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Mitigating the Contamination Challenges of Hydrogen Halides in Semiconductor Manufacturing

White paper

The toolkit of semiconductor gases has grown steadily in recent years with the introduction of new deposition and etch chemistries to enable advanced device architectures in memory and logic. Use of hydrogen halides – hydrogen fluoride (HF), hydrogen chloride (HCl), and hydrogen bromide (HBr) – has also grown as these molecules find use in epitaxy, dry etch, and cleaning processes in every fab, introducing additional moisture and metals contamination that leads to increased wear-and-tear on process equipment and corrosion-related device defects.

Hydrogen Halide	Role in Semiconductor Processing	Chemical Behavior
HF	Etching (SiO_2 , Si_3N_4), cleaning	Reactive gas
HCl	HVPE, cleaning	Reactive gas
HBr	Etching (Si , Si_3N_4)	Reactive gas; mild reducing agent

This trio of compounds is often broadly described as corrosive due to similar chemical reactivity, and they also share similar contamination profiles including the moisture and intrinsic volatile metals present in ultra-high purity (UHP) supplies. The corrosive nature of these gases enables valuable chemistries but also promotes the attack of expensive 316/316L stainless steel components ubiquitous in the semiconductor ecosystem,¹ contributing additional metals release into the gas delivery system. To combat this, many end-users of hydrogen halides have replaced 316SS delivery systems with more costly and exotic alloys only to see problems resurface.

To effectively purify hydrogen halide gases, it's essential to target moisture and metals removal. Metals contamination signatures depend on many factors; the source and moisture level of gas, delivery system, temperature and pressure all play a role in determining the type and level of metal-containing molecules possible in the supply. Two common alloys and resultant volatile metal compounds are provided in the table below.

EXPECTED VOLATILE METAL COMPOUNDS ^{2,3} PRESENT				
Alloy	Constituents	HF	HCl	HBr
316/316L	Co, Cr, Fe, Mo, Ni	CrO_2F_2	CrO_2Cl_2	CrO_2Br_2
		MoF_6	FeCl_3	FeBr_3
		MoF_5	MoCl_5	Mo(O)Br_4
C-22 Hastelloy	Co, Cr, Fe, Mo Ni, W	CrO_2F_2	MoO_2Cl_2	CrO_2Br_2
		MoF_5	MoCl_5	FeBr_3
		MoF_6	W(O)Cl_4	MoO_2Br_2
		WF_6	WCl_5	Mo(O)Br_4
			WCl_6	W(O)Br_4

Despite similarities in chemistries, differences in how HF, HCl, and HBr are manufactured, handled, and their intrinsic properties, demand a tailored solution for each gas to address their unique challenges. An aggressive purification strategy – implemented at the process design stage – remains the best insurance against costly repair downtime and for mitigation of process issues. The illustration below shows potential locations for purifiers within the delivery system, along with typical pressure conditions at each stage.

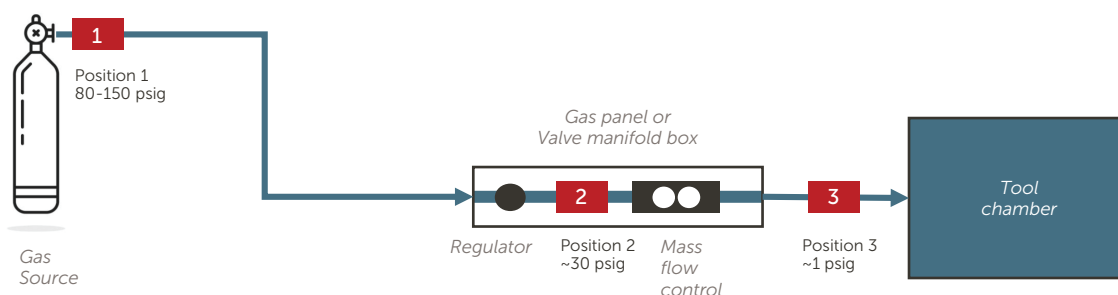


Figure 1. Potential locations of purifiers in gas delivery pathways.

HYDROGEN FLUORIDE

The global movement away from the use of polyfluorinated alkanes (PFAs) has brought significant challenges to the semiconductor industry. One effort to counter PFA use is the move towards hydrogen fluoride as a vapor-phase etchant to supersede PFAs. HF is capable of high etch rates for SiO_2 and Si_3N_4 , but its use poses difficulties uncommon to the etch process. The most significant of challenges is overcoming the compound's relatively high boiling point, which at 19.5°C requires the use of heat to generate gaseous HF at usable pressures. Entire delivery paths must therefore be heated to avoid process-killing condensation. Purification can contribute significantly to this problem; the standard high-efficiency outlet filters contained in most gas purifiers have significant pressure drop. This problem is exacerbated by the low 2-5 psia delivery pressure in the HF system, creating a "perfect storm" for HF condensation within the purifier itself.

Placing purification at the gas source (position 1) provides maximum protection for the system. Additional purification at the gas panel or valve manifold box (position 2) provides another layer of protection for critical and expensive tool components. Note: Placing purification closer to the process tool chamber (position 3) may seem advantageous, but the combination of very low pressures and inevitable incompatibility with purification media introduce additional issues.

The purification problem therefore becomes three-fold:

- Removing moisture and metals contamination at elevated temperature
- Providing adequate protection against particles
- Minimizing pressure drop and HF condensation

In this unusual case, less restrictive outlet filtration in the purifier is the most effective defense against condensation. This can be accomplished in two ways, depending on the system configuration surrounding the purifier. One method employs a coarser (and less retentive) integrated filter followed by a discrete, dedicated high efficiency filter. This method maximizes internal purifier volume and lifetime. The second method uses a much larger high-efficiency integrated filter with lower differential pressure within the purifier itself, which saves space at the expense of reduced purifier lifetime.

HYDROGEN CHLORIDE

When considering corrosive gas usage by volume in the semiconductor ecosystem, HCl is clearly the frontrunner. UHP HCl flows can span from less than one to hundreds or thousands of liters per minute, depending on the process. Hydrogen chloride is a byproduct of many industrial processes and is globally produced on a large scale, with over 1.7 million metric tons produced annually.⁴ Much of the UHP HCl supply is recovered from industrial processes such as vinyl chloride manufacture, where upstream process changes or upsets can result in organics contamination that is not present in HF or HBr. These organics can manifest as residues on the wafer, or they can become airborne and contaminate wafer handling devices and even other downstream processes. The appearance of organic compounds such as 2-chloropropane can be indicators of HCl manufacturing process upset, and at times can be found in high levels. While efficient removal of organics is not uncommon and relatively straightforward for many gases such as nitrogen and clean dry air (CDA), materials compatibility concerns make many commonplace adsorbents ineffective, unsafe, or even unusable in HCl. To ensure an effective, complete purification solution for hydrogen chloride, organics must be mitigated along with ubiquitous moisture and volatile metals contaminants.

HYDROGEN BROMIDE

HBr is more acidic than HF and HCl, based on literature pK_a values.² For this reason, moisture (and subsequent moisture-induced corrosion) in hydrogen bromide supplies are extremely problematic. 316SS can suffer damage of electropolished surfaces and weakened weldments, and moisture-laden HBr is notoriously aggressive towards costly UHP valves and mass flow controllers. Naturally, this raises serious safety concerns and drastically shortens gas delivery system lifetimes while increasing volatile metals contamination-related problems. Highly efficient removal of moisture in HBr delivery is critical, and when under control, corrosion is essentially eliminated.⁵

SOLUTIONS

Point-of-use purifiers, such as those in the Entegris [Gatekeeper GPU](#) product line, are designed and manufactured to meet the unique purification needs for hydrogen halides. These purifiers are ubiquitous in specialty gas delivery systems and reduce contaminants below critical thresholds. As expected in semiconductor applications, these purifiers incorporate high-efficiency particulate filtration to provide additional process protection.

GAS	CHALLENGES	SOLUTIONS
Hydrogen Fluoride (HF)	High boiling point (19.5°C) and low delivery pressure causes condensation risk; Moisture and metals contamination; Particle control at elevated temperatures	Heated delivery paths; Less restrictive outlet filtration; Two purifier configurations: 1) Coarse filter + external high-efficiency filter, 2) Large integrated low-pressure-drop filter
Hydrogen Chloride (HCl)	Extremely high flows; presence of organic contaminants	Removal of organics, moisture, and metals
Hydrogen Bromide (HBr)	Highly corrosive in presence of moisture; Causes damage to UHP components; Safety and equipment longevity concerns	Highly efficient moisture removal; Use of point-of-use purifiers with high-efficiency particulate filtration

Join us as collaboration partners or bring your individual process needs to solve these hydrogen halide purity challenges. [Contact our Experts to get started.](#)

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References

¹ SEMI F20-0923, Specification for 316L Stainless Steel Bar, Forgings, Extruded Shapes, Plate, and Tubing for Components Used in General Purpose, High Purity and Ultra-High Purity Semiconductor Manufacturing Applications, 2025.

² P.L. Daniel et al., Advances in Corrosion Science and Technology, Vol 5, 1970, p 55.

³ O. Kubaschewski, et al., Metallurgical Thermochemistry, Pergamon Press, 1958.

⁴ "Global Hydrogen Chloride Market Size, Share, and Business Benefits" <https://market.us/report/hydrogen-chloride-market/>, 2025.

⁵ Fine, et al., J. Electrochem. Soc., 1995, Vol 142 (4), pp 1286-1293.

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