Getters and Design to Reliability: A Tool For Lifetime Assurance

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Abstract

The key to reaching multi-decade package lifetimes and device reliability is to not just take a snap shot with a RGA and declaring a part passed per MIL-STD-883. It requires a deep understanding of the sources of unwanted gases in a package, characterizing their true flow rates within, without and through the package system, and carefully choosing processes and materials, including getters, to manage the unwanted gases. This is true whether the package is hermetic or non-hermetic.

A multi-step process is discussed to include identifying the gas sources, the species present and their quantities, modeling the true quantities of gas generated over the lifetime of the package, and removing it, either through process or materials. When package service lifetimes reach decades, traditional understandings start to fall apart and careful quantitative analysis is rewarded.

Getters play a key role in attaining multi-decade lifetimes. Getter selection and sizing is discussed. Included in the discussion will be a brief synopsis of the current state of the art of gettering technology.

Key words: getters reliability hermetic packaging leaks outgassing

Introduction

To truly understand the service life impacts of contaminants like water vapor on the wide array of modern package designs and sizes requires a deep understanding of the sources of unwanted gases in a package, characterizing their true flow rates within, without and through the package system, and carefully choosing processes and materials, including getters, to manage the unwanted gases. This is true whether the package is hermetic or non-hermetic.

Indeed, the science and technology behind these understandings has reached a juncture where it has been strongly suggested that academia and the national labs clean sheet the issue as a whole. [1]

The Problem

The problem of unwanted gases within a package is conceptually simple: [2]

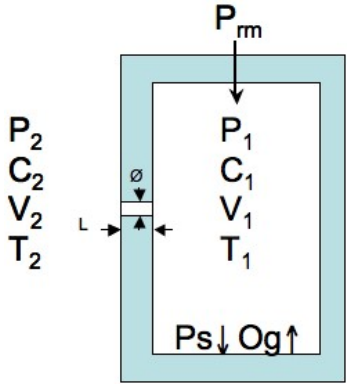

Figure 1: [2] A simple schematic of mass flows within a microelectronic package where:

P = pressure

C = the concentration of the species of interest

V = volume

T = Temperature

P_{rm} = the permeation rate of a species into the internal volume of a package

P_s = the physisorption rate of the species onto the interior surfaces of the package

O_g = the outgassing rate of the species from the interior surfaces of the package

⌀ = the diameter of a leak path

L = the length of a leak path.

Industry and the standards community have historically focused on leaks and the internal concentration of the species of interest, e.g. water vapor and hydrogen. This made sense given that packages were typically made of impermeable materials like metals. In addition, the typical internal pressure of 1 atm and volumes on the order of a few cm^3 masked the impact of mass flow mechanisms such as outgassing and physisorption.

As the interior volume of packages continue to shrink, the impact of outgassing in particular becomes an ever more significant contributor of mass flow into the total system. Consider matters from a simple mass flow perspective. Taking guidance from MIL-STD-883H, Test Method 1014, a leak rate of $5x10^{-8}$ atm cc s^{-1} is the maximum acceptable for volumes of 0.01 cm^3 or less. Indeed it is the lowest leak rate mentioned for any volume device in the test method. Compare it with other leak rates for the time to reach 1 atm from a perfect vacuum:

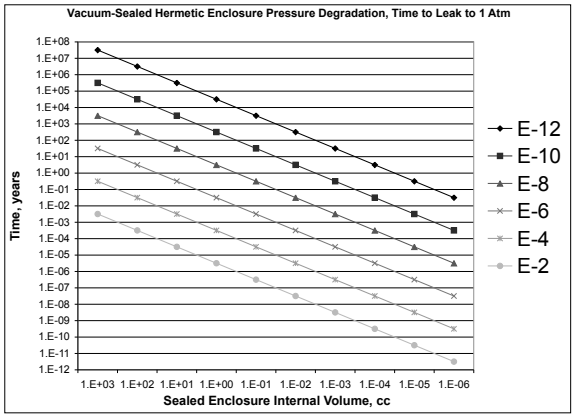

Figure 2: Time to reach 1 atm from a vacuum for various leak rates and device volumes. [3]

At low levels the rates of leak mass flow and outgassing mass flow begin to overlap. This begins to create diagnostic difficulties at mass flow rates on the order 10^{-11} atm cc s^{-1}

The response of industry and the standards bodies to this changing reality has been to focus on reducing permissible leak rates, as much because they can arguably be measured, as for any other reason. The debate over the issue of leaks and their real impact has reached the point where calls have been made to start fresh on the whole issue. [4] [5]

This becomes painfully clear when considering the different estimated package life times that can be calculated when using different leak models ranging from pure Fickian diffusion to the latest empirical work by Rossiter and Neff:

Time to 5000 ppmv Moisture [6]

	200 cc internal volume	**0.01 cc internal volume**
Fick	160 years	0.008 years
Davy	89 years	0.004 years
Rossiter & Neff	850 years	4 years

Quantifying the Problem

Quantitative and scientifically applicable data on the mass flows within a package is crucial to understanding the scope of the problem to be solved. That is if there is a problem to be solved! Historical observations based on a study of archival parts have shown that if a part is hermetic and properly processed it tends to have excellent service life. Good

material and process engineering continues to be critical for success. [7]

The two main mass flows that impact package life are leaks and outgassing. The primary methods of quantifying this mass flows and their constituents are the various forms of leak testing and residual gas analysis, or as it is known in MIL-STD-883, internal gas analysis. In recent years the sensitivity of these methods has increased significantly through the use of time of flight spectrometers and Kr85 leak testing. [8][9]

Sensitive determination by mass spectrometer of the species present is critical to determine if a leak or outgassing is the source of the species of concern.[10][11] Mass spectrometry is also used to measure outgassing rates.[12] Outgassing is a significant source of gas in small volume systems.

In order to estimate the total mass flow into a package of a species of interest, leaks and outgassing are of the most interest in terms of magnitude. When calculating the total mass flow of a leak there are a number of conflicting approaches. Given the actual conditions observed in most packages, the authors and their colleagues lean towards the Fickian understanding of what is occurring.

Outgassing is a much simpler mechanism to model. Quantitative models have been developed that are in daily use in industry. [13] [14]

To calculate the total quantity of gas outgassed over a time period (t) measured in hours, it is customary to assume a time dependence of the outgassing rate q of the type:

(1) $$q = q_0 t^{-v}$$

where the time factor (v) is normally estimated to be equivalent to 1 for gases, such as carbon monoxide (CO) or nitrogen (N_2), which are desorbed from the surface of a material, and is estimated to be equivalent to 0.5 for gases, such as hydrogen (H_2), which desorb by diffusion from the bulk of a material.

The quantity of gas released can be obtained by integrating equation 1 over the desired time period, t:

(2a) $$q = \int q_0 t^{-v} dt = q_0 \int t^{-v} dt$$

(2b) $$= q_0 \frac{t^{1-v}}{1-v} \qquad \text{for } v \neq 1$$

(2c) $$= q_0 \ln t \qquad \text{for } v = 1$$

Evaluating the resultant equations over the range t = 1 to t = t gives us the following:

(3a) $$q_0 \frac{t^{1-v}}{1-v}\Big|_{t=1}^{t=t} = q_0 \frac{t^{1-v}-1}{1-v}$$

(3b) $$q_0 \ln t\Big|_{t=1}^{t=t} = q_0 \ln t - 0 \qquad \text{at } t = 1, \ln t = 0$$

With a quantitative estimate in hand of the mass flows of interest over the service life of the package a getter solution for removing that mass can be developed based on the amount and type of getter needed.

Getters

Getters have a long history of solving contamination issues within hermetic systems. Research on inorganic or organic getter materials that are able to sorb small quantities of reactive gases in vacuum devices began late in the 19th century. The first use of the term "getter" was by Edison's assistant Malignani in 1882. Malignani developed the technique of coating components of incandescent lamps with red phosphorous. Red phosphorous reacts with, or getters, water vapor, thereby breaking the water-tungsten cycle that limits lamp lifetime. This process is still used today in the lamp industry, over a century later.

During the early 20th century successful electron tubes were first developed, but tube lifetimes proved to be impractical. Tube lifetime was limited by degradation of the internal vacuum due to outgassing. New forms of getters were developed as a successful solution to this problem. Getters based on alloys or compounds of barium were developed to supply the necessary sorption capabilities. These getters are referred to as evaporable getters because they are heated to deposit a barium as thin film on the inner surface of vacuum tubes. Such films maximize the available gettering capacity.

Early forms of evaporable barium getters included pure barium encapsulated in small iron or nickel tubes, barium-thorium alloys (Telefunken) and barium-strontium carbonate mixtures (RCA). All of these approaches had stability problems. These problems were solved by the development of the

$BaAl_4$ alloy by Paolo della Porta of SAES Getters S.p.A. in the early 1950s. This alloy is stable in atmosphere and made the high volume use of getters much more practical. $BaAl_4$ getter technology extended vacuum tube life to thousands of hours. [15]

Metal getter technology expanded beyond Ba to include Ti, Zr and their alloys. Metal getters work well for removing gases like O_2, N_2, CO, CO_2, and H_2O from a hermetic device with an internal pressure in the vacuum regime. An example gettering reaction is:

$$Ti + O_2 \rightarrow TiO_2$$

It must be noted that H_2 does not follow this mechanism. When H_2 physisorbs on a chemically active site on a metal getter surface it is split into monoatomic hydrogen which then dissolves into the bulk metal, going into solution. The amount of hydrogen that can go into solution in a metal getter is inversely proportional to temperature and follows a Sievert's Law relationship.

The hey day of classical metal getters was the barium ring era from the 1950s through the 1990s. Hundreds of millions of barium getters were produced every year in the US, Asia, and Europe. With the passing of vacuum tube technology both in electronics and in displays (CRTs) this era has passed, albeit there are still small specialty applications in industries spanning the gamut from aerospace to high end music playback systems.

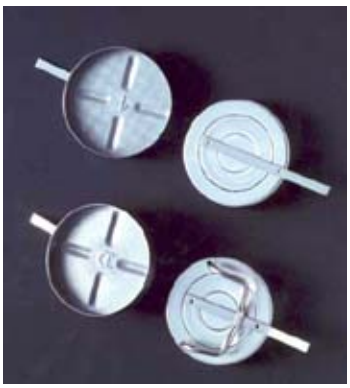

Figure 3: Typical barium getter of the type developed by Dr. Paulo della Porta of SAES Getters S.p.A. [16]

The second wave of metal gettering technology is based on Zr and Ti alloys. These alloys are typically called non-evaporable or NEG getters. The classic application for NEGs and their derivatives such as sintered porous structures is to maintain a vacuum used for thermal isolation in applications like thermos bottles or IR detectors.

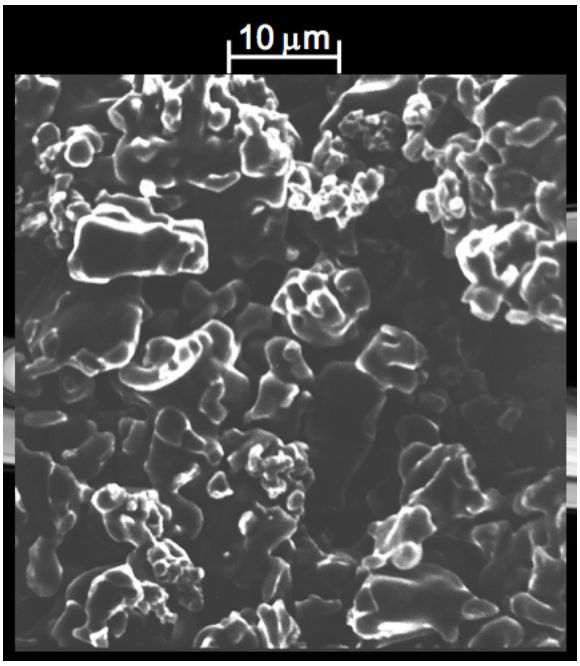

Figure 4: Sintered porous getter structure of a Zr alloy. [17]

Beginning in the 1990s growing issues with contaminating species like hydrogen in non-vacuum packages became more common. A classic example is hydrogen induced degradation of GaAs devices. [18] To solve this problem a new generation of getters was developed.

From a gettering perspective a package filled with a gas as opposed to a vacuum presents significant difficulties. A broad spectrum metal getter that can remove everything from O_2 to H_2O is passivated in short order by the immense (from a metal getter perspective) amount of gas present. In order to provide a useable getter solution two factors came into play. First the focus shifted from taking all potentially harmful species out of a system, as is the norm in a vacuum system, to taking out the critical species, typically H_2 and H_2O. The second factor was to develop active gettering materials that can remove one or two species in an atmosphere of gas without being destroyed by the other gases present.

There are four mechanisms by which H_2 can be gettered from a package. These mechanisms include the formation of metal hydrides, reducing metal oxides, hydrogen re- combination (forming water while in the presence of oxygen) and hydrogenation.

The metal getter community took a thin film deposition path. The original gas of interest was H_2. It is possible to deposit a thin film metal structure that will effectively sorb H_2 without being passivated by the other chemically active gases present. [19] Another pathway was to take gettering approaches used in other industries, for example PdO as used cryogenics to sorb H_2, and incorporate them in structures suitable for use in microelectronic packages. [20]

Both of these approaches present difficulties to the packaging engineer. A metal thin film needs an adequate footprint within a package for deposition. This deposition typically occurs at an outside facility, complicating the workflow. The use of PdO addresses the footprint and workflow issues, but the gettering reaction creates its own issues:

$$PdO + H_2 \rightarrow Pd + H_2O$$

Introducing additional water into a package that the user is already working to keep dry is disconcerting to say the least. The supplier of these formulations does address the issue with the addition of a desiccating agent, but it is still an ongoing concern.

At the current time the most advanced solutions for removing H_2 side step the whole issue of metal films or metal oxides entirely by leveraging hydrogen gettering compounds developed by Sandia National Labs. These compounds work by hydrogenation and can incorporate the end user's desiccating agent of choice.

Originally pioneered by Sandia National Laboratories, these materials are based on the selective hydrogenation of unsaturated carbon-carbon triple bonds and double bonds to their saturated carbon-carbon single bond analogs. These materials scavenge hydrogen in an irreversible manner in contrast to the aforementioned metal hydrides. Additionally, they do not generate water as a part of the reaction chemistry, in contrast to the metal oxide systems such as PdO. The organic hydrogen getter materials offer package designers another option in dealing with the removal of hydrogen from hermetically sealed devices. [21] [22]

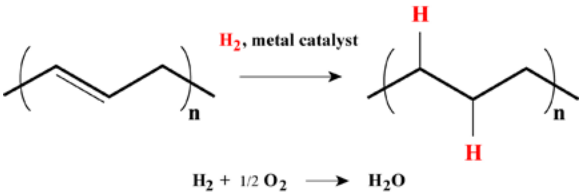

Figure 5: Typical Hydrogenation Getter Reaction

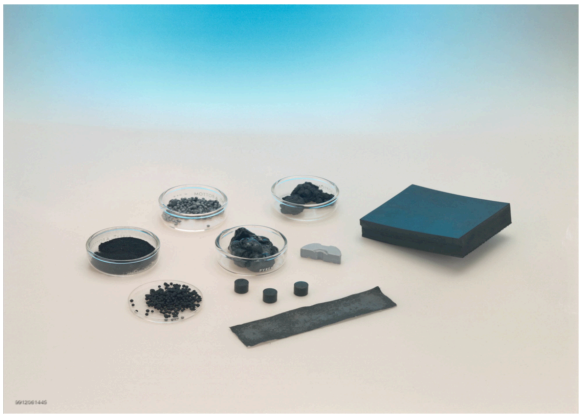

Figure 6: Typical Vacuum Energy polymer hydrogen getters. [23]

Choosing a Getter

Based on this short discussion of the types of getters commonly in use, simple guidelines for choosing a gettering technology to investigate can be given.

Is your package under vacuum or is it gas filled? If it is under vacuum a traditional metal getter system is the most likely candidate. These systems are well understood and the suppliers can assist you in engineering a solution. Caution is urged however, in the MEMS case given the typically very high surface area to volume ratios in these packages as well as limited footprint availability for getter integration. These factors make careful evaluation of the outgassing load critical, as well as absolute hermeticity with no actual leaks.

If a package is gas or air filled matters become more complex. Careful needs analysis is required to identify the actual problem to be solved. Some of the questions to be answered during such analysis are the actual species of concern (H_2, H_2O or something else entirely?), the desired service life, which leak model and test method are most applicable, and more. As volumes decrease and surface area to volume ratios increase mechanisms

like outgassing or the formation of addition water within the package due to hydrogen reducing any metal oxides present becomes more critical to understand.

Removing moisture vapor only from a package is the simplest scenario, solvable by introducing a desiccating agent. Typical agents used in microelectronics include molecular sieves or anhydrous CaO. Usage should be per the manufacturer's directions for best results. Do note that both approaches present issues either of activation for the molecular sieves or preventing hydration of the CaO until the package is sealed. The addition of desiccating agents does present a useful tool for the packaging engineer.

Desiccating agents work by two different mechanisms. These are physisorption and chemisorption. Historically the bulk of water sorbing materials used have been of the physisorption variety, e.g. mole sieves and zeolites. These materials work by presenting very large surface areas to a system for water to sorb on. Molecular sieves and zeolites are often used in conjunction with metal oxide hydrogen getters, where they are used as much to getter the water generated by the hydrogen guttering reaction, as to getter any other water present in the package. To say that it seems somewhat incongruous to create water in moisture sensitive packages is a bit of an understatement.

As packages shrink and have ever higher surface area to volume ratios, the MIL-STD-883 5000 ppmv maximum permissible water vapor concentration specified to keep the number of water monolayers at 3 or less, is ever less applicable to the real world. There are programs now specifying maxim water concentrations as low as 1000 ppmv to prevent corrosion and stiction. When operating at these very low maximum water concentrations, vapor pressure issues become important as well.

In such circumstances a better technical choice (albeit not necessarily the better choice from a process flow perspective) is a chemisorbant like anhydrous CaO. Anhydrous CaO irreversibly (in a practical sense) getters water from a system. CaO provides much lower water vapor pressures that range from 10^{-11} torr at 0 C to 10^{-9} torr at room temperature to 10^{-5} torr at 100 C. Consequently, under normal room temperature operating conditions, the water vapor pressure is 6 orders of magnitude lower than that of a typical zeolite.

H_2 only removal can be equally simple in principle given the available thin film and polymer gettering materials. Both options will sorb H_2 without activation or the generation of H_2O. In the case of the polymer materials a desiccating agent, complete with the associated issues previously discussed, can be incorporated into the final part.

Designing a hydrogen getter is complicated by the source of hydrogen within a package. Hydrogen outgasses from metal components, plating, and metallization of the various internal surfaces within a package. Uniformity of this outgassing rate can not be assumed even within the same lot of materials. It has been observed to vary by up to two orders of magnitude in packages assembled from the same lots of source materials and parts.

A design rule has been developed to accommodate this extreme variability. Historical data shows that H_2 concentrations typically fall within a range of a few hundred PPMV to 27,000 ppmv. An outlier population of approximately 7-8% of the total exceed 27,000 ppmv. Experience shows that even this population rarely exceeds 50,000 ppmv. Consequently hydrogen getters can be engineered to the 50,000 ppmv case plus the desired factor of safety. [24]

Factors of Safety

It is very common for hermetically sealed systems to be used in mission critical components. Applications for gettered systems literally range from the bottom of the ocean to the moons of the outer planets. [25] [26] Getters play a key role in mission assurance for these types of applications.

When considering a getter solution not only must the cost of the getter material and its integration into the package be considered, but also the price of failure should adverse species be allowed to increase in concentration to the point where failure mechanisms are induced. Factors of safety in getter capacity of 2-3 are very common and it is not unheard of to reach factors of safety as high as 10 in applications like space flight.

Conclusions

Getters are not a black art nor do they consist of magic pixie dust. Rather they are highly engineered materials that have solved real world problems for over a century at the leading edge of technical developments from the light bulb to the latest in MEMS based sensor systems.

In Memoriam

The authors would like to dedicate this paper to a key figure in the history of getters. Dr. Paolo della Porta, the founder of SAES Getters S.p.A., passed away this year. His technical rigor and entrepreneurial drive continue to inspire.

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