metal oxides in supercritical water, [27] in SCCO₂, [28] and in supercritical alcohol, [29,30] and rare-earth-based phosphors in SCCO₂. [31].

1.4. Supercritical CO₂ as a media for film etching

Conventional etching processes, such as RIE, use directed beams of highly reactive species. These reactive species interact with the material to be etched, producing a volatile compound, which is swept away by a carrier gas. An etching process using supercritical fluids would be phenomenologically similar. There does not appear to be as much research done in this area as in the previous two applications, but there is nothing that would preclude the use of a reactive component, dissolved in an appropriate supercritical fluid, to etch Si, SiO₂, or metals. The potential advantage of SCCO₂ etching is an enhanced etching rate resulting from the low viscosity and high diffusivity.

The cleaning of etching and CVD chambers relies on the use of perfluoro-compounds (PFC's). There has been a great deal of work on the reduction of PFC use and/or abatement of downstream reaction products, such as HF. It turns out that the two general

classes of polymers having large solubilities in SCCO_2 are siloxanes and perfluorinated alkanes. We suggest that a significant reduction in PFC use can be achieved by using PFC's, dissolved in SCCO_2 .

1.5. Supercritical CO_2 as a photoresist fixer/developer

It has been demonstrated that the lower molecular weight fractions remaining after the exposure of specially formulated, positive-tone [32] and negative-tone [33,34,35] photoresists to UV radiation can be selectively solubilized in SCCO_2 .

This type of matched supercritical fluid/photoresist system offers considerable promise as an environmentally friendly lithography process, owing to the greatly reduced waste volume that would be generated.

It has been shown that the baking, or thermal "fixing", step of x-ray photoresist processing can be replaced by SCCO_2 extraction.[36] Instead of driving off the volatile solvent by oven heating, SCCO_2 can selectively extract the volatile components. The advantage, once again, is the greatly reduced levels of airborne solvent vapors.

The performance of conventional photoresists, such as those based on Novolak resins, can be enhanced by pre-processing in supercritical fluids. It is well known that the chemical and thermal properties of photoresists, such as dissolution rate and glass transition temperature, T_g , are sensitive functions of molecular weight. A typical photoresist polymer is made up of a large range of molecular weights, and the variability in this molecular weight distribution has been implicated in observed variations in lot-to-lot photoresist performance. A photoresist, dissolved in a supercritical fluid can be fractionated, or separated into a number of discrete molecular weight fractions. Once the photoresist has been "sorted" by molecular weight, these fractions can be recombined, or re-blended, into a formulation having a more optimal combination of properties.[37] For example, the very low molecular weight fractions, having a very low T_g and very high dissolution rate, as well as the very high molecular weight fractions, having a very high T_g and very low dissolution rate, can be removed or added in lesser proportions, to give a photoresist with a better overall combination of properties.[38]

1.6. Supercritical CO_2 as a photoresist-stripping solvent

The use of dense (liquid/supercritical) CO_2 for the selective removal of components during the

developing stage of photoresist patterning has been previously described. A more difficult problem is the complete removal of photoresist after "fixation" by hard-baking. This baking treatment renders the resist much more resistant to chemical and physical attack, which is required for subsequent component fabrication. Consequently, the stripping of these materials has not received the level of attention, or success, as have the other applications.[39] It is this application which has been the focus of our research, and will be described in the Experimental section of this paper.

1.7. Supercritical fluids for waste treatment

The use of supercritical fluids, particularly supercritical water, for the destruction (complete oxidation to CO_2 and H_2O) of organic compounds has been an industrial process for some time.[40,41] A recent example of its application to semiconductor manufacturing wastewater is given by Tomioka *et al.*[42] who report the complete conversion of tetramethylammonium (TMA) hydroxide, used as a positive photoresist developer, into CO_2 , H_2O and N_2 using a Pd catalyst in supercritical water.

The advantage of supercritical water oxidation is the possibility of complete destruction of the target materials, into an environmentally benign form, in a semi-continuous process.

2. EXPERIMENTAL

2.1. Supercritical CO_2 as a photoresist-stripping solvent

The stripping of hard-baked photoresists generates more waste than any other step in the IC manufacturing process. Unfortunately, alternative processing strategies, which can significantly reduce waste generation and personnel exposure, have not been forthcoming. This is due, in part, to the severe requirements placed on the stripping process, in terms of residual contamination and materials compatibility.

It has been found [43] that pure, liquid propylene carbonate, (1,3-Dioxolane-2-one, 4-methyl; CAS # 108-32-7), hereafter referred to as PCO_3 , is an effective, low-toxicity replacement for methylene chloride and methyl chloroform in the debonding of a negative, PMMA-based photoresist (RISTON T168). This finding, and the fact that PCO_3 is not expected to adversely affect thin-film metallizations, prompted us to investigate the use of PCO_3 , as a SCCO_2 modifier, for its ability to remove hard-baked photoresists currently used by the Hewlett-Packard Company.

PCO₃ is an environmentally friendly solvent, having no Personal Exposure Limit (PEL). It is non-flammable, non-toxic, biodegradable, and has a low vapor pressure.[44,45] It is readily available in high purity and in large quantities. Finally, PCO₃ is completely miscible with high-pressure CO₂. [46]

We have performed experiments on metallized Si wafers coated with hard-baked, positive-tone photoresists, and unmetallized Si wafers with positive-tone photoresists after ion-implantation.

2.1.1. Nuclear Reaction Analysis (NRA)

Nuclear Reaction Analysis (NRA) was used to evaluate the degree of removal of photoresist from the treated Si wafers. NRA is a rapid (<15 min.) analytical method, which probes a relatively large surface area ($\approx 10 \text{ mm}^2$). The method provides a high degree of sensitivity to carbon (the main component of photoresists), and is non-destructive both to the substrate and to the metallizations. As a result, we are able to obtain high-precision, quantitative data on residual carbon concentration at the sample surface, while preserving the samples for subsequent electron microscopy analysis.

In an NRA experiment, Figure 4, a beam of 1.2 MeV deuterons is directed onto the wafer surface. Carbon nuclei have an absorption resonance for deuterons at this energy, so that the deuterons are "absorbed", temporarily raising the carbon nuclei to an excited-state. The carbon atoms relax by emitting a high-energy proton, which is detected. The overall nuclear reaction can be written :

where d^+ is the incident deuteron and p^+ is the emitted proton. The sensitivity of NRA is high, owing to the fact that the emitted protons are of much higher energy than the incident deuterons, producing a high signal to noise ratio.

The fundamental equation relating areal density of surface carbon nuclei to resonance absorption cross-section of carbon nuclei is

$$nt \left(\frac{\text{atoms}}{\text{cm}^2} \right) = \frac{[Y (\text{yield})]}{\left[\sigma \left(\frac{\text{cm}^2}{\text{str}} \right) \right] [Q (\text{atoms})] [\Delta\Omega (\text{str})]} \quad (2)$$

where σ is the resonance cross section, Y is the experimental yield (in detected number of protons for

¹²C(d,p)¹³C Nuclear Reaction Analysis

Figure 4. Schematic illustration of the Nuclear Reaction Analysis (NRA) experiment.

a given number of incident deuterons), (nt) is the areal density of surface carbon atoms, Q is the number of incident, singly-charged deuterons, and $\Delta\Omega$ is the solid angle of the proton detector. For the beam line and experimental procedure used in these analyses, $\Delta\Omega = 2.5 \times 10^{-3} \text{ str}$, $\sigma = 90 \times 10^{-27} \text{ cm}^2$, $Q = 4 \mu\text{C}$. The areal density of carbon atoms, nt , is therefore related to the experimental yield (or number of detected protons), Y , by

$$\left[nt \left(\frac{\text{C atoms}}{\text{cm}^2} \right) \right] = 1.78 \times 10^{14} \cdot Y \quad (3)$$

To further enhance the experimental sensitivity for some of experimental runs, the sample is tilted, relative to the incident deuteron beam, to achieve a longer interaction, or 'path', length. For those experiments, the samples were tilted at 60° relative to the incident beam, so that the right side of Eq. (3) must be multiplied by $\cos(60^\circ) = \frac{1}{2}$. The experimental sensitivity, *in the absence of background*, is defined by an experimental yield of one count, $Y = 1$, so that we have

$$(nt)_{60^\circ, \text{min}} = 8.9 \times 10^{13} \left(\frac{\text{C atoms}}{\text{cm}^2} \right) \quad (4)$$

For comparison, an areal density of $1 \times 10^{15} \left(\frac{\text{atoms}}{\text{cm}^2} \right)$ is approximately equal to a monolayer of carbon atoms.

Column 2 in Table 4 gives the experimental yield (number of detected protons) for positive-tone resist-coated Si wafers containing Ti/Pt, In/Sn oxide, Al, and Ti/W metallizations, and two unmetallized,

ion-implanted positive-tone resist-coated wafers examined in this study. Column 3 gives the number of carbon atoms determined from the yield, while column 4 gives the equivalent number of monolayers of carbon remaining on the wafer surface, found by dividing the quantity (nt) by

$$1 \times 10^{15} \left(\frac{\text{C atoms}}{\text{cm}^2 \cdot \text{monolayer}} \right). \text{ It is seen that the}$$

residual carbon on the wafer surfaces, after the SCORR treatment, amounts to 1-10 atomic layers. This is not considered significant since the method used to correct the experimental gross yield for extrinsic carbon is only approximate, and will, if anything, be an underestimate. Further, the SCORR treatments were carried out in an open laboratory, and not in a clean-room environment so that the NRA results will include carbon in the form of CO_2 left absorbed on the substrate surface during the final "rinse" step of the treatment as well as atmospheric CO_2 adsorbed during sample transfer between the treatment facility and the analysis facility.

2.1.2. Scanning Electron Microscopy (SEM)

Verification of photoresist removal represents only the first step of our research goal. The required second step is to demonstrate that the SCORR treatment is not destructive to pre-fabricated thin-film metallizations. We therefore performed SEM analyses on the 'stripped', metallized Si wafers to see if the metallizations are in any way undercut or etched. All microscopy was done on the same samples, which were analyzed by NRA. No conductive coating was applied, so that low-voltage microscope operation was necessary. Further, all images were obtained with the sample tilted at 40° relative to the axis of the electron column to observe any undercutting of the metallizations.

Figure 5 shows a composite of four EM micrograph of the same Al/Si sample that was treated with the SCORR process and subsequently analyzed by NRA. No etching, pitting, or undercutting are evident. A similar absence of deleterious reactions was seen for the remaining metallized samples, indicating that the supercritical fluid composition and treatment parameters are compatible with existing IC processing procedures.

Figure 5. Composite of four electron micrographs of the SCORR-treated Si wafer with aluminum surface metallizations.

3. DISCUSSION

During the course of the SCORR experimental program, we have found that only by combining the PCO_3/CO_2 mixture in flowing system could complete photoresist removal be achieved. The mechanism by which the SCORR solvent removes the photoresist has not yet been determined. However, it is well known that polymeric materials can be made to swell by diffusion of CO_2 molecules and, in some instances, a significant reduction in the glass transition temperature can be produced. It is likely that such swelling occurs, effectively softening the resist. At the same time, the reactive ester group of the PCO_3 oxidizes the polymer, reducing its average molecular weight. This molecular weight reduction promotes solubility in the supercritical fluid, facilitating its removal.

Table 4. NRA results for the four Si/metallization systems treated by the SCORR process.

Sample description	Experimental gross yield, Y (counts)	(nt) $\left(\frac{\text{carbon atoms}}{\text{cm}^2}\right)$	Equivalent conc. of surface carbon atoms
Al on Si w/(+) resist	189 *	$(1.0 \pm 0.1) \times 10^{16}$	≈ 10 monolayers
In-Sn oxide on Si w/(+) resist	138 *	$(5.9 \pm 1.1) \times 10^{15}$	≈ 6 monolayers
Ti/W on Si w/(+) resist	97 *	$(2.4 \pm 0.4) \times 10^{15}$	≈ 2 monolayers
Pt/Ti on Si w/(+) resist	74 *	$(2.7 \pm 3.6) \times 10^{14}$	< 1 monolayer
Si w/(+) resist, implanted with $5 \times 10^{14} \text{ cm}^{-2} \text{ p}^+ @ 50 \text{ kV}$	84	$(3.4 \pm 1.8) \times 10^{15}$	≈ 3 monolayers
Si w/(+) resist, implanted with $6.2 \times 10^{15} \text{ cm}^{-2} \text{ As}^+ @ 40 \text{ kV}$	101	$(6.4 \pm 1.8) \times 10^{15}$	≈ 6 monolayers

* - sample tilted 60° relative to incident beam

4. CONCLUSIONS

Preliminary results indicate that CO₂-based supercritical fluids are attractive alternative solvents for photoresist stripping. Such fluids, as part of an appropriately designed, closed-loop treatment

system, have the potential to significantly reduce waste generation and water use. The reduction in water use is particularly significant, as the amount spent by the semiconductor industry on ultrapure rinse water, in 1996, equaled the amount spent on all other chemicals for wet cleaning.[47] The Semiconductor Industry Association (SIA) has set itself the goal of reducing the amount of ultrapure water used in 0.25 μm fab facilities by 50%.

The actual treatment schedule for the samples we have examined thus far was arbitrarily chosen, and only limited experimentation has been devoted to process optimization. We have determined, however, that increasing the treatment temperature significantly increases the amount of photoresist softening, for a given treatment time, and would therefore be expected to significantly reduce the required, overall treatment time.

It must be established by electrical testing that there is no adverse effect of the SCORR treatment on pre-fabricated surface and sub-surface structures. Finally, additional work needs to be done on characterizing, using completed, production-size wafers, contamination due to widely dispersed particulates and trace concentrations of transition metals. We are currently performing experiments on 6" production wafers to evaluate these issues.

Although our research has focused on the photoresist-stripping step of the fabrication process, there are other fabrication steps which may benefit from supercritical fluid processing, Figure 6. Clearly, the same system used for photoresist removal can be used for initial wafer cleaning, where highly efficient removal of greases, oils, and particulates is required. Further, it has been established that supercritical fluids can be used to deposit metallic and insulating thin films, and so could be used for generate interconnect lines, barrier layers and low-dielectric

Figure 6. Schematic illustration of the photolithography process, illustrating some of the processing steps, which could be preformed using or replaced by supercritical fluids.

constant films. It is also possible to use supercritical fluids, containing dissolved, reactive components, to etch metal and oxide films. Finally, supercritical water oxidation is a proven method for the complete oxidation of organic compounds, and so could be used for the treatment of wastewater.

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