

# Advanced Getter Materials for GaAs, RF/MW, MEMs and Other Microelectronic Packages

Richard C. Kullberg & Bradley L. Phillip, Vacuum Energy Inc.<sup>1</sup>

&

Timothy J. Shepodd, Sandia National Laboratories<sup>2,3</sup>

## INTRODUCTION

Various getter materials have been developed over the years to deal with hydrogen and moisture caused problems in microelectronic packages. These materials have ranged from adaptations of classical metal getter systems, to the currently prevalent PdO/desiccant mixtures in silicone RTVs, to esoteric metal thin film structures. All of these approaches have been successful when used appropriately, but all of them have also presented implementation difficulties to the packaging engineer. In addition, other issues can arise during a package's service life. A brief overview of these traditional materials and the design concerns they raise will be presented.

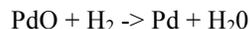
To meet community driven needs and concerns in regards to the primary family of getters used in microelectronic packages, i.e. the silicone RTV mixtures with PdO and desiccants, a new class of getter materials have been developed as a drop in functional replacement for them. Key design goals for these materials has been to increase the capacities for hydrogen and water, while minimizing outgassed VOCs, which is of particular importance to optical applications, while eliminating corrosion inducing ionics and lowering the attainable vapor pressures for moisture inside the package. In addition, the material system allows the incorporation of RF absorbers.

## IMPLEMENTATION ISSUES

To date the major approaches to gettering hydrogen and water from microelectronics have been based on traditional metal getters used in vacuum systems, mixtures of PdO and desiccants in silicone RTVs, and various thin film structures deposited by PVD techniques. All of these approaches have created implementation issues for the packaging engineer:

Traditional metal getters are exemplified by the classic barium ring getter used in CRT TV sets. Metal getter systems need to be used in a vacuum or noble gas environment and require a high temperature activation step. Mounting the getter is often an issue.

PdO/desiccant mixtures, while conceptually easier to implement, since they will operate in normal fill gases, still need an activation step at an elevated temperature in order to remove existing moisture from the desiccants used. In addition, the use of desiccants to capture water formed as part of the hydrogen gettering process is mandatory in these materials as hydrogen is gettered by the following reaction:



It is somewhat incongruous to put a material into a water sensitive device that creates water itself.

---

<sup>1</sup> Richard C. Kullberg & Bradley L. Phillip, Vacuum Energy Inc., 2714 W. Park Blvd., Shaker Heights OH 44120, 216-991-7000, rkullberg@vacuumenergyinc.com & bradlphillip@vacuumenergyinc.com

<sup>2</sup> Timothy J. Shepodd Ph.D., Materials Chemistry Department 8223, Sandia National Laboratories, 7011 East Ave., MS9403, Livermore, CA 94551-0969, 925-294-2791, tjshupo@sandia.gov

<sup>3</sup> Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Co., for the United States Department of Energy's National Nuclear Security Administration under Contract No. DE-AC04-94AL85000.

In order to deal with these issues recent work has been done to create thin film metal structures that pump hydrogen without creating water vapor. While these films are excellent hydrogen getters, they do nothing to pump water from a package and can be both difficult to integrate into a package design, as well as expensive.

## DESIGN GOALS

Based on the existing issues with current hydrogen and water getters for microelectronic packages a simple set of design goals was established:

- no activation
- irreversible pumping of hydrogen & water in any sort of normal operating conditions
- meet or exceed the requirements MIL-STD-883, Test Method 5011.4 for minimizing corrosion inducing ionics in polymer based materials used in microelectronic packages
- minimize outgassing of any organics into the headspace of the package

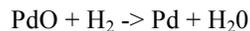
## MATERIAL CONCEPT

Extensive work has been done over the years at Sandia National Laboratories to develop hydrogen gettering materials for use in many different defense & industrial applications. The resulting materials, which work via hydrogenation, are completely passive, completely irreversible with no possibility of hydrogen re-emission, and non pyrophoric. They efficiently scavenge hydrogen down to the sub-ppm range in the cold conditions of the Arctic, as well as at temperatures as high as 300 °C.

In practical terms this means that compounds can be developed to getter hydrogen from microelectronic packages at room temperature that 1) do not require a thermal activation step, 2) will operate in air or other atmospheres, and 3) irreversibly sorb the hydrogen without creating water as a by product.

With these compounds in hand, gettering water from a package becomes a much simpler task as any moisture getter present need only deal with water already present in the system. Such a water getter becomes simple to define in that it should have a reasonably high capacity for moisture, not need any heat treatment to activate it, and pump water irreversibly under the desired operating conditions.

In some cases the presence of a desiccant is a by product of the hydrogen gettering chemistry used and additional desiccant is added to sorb any additional water present in the package:



Typical desiccants used in these scenarios are zeolites with an equilibrium water vapor pressure in the range of  $10^{-3}$  torr, which can be an appreciable amount of water vapor. A downside to the use of zeolites is that they need a bakeout step in order to prepare them for use. This step is typically accomplished at some phase of the material's introduction into the package.

As package volumes decrease the acceptable water concentrations inside the package decrease well below the 5,000 ppmv called out in MIL-STD-883. 5,000 ppmv is a historical compromise designed to prevent the formation of 3 monolayers of water on surfaces inside a typical package of the day. 3 monolayers is a critical metric as it is the boundary condition above which ionics begin to induce corrosion processes on a surface. It therefore becomes critical to not only remove the hydrogen from a package in a manner that doesn't generate water as a byproduct, but to use a desiccating agent that operates at much lower vapor pressures.

A typical desiccant considered in these scenarios is anhydrous CaO, which reacts with water in an irreversible manner under normal operating conditions:



CaO provides much lower water vapor pressures that range from  $10^{-11}$  torr at 0C 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.

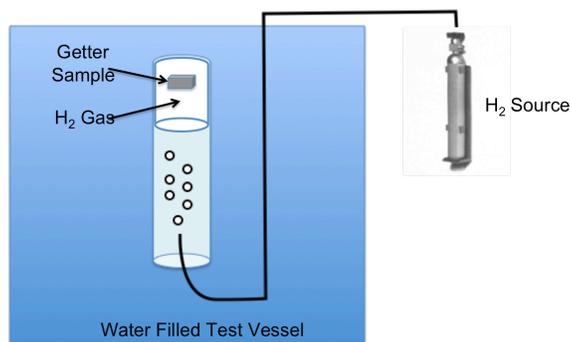
Lastly, any resulting gettering system should be able to be integrated in to a package using normal industrial methods. I.E. the getters should be able to be mixed into various polymer substrates in order to facilitate their use as molded forms, pastes, or dispensable liquids depending on the preferred method of integration into a package.

## MATERIAL PERFORMANCE VERIFICATION

### Hydrogen Sorption Measurement

While hydrogen sorption testing can get quite complicated, particularly when one is studying metal based getter systems, polymeric hydrogen gettering systems lend themselves to simple, yet still quantitative approaches that can be implemented even in incoming inspection scenarios.

There are two basic approaches to simple sorption measurement. These are based on the getter's pumping action changing either the pressure or the volume of a system. These are often referred to as the  $\Delta P$  or  $\Delta V$  methods. For this development effort we used the  $\Delta V$  method, as it is the simplest of all and takes advantage of the insensitivity of polymeric getters to water exposure.



Simple schematic of  $\Delta V$  set up.

To implement the  $\Delta V$  method cut off a piece of getter material with a mass of approximately 0.5 g. Note the actual mass. Wrap a thin copper wire around it and suspend it in a graduated cylinder. Place the cylinder in a vessel containing water and allow it to fill. Invert the cylinder without re-exposing it to air. Put the tubing from the hydrogen source into the vessel and flush with hydrogen for a few seconds. Then bubble a few tens of cc's of hydrogen at a pressure of 1 atm into the inverted cylinder and make note of how much gas is captured. Note the starting volume of gas and gather data over time until the captured volume of gas no longer decreases. The slope of the curve will tell you the pumping speed of the getter sample and the total volume of hydrogen pumped will tell you its capacity per unit mass.

### Water Sorption Measurement

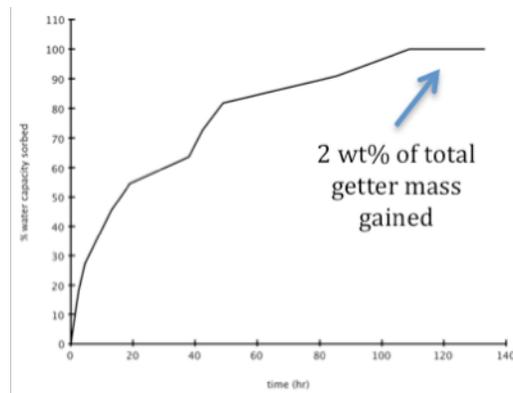
Verifying the performance of proposed materials for water sorption is a simple matter of measuring the change in mass of a sample over time. The purpose of such testing is more of a snap gauge test to ensure that the amount of water gettered approaches the stoichiometric endpoint of the reaction, rather than a detailed study of the reaction itself and any environmental impacts caused by the operation ambient. In other words, desiccants are well understood and all that is necessary for the current work is performance verification. To that end samples were exposed to normal laboratory ambients and the increase in mass over time measured with a normal electronic lab balance.

## RESULTS

For the purposes of this paper sample material was prepared containing both a proprietary hydrogen getter material and CaO as a desiccating agent. Testing on candidate materials began with exposure to atmospheric moisture to verify the water getting ability of the samples. Once water sorption performance was measured the samples were tested for hydrogen capacity as well as ionics content.

### Water

CaO desiccants have a high capacity for water. Stoichiometrically, one mole of CaO will getter one mole of water, or for every 3g of CaO 1g of water will be getter. For testing purposes a small batch of getter material was prepared with 5.5 wt % CaO for sorption testing. The amount of desiccant added was purely arbitrary and can be engineered over a broad spectrum to meet customer needs. At the end of the test the sample gained 2 wt%, or within the theoretical water capacity of the CaO used.

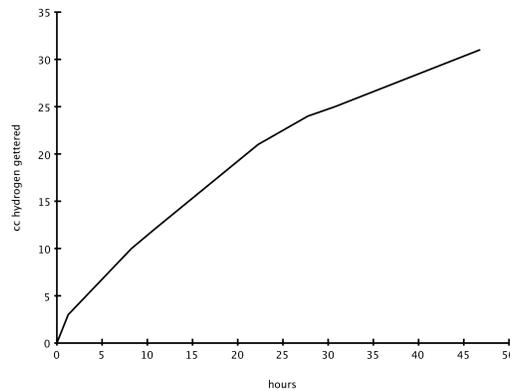


Performance of a polymeric getter structure with CaO desiccant.

As can be seen from the data, appreciable water pumping speed is available but there is also adequate 'throttling' of water diffusion into the getter structure to allow reasonable working times.

### Hydrogen

A 0.5g sample of the original polymeric getter structure, after exposure to water vapor, was tested for hydrogen sorption performance via the  $\Delta V$  method.



Performance of a 0.5g sample after moisture saturation.

As can be seen, even after getting water to capacity and subsequent exposure to liquid water as part of the  $\Delta V$  method set up, the getter was on track to its nominal 50 cc/g hydrogen capacity when the test was ended.

### **Ionics**

Testing materials for ionics per MIL-STD-883, Test Method 5011.4 is an established procedure and is supplied by DSCC certified laboratories. For this talk, rather than reinvent the wheel, we had samples tested by Pacific Testing Laboratories, who is DSCC certified:

<b>MIL-STD-883G Requirements</b>	<b>Vacuum Energy Inc. PolyGetter™ 1B</b>	<b>Vacuum Energy Inc. PolyGetter™ 6D</b>
Total ionic content: $\leq 4.5$ mS/m	Total ionic content: 2.23 mS/m	Total ionic content: 2.22 mS/m
Hydrogen: $4.0 < \text{pH} < 9.0$	pH = 7.9	pH = 7.5
Chloride $\leq 200$ ppm	3.9 ppm	1.4 ppm
Sodium $\leq 50$ ppm	0.8 ppm	4.2 ppm
Potassium $\leq 50$ ppm	$< 0.5$ ppm	$< 0.5$ ppm
Fluoride $\leq 50$ ppm	$< 0.5$ ppm	$< 0.5$ ppm

### **Outgassing**

At this time outgassing testing is still underway and is planned to incorporate concepts incorporated in standards and guidelines currently under development by SEMI. Consequently we will report on this work in a future paper.