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Progress in improving cylinder gas purity

COVER ARTICLE

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overview
Use of cylinder gases in semiconductor manufacturing presents a set of unique challenges for microcontamination control. Here, success requires tight control of the cylinder material of construction, gas fill and delivery techniques, and knowledge of the dynamics of cylinder gas contamination levels during use. As a further aid, the industry's use of external filtration is now supplemented with built-in cylinder filtration that ensures gas purity and can be implemented with cost savings.

The consistent delivery of high-purity process gases from cylinder sources represents one of the biggest microcontamination-control challenges in semiconductor processing. If not properly controlled, impurities such as metals, moisture, atmospherics, particles, and hydrocarbons can seriously interfere with many wafer fab processes, leading to inconsistent results and adverse effects on device yields. Successful efforts have therefore been made in recent years to control all of these contaminants as industry roadmaps have demanded ever-decreasing impurity levels as device sizes are reduced.

Bulk inert gases such as nitrogen used for purging can be purified and handled in systems that can achieve sub-part-per-billion (ppb) levels of all impurities, and analytical techniques exist to confirm this purity. It has been a different order of challenge with cylinder process gases, however, because these are often corrosive, toxic, and more difficult to handle and analyze. Cylinder gases can also have a more immediate effect on processes because, in general, they directly participate in layer and device chemistries.

Much of the progress in reducing contaminants in cylinder gases has therefore centered on improvements in cylinder material selection, surface polishing and cleaning processes, vacuum purging and baking techniques for preparation, and ultra-high-purity (UHP) gas-handling techniques for filling.

Industrial gas cylinders

The need for safe operation in a pressure vessel at pressures up to 200barg (2900psig) and increasingly to 300barg (4300psig) means the high intrinsic strength of Cr-Mo mild steel makes it the preferred material of choice for industrial gas cylinders.

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Provided they are kept dry, even corrosive products, such as anhydrous liquefied HCl, Cl_2, and BCl3, can be reasonably safely contained, as corrosion only occurs when moisture is present.

Although austenitic stainless steels may appear to offer better corrosion performance than standard low-alloy steels in many environments, the protection afforded by these materials in the presence of halide ions is minimal. Further, the lower tensile strength of these stainless steels (~80% that of Cr-Mo steel) requires a much heavier cylinder to achieve the required pressure rating.

Stainless steel may provide some benefit with low-vapor-pressure products, such as $SiCl_2H_2$ and $SiCl_4$, but the more corrosive halide gases can lead to stress corrosion cracking and pitting corrosion. The greater susceptibility to the localized corrosion processes in stainless steels makes them unsuitable for pressure vessels containing corrosive halide gases such as HCl.

With the most extremely corrosive materials such as WF_6, pure nickel cylinders are often used to minimize Cr and Fe contamination in the product. Aluminum cylinders are restricted to noncorrosive applications. The majority of electronics specialty gas products are therefore still preferably supplied in Cr-Mo steel cylinders. Because they are produced by normal metallurgical processes, they can often exhibit surface corrosion in the "as-received state." This may be less critical in routine low-purity applications, but is completely unacceptable for UHP electronics gases.

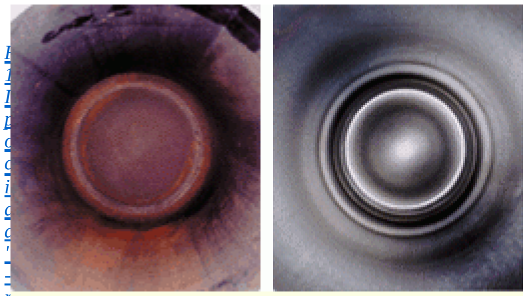

Figure 1. Internal photographs of cylinders in a) an "as-received" state and b) after surface treatment.

surface treatment.

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Cylinder preparation

To initially clean cylinders, they are typically subjected to a variety of mechanical and chemical polishing treatments that remove mill-scale and rust and improve the surface quality and appearance. These treatments are followed by final rinsing in UHP 18megOmega deionized water to remove any cleaning residues and contamination. Figure 1 shows a comparison between an as-received standard cylinder exhibiting some surface rusting, and one following an Air Products electronics-polishing treatment, where all the rust is removed and the surface roughness is improved from ~20mm Ra to 2.5mm Ra (800 to 100min.). Any surface corrosion and roughness provide sites to adsorb moisture and other impurities, as well as providing sources for ongoing metals and particle contamination. Thus, these must be removed.

This cleaning and polishing makes it easier to prepare cylinders for filling.

To provide rapid connection, purging, and filling, and minimize leak rates, the vacuum and gas manifolds used for filling cylinders are typically made from 316 stainless steel, with orbitally welded joints and face seal demountable connections. Similarly, to avoid oil and hydrocarbon impurities, state-of-the-art systems use dry turbomolecular pumps. Cylinders are typically baked under high vacuum (<10-6mbar) at 150°C for a sufficient period to remove most of the atmospheric contamination.

Figure 2 shows how a standard untreated industrial cylinder might result in an initial level of moisture of a few parts per million (1000ppb) when the cylinder is full of inert UHP gas (to

2900psig), which rises to >10,000ppb as the cylinder empties. The much improved electronics standard of treatment and preparation achieves much lower levels, in the example to around 150ppb as first filled, remaining flatter over a longer period, and rising to only 450ppb as the contents are exhausted. Improvement due to the electronics treatment and preparation is clearly demonstrated.

Similarly, although polishing and cleaning remove all particles from the surface, they can still remain suspended within the gas in the cylinder, so in a further purging step the particle level is reduced to <10 particles/ft^3>0.1mm in size. Figure 3 shows how in the electronics-treated cylinder the particle level can be reduced below this specification, whereas the untreated cylinder starts at a much higher level and does not purge down to the specified level in a similar time.

Cylinder filling

The approach with cylinder filling is similar as far as materials selection and design of gas-handling systems is concerned, but a different manifold design is needed.

Standard fill manifolds typically involve a number of cylinders connected linearly in series. Although suitable for many less stringent applications, such a configuration cannot ensure completely uniform fill conditions in each cylinder, as the length of pipe work between each cylinder and the filling point is different. To achieve improved consistency with electronics products, particularly mixtures, manifolds typically use a "radial" design where gas is distributed from the center to a group of cylinders arranged around a circle through pipe work of equal length.

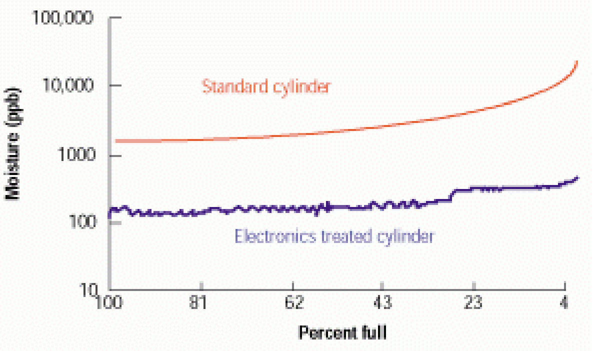

Figure 2. Concentration of moisture in gas cylinder contents.

The product pumped into the cylinder can if necessary be further purified prior to filling.

After fill, samples are taken directly from the fill manifold to analyzers (e.g., gas chromatography, GC, Fourier transform infrared, FTIR, and capacitance moisture detectors) to check quality against specification and to determine that no additional contamination has been introduced during the transfill process.

Returned cylinders that are reused are processed with special procedures. They may still contain unused residual product that must be removed and the cylinder purged before refill. "Top filling" onto residual material is not normally permitted because of the possibility of cross contamination during a customer process.

After both cylinder preparation and product disposal, and prior to each fill, mass spectrometry analysis is performed on the residual gas in the cylinder to check on remaining impurity in a "fitness to fill" check.

Such state-of-the-art approaches in designing and operating electronics specialty gas transfill systems, coupled with rigorous statistical quality control, allow consistent high-purity product to be supplied to the electronics industry and to meet the ever increasing demands on purity, consistency, and quality.

(Although the procedures described here involve some aspects of proprietary technology in their detailed implementation, the general principles and approach are followed by all reliable suppliers to the industry.)

Further areas of development

Although the approaches described so far meet current quality and consistency requirements, the need to achieve ever more cost-effective processing at increasingly demanding specifications means there are areas offering scope for further improvements.

First, as illustrated in Fig. 2, however well the cylinder is dried, there is always a level of moisture adsorbed on the walls that continues to desorb and provide a constant equilibrium vapor pressure in the gas within the cylinder. This causes the concentration of moisture to increase as the internal pressure of the contents falls.

Second, in liquefied products, volatile impurities concentrate in the headspace above the liquid, while less volatile impurities concentrate in the liquid, also contributing a varying purity level as the cylinder is emptied. As a cylinder approaches and becomes liquid dry, moisture levels may well break through the 1000ppb level. Because of these effects, it is common practice to leave a "heel" of unused product in the cylinder, typically 2.5-10%.

Third, ongoing chemical interaction between the walls and the contents can generate additional impurities with time. Concern over this potential source of contamination has led to the imposition of a shelf life or date by which product should be used. For example, reactive gases are typically specified with a shelf life of 24 months, compared with much longer periods for inert gases.

External purification

These three issues, together with the intrinsic impurity levels in some products, can lead customers to consider external point-of-use purifiers and filters to control consistency (Fig. 4). Here, the materials of construction are 316 stainless steel, with welded permanent joints on 6mm (1/4 in.) tubing, and with face-seal demountable connections. In Fig. 4, a separate filter is shown in the outlet line, together with tied diaphragm isolation valves. A 1 x 10-9 atm-cc/sec leak integrity specification, together with the proprietary purification materials to achieve ppb impurity levels means that designs of this type can add significant costs to a gas distribution system.

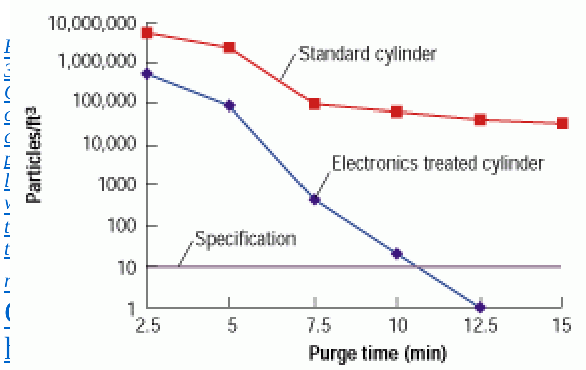

Figure 3. Comparison of cylinder particle levels with two treatment methods.

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When cylinders are changed out, the impurity loading on an external purifier from atmospheric contaminants can sometimes be more difficult to quantify. Since there is usually no indication of purifier lifetime, it can therefore require additional management and maintenance to ensure that the purifier is always operating correctly.

Purification built into cylinders

In an effort to deliver purer gases more consistently, Air Products has developed a new gas supply system that builds a process gas purifier within the compressed gas cylinder, dubbed built-in purifier (BIP) and MegaBIP technology for electronics. This arrangement improves gas purity and minimizes both inter-cylinder and intra-cylinder variability. Any purifier maintenance issues are essentially eliminated with BIP technology, because the gas supplier controls the integrity of the purifier as well as the impurity challenge it experiences.

Figure 5 shows how gas quality is controlled by filling the cylinder through a separate pathway. But when the standard customer valve is opened, gas is removed through the purifier, providing gas with oxygen and moisture levels below 1ppb directly from the cylinder. The BIP cylinder contains an integrated residual pressure valve that is essentially a spring-loaded check valve with

high cracking pressure. Because there is a residual pressure valve within the system, there is no possibility of back contamination compromising the purifier, or of the cylinder running empty. In addition, with the purifier completely sealed within the high-pressure cylinder, it is immune to atmospheric leaks.

inert gases.

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By operating at the higher pressure within the cylinder, the efficiency of purification is enhanced over ambient pressure operation. Unlike conventional low-pressure external purifiers, the high-pressure piping upstream of the process regulator in BIP systems is also protected, since the purifier is already delivering pure gas directly from the cylinder. This is important in corrosive gas systems where piping is thermodynamically more vulnerable to corrosion at higher pressure than in standard systems.

The significant impact of BIP technology on moisture in the gas emerging directly from the cylinder can also be seen in Fig. 6, where the level remains below 1ppb to the end of the cylinder.

This radical new approach gives totally consistent quality every time. Initially introduced for UHP analytical carrier gas applications, BIP technology gases have given significant performance and cost benefits. In many GC applications, the two key impurities in the carrier gas are oxygen and moisture, which can increase baseline noise and reduce sensitivity, thus degrading limits of detection (LOD). A number of studies have shown significantly improved performance in baseline and LOD by switching to BIP technology gases [1-3]. In addition, the use of BIP technology gases has been reported to significantly reduce overall costs by up to 70% by improving column and purifier lifetimes in GC applications [3, 4].

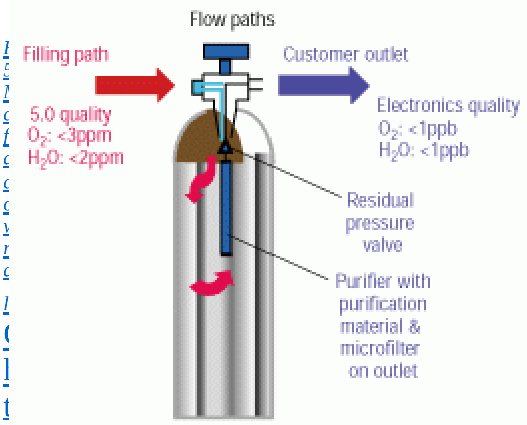

Figure 5. MegaBIP cylinder filling and customer outlet, with respective quality levels.

R&D analysis by atmospheric pressure ionization mass spectrometry of the inert BIP technology gases for purging has demonstrated residual impurity levels at the detection limits of the analysis, typically <1ppb for oxygen, moisture, and hydrocarbons. Metals have been shown to be lower than ppb levels by inductively coupled plasma mass spectrometry.

Inert gas purging

The first application of MegaBIP technology was with high-purity inert gases such as helium, nitrogen, and argon used for purging corrosive toxic or flammable gases. In many applications, these process gases are handled in gas cabinets, where the gas from the purge cylinder is passed through an external inline purifier.

The extension of BIP technology to meet the additional demands of the electronics industry was achieved through the use of electropolished stainless steel materials, a tied diaphragm valving design to minimize contamination, use of dedicated electronics valve outlets for greater integrity, and incorporation of 0.003mm microfiltration. In a number of customer trials using this approach, it has been possible to eliminate costly external purifiers with substantial savings in operational costs, with no detriment to process and product performance over a substantial period.

Although BIP technology gases are more costly than standard gases, the elimination of the external purifier has demonstrated overall cost savings of >60%, as well as reducing capital cost up front. In cases where purifiers continue to be used, the reduced loading from using BIP technology gas extends the time between change outs but still reduces overall costs.

Process gases

BIP technology has also been used with electronics grade carbon monoxide (CO), which is of increasing interest for use in selective oxide etch chemistries, where it scavenges fluorine by forming COF2. One of the main challenges in delivering CO to the electronic marketplace is the potential for CO to form volatile metal carbonyls such as $Fe(CO)_5$ and $Ni(CO)_4$ when in contact with these metals at high pressure. These contaminants can form from reaction of the CO with iron- and nickel-containing components, both within the production and transfill systems, as well as within the cylinder package itself. The use of BIP technology to remove these volatile metallic contaminants has already been demonstrated. Control of metal carbonyls to below 10ppb is possible by the correct selection of purification media.

Conclusion

Although advances in conventional technology have enabled significantly improved purity levels in electronics specialty gases to be achieved on a consistent basis, a new cylinder technology based on built-in purification offers the prospect of further driving the state-of-the-art in achieving improved purity and consistency in these gases. It has already been introduced for inert gases, with the prospect of application to a family of process gases as the technology is adapted to the particular demands of each candidate.

Acknowledgments

BIP and MegaBIP are trademarks of Air Products and Chemicals Inc.

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