

CONTENTS

1. Entegris News

- Entegris i2M Center for Advanced Materials Science
- Entegris @ SEMICON® Europa

2. Cost Reduction

- Customized Valve Manifolds Improve Tool Uptime on High-temperature Applications

4. Innovation

- HF Contamination Control by Clean Gas Purge

5. Yield Improvement

- Reduction in Wafer Defects in IPA Solvent Drying Application

6. Safety

- Pressure Relief: 20 Years of Safety and Efficiency for Storage and Delivery of Highly Toxic Gases

7. Product Highlight

- Advanced Filtration Solutions with Improved PTFE Membranes: Fluorogard® FP/FP-HP and FluoroLine® DF Plus Filters

ENTEGRIS EUROPE

A question about Entegris products?
Call your customer service center

France

Tel. +33 (0)4 76 35 73 50
Fax +33 (0)4 76 35 73 80

Germany

Tel. +49 (0)351 795 97-0
Fax +49 (0)351 795 97-498

Israel

Tel. +972 (0)73 221 0000
Fax +972 (0)73 221 0030

A question about cleaning services?
Call **Entegris Cleaning Process ECP**

Tel. +33 (0)4 67 22 40 95
Fax +33 (0)4 67 22 49 90

www.ecp-entegris.com

Publisher: Entegris Europe
Editor: Françoise Moign
Please contact francoise_moign@entegris.com for permission to reproduce Zero Defects articles

Entegris i2M Center for Advanced Materials Science



June 18, Entegris celebrated the grand opening of the i2M Center for advanced materials science.

"The i2M Center is a place where the most talented and creative materials scientists and chemical engineers can come together to solve some of the industry's most complex technical challenges. I look forward to seeing the breakthrough science and collaborations that emerge from this one-of-a-kind facility."

– Entegris' CEO, Bertrand Loy.

Entegris' i2M Center is one of the world's most advanced centers for the research, development and manufacturing of filtration media technologies and proprietary, innovative low-temperature coating technologies. These products are core components for filtration and electrostatic clamp (E-Chucks) solutions used in

semiconductor and other demanding manufacturing environments.

Located in the US (Bedford, MA), the 80,000 square foot i2M Center includes approximately 6,000 square feet of cleanroom space. Entegris has invested more than \$55 million in building infrastructure upgrades and equipment to create the i2M Center.

"i2M" stands for "ideas to market" and represents the focus of the new facility on innovation in the area of materials science. The i2M Center is home to approximately 100 employees, many of whom hold advanced engineering degrees in chemical engineering and related sciences.

- ▶ To view live key moments of this celebration, type #i2MCenter on [Twitter](#)
- ▶ To get an overview of the i2M Center, watch this video: [link](#)

Entegris @ SEMICON® Europa

This was the first year SEMICON Europa was hosted in Grenoble on October 7-9. This exhibit was very successful with an increase of 40% exhibitor space and 20% visitors.

For Entegris it was also a first positive experience to co-exhibit with the French [Minalogic](#) cluster.



Key highlights included presentations by Jorgen Lundgren – in the 3D and 450 mm sessions on the:

- ▶ Next Generation Contactless Shipping Solution – for bumped wafers/glass substrate (80 µm – 1100 µm thickness)

- ▶ FOUP (Pod) contamination control solutions for 200 mm, 300 mm and 450 mm substrates.

We thank you for visiting us and hope to see you next year in Dresden!



Cost Reduction

Customized Valve Manifolds Improve Tool Uptime on High-temperature Applications

By Marc Hanotte, Account Manager and Shane Collis, Regional Product Support – Entegris Europe

The aggressive chemicals required for semiconductor wet process applications have created challenges for ultrapure, chemically resistant polymers including shortened equipment lifetime, increased component replacement costs and reduced tool uptime. To combat these challenges, Entegris has developed a suite of fluid handling components that ensure high-performance operation and reliability in the most difficult environmental conditions.

STMicroelectronics® in Tours, France, recently achieved tool productivity improvements by introducing Entegris fluid handling components into their processes. The semiconductor fabrication plant uses a Piranha chemical solution, a blend of sulfuric acid and hydrogen peroxide heated to an operating temperature of 130°C to clean photoresist from wafers. The wafers are immersed in a tank, while the heated chemicals circulate throughout the tank.

Historically, wet benches were built with standard polymer-based valves and fittings. Although those parts were made of ultrapure fluorinated polymers, the elevated temperatures caused more frequent fitting leakage and valve failure. Some components within the valve tended to become deformed and damaged due to increased temperatures. These issues also occurred outside the wetted flow path because of the intense heat radiating from the Piranha chemical solution. Consequently, the sealing capacity of the components was compromised, causing the fluid flow pressure to be impacted. These components had to be replaced each time, causing numerous tool shutdowns lasting several hours.

▶ To avoid the costly tool downtime, STMicroelectronics addressed the situation to Entegris. The Entegris team proposed that STMicroelectronics replaced their standard valves and fittings with components designed for harsh operating conditions.

High-temperature Applications Valves

On the standard valve, some components are made of PVDF, because they are exposed neither to corrosive chemicals nor to elevated temperatures.

Entegris proposed the use of the Integra® DH12 valve (3/4" orifice), a component designed for elevated temperature applications. The diaphragm valve is constructed of either PTFE or PFA to improve chemical and thermal resistance. The DH12 valve consists of a stem and diaphragm comprised of a single PTFE component, as using fewer components improves the compatibility in aggressive environments (Figure 1).

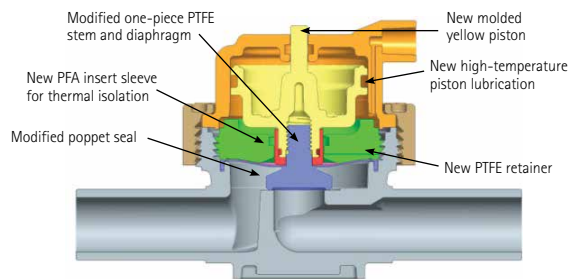


Figure 1: DH12 Integra Valve Cutaway View

PrimeLock® Connections

Entegris also proposed PrimeLock series fittings, a high-performance connection technology that significantly increases tool uptime. PrimeLock fittings are designed for use in elevated temperatures up to 200°C at 276 kPa (40 psig). An insert is assembled into the tubing of the fitting, and a primary face seal and three backup seals ensure leak-free performances (Figure 2).

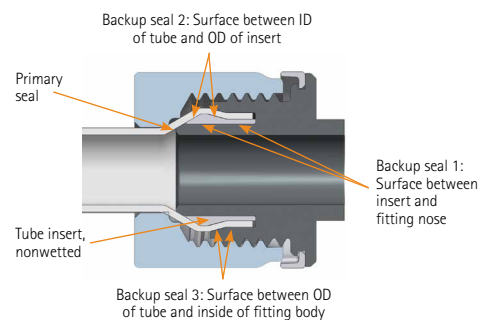


Figure 2: PrimeLock Cross-section, Three Back-up Seals

The insert, which is not wetted, is designed with a specific geometry that increases connection-sealing performance and reduces chemical entrapment and flow interruptions when compared to comparable wetted insert designs. All wetted parts are made of PFA, enabling broad a chemical compatibility.

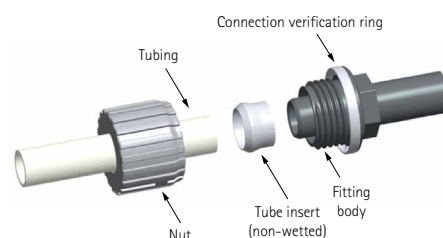


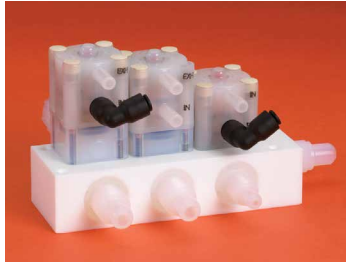
Figure 3: PrimeLock Fitting Design

(continued)

Cost Reduction

Dymension® Manifolds

Even with the best connection technology, reducing the number of fitting connection points is highly recommended to limit pressure drop and potential leak points. Moreover, **STMicroelectronics** engineers needed easier access to service and maintain the valves and to eliminate dead volumes within the flow stream.



Entegris proposed Dymension manifolds, which consist of multiple valves on a single component, allowing for fewer tubing runs and fitting connections. The valve type and inlets/outlet sizes can be customized for various application requirements. The considerable space savings and lower overall component costs surpass the benefits of STMicroelectronics' previous configuration.

Figure 4 shows an Entegris three - DH12 valve manifold with PrimeLock connections. The design includes a single 1" inlet and three 3/4" outlets. **The footprint savings (compared to three standard DH12 valves in parallel) is approximately 40%, and the resulting price is reduced by 15% with the DH12 valve.** Various manifolds were designed and manufactured, based on the STMicroelectronics specific requirements.

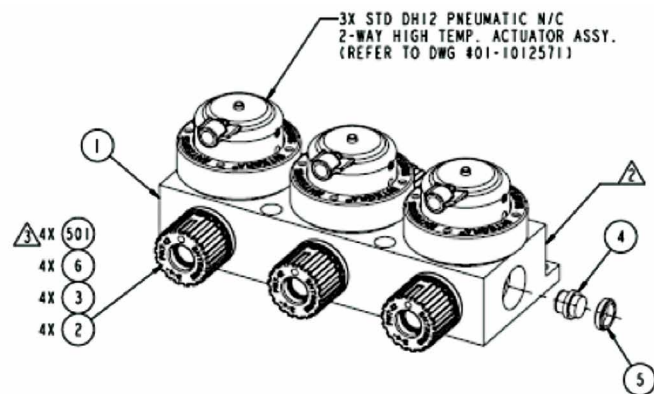


Figure 4: Dymension Manifold Designed for STMicroelectronics Tours

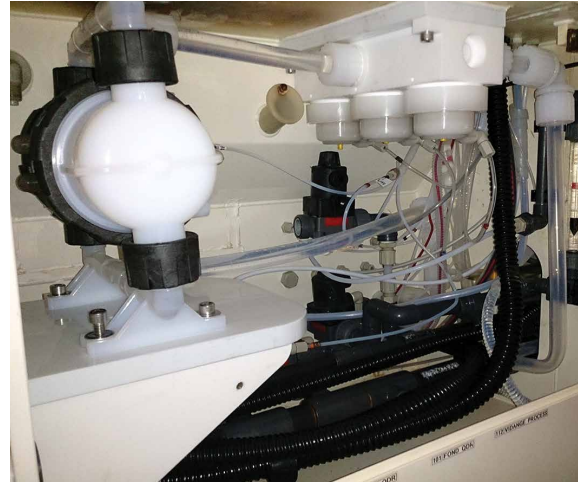


Figure 5: Dymension Manifold Installed in STMicroelectronics Tours Tool on Hot Sulfuric Acid

Conclusion

After employing these reliable, high-temperature solutions for over a year, **STMicroelectronics has achieved increased tool uptime and greater productivity** (Figure 5). They continue to research the use of customized manifolds to upgrade additional tools on other wet processes.

We acknowledge ST Tours employees who have worked on this project.

HF Contamination Control by Clean Gas Purge

By Paola Gonzalez Ph.D., Engineer Application Development | CEA-Leti Assignee - Entegris Europe

Front Opening Unified Pods (FOUPs) are designed as controlled microenvironments (MEs) that protect processed wafers from AMCs during storage and transport. However, it has been demonstrated that FOUPs are able to accumulate by sorption molecules outgassed by processed wafers. Such contaminants are then able to be subsequently released and transferred to other sensitive wafers, leading to detrimental impact. Microenvironments purge provides several advantages; for example, wafers are not easily oxidized thus preventing oxide layers, deposition of hydrocarbon compounds and metal defects. However, there is no measured information about the purge impact has on AMC control inside a FOUP.

► The purpose of this paper is to **show and quantify what effect two different FOUP polymers using nitrogen and clean dry air (CDA) purge have on the HF volatile acid control.**

FOUPs and Polymers Materials Tested

FOUP Tested	FOUP Platform	Shell Material	Wafer Capacity	Side Columns Material	Inner Door Material	Wafer Planes Material
EBM/CNT	A300	EBM/CNT	25	EBM/CNT	EBM/CNT	EBM/CNT
PEI/CNT	Spectra™	PC	25+1	PC	PC/CP	PEEK/CF

EBM: Entegris Barrier Material
 PC: ultrapure polycarbonate
 PEEK/CF: carbon fiber polyetheretherketone
 CNT: Carbon-nanotubes
 PC/CP: STAT-PRO® 500 carbon filled PC

Experimental

- FOUPs were first conditioned at cleanroom conditions (21°C, 45% RH). To contaminate the FOUP a 10 µL droplet of HF 2% is deposited into a PTFE cup, and then placed into the FOUP for 24 hours. Then after the 24-hour contamination, the FOUP is briefly opened and four 200 mm silicon wafers with a copper layer were exposed inside contaminated FOUPs in slots 11 to 14 using 300 mm silicon wafers as supports adding two additional 300 mm wafers in slots 10 and 15. Clean Cu surface was selected to quantify the HF transfer due to its quite higher affinity than any other surfaces (then no significant disturbance is expected due to Si supports).
- After the wafers were inserted the FOUPs were purged using 25 L/min of clean dry gas, i.e., CDA or nitrogen (HC < 100 ppb, H₂O < 10 ppb) for ten minutes and then the purge flow was set at 5 L/min for 24 hours. Same protocol of contamination and wafer storage was used in a non-purge test in order to evaluate the purge effect. A thermo/humidity sensor (TR-77Ui) was introduced into the FOUP through one of the outlet port purge of the FOUP.
- HF deposited on wafers was collected by a liquid phase extraction (LPE) of the surface using a low-volume of UPW and analysis of the solution by ion chromatography (IC). LPE-IC allows HF quantification as fluoride ion with low limits of detection better than 5E+11 ions/cm².

Results

► Non-purged results confirm the significant HF cross-contamination from contaminated FOUP to Cu-surfaces as well as the effectiveness of the Entegris barrier material (EBM/CNT) in comparison to polycarbonate with respect to the lower rate of HF transfer over stored Cu wafers, especially after the 24th hour of exposure (5.3E+13 vs 1.6E+14 F-atoms/cm²). Regarding the implementation of continuous purge (Figure A), the process has a dramatic reduction in the transfer of HF from the FOUP polymer to the Cu wafer. Indeed, contamination levels decrease about a factor ~33 over 24 hours for PC and no HF transfer is shown in the case of EBM/CNT.

► Once purge efficiency has been established, the next question is what kind of gas is better to use and today there are no technical data available about the difference between purge with nitrogen or clean dry air. CDA and N₂ purges were tested and are compared in Figure B in case of PC FOUPs. No significant difference is observed. Indeed, LPE-IC measurement uncertainties (reported as error bars) without taking into account that FOUP tested is not the same, handling, slight wafer position variation, etc., clearly shows this point. This means that the contaminant and humidity removal lead to control the HF transfer whatever the purge gas nature (on a centered 200 mm wafer).

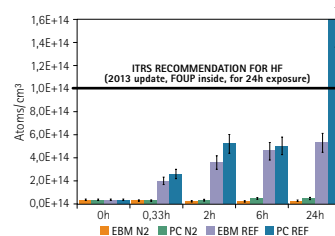


Figure A

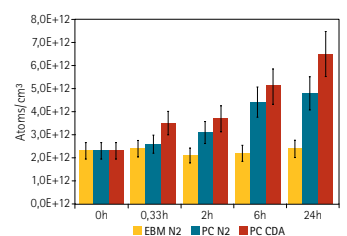


Figure B

Conclusion

Continuous FOUP purge appears as a very effective way to control HF cross-contamination and to guarantee an optimum yield thanks to low humidity, and chemically clean environment from the AMC point of view. In addition, the use of FOUPs made of barrier materials such as EBM/CNT allows complete control of volatile acids cross-contamination.

To reach a complete wafer environment control it is necessary to implement advanced solutions to address upper slot and wafer edge issues. One option to reduce both contamination transfer and upper slot effect could be the **Spectra FOUP configuration with 25+1 wafer capacity**, which allows the use of desiccant as a moisture getter (Clarilite® Purification Wafer). In addition, Entegris is currently developing new advanced solutions in terms of purge configuration (diffusers placed in the back side of the FOUP that offers a more homogeneous clean gas flow distribution) and the results of these new solutions will be reported in future communications.

Yield Improvement

A Reduction in Wafer Defects in IPA Solvent Drying Applications

By Tetsu Kohyama, Application Solution Development – Nihon Entegris K.K.

The IPA solvent drying process is one of the most important advanced wet cleaning steps because it's critical in reducing water marks after DI water rinsing steps. In general, IPA transport to the wafer has utilized stainless steel pipes. As a result, IC manufacturers have observed associated metal contamination including Cr, Ni and especially Fe. Removal of these metal ions has become increasingly critical as semiconductor manufacturing processes migrate to smaller technology nodes.

In this article we introduce a new, purpose-built purifier for IPA solvents, as well as a discussion of some history regarding the development of this product including associated challenges and solutions specific to the development of an IPA specific purifier.

Traditional Purification Solutions are Incompatible with IPA Processes

Traditional purifiers in the semiconductor market have been targeted at DI water. In a representative example, a legacy Entegris product designed as a general use purifier, the Protego® Plus, purifier was tested by a customer on wafers with an IPA drying process. Although the customer was able to confirm a reduction in metal ions, defects were observed due to particles from the purifier.

Particle Types and Implications for Purifier Design

Two types of foreign particles were observed: hard (Figure 1), and gel-like particles (Figure 2).

Hard particles are typically the result of an insufficiently robust cleaning process and defects are caused by adhesive particulates released onto the wafer. In contrast, gel-like particle formation is related to chemical compatibility. There is always some leeching of organic extractables from purifiers into any solvent, and even at trace levels, the concentration of particles due to evaporation can lead to defects on the wafer. These results underscore the importance of cleaning processes as part of the product manufacturing process as well as ensuring chemical compatibility of all components materials of construction with the target chemicals.

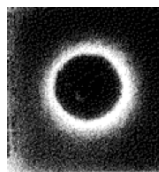


Figure 1: Solid Particulates

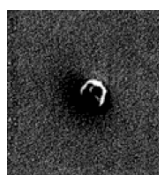


Figure 2: Gel-like Particulates

Protego Plus IPA

Based on experiences with the Protego Plus (DI water) in IPA, Entegris developed a new purifier: the Protego Plus IPA purifier, which was purpose-built for IPA purification. In customer testing, the particles described above were not observed on the wafer and yield was improved. The Protego Plus IPA purifier is the premier solution for IPA purification.

Discussion

The following table compares the Protego Plus (DIW) and the Protego Plus IPA purifiers. As previously described, even trace

extractables can cause defects on the wafer. While polyethylene is perfectly compatible in DI water and some solvents, it is not suitable for the IPA drying process due to chemical compatibility limitations between the polyethylene purifier membrane and the IPA solvent. The Protego IPA purifier addresses this with an all fluorocarbon polymer construction. **Fluorocarbon polymers are among the least reactive materials available and provide the best chemical compatibility. These materials, combined with an improved cleaning process to reduce residual particles, resulted in an exceptionally clean purification device, which delivered great improvement on yields.**

	Protego Plus	Protego Plus IPA
Materials	All Polyethylene	All Fluorocarbon Polymer
Cleanliness	NVR	⊙
	Metal Extractable	⊙
	Particle Shedding	⊙
Chemical Compatibility	○	⊙
Heat Stability	◇	⊙
Ion Exchange Capacity [meq/device]	For Cations 16 [1,000 cm ²]	For Cations 0.48 [2,000 cm ² /P1500] 0.18 [4,900 cm ² /P3000]
Metal Removal Capability	⊙	○
Life Time	⊙	◇
Main Application	DIW or Bulk Chemicals	IPA Drier

⊙ Excellent ○ Good ◇ Poor

Performance

The new Protego Plus IPA purifiers possess the same metal removal efficiency as the current Protego Plus purifier (see Figure 3). In part, because of their fluorocarbon polymer construction, the IPA purifiers demonstrate exceptional stability at high temperatures even when installed in close proximity to a heating element. Particle removal functionality was added to the purifier via a high-retention PTFE membrane to capture metallic colloid particles such as Fe.

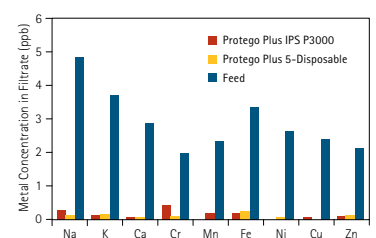


Figure 3: Protego IPA purifier shows an excellent metal removal performance

Conclusion

The Protego IPA purifier represents a first-of-its-kind purifier optimized for the IPA drying process, neutralizing a previously unaddressed source of contamination. Since its introduction, customer feedback has been favorable with demonstrated yield improvements on the customer's processes. Please reach out to Entegris with any questions on this solution or others.

Pressure Relief: 20 Years of Safety and Efficiency for Storage and Delivery of Highly Toxic Gases

By Al Botet, Director, Product Management, Specialty Gases & Delivery Systems - Entegris Inc.

Twenty years ago, the semiconductor industry accepted an innovation that dramatically improved safety conditions and increased process efficiency in the ion implant process of manufacturing semiconductors. Today, that innovation has become the optimal method for storing, transporting and delivering toxic or corrosive gases for implant applications.

Hazardous gases are used in a number of semiconductor fabrication process steps in the semiconductor industry. Traditionally, this was accomplished by compressing the gas in conventional high-pressure gas cylinders. While high-pressure cylinders are still widely used today, it is no longer the preferred method for storing and delivering the most toxic gases, where an accidental gas release or a compromised cylinder could lead to immediate death for workers in the area. The alternative implant delivery system uses a medium that adsorbs (or bonds) gas molecules inside nano-size pore structures in the cylinder, effectively reducing cylinder pressure and virtually eliminating accidental gas releases.

This technology was first introduced by Advanced Technology Materials, Inc. (ATMI) under the brand name Safe Delivery Source®, or SDS®, in the early 1990s as a much safer way to store and deliver dangerous gases. Today, ATMI's advanced cylinder-based systems known as SDS 2 and SDS 3 (now owned by Entegris, Inc.) are often the methods of choice to deliver toxic hydrides (arsine and phosphine) or corrosive gases (such as boron trifluoride).

Gas Adsorption and Intrinsic Safety

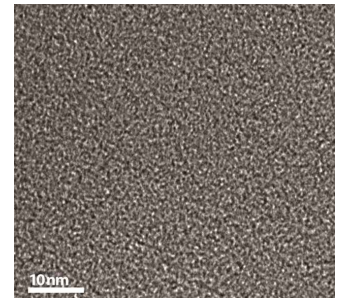
Inside traditional high-pressure gas cylinders (for example oxygen, propane and helium tanks), gas molecules are free to move and collide against the inner walls of the vessel pressurizing the system. With these pressurized cylinders, a simple turn or push atop an unconnected cylinder can open the cylinder valve. Once open, the pressure conditions inside the cylinder force the gas through the valve and out of the cylinder. This, of course, is not optimal for handling lethal gases, but years ago it was common.

In the SDS system, **molecular gases are weakly bonded (adsorbed) inside the surfaces of nanoporous BrightBlack® carbon material**, also developed by ATMI.



SDS cylinders remove the pressure of standard high-pressure cylinders by filling the interior space with nanoporous BrightBlack carbon pucks that adsorb gas molecules and create a sub-atmospheric (less than room pressure) gas environment. This technology and approach virtually eliminates accidental release of dangerous gases.

These adsorption forces allow the material to capture the gas molecules on its surfaces, reducing the pressure inside the cylinder to below atmospheric conditions. Process conditions inside the ion implant process reactor that will use the gas provide adequate negative pressure to pull the gas molecules from the carbon into the process chamber. **This type of cylinder technology and gas delivery system has greatly reduced the amount accidental gas releases in the semiconductor industry—potentially saving lives in the process.**



Magnified look at the surface structure of BrightBlack precision carbon adsorbent in the round puck form. Special thanks to Dr. Georgina Laredo at IMP for the use of this Micrograph.

Regulatory Bodies Have Acknowledged SDS

When it comes to SDS technology, chip manufacturers were not the only group to have noticed. Several regulations and codes have been updated and/or changed, especially related to how an SDS system holds and delivers gas. In fact, the National Fire Prevention Association created a new classification for SDS cylinders, calling them sub-atmospheric gas systems (SAGS), which is now part of the International Fire Code. And more recently, the United Nations' Sub-Committee of Experts on the Transportation of Dangerous Goods (SCETDG) acted to amend the "U.N. Model of Regulations for the Transportation of Dangerous Goods" (Model of Regulations) to create the new "Adsorbed Gases" condition of transport classification. The 18th revised edition of the regulations also added 17 new proper shipping names and U.N. numbers to allow expanded transportation options for adsorbed gas materials and packages, such as those using an SDS type of technology.

Delivering on the Promise

As SDS technology continues to enable safer, more efficient, less costly operations, semiconductor manufacturers continue to leverage it. While other approaches try to emulate the physics of the SDS nanotechnology by using mechanical-based systems, none can compare to the intrinsically-safe capability of the SDS system. Often, new solutions are slow to be adopted, but in the end, if they prove their worth, they become the new industry standard and realize their potential. That's how it unfolded over 20 years for SDS technology. **And it's all because a nanoporous carbon material relieved the pressure of dealing with dangerous gases and rendered them safer to use.**

Product Highlight

Advanced Filtration Solutions with Improved PTFE Membranes: Fluorogard® FP/FP-HP and FluoroLine® DF Plus Filters

Entegris recently launched two liquid filtration solutions constructed with improved PTFE membrane: Fluorogard FP/FP-HP and FluoroLine™ DF Plus filters.



Constructed with polypropylene supports and rugged PTFE membranes, Fluorogard FP/FP-HP deliver enhanced durability and superior cleanliness in point-of-use (POU) and chemical delivery system (CDS) filtration applications. The filters, available in retention rating from 0.02 µm to 10.0 µm, efficiently remove critical defect-causing particles to improve yield and increase process reliability.

Features and Benefits

Durable PTFE fluoropolymer resin and polypropylene construction	<ul style="list-style-type: none"> Reduces particle contamination with superior downstream cleanliness and faster startups Contains low levels of organic and metallic extractables Ensures longer filter life and excellent chemical compatibility
Retention ratings from 0.02 µm to 10.0 µm	<ul style="list-style-type: none"> Can be used in a wide variety of process chemicals in bulk or point-of-use applications Removes critical defects
Available with hydrophobic (Fluorogard FP) and hydrophilic (Fluorogard FP-HP) PTFE membranes	<ul style="list-style-type: none"> Eliminates the need for time-consuming prewetting steps Ensures lower operational costs, improved yields and process reliability

FluoroLine DF Plus disposable filters deliver excellent particle retention and flow rate capabilities for liquid crystal (L/C) chemical filtration in flat panel display manufacturing applications. With its unique core design, the filters eliminate air bubbles and provide superior chemical resistance during one-drop-filling (ODF) process.



Features, Advantages and Benefits

Improved PTFE membrane	<ul style="list-style-type: none"> Excellent chemical compatibility Good wettability with L/C Better flow rate Better retention 	<ul style="list-style-type: none"> Clean filtration for liquid crystal chemicals Strong flow performance at start up Decreased bubble generation High resolution requirements Lower particle defects
Optimized core design	<ul style="list-style-type: none"> More open window for L/C flow path 	<ul style="list-style-type: none"> Improved flow performance
PFA molded parts	<ul style="list-style-type: none"> Excellent chemical compatibility 	<ul style="list-style-type: none"> Clean filtration
Filter with buffer tank	<ul style="list-style-type: none"> Filtration and trapping bubbles 	<ul style="list-style-type: none"> Minimized bubble issues



Feedback

We value your feedback and suggestions to help us improve Zero Defects. Please send your questions, suggestions and comments to europa_region@entegris.com

If you would like more information regarding Entegris products and services, please contact your customer service centers (page 1) or refer to Entegris on-line at www.entegris.com

Free subscription Form

email to europa_region@entegris.com
fax to +33 (0)4 76 35 73 80

Zero Defects Entegris Newsletter

Name*: _____ Job title*: _____

Company name*: _____ Dept: _____

Address: _____

Postal code: _____ City: _____ Country: _____

Tel. : _____

E-mail*: _____

Send me the Zero Defects pdf file

Send me the direct link to Zero Defects

* required to complete

Entegris® and the Entegris Rings Design®, creating a material advantage®, Fluorogard®, FluoroLine®, Integra®, PrimeLock®, Dymension®, Spectra™, STAT-PRO®, Clarilite®, Protego®, BrightBlack®, Safe Delivery Source® and SDS® are trademarks of Entegris, Inc. SEMICON® is a trademark of Semiconductor Equipment and Materials International Corporation.

STMicroelectronics® is a registered trademark of STMicroelectronics, Inc.
Lit. #: 9000-7688ENT-1014EU
©2014 Entegris, Inc. All rights reserved.