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Contamination Considerations for Perfluoroelastomer Seals used in Deposition Processes

Introduction

Semiconductor fabricators have found that plasma is a versatile and powerful tool for etching, deposition, stripping, ashing, etc.1,2 Fluorine-containing plasmas and gases, e.g., NF_3, CF_4, ClF_3, etc., are commonly used for deposition chamber cleaning due to their high reactivity towards materials to be removed. In addition, gases such as NF_3 can be used during deposition to enhance gap fill performance in HDPCVD STI processes. However, they also create extreme challenges for sealing materials. Since all materials are consumed in plasma, the desired sealing material needs to withstand plasma attack, i.e., exhibit low weight loss (erosion) and leave minimal particles after being etched.

Plasma Resistance

Different plasma reactors such as reactive ion etch (RIE), inductively coupled plasma (ICP) and downstream reactors are typical plasma configurations used in IC processing. However, they can create extremely different plasma environments resulting in very different sealing material performance. In addition to reactor configuration, plasma recipe and processing parameters, such as power, pressure, temperature, flow rate, etc., as well as the location of the seal in the plasma reactor are important factors in determining the attack mechanism towards the sealing material.

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), physical (seal surface subjected to energetic ion bombardment) or both. “Chemical” plasma attack 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 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 wafer processing seal locations, the plasma attack mechanism is mainly chemical. This is particularly true for 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 elastomers such as fluoroelastomer (FKM, e.g., DuPont™ Viton®, etc.) and silicone (MQ).

Fig. 1 shows the effect of chemical and physical plasma attack (% weight loss) 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.

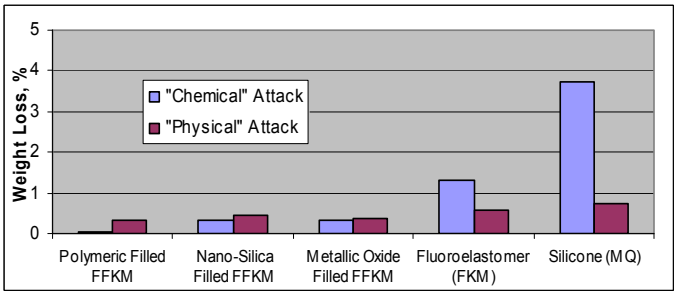

Fig. 1. Effect of Plasma Attack on Elastomeric Materials
CF_4/O_2 (10:1) Plasma, 6 Hours at 200 Watts, 0.5 Torr, Direct Exposure, Reactive Ion Etch and Downstream Plasma Reactors

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Particle 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 and SiO_2, it can "shield" the polymer to reduce erosion, but have high potential for particle generation by leaving discrete particles behind once the polymer has become etched.[3]

Unfilled/polymeric filled compounds can be completely etched to form volatiles, thereby significantly reducing the potential for particle generation. Since perfluoroelastomers and perfluoropolymers degrade similarly in plasma to form volatile products, perfluoropolymer-filled FFKMs offer minimal potential for both particle and metallic contamination. In addition, the dispersed perfluoropolymer provides added mechanical reinforcement to help improve sealing functionality, which is especially important for dynamic sealing applications.

Fig. 2 illustrates the relative particle generation of three different FFKM compounds in CF_4/O_2 (10:1) Plasma. An ultrasonic bath containing UPDI water was used to collect the particles on the exposed surface of the FFKM compound. The number of particles as well as the particle size distribution were counted/measured using a liquid particle counter. Analytical techniques, such as SEM/EDX, can also be used to determine the shape and composition of the particles detected.

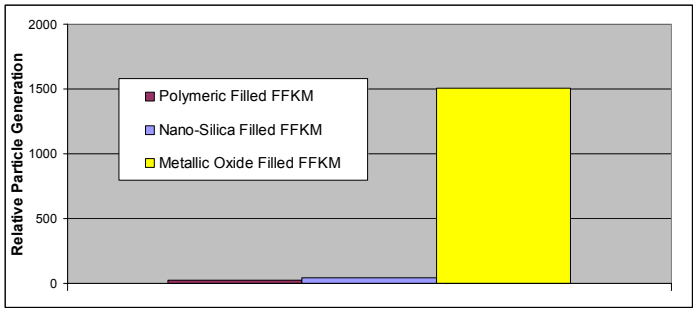

Fig. 2. Relative Particle Generation
6 Hours at 200 Watts, 0.5 Torr, Direct Exposure, Downstream Plasma Reactor

Metallic Contamination

In addition to contamination from particles, metallic contamination, i.e., copper, titanium, magnesium, 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 (weight %) can be determined by XRF analysis. This 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 metal analysis. These 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. Fig. 3 provides a breakdown of the bulk elemental content of three different FFKM compounds using XRF analysis.

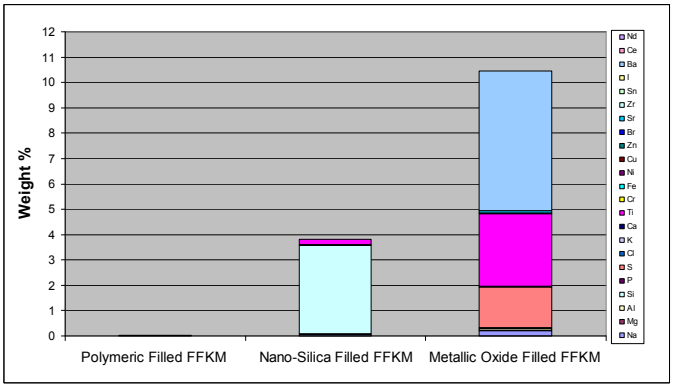

Fig. 3. Bulk Elemental Content Using XRF Analysis

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.

Fig. 4 shows outgassing from room temperature up to 200 °C ("Stage 1" Outgassing) and is representative of adsorbed atmospheric gases, i.e., H_2O, CO_2, N_2, O_2, etc. Fig. 5 shows outgassing as a result of continued heating up to 330 °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. 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.[4] It can be harmful to both the environment as well as the process equipment, especially to quartz and stainless steel components.

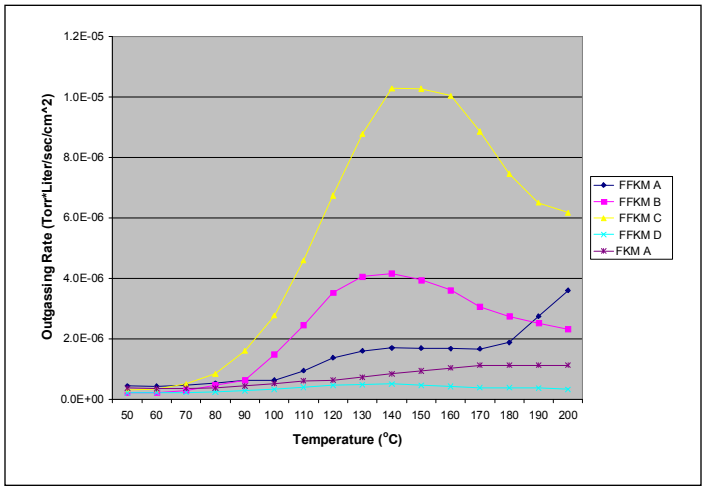

Fig. 4. "Stage 1" Outgassing (50–200 °C)

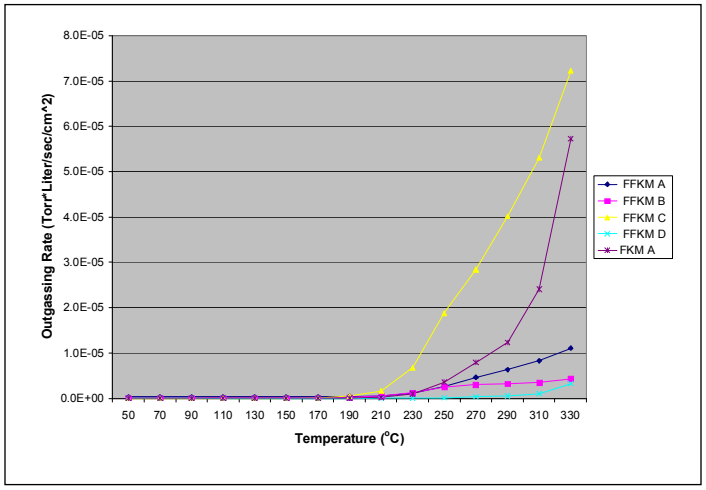

Fig. 5. "Stage 2" Outgassing (50–330 °C)

In general, the outgassing properties of FFKM are typically superior to FKM based on the thermal stability of the polymer and cure system employed.[5] However, the outgassing properties of FFKMs can be significantly different depending upon their chemical composition. For example, FFKM D, employing a high thermal stability polymer and cure system along with a polymeric filler, exhibits improved (lower) outgassing properties than FFKM Compounds A, B and C. Thus, an FFKM that provides excellent (high) thermal stability while significantly reducing outgassing at elevated temperatures is desired. It 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. The chemical composition of the FFKM and FKM Compounds referenced in Figs. 4 and 5 above is contained in Table 1.

Summary

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

Table 1: Chemical Composition of FFKM and FKM Compounds

Compound	Polymer Type	Filler System	Cure System
FFKM A	TFE/PMVE	Carbon Black	Triazine
FFKM B	TFE/PMVE	Metallic Oxide	Heterocyclic
FFKM C	TFE/PMVE	Silica	Organic Peroxide
FFKM D	TFE/PMVE	Polymeric	Heterocyclic
FKM A	TFE/HFP/VF2	Polymeric	Organic Peroxide

References

1. S. Wang and J. Legare, “Perfluoroelastomer and fluoroelastomer seals for semiconductor wafer processing equipment,” J. Fluorine Chemistry, vol. 122, pp.113-119, 2003.
2. S. Wang, J. Legare and B. Rai, “Perfluoroelastomers seals for semiconductor wafer processing equipment,” ISTC 2005, Shanghai, China.
3. Bletsos and J. Legare, “The role of additives in perfluoroelastomer sealing parts exposed to reactive plasmas,” Microcontamination ’93 Conference Proceedings, Canon Communications, pp. 625, 1993.
4. DuPont Technical Bulletin KZE-H82172-00-F0607 (June 2007).
5. M. Heller, J. Legare, S. Wang and S. Fukuhara, “Thermal stability and sealing performance of perfluoroelastomer seals as a function of crosslinking chemistry,” J. Vacuum Society & Technology A, vol. 17, pp. 2199-2124, 1999.

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