PERFLUOROELASTOMER SEALS FOR SEMICONDUCTOR WAFER PROCESSING EQUIPMENT

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ABSTRACT

Perfluoroelastomers (e.g. those used to make Kalrez® perfluoroelastomer parts) are widely used as seals on semiconductor wafer processing equipment. They have extraordinary resistance to harsh chemicals and heat, enabling them to withstand virtually any process media, including reactive plasmas, at temperatures as high as 327°C.

This paper is a review of perfluoroelastomers used as seals in semiconductor wafer processing. These seals offer cleanliness and lack of contamination while maintaining sealing functionality in aggressive "wet", "dry" and "thermal" processes. Applications include etching, ashing, stripping, cleaning, PECVD, HDPCVD, LPCVD, diffusion furnace and rapid thermal processing, etc. The ability of perfluoroelastomers to resist aggressive chemicals, plasmas as well as high temperatures will be discussed. A relative comparison of the various types of perfluoroelastomers used as well as a comparison to other elastomeric materials will also be presented.

INTRODUCTION

Semiconductor wafer processing involves many aggressive chemicals and operates under very severe environments. Perfluoroelastomers are widely used as seals on semiconductor wafer processing equipment due to their extraordinary resistance to chemicals and heat. Their outstanding chemical resistance and thermal stability enable them to withstand virtually any process media, including reactive plasmas, at temperatures as high as 327°C. A relative comparison of perfluoroelastomers to other elastomers in terms of thermal stability, i.e., service temperature, and chemical compatibility can be seen in Figure 1.

The first commercial perfluoroelastomer was developed in the 1960's by E. I. du Pont de Nemours. It was used in parts sold under the trade name Kalrez®. From this early beginning the use of perfluoroelastomers has increased steadily. Today there are four major global manufacturers of perfluoroelastomer polymers: DuPont Dow Elastomers L.L.C., Dyneon, LLC, Solvay Solexis, and Daikin Industries Ltd. Perfluoroelastomer seals are manufactured by a number of companies worldwide.

This paper is designed to be a review of the chemistry of perfluoroelastomers and their use in semiconductor wafer processing. Perfluoroelastomers offer the cleanliness and lack of contamination that are crucial to this industry while maintaining sealing functionality in aggressive media. Applications requiring resistance to "wet" process chemistry (i.e., acids, bases, amine-based strippers, etc.) include etching, rinsing, cleaning, stripping and copper plating. Applications requiring resistance to "dry" process chemistry (e.g., gases, reactive plasmas, plasmas used for chamber cleaning, etc.) include etching, ashing, chemical vapor deposition, high density plasma chemical vapor deposition and plasma enhanced chemical vapor deposition. Applications requiring thermal resistance include low-pressure chemical vapor deposition, oxidation, diffusion furnace, lamp annealing and rapid thermal processing. A relative comparison of the various types of perfluoroelastomers used as well as a comparison to other elastomeric materials is also presented and discussed.

Structure and Properties of Perfluoroelastomers

Perfluoroelastomers contain a completely fluorinated backbone [1]. The carbon-fluorine bond is the most stable single bond in fluorinated polymers that have a carbon backbone. The high bond dissociation energy of the C-F bond is the main reason for a perfluoroelastomer's thermal, oxidative and chemical stability. Table I lists typical bond dissociation energies of single bonds. Homo-polytetrafluoroethylene (PTFE) contains all C-F substitution, which makes it one of the most thermally and chemically stable polymers. However, PTFE has very high crystallinity. As a result, it is a rigid thermoplastic, not an elastomer. In order for a material to be rubber-like, it has to be capable of very high deformation. It must also be able to maintain retractive force when external stress is applied, recover substantially to its original dimension after removal of an external stress and retain its shape after swelling. To accomplish this, polymers with long flexible chains having a three-dimensional network structure are essential. Randomly incorporating other monomers into homopolymers breaks the regularity and forms amorphous polymers consisting of randomly coiled flexible chains. These polymers then have flexibility and mobility and can deform when acted upon by an external force. In addition, these polymers need to be crosslinked to form a three-dimensional network structure to ensure recoverability. A schematic view of elastomeric crosslinked network structure can be found in Figure 2. The structure and properties of the resulting network depend largely on the polymer backbone, the cure site functionality and curing chemistry [2 and 3].

Perfluoroelastomer parts are normally made from perfluoroelastomer polymer. In addition, reinforcing fillers, such as carbon black and mineral fillers, and other organic fillers, are incorporated along with curatives, processing aids, etc. The properties of the final compound not only depend upon the polymer, but also on other ingredients as well. Therefore the performance of perfluoroelastomer seals can be very different and proper selection of the right compound for a specific application is very important. Main applications in semiconductor wafer processing equipment and recommended sealing materials are discussed in the following sections.

Applications for Perfluoroelastomers in Plasma and Gas Deposition Applications

Semiconductor fabricators have found that plasma is a very powerful tool for etching, chemical vapor deposition and stripping because all materials are consumed in plasma and plasma can increase reactivity. Seals made from perfluoroelastomers are used in these processes because of their exceptional resistance to aggressive media. Despite this, prolonged exposure to plasmas can degrade their surface resulting in particulate contamination before sealing functionality is lost. The ideal seal for plasma applications, therefore, would resist surface degradation while maintaining sealing functionality.

Perfluoroelastomer seals are designed to withstand chemical attack and provide extended seal life in plasma. They exhibit low weight loss (etch rate) and particle generation, thus improving wafer yield, increasing process reliability and reduced frequency of equipment maintenance.

Fluorine plasma is the most common process chemical used in semiconductor wafer processing. NF_3 plasma, due to its high reactivity, is typically used for etching and chamber cleaning. Oxygen and mixture of oxygen and fluorine plasma are also common chemicals used in etching and ashing processes. Figure 3 illustrates the low weight loss properties of perfluoroelastomers compared to fluoroelastomer and silicone rubber in NF_3, a 50/50 mixture of C_2F_6/O_2, and oxygen plasma. However, the plasma resistance of fluorinated elastomers can vary widely depending upon other process parameters employed, i.e., power (wattage) level, flow rate, etc. The plasma performance of perfluoroelastomers also depends on other ingredients contained in the compound. Legare, et al discusses the impact of fillers on plasma resistance [4]. Another important performance requirement for seals used in plasma applications is low particle and metal contamination. A comparison of relative particle generation can be found in Figure 4. SEM/EDX on exposed seals can be used to check surface morphology and possible metal contamination as in Figures 5(a) through (c). A new generation of perfluoroelastomer compounds, such as Kalrez® Sahara ™8085 and Kalrez® 8002, are designed to minimize particle generation [5,6].

Figure 6 shows the excellent chemical resistance exhibited by perfluoelastomers compared to a fluoroelastomer in chlorine trifluoride (ClF_3) used for chamber cleaning. Typical applications for perfluoroelastomer seals in plasma and gas deposition wafer processing equipment include gate valves, door seals, chamber lid seals, electrode seals, lamp seals, exhaust seals, gas inlet/outlet seals, window seals, seals for centering rings, fittings, etc.

Applications for Perfluoroelastomers in Thermal Applications

High heat and temperature spikes can "cook" elastomeric seals beyond recognition, causing them to become hard and brittle. When this occurs, their crosslinking structure, the key to their elasticity, becomes irreversibly damaged. This loss of elasticity makes effective sealing impossible. In addition, elastomers can degrade under high temperatures, causing outgassing to occur, thereby contaminating the process environment. The result is unscheduled downtime, or even worse, product loss. Table II shows the extremely low outgassing properties of a typical perfluoroelastomer compound from room temperature up to 400°C. A relative comparison of the outgassing performance of typical perfluoroelastomer compounds versus a typical fluoroelastomer compound can be found in Figure 7.

Thermal processes like rapid thermal processing (RTP), low-pressure chemical vapor deposition (LPCVD), oxidation, diffusion, lamp annealing, etc., need seals that resist not only the process chemicals, but also the extreme temperatures required. Reliable, in service temperature ratings for sealing materials are best defined by long-term (672 hour) testing for seal force retention [6]. Figure 8 shows the excellent long-term seal force retention properties of perfluoroelastomers versus fluoroelastomer and silicone rubber. Applications for perfluoroelastomer seals in thermal processing equipment include quartz chamber seals, plenum seals, seals for centering rings, etc.

Applications for Perfluoroelastomers in “Wet” Process Applications

To transform raw semiconducting materials into useful devices requires hundreds of chemical processing steps. A significant number of these steps involve aggressive acids, solvents (including amines), and bases used to clean, rinse, etch or strip unwanted materials and contaminants from the wafer surface. These chemicals can attack elastomeric seals causing them to swell and degrade or leach undesirable metallic and ionic extractables that affect integrated circuit functionality.

Perfluoroelastomer seals are used in wafer cleaning wet etching, photolithography and copper plating applications. Specially designed perfluoroelastomer compounds, such as Kalrez® 6375UP, feature low metallic, ionic and total organic carbon (TOC) extractables as well as excellent chemical resistance and provide superior contamination performance as presented in Table III [8]. Tables IV and V show the extractables performance of several perfluoroelastomer compounds versus a typical fluoroelastomer compound in ultrapure deionized water (UPDI) and “piranha” (H_2SO_4:H_2O_2) after 1 month @ 80°C [9]. Applications for perfluoroelastomer seals in “wet” chemical wafer processing equipment include drain seals, seals for chemical containers, filter seals, door/lid seals, flow meters, etc.

The trend towards larger 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. Chemical and equipment manufacturers go to great lengths to minimize the potential for contamination that could result in chip defects. Demand for perfluoroelastomer seals has steadily increased as wafer process requirements have become more stringent.

ACKNOWLEDGEMENTS

The authors appreciate all the discussions and support from their colleagues at DuPont Dow Elastomers L.L.C.

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Table I. Typical Bond Dissociation Energies for Aliphatic Bonds (KJ/mol)

C-C	284-368
C-H	381-410
C-Cl	326
C-F	452
C-O	350-389
C-N	293-343

Table II. Outgassing Properties of a Typical Perfluoroelastomer Compound∗

TG-MS Outgassing Analysis
(Room Temperature to 400°C @10°C/min)

Gas Evolved	R.T. to 100°C (ppm)	R.T. to 200°C (ppm)	R.T. to 300°C (ppm)	R.T. to 400°C (ppm)
H2O	2	255	324	345
HF^+	0	0	0	1
CF+	0	0	0	12
CO2	0	0	2	103
CF2	0	0	0	19
CHF+	0	0	0	20
CF3+	0	0	0	119
C2F3+	0	0	0	23
CF3O+	0	0	0	0
C2F4+	0	0	0	9
C2F5+	0	0	0	1
C3F5+	0	0	0	31
Total Outgas (%)	**0.00**	**0.03**	**0.03**	**0.07**
Weight Loss (%)	**0.00**	**0.00**	**0.01**	**0.07**

∗ DuPont Dow Elastomers Proprietary Test Method

Table III. Typical Volume Swell of A Perfluoroelastomer Compound in "Wet" Chemistry [7]∗

Immersion Chemistry	Exposure Condition	% Volume Swell
UPDI Water	85°C, 30 days	0.7
Pirahna	25°C, 30 days	0.1
SC-1	25°C, 30 days	0.6
SC-2	25°C, 30 days	0.1
49% HF	25°C, 30 days	2.8
$NH_4(OH)$	100°C, 7 days	2.6
H_2SO4	120°C, 28 days	1.3
H_2SO4	150°C, 28 days	6.6
HNO3	85°C, 7 days	2.1
ACT ®690C	95°C, 10 days	1.5
ACT ®970	80°C, 10 days	2.0
ACT ®935	80°C, 10 days	1.6
ACT ®NE-14	25°C, 10 days	0.0
ACT ®CMI	80°C, 10 days	2.7
EKC 265™	75°C, 7 days	1.0
EKC 830 ™	75°C, 7 days	3.1
EKC 4000 ™ PCT	75°C, 7 days	0.7
PRS-1000 ™	85°C, 7 days	1.9
PRS-3000 ™	85°C, 7 days	4.2

∗ ASTM D1414 and ASTM D471 (AS568A K214 O-ring Test Specimens)

Table IV.
Extractables Performance of Fluorinated Elastomers in 18 Mega-ohm Ultrapure Deionized Water - 1 Month @ 80°C – Parts Per Billion (ppb)
ICP-MS/GF-AA/IC/TOC∗

Extractable Detected	Perfluoroelastomer (Black)	Perfluoroelastomer (Brown)	Fluoroelastomer (Black)
Aluminum	9.5	-	4.5
Copper	0.9	0.2	0.4
Magnesium	2.7	3.9	61.2
Zinc	0.5	0.9	0.2
Barium	-	-	23.6
Iron	3.6	0.1	0.9
Calcium	15.4	28.0	400.0
Potassium	-	-	8.0
Sodium	-	-	16.5
Fluoride Ion	1100.0	17.0	268.0
Total Organic Carbon	1540.0	866.0	2650.0

Table V.
Extractables Performance of Fluorinated Elastomers in "Piranha" (3:1 (v/v) 96% H_2SO_4: 30% H_2O_2) - 1 Month @ 80°C – Parts Per Billion (ppb)
ICP-MS/GF-AA∗

Extractable Detected	Perfluoroelastomer (Black)	Perfluoroelastomer (Brown)	Fluoroelastomer (Black)
Aluminum	-	-	7.8
Copper	-	2.0	-
Magnesium	17.0	20.0	195.7
Zinc	-	2.0	-
Barium	-	-	33.7
Iodine	-	-	53.0
Tin	234.0	-	-
Chromium	-	-	2.4
Iron	-	-	30.5
Calcium	-	17.0	572.0
Sodium	-	-	10.1
Potassium	-	-	2.9

∗ DuPont Dow Elastomers Proprietary Test Method (AS568A K214 O-ring Test Specimens)