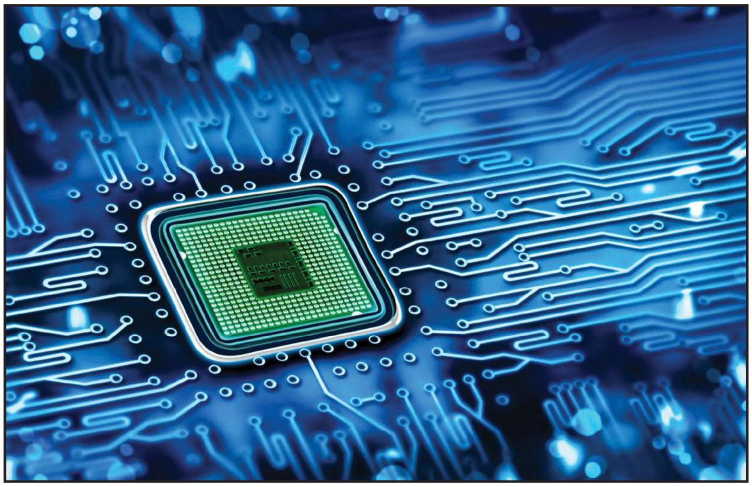
IES Technical Sales
A Gallagher Vacuum & Semiconductor Company

Perfluoroelastomers for the Semiconductor Industry

White Paper

The semiconductor industry, one of today's major industries, produces integrated circuits (chips) which have found their way into everyday devices from toasters to smartphones to high speed computers. Integrated circuits are expected to perform operations faster and faster while attaining ever higher levels of reliability. As these chips become more complex and powerful the process for their manufacture becomes more complicated. Years ago a chip may have gone through 100 steps as underlying circuits were constructed. Now chips may go through more than 400 steps and the complexity of these circuits, and their capability, has greatly increased. This also results in more opportunities for problems during manufacture. Line widths, the width of the electrical pathways, have decreased in order to pack more capacity into each chip. This dictates that contaminants from the production equipment, gas streams, seals, etc., must be essentially eliminated to avoid contamination and chip malfunction.

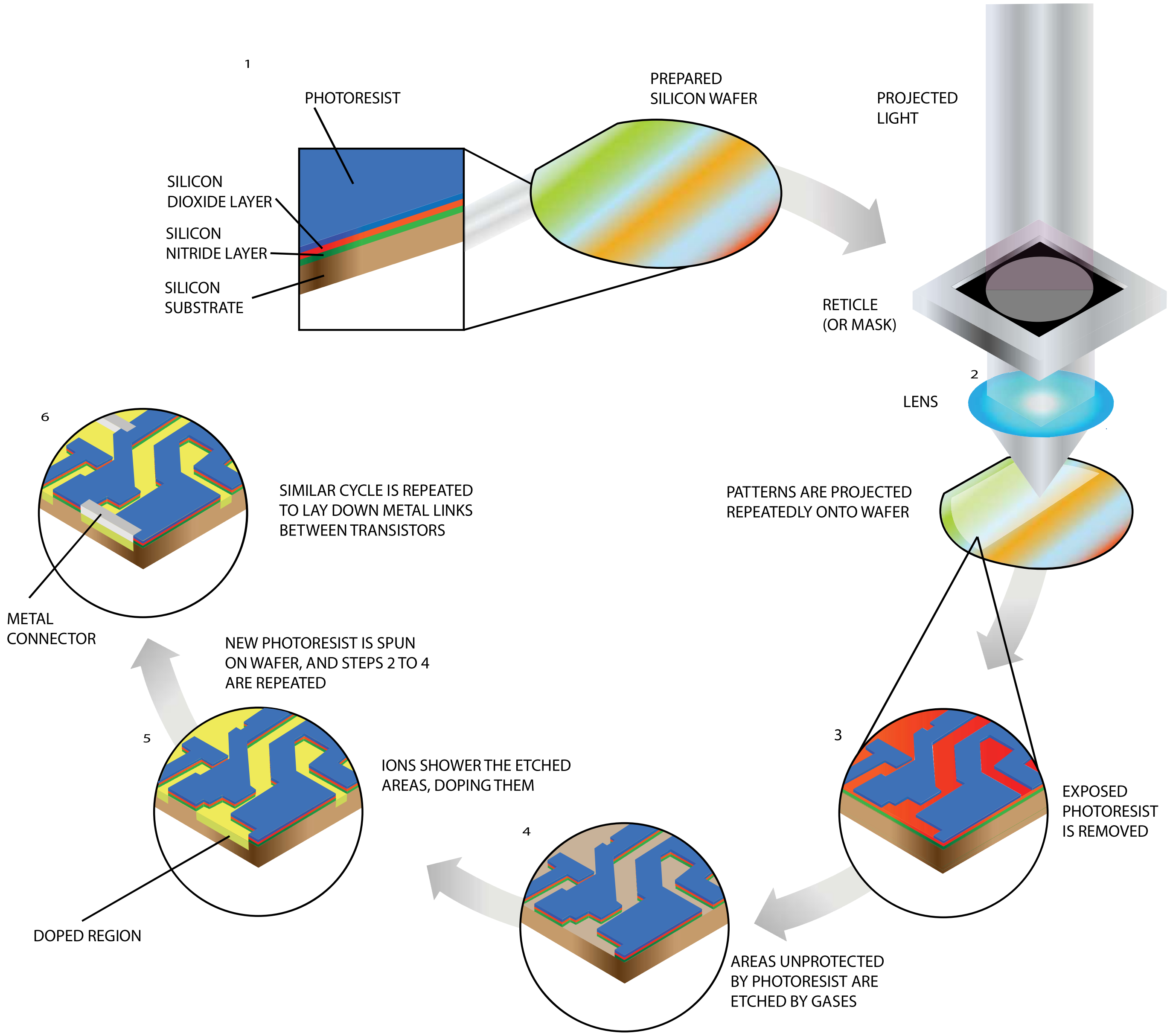


As processes become more complex, the need for continuous evaluation of equipment quality and cleanliness increases. One part of this equipment that has received much attention is the elastomer seals which are critical for maintaining an airtight seal for many different processes in plasma, thermal and wet manufacturing applications. These processes include deposition, etching, and cleaning. Unfortunately the elastomer seals can be degraded by the aggressive chemicals in the manufacturing equipment. Further, as manufacturing processes raise temperatures and use more exotic chemicals to improve throughput, the elastomeric seals must continue to function without incident. Perfluoroelastomers (FFKMs) continue to see increased use due to their high temperature capabilities, low contamination and chemical resistance when compared to other elastomers. Product yield continues to be a major factor in chip production, hence a premium is placed on high performance elastomer seals as well as manufacturing equipment.

This paper will briefly review several specific semiconductor processes. The purpose is not to teach semiconductor chip manufacture, but rather to explain how and why perfluoroelastomers are used.

Basic Semiconductor Process

The following is a simplified process chart for chip manufacture in the semiconductor industry:



Following the process shown above:

1) A silicon wafer has been prepared from an ingot by cutting and polishing. The wafer then has layers of material applied. These include a silicon oxide layer, a silicon nitride layer and a layer of photoresist.

2) A light is then projected through a reticle and a lens unto the wafer surface. This pattern is projected

numerous times onto the wafer for each chip.

3) The photoresist that was exposed to the light can now be chemically removed.
4) The areas where the photoresist has been removed can now be etched, which in the case above, is done by gases.
5) An ionic gaseous stream showers the chip and "dopes" those regions that were exposed due to etching. New photoresist can be applied to the wafer and steps 2-4 are repeated.
6) In a similar repeated cycle, metal links can be laid down between transistors.

Every step of the process requires elastomer seals to isolate the process from the outside atmosphere. The processing environment is very aggressive and often requires high performance perfluoroelastomer (FFKM) seals for longer service life.

There are three standard processes that are used to accomplish the above tasks: plasma process, thermal process and wet process. Each has unique requirements for seal use and performance. This discussion will focus on elastomer, and more specifically, perfluoroelastomer seals in these applications.

Plasma Process

This is one method to accomplish a number of the steps outlined above. In this process, a remote plasma source generates a plasma gas. Note that this type of process is run in a vacuum environment. This gas is composed of ions, electrons, radicals and neutral particles. The flow of these particles must be carefully controlled for etching, deposition, or ashing/stripping processes. These processes often use oxygen, fluorine, and other exotic plasma gases, which are extremely aggressive to many materials. In addition, cleaning processes often use oxygen plasma. Precise control of the plasma gas in the chamber is critical so processes perform as expected, for all the individual chips, across the entire diameter of the wafer.

In plasma processes, which typically operate under a high vacuum, FFKM seals can be critical for maintaining system integrity and providing a long seal life. The term "long seal life" is relative. However these seals must perform at high temperatures, up to 250°C, and still maintain low offgassing and low particle generation to prevent contaminating the manufacturing process. In some cases, under extremely aggressive conditions of plasma gases and high temperatures, 6-8 weeks may be considered a long service life for an elastomer seal.

Perfluoroelastomer Seal Requirements in Plasma Processes

Depending on the elastomer seal location, different performance requirements may be needed. Close to the plasma source and leading up to the wafer, numerous ions are present in the plasma gas, making this a "physically" aggressive environment to the elastomer surface. When the ions directly bombard the elastomer surface, they can physically erode the polymer. In these locations, some type of filled elastomer is preferred. Unfilled elastomer seals may degrade too quickly, resulting in a leak. Unfortunately the use of a "standard" filler, such as carbon black, is not suggested. When a carbon black filled elastomer is eroded away, carbon black particles are released and can land on the wafer and cause short circuits in the electrical pathways of chips. In recent years, the development and use of polymeric fillers has provided increased protection to the elastomer polymer backbone while eroding away cleanly and not causing chip contamination. For example, DuPont™ Kalrez® 9100 o-rings utilize a polymeric filler for improved resistance to plasma gases and extremely low contamination.


DuPont™ Kalrez® 9100 O-Ring

Other particles in the plasma gas are also present in the plasma stream. However these particles, for example radicals, are considered less aggressive and are sometimes referred to as "chemical" plasma. These particles can still erode the elastomer surface, but at a slower rate than ions. Elastomers seals that are further from the plasma source, not directly in line with the ions generated by the plasma source, or the chamber area below the wafer will mainly see this type of exposure. Seals in this area still need to be "clean", however non-filled or lightly filled elastomers may be used here because surface erosion is lower. Finally, for the exhaust piping, elastomer cleanliness is of less concern since any elastomer particles generated should be swept out of the system with the exhaust gas.

In plasma processes, especially deposition, material will eventually build up on the chamber walls. The chamber then requires a cleaning process, typically an aggressive plasma gas to strip away the deposits. These gases may include oxygen plasma, which can be extremely harsh on elastomers by attacking the elastomer surface.

Plasma Process Applications

Elastomers can be used in a variety of sealing applications. These applications include: chamber lid seals, window seals, centering rings for flanges, exhaust valves, door seals, valve seals, and as cushioning for wafer transport. These applications have different requirements, so understanding the exact needs for each type of application can maximize service life and yield optimal elastomer performance.

Door Seals

These seals can also pose problems a number of problems for elastomers. Door seals usually offer one of two options regarding the seal. In the first case, the door contains a groove, into which an elastomer seal (usually an o-ring) is inserted into a dovetail groove. In the second case, the elastomer seal (cross section can vary) is permanently bonded to the door. Each case is reviewed separately below. Note that many of the concerns regarding door seals are similar to those for other types of seals such as gate or pendulum valves.


DuPont™ Kalrez® Bonded Door Seal

Door seals that contain a groove into which a circular cross section elastomer seal is inserted allow for easy replacement of the seal when required due to leakage or particle generation. The seals itself is often an o-ring. Unfortunately the action of the door, when opening or closing, often causes the o-ring to move or roll slightly, which can result in particle generation. In addition, if there is any sticking between the o-ring and the metal against which it seals, the o-ring may partially pull out of the groove when the door opens. This can result in pinching and damage to the o-ring seal the next time the door closes.

Finally, o-rings are not often the best choice for door seal grooves, which have a racetrack design. The use of o-rings can result in localized areas of high stretch when fitted around the groove corners. Excessive localized stretch can result in plasma cracking, if the seal is exposed to plasma gas. A custom seal, which is in a racetrack shape, like the groove, is a better choice. If this design is satisfactory for the application, this door seal is the lower cost option of the two listed.

Bonded door seals offer a number of advantages over the previously mentioned design. Bonded doors can have elastomer seals with custom cross sections to give the best sealing results for the application. Because it is bonded, the elastomer cannot roll when the door is opened or closed, which minimizes particle generation. The elastomer will not pull out of the groove if there is sticking when the door opens. Lastly, the seal is molded to the door so there is no localized excessive stretch to cause part damage while in use. However, bonded door seals are more expensive than doors utilizing a groove and an o-ring for a seal. Further, when a bonded door fails to seal, it must be thrown away and a new door installed. The choice between these two options comes down to the application and performance requirements.

Chamber Lid Seals

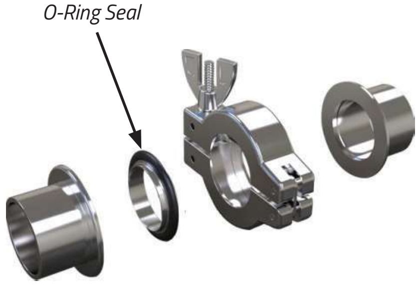
Applications such as chamber lid seals often involve the use of large o-rings. The large surface contact area can result in sticking of the o-ring to the lid, making it very difficult to open. In general, perfluoroelastomers tend to be stickier than other elastomers, for example, fluoroelastomers (FKM). Filled elastomers tend to be less sticky than non-filled elastomers. If this is a problem, look for information on which products have lower stickiness. Alternatively, perfluoroelastomers tend to be less sticky at elevated temperatures. Hence if the chamber lid needs to be opened and is sticking at room temperature, raise the equipment temperature to 50°C, before opening the lid.

Exhaust Valves

These valves are located at the bottom of the chamber and exhaust the chamber. An example is a butterfly valve that is throttled to achieve the desired level of vacuum in the chamber. The constant movement (fluttering) of this type of valve can result in seal wear. Low seal friction and abrasion resistance is important for these types of services. Also, since these valves are located away from the wafer and exhaust gas away from the wafer, the seals do not have the same rigid particle generation requirements as those used in the chamber. A final consideration is that the area near the exhaust valves may be heated to minimize build-up of material from the process stream. This then becomes a high temperature area and will require the use of high temperature perfluoroelastomers in order to maximize service life.

Flanges

Elastomers can be used in flanges, e.g. KF flanges, for piping connections in the gas system. These flanges have a centering ring that contains an o-ring as a seal. Proper sizing of the o-ring is critical or else elastomer extrusion and seal failure will occur. Some AS size rings are often listed as options when the proper size o-ring is a metric size. The AS size o-ring "equivalent" is often larger than the metric size and will result in extrusion of the seal at elevated temperatures. Selection of the correct o-ring size is especially important for perfluoroelastomers since they have a higher coefficient of thermal expansion compared to other elastomers.



Metallic Flex ISO-KF-Flange

Wafer Transport
As the wafers are moved from one chamber to another via a robotic arm, care must be taken that the wafers do not shift position or fly off the arm. Elastomer parts are often used to support, cushion and hold the wafer in place while it is moved. The elastomers must provide sufficient friction to eliminate movement of the wafer while the robotic arm quickly moves in a horizontal plane. However, there should not be any sticking when the arm sets the wafer into position, on a support, in a chamber for a subsequent operation. That is, the wafer must not stick to the elastomer supports when it is placed in the chamber. Any sticking may cause a shift in wafer positioning. Finally, the elastomer should not leave any residue on the wafer after release. These elastomer parts may be either custom parts, or o-rings, depending on the support design.

Another consideration is the wafer temperature. Often wafers may be 300°C or higher when picked up by the robotic arm and contacting the elastomer. Although the wafers cool relatively quickly, the elastomer will see this high temperature for a short period of time. This repeated high temperature exposure can cause the elastomer surface to change its frictional and sticking (stiction) characteristics. Hence the wafer may start to slip slightly on the elastomer pads of the robotic arm after a number of high temperature wafer transports. Care must be taken in the selection of an FFKM material, choosing one that has performance characteristics that resist change over time while in contact with high temperature wafers.

Thermal Process

The term "thermal process" covers a fairly wide range of applications. Per the name, these application temperatures are generally higher than plasma processes, ranging up to 300°C. This general term can cover processes including: Sub Atmospheric Chemical Vapor Deposition (SACVD), Metal CVD, Low Pressure CVD (LPCVD), Rapid Thermal Processing (RTP), and Oxidation or Diffusion furnaces. In these applications the wafers and the equipment that surrounds them, are heated to extremely high temperatures. In the case of thermal deposition, the high temperatures aid in the uniformity of the coating thickness.

Rapid Thermal Processing is used to very rapidly heat a wafer up to temperatures of 1000°C or greater for short periods of time. "Rapid Thermal Processing (RTP) can be used to reduce the thermal redistribution of impurities at high temperature…. RTP was originally developed for ion implant anneal, but has broadened its application to oxide growth, chemical vapor deposition, and silicidation."[1] For oxidation or diffusion furnaces, the applications are different, but still involve high temperatures. For oxidation applications, the procedure involves formation of a thin oxide film on the wafer surface. For diffusion applications, the furnace may assist in silicon dioxide formation on the wafer surface or it may be used to diffuse dopants in the wafer. For these applications, temperatures may range up to 1200°C.

Perfluoroelastomer Seal Requirements in Thermal Processes

For these processes, the main factor in elastomer selection is high temperature performance. Many of these applications use elastomers which are filled with standard fillers such as carbon black. These elastomers are not subjected to aggressive etching requirements as in plasma processes. Primarily the elastomer must survive high temperatures and be able to maintain sealing force after exposure to high temperature cycling, which is extremely hard on elastomers and hastens loss of sealing force. Carbon black fillers provide the best resistance to compression set (loss of sealing force) for carbon backbone elastomers.

Another primary consideration is minimal outgassing at high temperatures in order to avoid contamination of the wafer surface. Perfluoroelastomers provide the lowest outgassing at high temperatures. The high application temperatures may be achieved by various methods, for example, high temperature lamps. Specific FFKM products are available and should be selected for the best performance in these types of applications.

Thermal Process Applications

Some of the applications are similar to those listed for plasma processes, except that thermal processes usually have higher application temperatures. For these applications, proper elastomer groove design becomes even more critical. High service temperatures result in large thermal expansion for perfluoroelastomers. The volume of the groove design must be sufficient to accommodate this thermal expansion or the FFKM seals will overfill the groove, extrude and subsequently fail in service.

Quartz Chambers

These chambers may be used as the “hot” section of the furnace. Quartz can withstand very high temperatures without yielding contaminants that could cause problems with the wafer being treated. Elastomer seals for these applications are exposed to very high temperatures and shielding is often needed, or at least helpful, to reduce direct exposure of the elastomers to the high temperatures. Shielding is even beneficial for perfluoroelastomer seals to improve service life. For lamp anneal processes, non-black elastomers are often used because they reduce the absorption of heat from the lamp source, increasing elastomer service life.

Plenum Seals

Plenums provide space for equipment such as cables and chambers. These seals are also exposed to extremely high temperatures. As mentioned previously, elastomer seals must resist degradation at high temperatures and perfluoroelastomers are the seal of choice. Proper groove design is critical for these services to avoid elastomer extrusion. Any methods for cooling and reducing the temperature at the seal location will help prolong seal life.

Wet Process

Although this is a smaller segment of the semiconductor chip manufacturing industry, it still plays an important role. Wet processes can be used in cleaning, etching, and other steps in chip manufacture. Wafers may be cleaned and rinsed after initial wafer preparation. This step removes residual particles and other contamination on the wafer surface. The wafer may then be exposed to chemicals for adhesion promotion and/or photoresist deposition. After photoresist is applied to the wafer surface, the wafer can be exposed to a number of photolithography steps. The wafer may then be exposed to liquid developer solutions and photoresist stripping solutions. Resist strippers usually involve aggressive acids or organic solvents. Finally, wet processes can also be used in etching processes, which typically involve strong acids.

Perfluoroelastomer Seal Requirements in Wet Processes

Wet processes by their very nature do not involve high temperatures as in many plasma and thermal applications. However, elastomers must resist attack by aggressive chemicals such as acids, amines, and aggressive “stripper” chemicals. Perfluoroelastomers provide the broadest range of chemical resistance and can be used in most wet process applications. Unlike many plasma processes, the elastomers must be resistant to wet chemical attack. Chemical attack often causes swelling of an elastomer, which can lead to extrusion and/or general elastomer degradation over time. For example, fluoroelastomers are resistant to a wide range of chemicals, but amines strippers can quickly degrade these products. The elastomers used in these processes may employ standard filler systems, such as carbon blacks, and still perform satisfactorily in this environment. However care must be taken to avoid contamination due to metallic ion extraction and/or carbon black particles. Perfluoroelastomers remain a top choice for these applications due to their near universal chemical resistance and low extractables/contamination.

Wet Process Applications

The applications for perfluoroelastomers in wet processes are not unlike applications that are seen in the general chemical process industry. Groove design does not need to account for elastomer thermal expansion, however proper groove design is still critical for seal performance. Leakage of process chemicals can cause issues with environmental and operator exposure.

Chemical Containers

Liquid chemicals must be transported and hence containers must be properly sealed to avoid leakage of liquids or gases into the environment. The elastomer seals need to maintain integrity considering that containers may set for a relatively long time before use. The seals should not swell in aggressive chemical solutions and should resist compression set.

Flange Fittings

Piping and transport of chemicals, both new and spent, require flange seals. The seals must resist all types of aggressive chemicals without leakage or degradation. Elastomer seal degradation could result in the release of particles or metallic ions into the process stream or cause leaks to the environment.

Instrumentation Seals

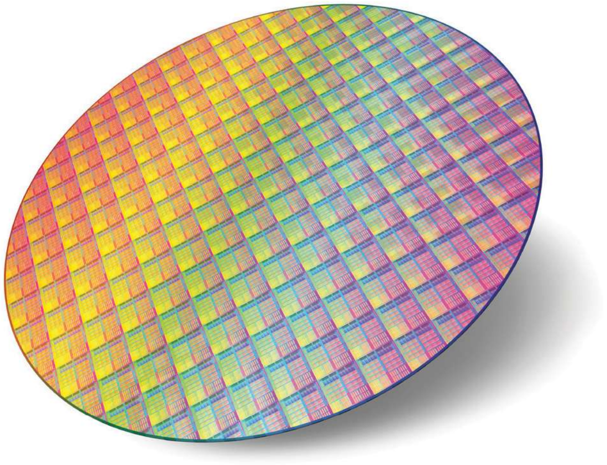
Examples of these include seals for temperature probes, flow meters, and conductivity probes. These are typically o-ring seals and they must maintain their integrity against numerous aggressive solvents without degradation. Proper seal design is critical for these applications.

Summary

Perfluoroelastomers (e.g. Kalrez® Parts), often replace fluoroelastomer (e.g. Viton®) in semiconductor applications. However, even though perfluoroelastomers are the highest performance elastomers, there are still subtle differences between products. It is suggested that the elastomer supplier be contacted regarding the optimum product and seal design for specific applications. As mentioned above the key characteristics of perfluoroelastomers include:

- Lower offgassing than other elastomers, especially at temperatures above 200°C, which lowers the risk of product contamination.
- Better sealing force retention (lower compression set) at temperatures over 200°C, which is critical for longer service.

- Best overall chemical resistance of any elastomer family.
- Formulations with extremely low particle generation in aggressive process environments.
- Generally higher gas permeation than fluoroelastomers.
- Higher coefficient of thermal expansion when compared to fluoroelastomers. Proper seal design will account for this and optimize performance.



Perfluoroelastomers play a critical role in the semiconductor environment by providing longer service life than other elastomers in terms of offgassing, sealing force retention at high temperatures, low contamination and chemical resistance. Manufacturers rely on this type of performance to minimize the maintenance cycles on their equipment. Longer run times result in higher production capability and higher profits. Processing environments are becoming harsher and process temperatures are increasing to improve product throughput, and perfluoroelastomers are the product selected to meet these stringent processing requirements.

References

Kalrez® is a registered trademark of the DuPont™ Company
Viton® is a registered trademark of the Chemours Company
[1] Dr. Lynn Fuller (March 27, 2010). "Rapid Thermal Processing (RTP)"

About the Author

Russell Schnell spent more than 37 years as an engineer with DuPont, the last 26 years as a Senior Application Engineer with the Kalrez® perfluoroelastomer parts business. Recognized for his expertise in elastomer applications, seal design and failure analysis, he provided technical support for a wide range of industries including: chemical processing, aerospace, oil and gas, pharmaceutical and semi-con. He created and conducted hundreds of training seminars and workshops in this field and was solely responsible for the development of the Kalrez® Application Guide software tool.
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