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Kalrez® perfluoroelastomer parts

From DuPont Performance Elastomers

CONTAMINATION CONSIDERATIONS FOR PERFLUOROELASTOMER SEALS USED IN DEPOSITION PROCESSES

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Deposition processes i.e., HDPCVD, PECVD, SACVD, ALD, etc., primarily operate at elevated temperatures and involve reactive gases and plasmas for both deposition and/or chamber cleaning. The trend towards larger semiconductor wafers, smaller feature sizes and decreasing thickness of deposited layers has placed increased emphasis on the need to minimize or eliminate unwanted sources of process contamination that could result in chip defects. Precise control of film composition and morphology is critical as deposition layers approach the atomic level. Furthermore, since surface integrity at the interface level is at least as relevant as the intrinsic bulk properties of the film, minimal perturbations of surface properties can result in integration problems at both the front-end and interconnect levels.

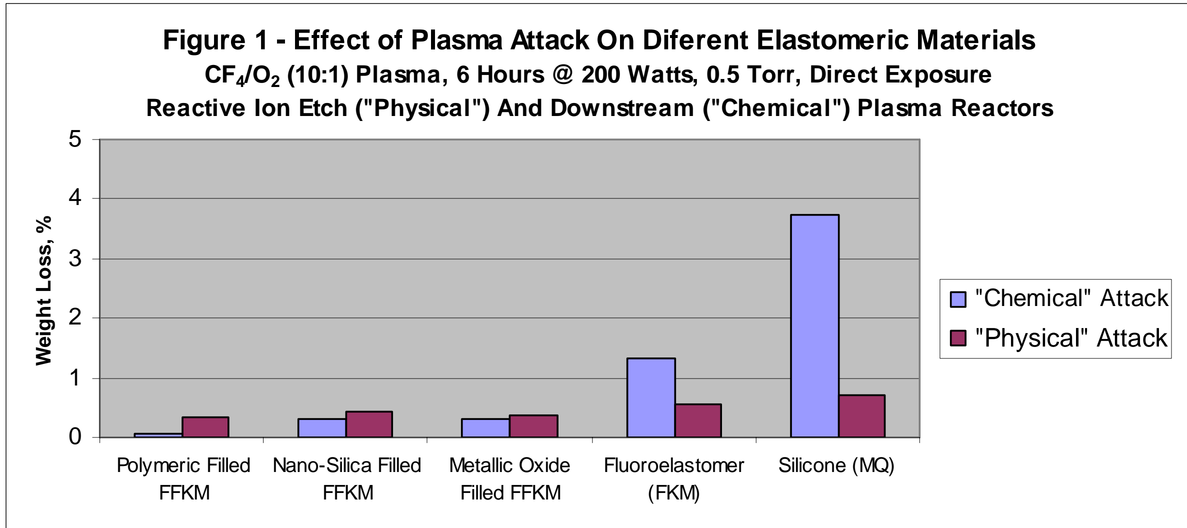
Since purity is critical to high wafer yield, reducing contamination from particles, metallic contaminants and outgassing caused by seal deterioration are major goals of semiconductor fabricators. Perfluoroelastomers (FFKMs) are widely used in critical seal locations in deposition processes due to their extraordinary chemical resistance and thermal stability. Despite these qualities, FFKM performance can vary widely depending upon chemical composition. Specially formulated perfluoroelastomer products, such as Kalrez® 9100 perfluoroelastomer parts, are designed to reduce contamination while maintaining sealing functionality in aggressive plasma environments.

Plasma Resistance

Semiconductor fabricators have found that plasma is a versatile and powerful tool for etching, cleaning, deposition, stripping, ashing, etc. Fluorine-containing plasmas and gases, e.g., NF_3, CF_4, ClF_3, etc., are most commonly used for deposition chamber cleaning due to their high reactivity towards materials to be removed. In addition, gases such as NF_3 can also be used during deposition to enhance gap fill performances in HDPCVD STI processes. However, they also create extreme challenges for sealing materials. Since all materials are consumed in plasma, the desired sealing material in such environments needs to withstand plasma attack, i.e., exhibit low weight loss (erosion), etc., and leave minimal particles behind after being etched.

Processing conditions can also vary within the same plasma chamber resulting in very different sealing material performance. In order to better predict seal life, a more thorough understanding of the plasma attack mechanism is required. Plasma attack can be chemical (seal primarily exposed to radicals, e.g., plasma “after-glow” condition), physical (seal surface subjected to energetic ion bombardment, e.g., high density plasma) or both. “Chemical” plasma attack (etching) tends to be very selective, i.e., radicals will react with the sealing material to form volatile products that can be pumped away. “Physical” plasma attack (etching) is highly dependent on the kinetic energy of the ions and is typically less selective, i.e., ions will strike the surface of the sealing material and “sputter” material away.

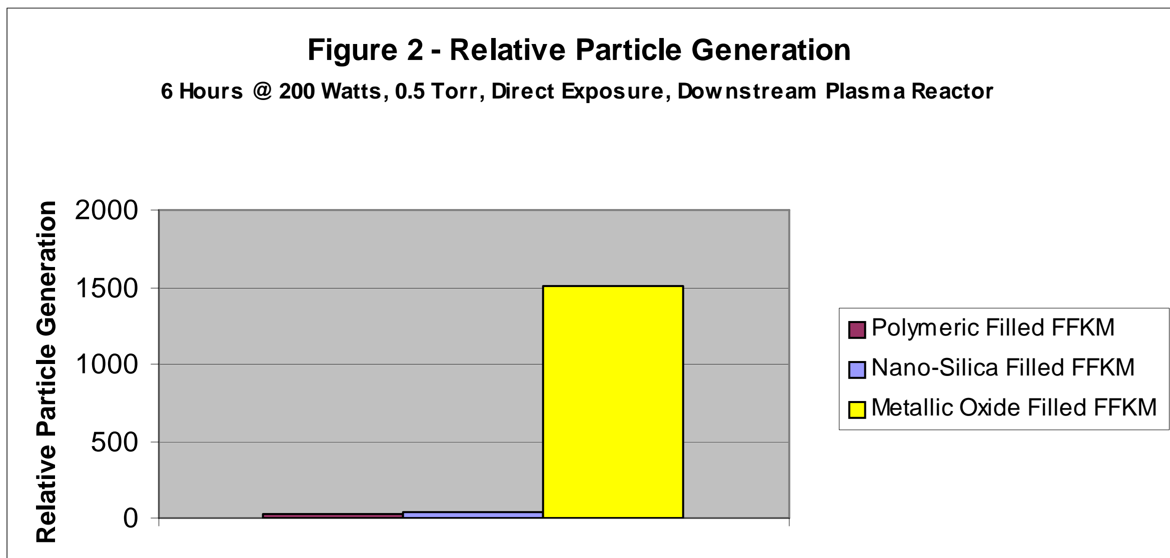
In most seal locations on semiconductor wafer processing equipment, the plasma attack mechanism is mainly chemical. This is particularly true for processing equipment that utilizes remote plasma sources and also where in-situ plasma sources are employed in which the ion density is low or the plasma glow is confined. FFKMs exhibit better resistance to such environments versus other elastomeric materials such as fluoroelastomer (FKM) and silicone and are therefore the preferred sealing choice. Figure 1 shows the effect of chemical and physical plasma attack on different types of elastomeric materials. The surface of the exposed test samples can be also analyzed by analytical techniques such as ESCA, SEM/EDX, etc., to measure changes in chemical composition and morphology.



Particle/Metallic Contamination

Conventional FFKM sealing materials normally contain carbon black and/or mineral fillers. Newer compounds are either unfilled or formulated with polymeric fillers. Plasma resistance can be significantly different depending on the type of filler used. If the filler has high resistance to plasma, such as $BaSO_4$, TiO_2, SiO_2, aluminum oxide and aluminum silicate, it can “shield” the polymer to reduce erosion or weight loss, but have the high potential for particle generation by leaving discrete particles behind once the polymer has become etched.

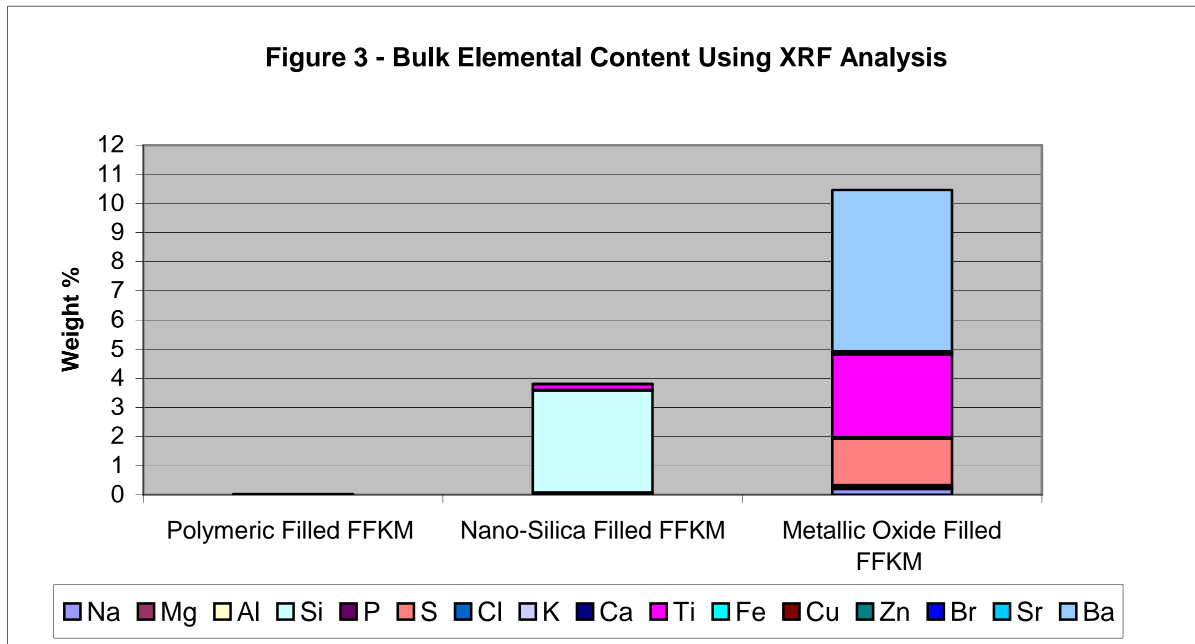
Unfilled or polymeric filled compounds can be completely etched to form volatiles, thereby significantly reducing the potential for particle generation. Figure 2 illustrates the relative particle generation of three different FFKM compounds in $CF_4/0_2$ (10:1) Plasma. Analytical techniques such as SEM/EDX can also be used to determine the shape and composition of the particles detected.



In additional to contamination from particles, metallic contamination, i.e., copper, titanium, magnesium, calcium, iron, etc., is another concern in plasma processes. Metallic contamination can produce negative effects at different levels of CMOS manufacturing. For instance, it can modify intrinsic properties of the film such as the dielectric constant or negatively affect interface properties which are critical for integration.

Plasma can break materials down to atomic or ionic species that can contaminate the deposited layer composition. Conventional mineral filled compounds contain metallic fillers as primary components, whereas newer polymeric or unfilled grades essentially contain no other elements other than carbon, fluorine and oxygen. Thus, sealing materials containing metallic fillers have the potential to generate metallic ions.

Relative bulk metal content (%) can be determined by XRF analysis. This semi-quantitative analytical method can detect all of the elements present in the sealing material. Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) or Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) can also be used for trace metals analysis. These analytical techniques provide a higher degree of accuracy for “clean” products, i.e., unfilled, polymeric filled, etc., that have a residual metallic ion content in the ppm to ppb range. Test results can vary depending upon the digestion method and the detection techniques used. Figure 3 provides a breakdown of the bulk elemental content of three different FFKM compounds using XRF analysis.



Outgassing

Precise control of deposition processing is critical as layers become thinner and approach the atomic level. A major concern is outgassing from sealing materials as it can interfere in the process by changing the composition and morphology of the deposited layer. In particular, outgassing contaminants absorbed by the exposed substrate during the initial steps of the deposition process can induce undesired interactions at the interface level and consequently affect the grown film as well as the overall process, i.e., the film properties at the interface can change, the deposition process can be delayed as a result of increased incubation time, or adhesion degradation can occur during subsequent processing steps. Outgassing can also cause slow vacuum pump down to occur.

Outgassing can originate from volatiles existing or adsorbed in the sealing material or from small molecules resulting from seal degradation. The main components of outgassing at elevated temperatures are fluorine-containing molecules and/or fragments. Hydrofluoric acid (HF) is one of the

gases evolved when fluoropolymers and fluoroelastomers begin to degrade. It can be harmful to both the environment as well as the process equipment, especially to quartz and stainless steel components. The outgassing properties of FFKMs can be significantly different depending upon the crosslinking system employed.

Figures 4 and 5 illustrate the outgassing properties of a typical FKM and three different FFKM compounds. Figure 4 shows outgassing from room temperature up to 200°C (“Stage 1” Outgassing) and is representative of adsorbed atmospheric gases. Figure 5 shows outgassing as a result of continued heating up to 400°C (“Stage 2” Outgassing) and is representative of gases evolved during service. The upturn in the curve indicates that the polymer network is beginning to degrade and that small molecules or fragments are being formed.

Figure 4 - "Stage 1" Outgassing (50 - 200 ^{o}C)

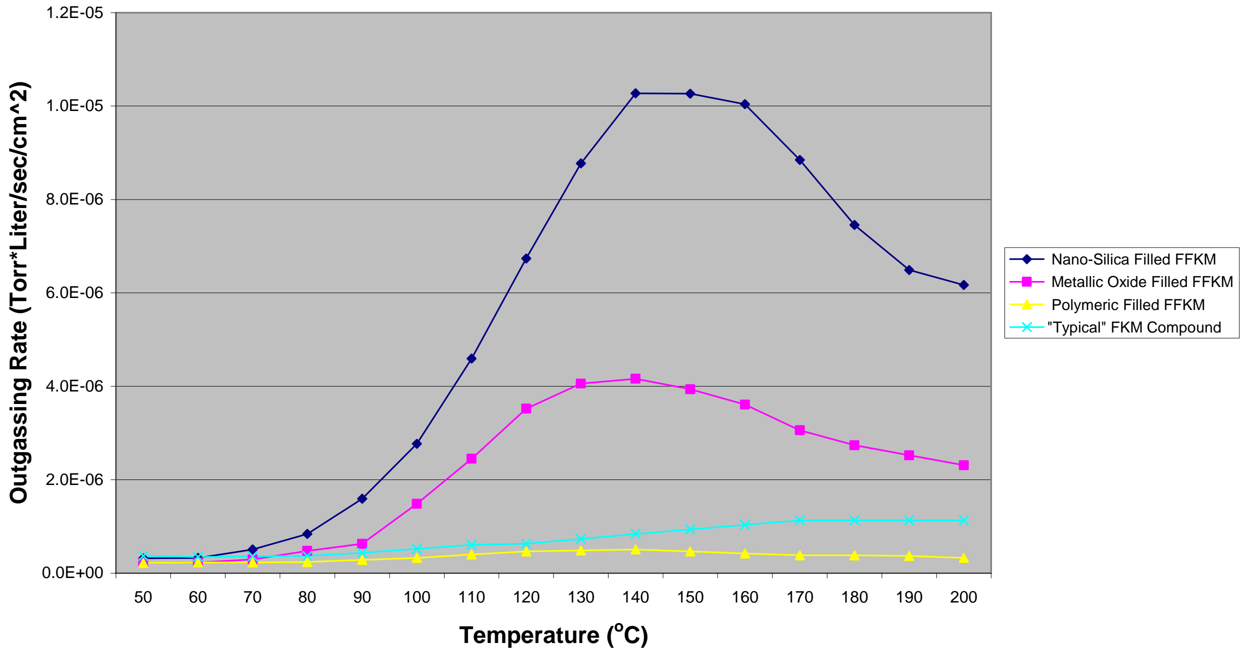
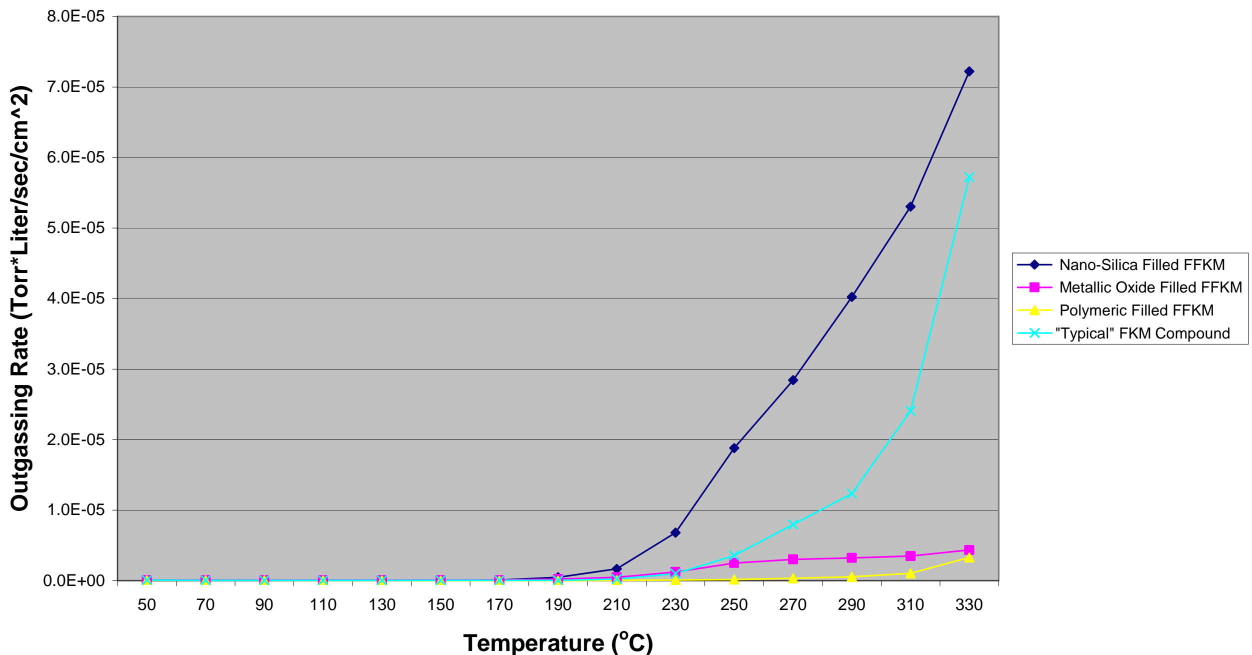


Figure 5 - "Stage 2" Outgassing (50 - 330 ^{o}C)



Kalrez® 9100 parts are polymeric filled. They are based on proprietary technology whereby the polymeric filler and perfluoroelastomer are incorporated to produce a fine dispersion of the polymeric filler in the perfluoroelastomer matrix. Since both perfluoroelastomers and polymeric fillers degrade similarly in plasma to form volatile products, Kalrez® 9100 parts offer minimal potential for both particle and metallic contamination. In addition, the dispersed polymeric filler provides added mechanical reinforcement to help improve sealing functionality as well as cracking resistance, which is especially important for dynamic sealing applications.

Kalrez® 9100 parts are also crosslinked using a proprietary curing system that provides excellent thermal stability while significantly reducing outgassing at elevated temperatures. A seal with high thermal stability allows equipment/process engineers a “larger window of process operation” with respect to minimizing/eliminating cooling devices, increasing the temperature of the chamber wall to help minimize condensation and shortening the cleaning cycle as a result of increased chamber wall temperature.

Outstanding resistance to “dry” process chemistry combined with excellent mechanical strength properties and thermal stability suggest the use of Kalrez® 9100 parts in the most critical deposition process sealing applications, both static and dynamic. Case reports (success stories) from a number of fablines have confirmed the superior performance of Kalrez® 9100 parts with respect to longer seal life, improved process reliability and reduced frequency of equipment maintenance.

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