Carbon Dioxide:

Supply, Applications, and Purity in Semiconductor Manufacturing

White paper

INTRODUCTION

Globally, carbon dioxide (CO_2) plays a critical role in numerous manufacturing environments. It is a fully oxidized form of carbon, often generated as the unavoidable result of many industrial processes. CO_2 is a very stable molecule which requires costly energy and chemistry to transform into a usable feedstock. Despite having a bad reputation as a waste molecule and greenhouse gas (GHG), carbon dioxide is essential to life on earth, finding diverse uses ranging from oxygen-producing photosynthesis to carbonating beverages. In the growing semiconductor ecosystem, CO_2 plays an important role in solving major industry challenges across photolithography, deposition, dry etch, and cleaning applications.

SUPPLY

Sources of carbon dioxide are wide-ranging, and every source imparts a unique combination of contaminants, or signature. In addition to the source, geography may also influence gas purity, potentially adding region-specific atmospheric contaminants to the supply. The unique supply variability of CO_2 creates a moving target for purification. There are two important purity grades for CO_2: electronics grade (typically 99.999% or 5N) and beverage grade (99.9% or 3N). Plant-scale purification of carbon dioxide typically involves a combination of technologies including cryogenic distillation, catalytic oxidation, adsorption, and filtration to achieve required purity. Examples of common global CO_2 sources, contaminants, and resulting purity are presented in Table 1.

Most semiconductor processes require ultra-high purity (UHP) gas supplies, due to the process issues and on-wafer defects gas-phase contaminants can cause. In the specific case of CO_2, UHP (5N or better) supplies are challenging to source and many times more expensive than the 3N beverage grade gas. The International Society of Beverage Technologists (ISBT) is a global consortium that sets standards for beverage grade carbon dioxide (Table 2). For example, there are "not-to-exceed" thresholds for specific contaminants, due to either regulatory, sensory, or process rationale. It is the responsibility of CO_2 suppliers to meet this standard, and individual gas supplies can exceed the purity requirement but still have dramatically different contamination signatures.

By using advanced purification methods, end users may significantly reduce costs by switching to 3N-grade supplies. However, due to the handling and storage of beverage grade CO_2, metal particles are also a major concern. Carbon dioxide is not particularly aggressive toward stainless steel alloys such as 316 and 316L, but it is nevertheless imperative to incorporate high efficiency filtration to keep on-wafer metals counts below $10^8/cm^2$ as insurance against metal particle-related defects.

Table 1. Sources of carbon dioxide.

SOURCE	REGION	CONTAMINANTS	PURITY
Hydrogen production (SMR)	Global	CO, H_2, CH_4, H_2O	3N, 5N
Ammonia production	Global	NH_3, NO_x, SO_2, H_2S, H_2O	3N, 5N
Geological sources	US, EU	N_2, CH_4, H_2S	3N, 5N
Carbon capture, utilization and storage (CCUS)	Global	O_2, N_2, Ar, H_2O, SO_x, NO_x	3N, 5N
Biogas upgrading and fermentation	US, EU, TW	H_2S, VOCs, NH_3, CH_4, ethanol, acetaldehyde	3N, 5N
Ethylene oxide production	EU	ethylene, O_2, H_2O	5N
Methanol production	CN	CH_3OH, formaldehyde, CO, H_2, H_2O	3N, 5N

Table 2. ISBT standards for beverage grade (3N) carbon dioxide.[1]

CONTAMINANT	THRESHOLD, PPM	RATIONALE
H_2O	20	Process
Acidity	–	Regulatory
Oxygen	30	Sensory
Nitrogen compounds		
Ammonia	2.5	Process
NO/NO_2	5.0 (combined)	Regulatory
Phosphine	0.3	Regulatory
VOCs (total)	50	Sensory
Non-methane VOCs	20	Sensory
Acetaldehyde	0.2	Sensory
Aromatic hydrocarbons	0.02	Regulatory
CO	10	Process
Sulfur (total)	0.1	Sensory
Carbonyl sulfide	0.1	Sensory
Hydrogen sulfide	0.1	Sensory
Sulfur dioxide	1.0	Sensory

SEMICONDUCTOR APPLICATIONS

There are several semiconductor manufacturing processes which require the use of CO_2. Each process has its own purity requirements as well as sensitivity to specific contaminants. These applications may be separated into two categories based on the physical phase of the CO_2: gas-phase and supercritical fluid/solid-phase.

Gas-phase applications

Immersion lithography. CO_2 is used in immersion lithography to create gas curtains around the wafer, preventing defect-causing bubbles by displacing less soluble gases like nitrogen and argon from the immersion water layer. Carbon dioxide's high solubility and low tendency to form large bubbles make it an excellent choice for the critical interface between the immersion liquid, the photoresist, and the lens. Hydrocarbon contamination is of particular concern because it can poison photoresist and leave carbon residues on the wafer.

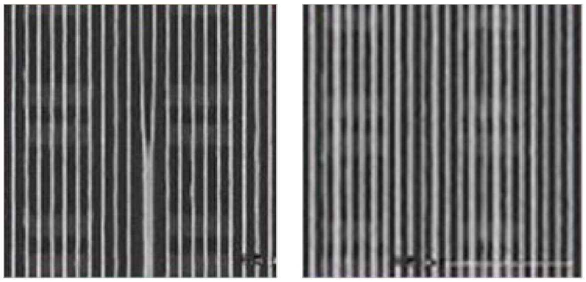
Deposition. There are two uses of CO_2 in deposition. The first is as a reactant to deposit carbon in chemical vapor deposition (CVD). Alternatively, carbon dioxide is used as a solvent or medium for depositing polymers, wherein its ability to form supercritical fluid or be cryogenically deposited allows for the controlled coating of surfaces. Contamination by other heteroatoms (nitrogen- and sulfur-containing molecules) are important sources of defects.

Dry etch. Carbon dioxide reduces damage to sensitive materials like low-k dielectrics by acting as a less aggressive etchant than oxygen. CO_2 also helps control polymer formation that provides stabilizing effects on etch profiles and enhances selectivity to other layers. Its low photoresist etch rate make it a useful additive or primary etchant for residue removal. In etch applications, contaminants such as carbon monoxide and methane may alter etch profiles. Sulfur-containing compounds like SO_2 and silicon-based refractory contaminants manifest as on-wafer residues.

Supercritical fluid/solid phase applications

Cleaning. Carbon dioxide is used in wafer cleaning because supercritical ($scCO_2$) and solid-phase CO_2 snow forms offer unique, effective, and relatively environmentally benign cleaning properties. To generate $scCO_2$, carbon dioxide is compressed and heated above its critical point, where it becomes a supercritical fluid and exhibits unique physicochemical properties, including low viscosity, high diffusivity, and tunable solvating power. This is particularly advantageous for high-aspect ratio (HAR) features, such as those found in 3D NAND memory device structures, as it avoids lithographic pattern collapse[2,3] (Figure 1) resulting from surface tension of cleaning liquids such as isopropyl alcohol (IPA). For $scCO_2$, high-efficiency particle filtration is equally critical to minimize defects, and this application presents unique design challenges not found elsewhere. Filters must operate under extreme conditions without destabilizing phase equilibrium in the dynamic supercritical system. The most critical-to-customer (CTC) considerations include the following:

- High mechanical strength
- Stable performance under supercritical conditions
- Resistance to $scCO_2$ absorption and phase-induced stress
- Consistent flow and minimal pressure drop



a) b)

Figure 1. SEM pictures[3] of a) Line flop-over (LF) pattern collapse due to liquid cleaning; b) pattern integrity maintained (no LF) after $scCO_2$ cleaning.

A solid-phase application, CO_2 snow provides a non-damaging, "all-dry" method for removing particulate and organic contaminants. In this process, liquid carbon dioxide is rapidly sprayed through nozzles, using expansion (Joule-Thomson) cooling to create a stream of solid CO_2 particles (snow) mixed with gas. These particles impact the wafer surface, providing abrasive cleaning action. This cleaning method eliminates the need for hazardous chemicals and deionized water, reducing waste and improving safety and sustainability.

SOLUTIONS

Addressing the wide range of carbon dioxide supplies and resulting variations in contaminant signatures demands advanced solutions. As the global leader, Entegris provides gas purity solutions that are engineered to exceed the requirements for carbon dioxide purity across all applications in semiconductor manufacturing, regardless of gas origin. Table 3 highlights the application-specific solutions available. To explore how the Entegris experts can optimize your process, please contact us.

Table 3. Entegris CO_2 purification and filtration solutions by application.

	APPLICATION	CONTAMINANT RISK	SOLUTIONS*	ADVANTAGE
Purification	Lithography	organics, refractories	POU, System	Yield Improvement, Tool Uptime
	Deposition	nitrogen- and sulfur-containing compounds	POU, System	Eliminates reactive impurities; maintains film integrity; ensures process stability
	Etch	methane, CO, sulfur compounds, refractories	POU, System	Protects etch uniformity; reduces contamination risk; enhances tool uptime
	Cleaning			
	Supercritical	heavy organics	POU, System	Residue Prevention
	Snow	organics, refractories	System	Yield Improvement
Filtration	Cleaning			
	Supercritical	particles	POU	Yield Improvement

** POU: point-of-use purifier; system: auto-regenerable purification system*

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References

[1] *Bulk Carbon Dioxide: Quality & Food Safety Guidelines and Analytical Methods and Techniques Reference*, www.isbt.com, 2025.

[2] Han-Wen Chen et. al., 2015 *ECS Trans.* **69** 119, **DOI** 10.1149/06908.0119ecst

[3] Sankarapandian, M. et. al. (2024). *ScCO$_2$ Drying for Preventing Pattern Collapse in Advanced Logic Device Structures*. 35th Annual SEMI Advanced Semiconductor Manufacturing Conference (2024). **DOI** 10.1109/ASMC61125.2024.10545479.

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Entegris

Corporate Headquarters
129 Concord Road
Billerica, MA 01821
USA

Customer Service
Tel +1 952 556 4181
Fax +1 952 556 8022
Toll Free 800 394 4083