Next Generation Safe Delivery Source® (SDS®4) Dopant Material Storage and Delivery Package

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Abstract *– The Entegris Safe Delivery Source® (SDS®) package has been the leader in providing subatmospheric specialty gas storage and delivery for ion implant dopant materials since its inception more than twenty years ago. As semiconductor devices advance, increased demands are placed on the purity, productivity, and safety of electronic gases. SDS4, the fourth generation of the SDS product line is designed to address these increasingly stringent demands. This paper presents key advancements in adsorbent-based packages for storing, handling, and delivering semiconductor dopant gases. Desirable characteristics and properties of adsorbents for use in this application are reviewed. The screening methodology and performance of various carbon and metal organic framework (MOF) adsorbents are evaluated against these characteristics. Further discussion is included on the testing, design, and selection of cylinder features to continuously improve the SDS product line, making SDS4 the safest and highest performing sub-atmospheric storage and delivery package to-date. Final product performance is demonstrated and verified through beamline ion implantation tool data.*

Keywords *– Ion implant, specialty gas, dopant, SDS, SAGS, carbon, metal organic framework, MOF*

INTRODUCTION

Subatmospheric gas storage and delivery systems, referred to as SAGS Type 1[1], were developed by Entegris and have been used to deliver gases in ion implant processes for many years under the tradename of SDS®. This technology stably and reversibly adsorbs pure dopant gases on an adsorbent substrate contained within a cylinder package. The SDS platform has been adopted industry wide and has proven to combine inherent gas cylinder safety with adsorption technology in an effective way to allow end users to safely deliver highly toxic materials, driving greater ion implant process efficiency.

As semiconductor nodes advance there is a need to continue to improve both the safety of the gas cylinder system as well as provide advancements in the features that have proven to be historically successful in this application. In this paper, we detail critical factors for selection of an adsorbent for the SAGS 1 application and introduce an improved performing carbon adsorbent found in SDS4. Also included in this paper are technical data generated during the development of new cylinder technology to provide a delivery package that has industry leading particle filtration capability and safety features.

CHARACTERISTICS OF SAGS1 PRODUCTS AND ADSORBENT SELECTION FOR IMPLANT DOPANTS

There are many characteristics of adsorbent-based gas delivery systems that must be met to effectively fulfill process application requirements. To accomplish this the adsorbent that is chosen must meet certain requirements to not only safely store these materials, but also to ensure that there is no unintended reaction of the adsorbate gas with the adsorbent that could result in either a decrease in performance or the generation of an impurity that could result in process issues.

For SDS4, the key mechanism driving subatmospheric gas storage and delivery is physisorption of gas molecules within a microporous adsorbent structure contained within the cylinder. Free flowing gas molecules are drawn into the microstructure wherein they are held by Van der Waals forces in close proximity, approaching the density of a liquefied gas. There is no chemical reaction or bonding between the gas and adsorbent. Gas molecules are neither broken nor complexed. Thus, the gas molecules can be extracted in an unchanged and high purity condition.

During the development of SDS4, the landscape of microporous adsorbents was evaluated for use in a SAGS I application; included in this screening was the use of MOF materials. MOFs are synthetic crystalline complexes that are formed by selecting a transition metal ion cluster or salt and linking the metal clusters with an organic ligand to form a porous cage-like structure capable of adsorbing the electronic gas. The production of these adsorbents often requires the use of a templating solvent during precipitation, followed by washing and drying steps. Maintenance of the crystalline structure can often be difficult during solvent removal and drying, in addition scalable and reproducible manufacturing processes are scarce.

Additional considerations such as density, toxicity of the adsorbent itself (particularly for MOFs), sensitivity to moisture, thermal instability, low volumetric adsorption and delivery capacity, gas contamination with trace metals, friability, particle generation, pressure instability, large undeliverable gas retention, transition metal reactivity, and decay of capacity and performance with cyclic filling/dispensing was considered when selecting the optimum adsorbent and should be assessed by the end user when considering a gas delivery system in the application.

Figure 1 provides an example of a test performed by Entegris to assess the pressure stability of phosphine stored on the improved SDS4 adsorbent along with several different MOF materials. As can be seen in the chart, the phosphine pressure for the SDS4 adsorbent is stable at the fill pressure over the entire testing time. This is related to the chemical inertness and physisorption mechanism that is employed by the SDS4 adsorbent. In contrast, several of the tested MOFs such as MOFs "K", "B", "E", and "G" shown in Figure 1 have substantial pressure changes, and in the case of MOF "K" the pressure went super atmospheric. The cause of the pressure increase is due to reaction of the phosphine with the MOF; this was confirmed through GC analysis which showed reaction by-products.

Pressure Stability of PH_3 in 50 cc Adsorbent Canisters @21°C (Post-fill to 650 Torr)

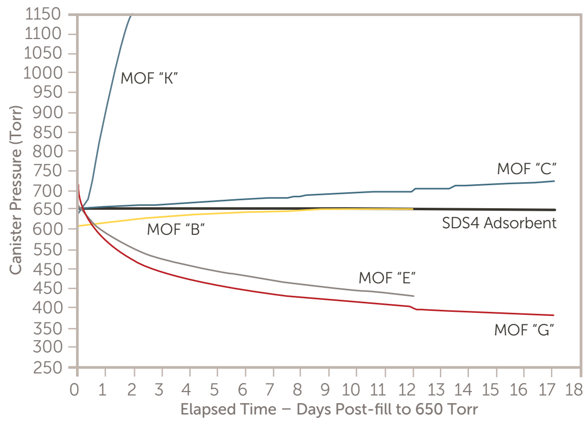

Figure 1. Comparison of pressure stability of SDS4 versus various Metal Organic Frameworks.

This is a clear indication that in certain instances there is a chemical reaction occurring between the MOF and the electronic gas. This is not wholly unexpected given that transition metals are known to be highly reactive. Inspection of the MOF materials after this test showed significant color change, further confirming that a reaction occurred and resulted in an oxidation state change of the transition metal.

In semiconductor applications where the process is sensitive to any contaminant it is the utmost importance to select an adsorbent that does not display any reactivity with the adsorbate gas, nor displays any signs of chemisorption as the mechanism for gas storage. The improved carbon utilized in SDS4 is inert, stores gas via physisorption, and exhibits long-term stable cylinder pressure for arsine and phosphine that makes it the optimal choice for storing electronic gases used in ion implant.

CAPACITY

The widespread popularity of SAGS I packages can partially be attributed to the large amount of gas delivered per unit of volume. When working within tight space constraints, such as the gas cabinet on an ion implanter, the optimal adsorbent for gas delivery is a high density microporous material. Having high surface area or gravimetric capacity is not enough if the density is low. Figure 2 shows the impact of bulk density on the volumetric capacity of various carbon adsorbents versus the tested MOFs for phosphine.

Deliverable Phosphine Capacities – 650 to 5 Torr

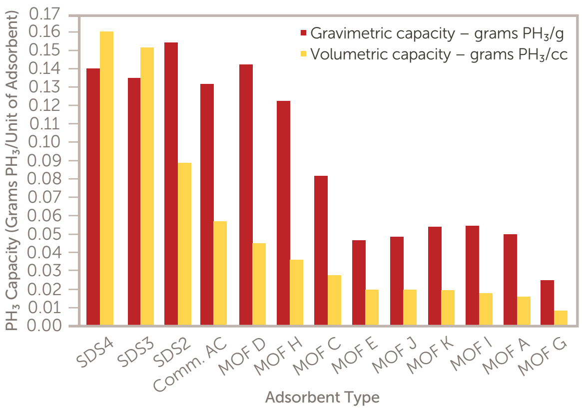

Figure 2. Comparison of gravimetric and volumetric capacity of various adsorbents.

As can be seen in Figure 2, SDS4 carbon has the highest volumetric capacity of any of the adsorbents considered. In SDS4 the carbon is further optimized and utilizes the SDS foundation of a highly pure, high density microporous adsorbent with a pore size distribution that is optimized for the gases to be adsorbed. The SDS4 adsorbent is a highly uniform microporous material with a very high bulk density that can be shaped into monoliths or space filling forms. This has enabled SDS4 to have the highest gas deliverables over any commercially available alternative. The SDS4 platform provides various options for scaling deliverable material quantity to meet process requirements for cylinder change out intervals. Standard cylinder sizes include a 2.5 liter option and a 7.6 liter option having a larger diameter and height, providing approximately three times the deliverable quantity. By taking advantage of the modular carbon monolith design, the 2.5 liter cylinder height and internal carbon stack can be scaled to increase the deliverable material quantity by up to 30%.

PURITY

Increasingly stringent demands and controls are placed on raw material suppliers to provide reliable, stable, high purity materials for electronic device manufacturing processes. Entegris has addressed this demand with SDS4. Adsorbent purification methods and processes have been developed through an extensive series of tests and designed experiments. The continued use of robust and chemically inert carbon adsorbent common to SDS3, combined with advanced handling and processing techniques has enabled an improved final product purity for SDS4.

While evaluating various adsorbents, a screening experiment was conducted on the improved SDS4 adsorbent along with a zinc based MOF for the presence of volatile metals in the gas delivered from the cylinder. The liberation of metals from an adsorbent should be a consideration, especially when evaluating a MOF as not only can the transition metal be reactive, the crystalline structure can break down due to changes in temperature or vibration during cylinder transportation.

Metals testing was performed by an independent third party utilizing ICP-MS as the analytical technique. The results show that zinc was not present in the SDS4 sample, however it was in the zinc based MOF at a level of 13X the detection limit.

This result shows the potential for the metal in the framework to be volatilized and liberated from the gas cylinder that could present a contamination issue in the application. It should also be noted that this laboratory test should be considered as an ideal condition as the MOF cylinder was not exposed to typical transportation conditions which include vibration and elevated temperatures that often occur during normal shipment. For SDS4 the carbon monolith is robust to these transportation conditions and has been proven in SDS3 usage not to break down over the lifetime of the cylinder.

Another aspect of achieving high device yield is the mitigation of particle shed from the adsorbent and cylinder. The SDS4 monolith adsorbent is robust and does not break down over use, however other potential adsorbents in a beaded or powder form, such as MOFs, may be more apt to shed particles. An extra level of protection against particle migration is employed with SDS4 via the utilization of an ultra-high efficiency outlet filter featuring an improved particle size rating. The broad capabilities of Entegris have been leveraged to develop a filter in-house specifically for SDS4. This filter features a grade of 3 nanometers with a log reduction value of 9 for the retention efficiency of particles greater than 10 nanometers at a flow rate of 10 standard cubic centimeters of air per minute. Testing has shown this filter to be capable to meet the flow and cylinder end-point requirements of the ion implant processes while still offering a significant improvement in filtration efficiency.

With the ultra-high material purity demands of the semiconductor market, one must consider potential sources of contamination of the entire system, not just the raw incoming material. A key, yet easily overlooked, aspect of this is the efficient cycle purge and evacuation of the dead volume up to the cylinder valve. The valve internal area between the valve closure sealing seat and valve outlet is one potential location that can greatly impact the efficacy of a cycle purge while changing a source cylinder. This section of a valve can contain complex features that can trap contaminants, especially when combined with the repeated cyclic exposure between process gas while in-use and wet atmospheric air during transportation. It is common for specialty gas cylinders to feature high integrity Stainless Steel Ultra-High Purity (UHP) diaphragm valves, but there are design differences that could affect performance. Many UHP diaphragm valves, as depicted in Figure 3, have a large internal wetted volume and surface area containing return springs, seats, and other components. The SDS4 valve, shown in Figure 4, features a tied-diaphragm design, where the diaphragm is mechanically linked to the valve handwheel spindle, eliminating the need for these internal wetted components. Utilizing this valve design reduces the valve's internal wetted volume by 40% and its' wetted surface area by 68%. This reduces the amount of contamination that can accumulate in this area, thereby improving safety, cleanliness and process purity.

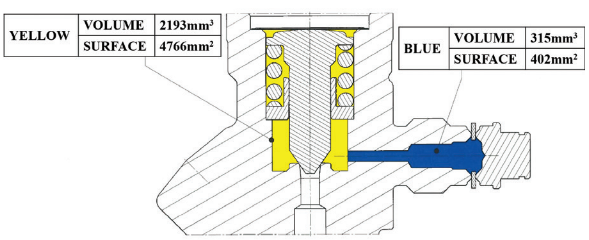

Figure 3. UHP valve cross-section showing internal components.

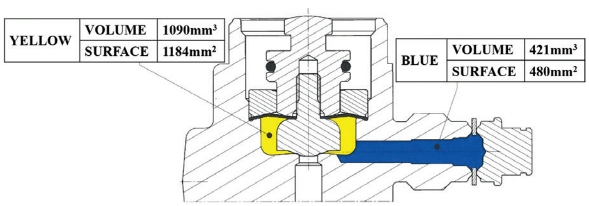

Figure 4. SDS4 valve cross-section showing improved design with decreased wetted volume.

SAFETY AND CYLINDER PACKAGE IMPROVEMENTS

Due to the extremely hazardous nature of many electronic gases, safely storing and delivering these materials is an utmost priority. To this respect, testing and theoretical calculations have shown SDS cylinders to nearly eliminate the potential of a hazardous gas release[2]. The need for safe material handling is even more important when considering the point of use in ion implant gas boxes. While designing the SDS4 package, every opportunity was taken to continuously improve and extend this safety record into the next generation of this technology. One key improvement that has been developed for SDS4 is a visual valve open/closed indicator.

Entegris has worked closely with the valve supplier to develop an application-specific valve state indicator for ion implant cylinders. Depending on the design of ion implant gas boxes, cylinders can be installed in either an upright vertical or laying down horizontal orientation. This variation in orientation was accounted for during the valve development and has resulted in a valve indicator that can be viewed from the top or side orientations as shown in Figure 5.

Figure 5. Depiction of SDS4 valve with open/closed indicator to communicate valve seat position.

The indicator is tied directly to the valve seat position and will display the state of the valve in both a text form ('Open' or 'Closed') as well as provide color indication (red = closed and green = open). Though SDS4 inherently limits the release potential, this added feature protects against inadvertent mis-operation and provides a real-time indication if the valve is open or closed. The SDS4 cylinder design includes other features such as QR codes, allowing for real-time data to be communicated to the cylinder user when needed, increasing the safety and efficiency of cylinder handling. The QR code can be scanned using any smartphone to retrieve important product documentation such as the MSDS or user guide.

The safety of a specialty gas cylinder package needs to be considered over the entire service life as it is subject to years of variable conditions throughout its use in the field. The new valve design utilized on SDS4 features a dual-seat design with a primary soft closing seat ensuring a reliable leak-tight closure and a secondary hard seat providing protection against over-torqueing the handwheel, which can potentially damage the sealing components. All valve designs are tested by the manufacturer per existing Compressed Gas Association (CGA) standards, however Entegris has expanded upon this, developing in-house accelerated cycle testing capability to verify valve performance and longevity under various process application conditions. It is critically important that hardware design decisions made at the time of product release be tested to confirm reliability throughout the full product lifecycle. This capability is one aspect that confirms component selections are reliable and robust to variations of use. Figure 6 shows an example of this testing output where the valve is subjected to repeated open/closed cycles while the torque and downstream pressure is monitored for any changes. This is then followed by periodic helium leak checking to ensure continued valve seal integrity.

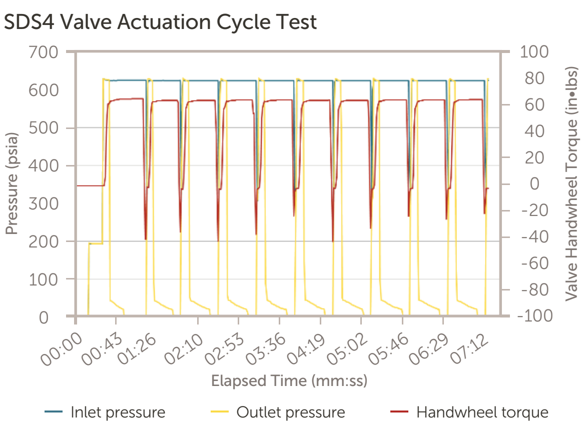

Figure 6. Example of reliability testing performed on SDS4 cylinder valve to ensure robust operation over intended cylinder service life.

APPLICATION VALIDATION OF SDS4

With the potential for any material change to cause subsequent undesirable impact to downstream wafer production, Entegris has provided several SDS4 Arsine and Phosphine cylinders to the field for validation and qualification. Feedback has shown comparable As+ and P+ beam spectra to SDS3 as shown in Figure 7 and 8. No beam glitching was observed.

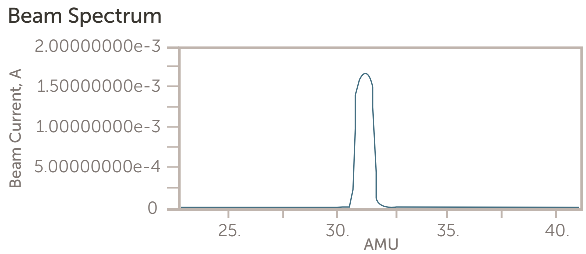

Figure 7. P+ Beam spectra from SDS4 PH_3 source.

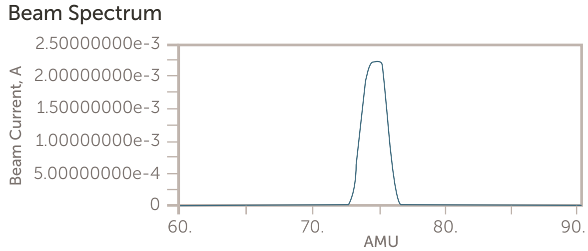

Figure 8. As+ Beam spectra from SDS4 AsH_3 source.

Vapor Phase Decomposition Inductively Coupled Plasma Mass Spectroscopy (VPD-ICPMS) analysis for trace elements matched with the control tool with all results well below an upper limit of 5E11 atoms per centimeter squared.

Measured sheet resistivity of samples generated from these sources also matched within 1 ohm of the control tool. In addition, Secondary Ion Mass Spectroscopy (SIMS profiles were run for both SDS4 arsine and phosphine and compared to the respective SDS3 controls, as shown in Figure 9 and 10. Particle monitoring test results for SDS4 were also slightly lower and matched within 1.5% of the control tool.

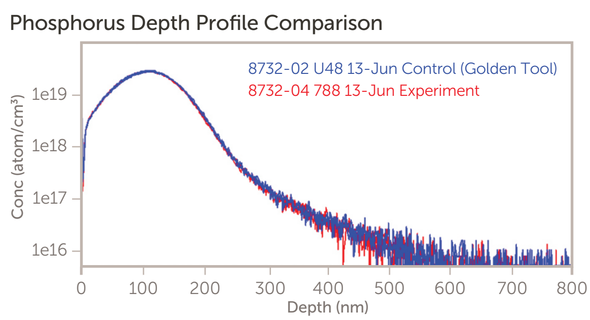

Figure 9. SIMS profile for SDS4 PH_3 in comparison to SDS3 PH_3.

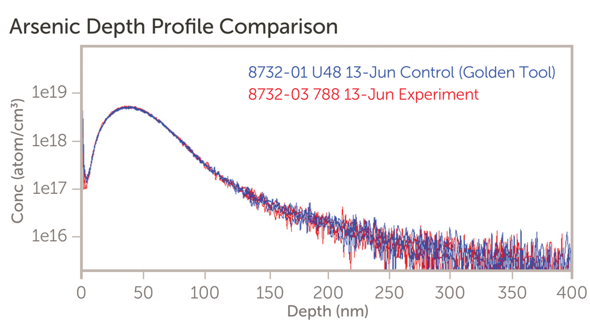

Figure 10. SIMS profile for SDS4 AsH_3 in comparison to SDS3 AsH_3.

CONCLUSION

Entegris has utilized its extensive historical product and application knowledge combined with a broad internal capability in material science and hardware design to develop the next generation Safe Delivery Source. A wide array of microporous adsorbents have been considered and screened based on the requirements of the ion implant application and these results show that the SDS4 carbon adsorbent is the best candidate for this application. Advanced handling and carbon media purification processes have been developed to enable improved purity and capacity. The SDS4 cylinder package has been carefully designed for unparalleled safety, performance, and reliability. Design characteristics have been confirmed through internal and external product testing at multiple customer sites, where the performance was validated, confirming SDS4 exceeds ion implant application requirements.

REFERENCES

[1] International Fire Code (2012), *Semiconductor Fabrication Facilities*. Section 2703.16.

[2] Despres, J. et al., *Gas Cylinder Release Rate Testing and Analysis,* ATMI, IIT 2012.

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