Bowling for Contaminants:

The New Science of Gas Purification

White paper

INTRODUCTION

Purity of gases and chemicals has always played a critical role in the performance and reliability of advanced semiconductors and memory devices. Over the past few years, fab-cleanroom purity requirements themselves have changed exponentially in key process areas and are now approaching parts per quadrillion.

To remain competitive, many semiconductor manufacturers have increased manufacturing volumes which subsequently increases the overall consumption of gases. In addition to increased volumes, both logic and advanced memory devices require significantly higher gas consumption per processed wafer to support shrinking geometries and multi-layer device architectures such as finFETS and 3D NAND. For example, the move from 20 nm logic to 7 nm logic doubled the number of process steps. As a result, process gas consumption is expected to increase over the next five years.

Concurrently, the industry is looking to achieve higher density at lower power which also increases the complexity of the processes.[1]

These additional process steps impact yields as there are more opportunities to expose wafers to process excursions. Even trace contaminants in the gas supply can cause measurable shifts that affect chip performance by interacting with a process, potentially costing the manufacturer thousands or even millions of dollars.[2]

As a result of this heightened sensitivity to molecular contamination and increased gas consumption, semiconductor manufacturers are placing new requirements on suppliers of both bulk and specialty gases to deliver process gases customized to meet purity requirements. This article explains the importance of applying purification science to managing the gas supply purity from the source throughout all the wafer process steps to ensure the highest device yield.

THE ROLE OF PROCESS GASES IN SEMICONDUCTOR MANUFACTURING

With hundreds of gas and specialty gas mixtures used in an ever-increasing number of manufacturing process steps, there are many opportunities for wafer contamination caused by the gas supply.

Of all the bulk gases, nitrogen is currently used in the highest volume. This ubiquitous gas is used for countless purging applications, including pumps and vacuum chambers. Wafer fabrication facilities making chips with 28 nm or 20 nm features can go through 20,000 to 30,000 cubic meters of nitrogen per hour.[3] Extreme clean dry air (XCDA®) is also employed for purging and sweeping cleanrooms. This has become increasingly important as newer generations of tools are specified to guarantee that processes are performed using XCDA. With the forthcoming adoption of extreme ultraviolet lithography (EUV), the use of hydrogen is expected to increase.

WHERE DO CONTAMINANTS ORIGINATE?

Intrinsic contaminants originate at the gas supplier; additionally, for corrosive gases, contamination can be picked up in the gas stream as a result of corrosion of the delivery system and tool. As such, the wafer's relationship with the gas supply and their journey together begins well before they even come in contact with each other.

WHAT DO CONTAMINANTS LOOK LIKE?

Contaminants in both bulk and specialty gas supplies come in several forms. Categorized as particulates or molecular contaminants, even historically benign contaminants have become problematic and can cause defects in today's 7 nm node devices or 3D NAND structures.

In general, contaminant classes include moisture, acids, bases, refractory compounds, and organic molecules (Table 1), but contaminants can also develop in unexpected ways. For example, if oxygen (O_2) is inadvertently introduced during the silicon (Si) ingot growth process, the resulting silicon dioxide (SiO_2) deposition will cause defects before wafer processing even begins.

CONTAINMANT TYPE	STANDARD SURROGATE	TYPICAL IMPURITY LEVELS (OUTLET PURITY)
Acids NO_x, SO_x, Organic acids	SO_2	0.1 – 1 ppmV (<1 pptV)
Atmospherics CO_2, CO, O_2, N_2	CO_2, CO, O_2, N_2	0.1 – 1.0 ppmV (<100 pptV)
Bases Amines, organoamines, silazanes	Ammonia (NH_3)	1 – 100 ppbV (<1 ppbV)
Metals Fe, Mn, Mo, Ni, Cr, others	E34 list, Fe, Cr	1 – 100 ppbV (<1 ppbV)
Moisture	H_2O	0.1 – 25 ppmV (< 1 ppbV)
Organics Condensable (45 – 100 amu; butane, IPA, toluene) Non-Condensable (>100 amu; decane)	Toluene Decane	0.1 – 2 ppmV (<1 pptv)
Refractory compounds Halogen-containing HCs, silicon compounds	HMDSO	<100 ppbV (<1 pptV)

Table 1: Common gas-phase contaminant classes.

Moisture (H_2O) is always a contaminant and an unwanted source of oxygen atoms. Molecular hydrocarbon and refractory contaminants introduced during the lithography process can wreak havoc on the stepper lens, impeding the patterning process. Carbon dioxide (CO_2) can be either a process gas or a process challenge.

Metal contaminants are particulates that can be picked up in the gas stream. For example, hydrogen bromide (HBr) gas, used in dry etch processes, is very aggressive towards stainless steel. Extremely corrosive when contaminated with moisture, HBr leaches constituent metals out of the stainless steel and can carry these through the gas stream onto the wafer, creating shorting defects. However, this source of metal contamination can be mitigated by properly desiccating the gas at the delivery source.

The bottom line is that gas purification is a complicated science. Contamination profiles vary dramatically from gas to gas. In many cases, it is no longer sufficient for a gas supplier to provide a customer with a specification sheet that addresses common contaminants. Customization of gas purification requires an end-to-end solution that begins at the bulk supplier and requires the right purification approaches that can vary from system to system, gas to gas, and process to process as the wafer travels along its manufacturing journey.

CAPTURING THE FLAG VS. BOWLING FOR CONTAMINANTS

In simpler times, when processes were more forgiving and feature sizes were larger and planar, process excursions and root causes were easier to identify and mitigate from the gas stream. Like the childhood game, capture the flag, there was often only one cause to identify and remove.

Today, as the device designs become more complex, the sensitivities to gas contaminants rise. Processes have become so numerous and integrated, that it is often difficult to know how the many molecular contaminants are contributing to process problems. Likewise, the solutions have become much more complex. Contamination control has become more like bowling, with multiple pins to knock down, and where hitting one can cause a chain reaction. Depending on the spin of the ball, any number of combinations impact the end result (Table 2).

Process	Contaminaton effects
CMP	Corrosion
Wafer clean	Corrosion
Dry etch	Metallic contamination
Epi	Lattice defects, metal contamination

Process	Contaminaton effects
Metrology	Haze
Deposition	Film defects, metal contamination
Track	Pattern defects
Scanner	Haze, pattern defects

P = Particles *W = Water/Moisture* *M = Metals* *O = Oxygen*

Process	HCl	HBr	CxFx	NH_3	CO	BCl_3	SixHx	Inerts	Metallic precursors
45 nm	P,W	P,W	P,W	P,W	P,W,M	P,W	P,W,O	P,W	P
32 nm	P,W	P,W	P,W	P,W	P,W,M	P,W	P,W,O	P,W	P
28 nm	P,W,M	P,W	P,W	P,W	P,W,M	P,W	P,W,O	P,W	P
22 nm	P,W,M	P,W,M	P,W	P,W	P,W,M	P,W	P,W,O	P,W	P
14 nm	P,W,M	P,W,M	P,W	P,W	P,W,M	P,W	P,W,O	P,W	P
10 nm	P,W,M	P,W,M	P,W	P,W	P,W,M	P,W	P,W,O	P,W	P

Table 2: These charts demonstrate how different processes have different sensitivities to contaminants depending on node.

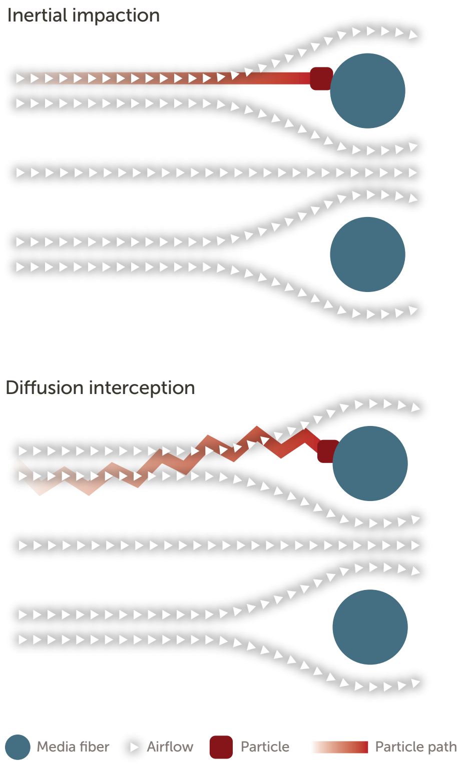
What was once a case of capturing one contaminant "flag" has become a multitude of contaminants to control. This requires a broad contamination control strategy and becomes more complex with each new design. This strategy requires close collaboration between the gas manufacturer, delivery provider, and the end customer. The goal: Achieve purity by controlling contamination at the molecular level to ensure the gas supply contains everything the customer wants, and nothing more.

THE SCIENCE BEHIND GAS PURIFICATION

Gas-phase contamination control calls for a combination of filters and purifiers installed in the right locations throughout the delivery system.

A filter is able to remove suspended particles from gas streams. Purifiers are able to remove molecular contaminants, such as H_2O, O_2, CO_2, hydrocarbons, and others. Due to the large number of contaminant types, gas purification is often more complex than filtration.

There are two dominant mechanisms in gas filtration. The first is inertial impaction (Figure 1), which is used when the particle is large and dense enough to pass out of the fluid streamline due to its inertia. The second mechanism is diffusion interception (Figure 2), which captures particles that are small enough to pass out of the fluid streamline due to Brownian motion. When used in concert, diffusion and interception can capture even the smallest particles, (about 0.001 µm or less). These are the most concerning to device manufacturers, as the current metrology tools are unable to detect these sizes.



Figures 1 and 2: Diffusion Interception.

Gas purification also employs two primary mechanisms. Physical adsorption (or physisorption) involves the physical interaction between the impurity being removed and the adsorbent. For example, physisorption is used to remove H_2O and hydrocarbons. Chemical adsorption (or chemisorption) involves forming a chemical bond between surface atoms of the adsorbent and the impurity. This is how reactive oxides like CO and O_2 are removed. (Figure 3) (See sidebar for list of adsorbent classes and types.*)

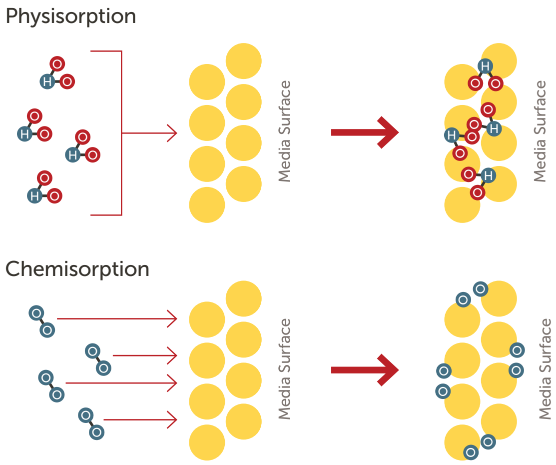


Figure 3: Comparison of how physisorption and chemisorption are used to remove common contaminants from the gas stream to prevent wafer defects.

USING GAS PURIFICATION SYSTEMS

Most gases entering the fab start out as 99.99% pure, but the actual contaminant profile can vary dramatically from lot to lot. Most modern processes require purity levels of 99.9999% (often called "six nines", or *6N*) or greater. Gas purification provides process stability by maintaining consistent purity levels, which improves yields rather than increases defects. This requires managing facility-wide control points that represent process risk. Table 3 illustrates these control points, the potential contaminant risks, and the effects these contaminants can have on the wafer as it makes its journey through the process tools.

*List of adsorbent classes and types

ADSORBENT: POROUS MATERIAL CLASSES	ADSORBENT TYPES
Crystalline materials Exhibit reproducible x-ray diffraction patterns Class includes zeolites, metal-organic frameworks (MOFs), ZIFs, ALPOs, SAPOs, some forms of carbon (i.e., CNTs, graphene) Vast array of structure types provides range of separation selectivities	**Activated charcoal (carbon)** Physical adsorption Removal of organic and strong acid AMC
Regular materials Do not exhibit reproducible diffraction (amorphous) Class includes activated carbons, amorphous silicas, and aluminas Can be modified to enable/enhance separations	**Coated carbons** Combination physical/chemical adsorption Removal of weak acids, special chemistry also some organic AMC
Catalytic and gettering materials Typically, a formulation that contains transition metals and alumina or silica binder Primarily used for removal of oxygen, oxidation of VOCs	**Ion exchange media** Chemical adsorption Base and acid AMC
	Catalysts Destructive adsorption/oxidation Special materials and formulations

Process	Contaminant	Effect
Track	Acids, bases, moisture, hydrocarbons	Pattern defects
Scanner	Acids, bases, refractory compounds, hydrocarbons	Haze, pattern defects
Metrology, reticle inspection, and wafer inspection	Acids, bases, refractory compounds, hydrocarbons	Haze, pattern defects
Piping welds	Moisture, oxygen	Discoloration, reduced weld integrity
Electrochemical deposition (ECD)	Moisture, oxygen, hydrocarbons, volatile metals	Film defects, metal contamination
Chemical vapor deposition (CVD) and Physical vapor deposition (PVD)	Moisture, oxygen, hydrocarbons, volatile metals	Film defects, metal contamination
Dry etch	Volatile metals	Metals contamination
EPI	Moisture, oxygen, volatile metals	Lattice defects, metal contamination

Table 3: Processes create different contaminant risks and process excursions on the wafer.

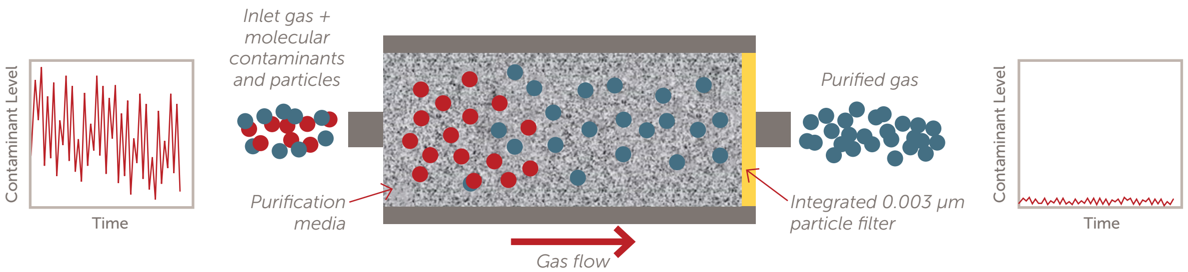


Figure 4: Better purity = improved yield. Consistent purity = process stability.

The intent of a gas purification system or cartridge is to create ultrapure gas as measured in “outlet purity”. The risks to mitigate or eliminate are the process excursions, which occur when the contaminant level spikes outside the baseline considered to be a safe operating range. (Figure 4).

Because a leading edge EUV scanner can cost as much as $300 million, with 10% of the cost in the lens stack alone, protecting, for example, the optics of a lithography scanner or other costly equipment that is highly sensitive to hydrocarbons, moisture, and other contaminants is important for cost control.

CONCLUSION

The journey of a semiconductor device is long, complex, and varied. The role gas purity plays begins long before the gas supply first meets the wafer in a process tool, and even before the first silicon crystal begins forming the ingot from which the wafers are sliced. To ensure the highest yield, gas purity must begin at the gas manufacturer, and follow the silicon through hundreds of processes before it becomes a finished device wafer.

Amplified sensitivities due to the increased number of processes, combined with the variety of process flow methods, is creating very customer- and process-specific problems, requiring more than off-the-shelf solutions. What’s needed is end-to-end collaboration between the gas supplier, semiconductor device manufacturer, and the end-customer.

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