# DuPont<sup>™</sup> Kalrez<sup>®</sup>

Outgassing Characterization of Elastomeric Seals Used in Semiconductor Wafer Processing

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Most integrated circuit manufacturing processes operate in high or ultra-high vacuum (UHV) environments. It is important that vacuum levels are maintained within specified limits to insure optimum process efficiency, uniformity and consistency. Specification of an appropriate size vacuum pump for the system is the primary mechanism for maintaining adequate vacuum levels for processing; however, seal outgassing can play a role in the ability to control this processing variable. Even more important is the ability to control the uniformity of the process environment within the chamber. While an adequately sized pump can typically

compensate for changes in vacuum level due to seal outgassing, it will not have the capability to control potentially harmful changes to gas uniformity or composition within the chamber. Changes in the partial pressures within the chamber caused by outgassing can cause quality problems in layering processes such as ALD, CVD, oxidation, diffusion, etc.

In general, it is accepted that elastomers outgas to a greater extent than metals. In many UHV systems, metal seals are used to avoid this issue. However, metal seals are not always effective and/or practical. Some of the difficulties associated with the use of metal seals are:

- · Difficult to install
- Expensive
- Non-reusable
- Poor sealing performance in dynamic applications
- · Potential for component damage in quartz and ceramic sealing applications

Therefore, it is important for vacuum system designers and process engineers to understand the outgassing characteristics of elastomeric seals. Currently there is no industry standard for measuring and characterizing elastomer outgassing performance and a limited amount of useful data is available.

This study evaluates and compares outgassing characteristics for three different classes of elastomeric seal materials typically used in semiconductor process environments using a test methodology developed by DuPont. Table 1 identifies the products/materials evaluated.



#### **Table 1. Materials Evaluated**

Elastomer Classification	Reference Identification	Polymer Type	Filler System	Cure System
Perfluoroelastomer	DuPont <sup>™</sup> Kalrez <sup>®</sup> 8900	TFE/PMVE	Carbon Black	Heterocyclic
Perfluoroelastomer	DuPont <sup>™</sup> Kalrez <sup>®</sup> 8475	TFE/PMVE	Silica/Metallic Oxide	Heterocyclic
Fluoroelastomer	FKM-K7	VF <sub>2</sub> /HFP	Carbon Black	Bisphenol
Silicone	VMQ-T1	Methyl Disiloxane	Silica	Organic Peroxide

\* FKM and VMQ are ASTM designations for the elastomer class indicated. K7 and T1 are internal DuPont references.

The test method and associated equipment developed uses a Residual Gas Analyzer – RGA (term for a class of quadrupole mass spectrometers) to evaluate the outgassing performance of elastomers. Other test methods/analytical equipment sometimes used for outgassing analysis are TGA-FTIR or mass spectroscopy, and head space GC mass spectroscopy. While these techniques are useful, they have some limitations and disadvantages. Table 2 compares the capabilities of each test method.

#### Table 2. Outgassing Test Method Comparison

Test Capability	DPP Method RGA/QMS**	TGA-FTIR/MS Thermogravimetric Analysis	HS-GC/MS Head Space Gas Chromatography
Measurement Under Vacuum	Yes, UHV*	No, 1 ATM	No, 1 ATM
Temperature Control	Programmable	Programmable	Isothermal
Max. Analysis Temperature	330 °C	1000 °C	230 °C
Gas Species Analysis Method	QMS (with electron multiplier)	MS or FTIR	GC/MS
Quantitative Results	Total Outgassing Rate (torr·liters/sec/cm <sup>2</sup> )	% Weight Loss	Difficult to Obtain (requires costly calibration)

\*Ultra High Vacuum, 1 x 10<sup>-8</sup> torr

\*\* QMS = Quadrupole Mass Spectrometer

The primary advantage of DuPont's test method is the ability to obtain quantitative outgassing data in an environment representative of typical semiconductor processes.

This paper presents the test methodology developed by DuPont, compares outgassing data from three commonly used elastomers (Table 1), and discusses how this data can be used to assist equipment and process engineers. Characteristics measured and compared include total outgassing rate as a function of temperature and total outgassing rate as a function of time at a given temperature. In addition, the methodology and equipment allows for the analysis/monitoring of select gas species associated with the mass-to-charge ratios (M/z) of the species during each rate test.

## 2.0 Experimental Procedure

The protocol developed by DuPont involves equipment and a test method capable of measuring the outgassing characteristics of elastomers under conditions similar to those found in typical semiconductor processing applications. It allows for the determination of total outgassing rate vs. time and temperature, and the monitoring of select gas species evolved while a sample is under vacuum.

Since elastomers are typically selected for use based upon a combination of their chemical resistance and thermal stability vs. the demands of the application, initial tests compared the outgassing characteristics for each class of material as a function of increasing temperature. In those tests, it became apparent that it would be necessary to measure the outgassing rate vs. temperature test in two stages. During initial heat up (from ~50 °C to >300 °C) some materials outgassed such that the partial pressure inside the chamber increased to > 1 x 10<sup>-4</sup> torr. At this partial pressure, the electron multiplier that enabled increased sensitivity in detection of ion currents/gas species could not be used. Furthermore, since two of the three materials evaluated are generally not recommended for continuous service above ~200 °C, the outgassing characteristics were examined in two stages. Stage 1 testing was conducted in a range from ~50 °C to 200 °C. After cool down to ~50 °C under vacuum, Stage 2 was carried out on the same sample from ~50 °C to 330 °C. More accurate monitoring (and a more thorough understanding) of the outgassing mechanisms was obtained using this approach. Figure 1 shows the outgassing test equipment.



# Figure 1. Residual Gas Analyzer/Outgassing Test Equipment

# 2.1 Sample Preparation

AS 568A size 214 O-rings were obtained corresponding to each material listed in Table 1. Each O-ring was weighed. Then a 1/16 section of the o-ring was collected and used for evaluation. Care was taken during sample preparation to avoid possible contamination due to handling that could affect outgassing results. The sample was placed in a quartz boat and the boat placed inside a quartz sample tube (See Figure 2).

## Figure 2. Sample in Quartz Boat and Heater Tube



# 2.2 Test Equipment Set-up and Operation



#### Figure 3. Residual Gas Analyzer/Outgassing Test Equipment Schematic

Prior to the evaluation of any elastomeric samples, the system was conditioned by allowing it to pump down for approximately two weeks to insure the system was clean and free of contaminants. With valve #2 closed, the turbo molecular pump (TMP) was used to pump down to approximately  $2 \times 10^{-8}$  torr. Vacuum was maintained at this level for 12 hours prior to performing outgas testing. After initial conditioning, the TMP operated continuously until the testing was complete. With valve #2 still closed, the quartz tube containing the sample was bolted in place. A Conflat seal (copper metal seal) was used to insure that any outgassing was from the evaluation sample only. Once the quartz tube was in place, valve #3 was opened and the dry pump was used to pump down the quartz sample chamber to a vacuum level of  $1 \times 10^{-6}$  torr.

## 2.3 Quantitative and Qualitative Outgassing Measurement and Characterization

**2.3.1.** Outgassing Rate vs. Temperature (Stage 1) — By closing valve #3 and opening valve #2, the system was allowed to equilibrate (P1 = P2 ~  $1 \times 10^{-7}$  torr). The vacuum line between ion gauge 1 and ion gauge 2 (vacuum chamber) has a conductance factor of 0.0005 liter/sec. Using this conductance factor, the outgassing flow rate was calculated as follows:

- Q = C (P2 P1), where
- Q = Gas flow rate (torr liter / sec)
- C = Conductance factor proportional to tube dia. and length = .005 liter / sec.
- P2 = Pressure reading at ion gauge #2 (torr)
- P1 = Pressure reading at ion gauge #1 (torr)

As the sample was heated at a controlled rate (1 °C/min), outgassing from the elastomer caused a change in P2, and the resulting flow rate was calculated. This flow rate was divided by the surface area of the evaluation sample to obtain the outgassing flow rate per cm<sup>2</sup> of surface area (torr-liters/sec/cm<sup>2</sup>). This flow rate was plotted vs. quartz tube temperature at 20 °C intervals. The quartz tube heater was ramped to a temperature of 200 °C. With valve #2 still open, the sample was allowed to cool down to approximately 50 °C overnight.

**2.3.2** Outgassing Rate vs. Temperature (Stage 2) — After the sample was allowed to cool down overnight, the sequence was repeated; however, the temperature was ramped to 330 °C at a rate of 2 °C/min. During this time, the outgassing flow rate vs. quartz tube temperature was calculated and plotted.

**2.3.3** Outgassing Rate vs. Time at Specified Temperature (275 °C) — For this test a new sample was prepared as outlined in Section 2.1. The sequence outlined in 2.3.1 was repeated; however, the temperature was ramped to 275 °C at a rate of 4 °C/min. and held at 275 °C for an additional 21 hours. During this time, the outgassing flow rate was calculated and plotted vs. time.

**2.3.4 Qualitative and Semi-quantitative Analysis of Evolved Gasses** — During each of the outgassing rate tests outlined in sections 2.3.1 through 2.3.3, the gasses evolved were analyzed using a quadrupole mass spectrometer. The relative intensity of select gas species, aligned with the appropriate charge-to-mass ratios (M/z), was plotted vs. temperature or time. This, in combination with the outgassing rate curve for each material, provides a semi-quantitative measurement and a comparison of gas species evolved. While it is possible to monitor all gas species evolved, only those species typically associated with the outgassing of absorbed / evolved atmospheric gasses (H<sub>2</sub>O, O<sub>2</sub>, N<sub>2</sub>/CO and CO<sub>2</sub>) and those gas complexes associated with crosslinking or thermal decomposition were monitored and plotted. For the perfluoroelastomers and the fluoroelastomers tested, these were HF, CF<sub>2</sub>H, CF<sub>3</sub>, and C<sub>2</sub>F<sub>3</sub>; for the silicone sample, these were (CH<sub>3</sub>)3-Si and (CH<sub>3</sub>)3-Si-O-Si-(CH<sub>3</sub>)3.

The specifications of the mass spectrometer used for analysis are as follows:

Manufacturer:	Anelva
Model:	M-QA100TS
Filament Type:	Tungsten
Mass Resolution:	M/delta M>2M
Detector:	CEM (Electron Multiplier)
Sensitivity:	3.8 A/Pa (CEM) for N <sub>2</sub>
Min. Detectable Partial Pressure:	1.0 E-12 Pa

## **Results, Observations and Discussion**

# 3.1 Stage I Outgassing (50 °C to 200 °C)

Figure 4 illustrates Stage 1 total outgassing rate vs. temperature data for all four materials identified in Table 1.



Figure 4. Stage 1—Total Outgassing Rate vs. Temperature (50–200 °C)

The data indicate that all four elastomers exhibited an increase in outgassing rate when initially heated from ~50 °C to 200 °C. This was expected. DuPont<sup>™</sup> Kalrez<sup>®</sup> 8900 and VMQ (silicone) exhibited the best performance in this temperature range. Both materials exhibited an increase in outgassing rate, but the slope of the curve was gradual and the magnitude of the increase was small relative to DuPont<sup>™</sup> Kalrez<sup>®</sup> 8475 and FKM-K7. To better understand performance, it is useful to compare selective ion intensity data. Figures 5, 6, 7 and 8 show selective ion intensity data for Kalrez<sup>®</sup> 8900, VMQ-T1, Kalrez<sup>®</sup> 8475, and FKM-7 respectively.



Figure 5. DuPont<sup>™</sup> Kalrez<sup>®</sup> 8900, Stage 1—Selective Ion Monitoring of Outgassing

Figure 6. VMQ-T1, Stage 1—Selective Ion Monitoring of Outgassing





Figure 7. DuPont<sup>™</sup> Kalrez<sup>®</sup> 8475, Stage 1—Selective Ion Monitoring of Outgassing

Figure 8. FKM-K7, Stage 1—Selective Ion Monitoring of Outgassing



Relative ion intensity data was plotted on a log scale. A number of observations were made from the data to help understand the difference in the rate performance of each material and the identity of the gas species that contributed to that difference.

For all the gas species monitored, M/z=18 (H<sub>2</sub>O) had the highest amplitude/intensity for each material.

As temperature increased, the H<sub>2</sub>O ion intensity for DuPont<sup> $^{\text{M}}$ </sup> Kalrez<sup>®</sup> 8475 and FKM-K7 was an order of magnitude higher than DuPont<sup> $^{\text{M}}$ </sup> Kalrez<sup>®</sup> 8900 and VMQ-T1. This appeared to be the primary contributor to the difference in outgassing rate.

The next group of gasses in order of ion intensity included absorbed/evolved atmospheric gasses ( $N_2$ ,  $O_2$ , CO,  $CO_2$ ).

The gasses with the lowest ion intensity were related to thermal degradation. These were HF and CF complexes for perfluoroelastomers and fluoroelastomers and  $CH_3$ -Si complexes for silicone.

The data indicate that all the material classes tested absorb atmospheric gasses (primarily moisture) which outgassed upon heating. It also indicates that outgassing performance within a class of material (Kalrez<sup>®</sup> 8900 and 8475) can be impacted by formulation/compounding differences.

## 3.2 Stage 2 Outgassing (50 °C to 330 °C)

Figure 9 shows the Stage 2 total outgassing rate vs. temperature data for all four materials. For comparison, Figure 10 shows Stage 1 rate data re-plotted using a vertical scale consistent with Stage 2 data in Figure 9.



Figure 9. Stage 2—Total Outgassing Rate vs. Temperature (50–330 °C)



Figure 10. Stage 1—Total Outgassing Rate vs. Temperature (50-200 °C)

Observations and comments regarding the Stage 2 results and the relationship between Stage 1 and Stage 2 are:

- During the second heat ramp cycle, outgassing rate remained very low and flat for all four materials until approximately 200 °C was reached. This suggests that once a material has been exposed to a given temperature and is allowed to outgas under vacuum, its performance will remain stable until a higher temperature is introduced to initiate further reactions.
- From 200 °C to 330 °C, DuPont<sup>™</sup> Kalrez<sup>®</sup> 8900 and 8475 exhibited the lowest outgassing rate while the VMQ-T1 and FKM-K7 showed a significant increase. This is consistent with the generally recognized thermal limitations associates with standard fluoroelastomers and silicones.
- Comparison of the Stage 1 and Stage 2 rate curves indicated a crossover point in rate performance between Kalrez<sup>®</sup> 8475 and VMQ-T1 at approximately 200 °C. It appears that Kalrez<sup>®</sup> 8475 exhibited higher initial outgassing, possibly due to the more hydroscopic nature of its filler system. However, as temperature was increased, the thermal limitations of VMQ-T1 caused it to outgas at a higher rate vs. Kalrez<sup>®</sup> 8475.

Figures 11, 12, 13 and 14 show the selective ion intensity data for Kalrez<sup>®</sup> 8475, Kalrez<sup>®</sup> 8900, FKM-K7, and VMQ-T1 respectively.



Figure 11. DuPont<sup>™</sup> Kalrez<sup>®</sup> 8900, Stage 2—Selective Ion Monitoring of Outgassing



Figure 12. DuPont<sup>™</sup> Kalrez<sup>®</sup> 8475, Stage 2—Selective Ion Monitoring of Outgassing



Figure 13. FKM-K7, Stage 2—Selective Ion Monitoring of Outgassing

Figure 14. VMQ-T1, Stage 2—Selective Ion Monitoring of Outgassing



Although water vapor and absorbed atmospheric gasses represented a significant contribution to the overall outgassing rate for each material, the data also indicates a significant increase in the relative intensity of the gas species associated with thermal degradation, especially for FKM-K7 and VMQ-T1.

Stage 1 rate and ion monitoring data provide a relative comparison of outgassing performance between materials for lower temperature processes. Similarly, Stage 2 data can help identify materials that are suitable for higher process temperatures. Both Stage 1 and Stage 2 data can be used to help select a product within an elastomer class, keeping in mind that variations in formulation can have an impact on outgassing performance. Finally, the very low and flat shape of the Stage 2 rate curve (up to 200 °C) indicates that pre-baking or equipment seasoning can be performed to reduce outgassing. However, conditions under which pre-bake is performed and the handling, packaging and timing between pre-bake and installation, are factors that must be controlled to avoid "re-absorption" of moisture and air. Obviously, the identification and specification of a low-outgassing material may reduce or eliminate the need for any pre-bake or equipment seasoning.

# 3.3 Outgassing Rate vs. Time at 275 °C

Outgassing rate vs. temperature data is not necessarily representative of conditions in a typical process cycle. A more typical process cycle would be to 1. pump down to process pressure and 2. ramp to process temperature and hold. As a result, the elastomers in Table 1 were evaluated when ramped quickly to a specified temperature (275 °C) and held for an extended period of time (21 hrs). Figure 15 shows the total outgassing rate vs. time for each material. In effect, this combines the Stage 1 and Stage 2 test but holds the temperature at an intermediate value.



Figure 15. Total Outgassing Rate vs. Time at 275 °C

A number of interesting and useful observations can be made from this data and this type of plot.

- The shape of the curve for all four materials is similar. However, the magnitude of the high/low rate values and the slopes of the curves are different.
- All three classes of materials (perfluoroelastomer, fluoroelastomer and silicone) experience a sharp rise in outgassing rate as the material is heated quickly to 275 °C. This would be expected based on the Stage 1 and Stage 2 rate data reported in section 3.1 and 3.2.
- At this temperature, DuPont<sup>™</sup> Kalrez<sup>®</sup> 8900 and 8475 offer the lowest steady state outgassing rate followed by VMQ-T1 and FKM-K7.
- While perfluoroelastomers appear to offer the best performance at this temperature, performance can vary due to compounding/formulation differences.

When the temperature is held constant, the outgassing rate decreases and approaches a steady state rate over time for each material. It is clear from this data that if an equipment/process engineer were choosing an elastomer for a UHV application at elevated temperature, DuPont<sup>™</sup> Kalrez<sup>®</sup> 8900 would be the best choice. It exhibits the lowest initial outgassing rate during heat up, the most rapid decrease and the lowest steady state rate. This relative performance is expected. Perfluoroelastomers are generally recognized as having a more thermally stable polymer backbone than fluoroelastomers and silicones. However, while they are recognized as having improved thermal stability and retained mechanical properties at elevated temperatures, not all perfluoroelastomers exhibit the same outgassing performance. This is demonstrated by the difference in Stage 1 and Stage 2 outgassing rate and the long-term data shown in Figure 9 for Kalrez<sup>®</sup> 8900 and 8475. Kalrez<sup>®</sup> 8900 was specifically formulated for low outgassing. As previously indicated, in addition to polymer backbone type, other compounding ingredients including the filler system and crosslinking agents can significantly impact both the short- or long-term outgassing performance of an elastomer. Kalrez<sup>®</sup> 8900 and 8475 are both perfluoroelastomer parts with the same basic polymer backbone which undergo very similar crosslinking reactions. However, they are formulated with different filler systems which appears to impact outgassing performance.

Equipment and process engineers can use this type of data to compare relative performance of elastomers and select materials that enable base pressure to be reached in the shortest period of time. It is not practical or economical to repeat this testing for multiple temperatures. However, it would be interesting to perform additional testing at select temperatures to bracket the performance for the same set of samples. For instance, if extended testing was performed at a lower temperature (e.g. 200 °C) for the same four materials, it is likely that the relative outgassing rate performance and curve shape would be similar but the magnitudes compressed. Similarly, if testing were performed at 300 °C, it is likely the curve shape would be similar but further separated. This is a theory that should be confirmed.

## Selective Ion Monitoring of Evolved Gasses at 275 °C vs. Time

As is the case for Stage 1 and Stage 2 testing, the selective ion intensity data captured during long-term testing at 275 °C can help explain the relative outgassing rate performance between materials. Figures 16, 17, and 18 are examples of ion species data generated.



Figure 16. DuPont<sup>™</sup> Kalrez<sup>®</sup> 8900, Selective Ion Monitoring of Outgassing vs. Time at 275 °C



Figure 17. FKM-K7, Selective Ion Monitoring or Outgassing vs. Time at 275 °C

Figure 18. VMQ-T1, Selective Ion Monitoring of Outgassing vs. Time at 275 °C



Note that the ion intensity data is plotted on a log scale. Figures 16, 17 and 18 compare the contribution of various gas species to overall outgassing of the materials.

Observations are consistent with those made from Stage 1 and 2 ion intensity data.

- For each material the intensity of the H<sub>2</sub>O signal is the highest.
- The overall ion intensity for gas species associated with absorbed/evolved atmospheric gasses (H<sub>2</sub>O, N<sub>2</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>) appears to be generally lower for VMQ-T1 vs. DuPont<sup>™</sup> Kalrez<sup>®</sup> 8900 and FKM-K7.
- While expected at this test temperature, the increased intensity of gas species associated with FKM-K7 and VMQ-T1 thermal degradation is consistent with the thermal limitations for these materials and supports the usefulness of this test method.

## 4.0 Conclusions and Summary

Outgassing is an important performance characteristic that should be considered in the elastomer selection process for applications that are particularly sensitive to small changes in process pressure or process gas uniformity. A number of methods have been used in the past to measure outgassing performance, but none that combined the exposure conditions (temperature and vacuum) that best reflect typical semiconductor processing.

DuPont Performance Polymers has developed a test method that characterizes outgassing performance (outgassing rate as a function of time and/or temperature and identification/monitoring of outgas species) in a vacuum environment. The data generated provides useful information for process and equipment engineers so that better decisions regarding elastomer selection and equipment operation can be made. The method was used to evaluate three classes of elastomers commonly specified in the semiconductor industry (perfluoroelastomer — FFKM, fluoroelastomer — FKM and silicone — VMQ). Results indicate that perfluoroelastomers offer the lowest outgassing performance, especially at elevated temperatures. However, care must be taken to select the appropriate FFKM product, since performance can vary within this or other classes of elastomers due to variations in compound formulation.

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