Reuther/EHP, Los Alamos National Laboratory

SCORR One

Love might once have made the world go 'round, but today, arguably, that job falls to semiconductor chips. These chips, which are the technical "brains" of everything from alarm clocks to supercomputers, exact a price in environmental health. Millions of gallons of fresh water are used in the manufacture of these chips. Also used are hundreds of thousands of gallons of organic solvents and corrosive mixtures of substances such as sulfuric acid and hydrogen peroxide. These substances require extreme care in production, storage, and handling. And because some of them are either suspected or known human carcinogens, concerns about health effects have prompted millions of dollars in lawsuits against the semiconductor industry by workers who claim their health was compromised by on-the-job exposures. A new alternative manufacturing process that uses carbon dioxide (CO_2) in place of solvents may put an end to such health risks.

Building Resistance

The fabrication of integrated circuits relies on a process known as photolithography, in which a photoreactive polymer, or photoresist, is applied to the surface of a silicon wafer. Integrated circuit manufacturers rely on photolithography to create the desired features in each layer of chip circuitry. The process requires the selective removal of hardened coatings (resists) from a wafer, leaving the intricate circuitry intact. The photoresist is hardened by exposure to light and then goes through several fabrication steps that uncover well-defined regions of the wafer surface and harden that surface to withstand subsequent fabrication steps.

The photoresist is intended to develop the pattern of the particular circuitry being built as the wafer is etched around it and the mask is then removed. The process could be roughly compared to putting a patterned doily on top of a cake, then dusting it with powdered sugar. When you remove the doily, the pattern is left. It's very much the same in wafer fabrication, but the "doily" is much harder to remove.

The exact makeup of the photoresist is proprietary information and varies from company to company. Generally, though, photoresists are made up of such ingredients as propylene glycol methyl ether acetate (a solvent), novolac (a phenol–formaldehyde resin), and diazonaphthoquinone (a sensitizer).

The problem for the industry lies in the removal of the photoresist. According to Craig Taylor, the principal investigator on a new photoresist removal technology at Los Alamos National Laboratory, the industry currently uses one of three general categories of photoresist removal technologies: aqueous-based acidic or alkaline solutions, nonaqueous organic solvents (usually containing some fraction of halogenated or polycyclic aromatic hydrocarbons), or radio-frequency plasmas of reactive species such as oxygen or fluorine. After one of these treatments, the chips are washed with highly purified water and then additionally processed with isopropyl alcohol to dry the chip's surface. On an average day of operation at a standard chip-making plant, millions of gallons of contaminated wastewater are produced.

In addition, as semiconductor chips get smaller and smaller, yet are expected to hold more information and work faster, it becomes even more vital to be able to remove the tiniest particles from the wafer surface. Taylor says that with the sizes of features—or portions of the integrated circuit being constructed—measuring less than 0.13 µm, it will be imperative to remove all particles .10 µm and greater in size.

for the Environment

"Existing cleaning technologies such as liquid or high-pressure [liquid] jet scrubbing cannot remove particles on the order of one-tenth of a micron because of surface boundary layer constraints," he says. Liquid flowing in a stream flows more quickly in the middle and increasingly more slowly toward the edges. A fluid being used in a wafer-cleaning process behaves the same way, so as the particles become smaller and smaller, it becomes more and more difficult to achieve a sufficient flow velocity to dislodge them from the surface of the wafer.

A boon for industry—and for the environment—would be the introduction of an environmentally benign method of removing photoresist and other residuals. To this end, Taylor's team has focused on using supercritical CO_2 in a process dubbed "SCORR," for Supercritical CO_2 Resist Remover.

Supercritical Cleaner

Supercritical CO_2 is formed by putting CO_2 gas under increasing temperature and pressure, creating first a liquid state, and then a "supercritical" state, which has many of the properties of both a gas and a liquid. Taylor explains it this way: "If you take a container half-full of a liquid and boil it, the vapor pressure builds as the liquid changes to a gas [steam]. The density of the liquid decreases, while the density of the vapor phase increases, until the two are of equal density. That's the critical point. If you continue beyond that point, you reach the supercritical phase, where you have something with the density of a liquid but many of the properties of a gas—no surface tension, low viscosity, the ability to diffuse into anything, including the bond that the photoresist forms with the semiconductor wafer surface." These gaslike properties also allow supercritical fluids to flow much closer to a surface, and thus they are able to dislodge much smaller particles than existing technologies.

The critical point of CO_2 is approximately 80°F and 1,080 units of pressure per square inch. According to Taylor, many substances can be made supercritical, but CO_2 has several advantages for cleaning microchips. "You can make water supercritical, or [solvents such as] argon, ethylene, or propane, but there are serious issues," he says. For instance, ethylene and propane are better solvents than CO_2, but they're highly explosive. Argon is safer, but is not as effective a solvent. Water requires exceptionally high temperatures—705°F—and pressures to go supercritical. "CO_2 is cheap, it's environmentally benign, and it's noncombustible," says Taylor. "And as chip manufacturing advances dictate smaller and smaller surface architectures, it's going to require a cleaning method that can reach into the integrated circuit's vias [vertical holes running through the layers of photoresist] and trenches. Supercritical fluids have virtually no surface tension and a gaslike viscosity, which enables them to clean these tiny spaces." The SCORR process has been shown to be effective at cleaning feature sizes down to the seven-micron level, which is the benchmark for the industry.

The SCORR process uses pure CO_2 for the final rinse step, says Taylor, thus saving millions of gallons of water, not to mention contaminants in the wastewater that would have to be disposed of. And instead of using alcohol in the drying step, the process merely lowers the pressure and temperature of the supercritical CO_2, allowing it to return to its gaseous phase and leaving the wafer dry and residue-free. This process could add to worker safety, says Taylor, because workers would no longer be exposed to the corrosive, toxic, highly flammable products used in current wet-stripping technologies.

Los Alamos research into SCORR began about four years ago, and was carried out in collaboration with Agilent

Technologies of Palo Alto, California, and GT Equipment Technologies of Nashua, New Hampshire. GT Equipment has since formed a company named SC Fluids to develop a prototype device to use the SCORR technology.

According to David Mount, vice president of technology for SC Fluids, photoresist removal is a key issue for the industry. "In the semiconductor wafer manufacturing process, an organic photoresist is used about thirty times as the wafer rides through the process," he says. The photoresist is layered on in 3-D, says Mount—that is, it is applied in layers to achieve a desired thickness, rather than being applied at a given thickness all at once—and later has to be removed. Current technology involves patterning the resist, etching it, and then removing the mask. That's usually done by using plasma to "burn away" unwanted material and then removing any residues in a solvent wet bench rinse. This is followed by a deionized water rinse and drying with isopropyl alcohol, exposure to which can cause irritation of the mucous membranes of the eyes, nose, and throat and increased risk of spontaneous abortion. "With supercritical CO_2, the wafer goes in dry and comes out dry, without using alcohol," says Mount.

Mount explains how the SCORR system works: A wafer is transported by robotic guidance into a pressure vessel, either stainless or carbon steel. The supercritical CO_2 is mixed with a small amount of a relatively benign cosolvent (typically 5% or less), which increases the solvent abilities of the supercritical fluid. The fluid doesn't dissolve the photoresist—although some researchers are working on a CO_2-soluble photoresist—but rather attacks the bonds at the wafer–polymer interface and in essence floats the photoresist off of the surface. "At the end of the process," says Mount, "we just drop the pressure, which allows the CO_2 to return to a gas, leaving us with a small amount of solution containing the cosolvent and photoresist. The cosolvent can be recovered and reused, and the photoresist is filtered out." One cosolvent used in tests at Los Alamos is propylene carbonate, which has a very high flash point, a very low freezing point, and no listed Occupational Safety and Health Administration exposure limits. It also is not a known human carcinogen.

SC Fluids has developed a fully automatic system called "Arroyo" that uses the SCORR process. The Arroyo system has the capacity to process 50 wafers in two 25-wafer lots. The process module for the system consists of a

A cleaner clean room. The Arroyo system uses supercritical carbon dioxide to clean semiconductor chips, thereby using less solvents, creating less toxic waste, and consuming less water resources.

SC Fluids

pressure vessel that can hold either 150 mm or 200 mm wafers and a fluid delivery/separator system. The delivery/separator system is designed to deliver CO_2 in a gas, liquid, or supercritical state at any appropriate temperature and pressure. It can also deliver to the pressure vessel precise concentrations of any cosolvent or surfactant mixtures with supercritical CO_2. (Surfactants would be used in a separate process to remove particles other than photoresist from wafers.)

After the wafers are cleaned, a separator mechanism separates the CO_2 from any of the cosolvents or surfactants, as well as the resist debris from the wafer. The CO_2 can be saved and later recycled, the cosolvent is recycled, and the debris is disposed of as waste.

A Supercritical Analysis

According to Mount, CO_2 is inexpensive. It is usually mined or recovered from alcohol fermentation plants or lime furnaces used in cement manufacturing, but it can also be recovered as a waste gas from coal, oil, and gas power plants. It offers many substantial benefits, both environmental and economic, he says. "Our estimate is that, if you compare CO_2 and the standard wet bench cleaning, you'll use ninety-nine percent less chemical," he says. "The environmental benefits are obvious. Keep in mind, though, we're after the organic solvent side of the processing equation. Cleaning with acids is still being done because that's what's used to remove oxides or metal contaminants. We're after the photoresist mask and sidewall polymers."

Mount says the equipment his company is designing will replace both a plasma asher (typical cost, $1.2 million) and the solvent wet bench where wafer cleaning is performed (typical cost, $2.5 million), and will cost an estimated $2.4 million. The major economic benefits, he feels, will come from the lower cost of running the equipment (because the user can skip the rinsing and drying steps) and the elimination of disposal costs for waste solvents. "With chemical and power costs, the traditional process runs about twenty-five dollars per wafer per layer," he says. "With our process, we're estimating close to eight dollars per wafer per layer. Solvents are expensive, have a short shelf life, and cost a lot to buy and then dispose of. The CO_2 is [less] expensive and our system is a closed system, so you can recover and reuse the CO_2. All you have to do is recharge it occasionally."

According to Mount, the system is in the alpha stage of development. SC Fluids expects to deliver two beta systems to IBM shortly for testing. Also waiting to see how the new system works is long-time Los Alamos collaborator Karl Tiefert, manager of product stewardship for the semiconductor products group at Agilent. Says Tiefert, "I started on this project because it offered, on the surface at least, a great opportunity for business and the environment. If it can be implemented in the semiconductor manufacturing process, it will replace environmentally hazardous strippers and will cut water use dramatically. This is a fantastic technology, and the key is to come up with a reliable piece of equipment."

According to Tiefert, whether the SCORR process becomes a commercial success depends upon the reliability of the equipment. "This is a high-throughput industry," he says, "and once you demonstrate reliability, there will be very little resistance."

Coleen Miller, director of environment, safety, and health for the Austin, Texas–based International Sematech, a consortium of 13 semiconductor manufacturing companies, says that, if proven, the supercritical CO_2 technology developed at Los Alamos could be a tremendous plus for the industry, as well as for the environment. "We're still in the very early stages on this technology," she cautions. "But one of our goals is to continue to identify more environmentally friendly methods for chip manufacture, as well as those that will allow us to effectively produce the next generation of semiconductor products. One of the characteristics that could make SCORR a win–win situation is not just its environmental friendliness, but also its potential to accommodate smaller feature sizes."

Chuck Fraust, director of environmental health and safety for the Semiconductor Industry Association, based in San Jose, California, says his organization sees no negatives, per se, in this technology. "Our only concern is on the commercialization side," he says. "The question now is the ability to integrate this system with our current set of lithography tools. The way dramatic changes like this take place is in next-generation clean rooms. It would be much more expensive to try and retrofit existing facilities to accommodate the process."

Fraust adds that any time a new process is put in place, extensive quality control is necessary to assure the user and the customer that they're getting at least as good a product as the one being replaced, if not better. "I would think anyone interested in using this technology would first have to do some extensive cost analysis, see how long it will take to equip a facility, and gear it up to meet customer demand," he says.

The question of demand may be one drawback of the technology. Says Fraust, "I think a single small company would have tremendous difficulty in meeting the kind of industry demand that could be triggered by a process such as this. They might well have to partner with a much larger production company."

Mount emphasizes that the system is indeed designed for next-generation products, to be used in new facilities rather than retrofitted into an existing process line. He says, "At some point in the future, it might become economical to backfit, but for now this is for new lines and new technology."

Says Miller, "The industry will have to evaluate this technology from a process perspective, and see what are its different infrastructure needs, and what that means in terms of its use in a production facility. If we can develop this technology and build it in as we're building a new facility, that would be the best opportunity to make an impact from an economic perspective. In any event, going to more benign resist-removal processes, processes that are safer for the environment and for our workers and that use fewer natural resources, would be a tremendous benefit for the industry and the world as a whole."

Lance Frazer

Suggested Reading

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