

Carbon Dioxide in Semiconductor Manufacturing

High-tech Uses for an Industrial Molecule

By Dr. Paul Stockman

Hundreds of millions of tons of carbon dioxide are used every year in diverse industrial applications. It is essential for the production of urea and other nitrogen fertilizers, and is the primary feedstock for methanol. Additional uses are numerous: specialty chemicals synthesis, refrigeration, dry cleaning, commercial greenhouse growth accelerant, and food and beverage additive, to name a few.

This same molecule that is used in large-scale industrial processes also enables a variety of highly precise semiconductor processes. This article reviews the properties of carbon dioxide (CO₂) that make it essential for leading-edge semiconductor manufacturing, details the specific processes that use carbon dioxide, and briefly illustrates the supply chain.

Important Properties of CO₂

Relatively inert: Although at high pressures and temperatures, or in combination with aggressive chemical agents, CO₂ can be reactive, at the temperatures (< 1,000° C) and pressures (< 1 bar) used in semiconductor manufacturing, it is inert.

Different accessible phases: At room temperature, most people are familiar with carbon dioxide as the solid commonly known as dry ice, which sublimates into a gas. At higher temperatures and pressures, different phases occur. Carbon dioxide has low triple point (5.1 bar, -57° C) and critical point (72.9 bar, 31° C). At the triple point, carbon dioxide is in triple equilibrium in gas, liquid, and solid phases. At pressures and temperatures above the critical point, carbon dioxide exists in a phase with properties of both a gas and liquid. In its

supercritical phase, carbon dioxide becomes a good solvent, especially for hydrocarbons. Supercritical fluids also have no surface tension at interfaces with solids.

Solubility: Carbon dioxide has a much greater solubility (1.5 g / L) than any other inerting gases, like nitrogen or argon. However, it does dissociate slightly in water to make a weak acid.

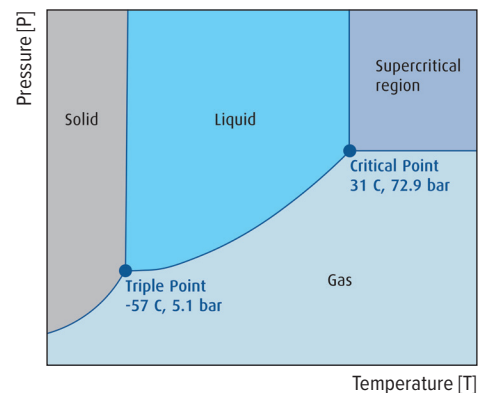
Process Applications

Photolithography

Semiconductor chips are built by depositing and then etching thin films of different materials to form transistors on a base silicon wafer. The elements of the transistors are patterned by a process called photolithography. UV laser light illuminates a master pattern mask before casting the image on photoreactive chemicals pre-deposited on the wafer. In addition to the mask, the light passes through a series of lenses to shrink and focus the pattern. The photolithography tool is the most expensive piece of equipment in the semiconductor factory, costing upwards of \$50 million.



The Linde facility in Medford, Oregon supplies high-purity CO₂ for semiconductor customers in the US and for export.



CO₂ Phases Diagram

While relatively inert, subtle distinctions in the properties of carbon dioxide versus other inerting gases, like nitrogen and argon, make it preferable to these gases for certain applications in the lithography process.

Photolithography – Immersion: Leading-edge semiconductor processes now employ a thin layer of water between the final optical lens and the wafer surface. This immersion lithography creates a sharper focus of the light, which in turn allows smaller patterns to be made. Rather than bathe the wafer in a large reservoir of water (the “bath tub” approach), a small disk of water is dispensed and moved around with the light source (the “shower head” approach). The disk is maintained by concentric rings of water jets, gas curtains, and vacuum ducts. Even though the water dispense and removal results in a short residence time on the wafer, gas from the curtain can dissolve and saturate in the water, resulting in bubbles, which distort the pattern image. By using more soluble carbon dioxide for the curtain gas instead of nitrogen or argon, the solubility limit is never reached and bubbles are avoided.

Photolithography – Extreme ultraviolet:

For more than 50 years of semiconductor fabrication, increasingly shorter wavelengths of light have been required in order to shrink the size of the chips, resulting in the observed phenomenon of Moore's Law, whereby the number of transistors per unit of silicon wafer doubles roughly every two years. The current series of light sources, excimer lasers, have been stretched to their limit, even with the immersion technique, and a new light source will be required in the next five years. This extreme ultraviolet (EUV) source will be powered by the emission of high excited tin atoms. High-power carbon dioxide lasers, around 10 kW, will be used to first atomize molten tin and then pump a large amount of energy into each atom.

Cleaning

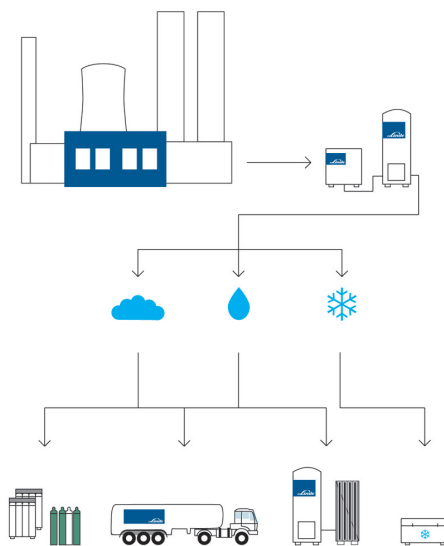
Maintaining product and process purity is critical throughout the semiconductor manufacturing process. Leading-edge processor chips have more than 2 billion transistors, and a single defect can render the whole chip worthless. Process gases are typically delivered at 99.999+ % pure, and are often further purified on-line to better than 99.9999999% pure. After nearly every deposition and etch step, the wafer is cleaned, typically in an aqueous bath, to remove all traces of chemical and particle impurities. Carbon dioxide offers unique improvements for cleaning at several points in the process flow.

Cleaning – Solid: Carbon dioxide snow cleaning is used in a number of industries, where small millimeter-sized particles, or "snow," are accelerated toward the part to be cleaned. The physical force can dislodge particulate impurities, while a thin supercritical fluid layer on the outside of the snow can dissolve chemical impurities. Instead of starting with dry ice, a high-pressure stream of liquid carbon dioxide is allowed to quickly expand and cool, resulting in the small flakes of snow.

In semiconductor manufacturing, liquid carbon dioxide can replace chemical solvents used to clean finished chips and assembled circuit boards to make the process much more environmentally friendly. In a more

critical application, the snow can be used to clean the semiconductor wafer between intermediate fabrication steps. Because the carbon dioxide is in physical contact with the unfinished circuits, extremely high purities greater than 99.9999999% are required.

Cleaning – Supercritical fluid: In other cleaning applications, impurities need to be removed from the very small features now associated with leading-edge semiconductors, sometimes as small as 10 nanometers. Here, carbon dioxide has been used in its supercritical phase. Individual or batches of wafers are sealed in a chamber, which is subsequently filled with high-pressure supercritical fluid. This is preferable to cleaning with aqueous solvents because the lack of surface tension prevents the collapse of the delicate features on the wafer.



CO₂ Production, Storage, & Transport

Cleaning – Eliminating streaming potential:

When ultra-high purity water moves quickly enough along a surface, like a dispense line or nozzle, it can pick up electrical charge created by the physical impact of water molecules with surface charges. Alternately called streaming potential, or tribo-charging, this electrical field can attract small particles directly, or cause downstream surfaces to charge and attract particles themselves, much like static electricity can attract small dust particles. Small amounts of carbon

dioxide added to the ultrapure water in such jet cleaning applications increase the conductivity of the water and allow charge to safely dissipate before it builds up to harmful levels. This is most often used when cleaning the chips while they are being sawed apart from the base wafer after transistor manufacturing.

Sources, Purification, and Supply

Carbon dioxide is not purposefully manufactured as a primary product, but rather is obtained as a by-product during the industrial manufacture of ammonia, alcohol, and fertilizers. There are also a few sources where it is obtained as a naturally occurring deposit, like natural gas and helium. The gas is captured, purified, and compressed in a multi-step process, and finally liquefied. Liquid carbon dioxide is stored and transported in pressurized tanks at a low temperature. Smaller volumes of liquid are stored in gas cylinders.

For semiconductor applications, source and purification process consistency, along with enhanced analysis, are essential to maintain the required quality. Carbon dioxide can be further purified to limit key impurities to less than one part per billion for the most demanding applications.

Conclusion

Carbon dioxide is essential in several steps of the key lithographic technique in semiconductor manufacturing and also enhances wafer cleaning processes. Linde has been a leading developer of the product grades and supply schemes that have enabled these advancements. Linde is the global leader for both the design and manufacture of carbon dioxide capture and purification plants, and for the supply of carbon dioxide for diverse applications. [SGR](#)

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