Hydrogen problems have concerned the microelectronics packaging industry since the beginning. Hydrogen cannot be totally eliminated, but it can be controlled and removed from a package. Special materials called getters have been developed to remove hydrogen from sealed systems like packages. Hydrogen getter technology has advanced to the point where getters can be deposited on existing package components like lids or on discrete substrates like ceramics that can be conveniently mounted inside a package. These new getters require no thermal activation, adhere well and are non-particulating. In addition, their capacity can be engineered to match the needs of the system they are to be mounted in.

Hydrogen contamination of hermetically sealed systems has been a problem for decades. Examples range from cryogenic dewars, to storage containers for hydrogen sensitive devices, to microelectronics packages. The problem really came to a head with advances into GaAs based devices in the 1990s as they cannot accept traditional solutions for ameliorating Hydrogen contamination issues. In order to understand how to solve these problems, it is important to step back from the immediate concerns with the impacted product and look at the mechanisms of Hydrogen contamination, its measurement, and mitigation.

Sources of Hydrogen

The sources of Hydrogen contamination inside a hermetically sealed system are varied. There are three typical sources encountered in the industry:

- Permeation from external sources
- Degradation of organics used inside the sealed system
- Outgassing from metals.

Permeation from external sources is not often encountered. Typically most sealed systems are used in an ambient surrounded by air. The concentration of Hydrogen in air is only 0.5 ppm by volume and therefore typically is inconsequential. When unexpected external sources of Hydrogen are encountered it is often as simple as a flow of forming gas coming from an adjacent lab or other normal process use of Hydrogen within a facility. Normal procedures for mitigating such sources and permeation into a system will solve this problem.

Hydrogen outgassing from metals is the classic case that historically has drawn the most attention. Several papers have been published on this subject, reporting both experimental data and theoretical considerations. Hydrogen is dissolved in the bulk of metals in the form of protons, after physisorption onto and dissociation on the surface of the solid. Consequently, desorption from the metallic surface takes place under vacuum after diffusing through the material. This behaviour has two important consequences: from the point of view of the outgassing kinetics, Hydrogen follows a different law with respect to the other gas species, since the desorption rate results as the combination of the diffusion of the protons through the metal lattice (depending on temperature) followed by the surface recombination before being released from the surface as H₂. From the point of view of the final outgassing characteristics, even after a strong baking cycle, Hydrogen remains the main gas species released from a metallic surface. Reducing the Hydrogen outgassing rate can be a key action to attain the required vacuum level or Hydrogen partial pressure for a specific application.

Controlling Hydrogen

Gas release from a solid surface depends upon both time and tempera-
ture. The time dependence can be expressed by the empirical relationship:

\[ q(t) = q_0 t^{-\nu} \]

Where \( q_0 \) is the outgassing rate measured one hour after starting of the pumping, \( t \) is the time elapsed after starting and \( \nu \) is a parameter, the value of which is typically 0.5 for Hydrogen (taking into account the diffusive kinetics).

The temperature dependence of Hydrogen gas release obeys an exponential law of the type:

\[ q(T) = \gamma n_o \exp(-E/RT) \]

Where \( \gamma \) is the vibrational frequency of the adsorbed atoms normal to the surface, \( n_o \) is the initial population site, \( E \) is the activation energy for the desorption process, \( R \) is the gas constant and \( T \) the temperature. A comparison between the two equations clearly shows that the outgassing rate is most sensitive to the temperature of the surface being treated, not to the time under pumping. Consequently, increasing the bake out temperature during processing has more immediate impact on reducing the amount of Hydrogen available to outgas into a package over its operational lifetime than increasing the time spent pumping out the package.

**Getters as a solution for outgassing problems**

When gas molecules interact with a solid surface, several phenomena can take place. Certain of these phenomena tend to remove or capture molecules from the gaseous phase. If the surface has suitable characteristics, the adsorption mechanism can prevail. Consequently, there is a net removal of molecules from gaseous phase and a decrease of the gas pressure within the system. This phenomenon is usually known as gettering and the solid materials which exhibit this capability are named getters. Typically the term getter is adopted when the capture of gaseous molecules is due to the presence of relatively strong forces (i.e. chemical forces) and it refers to special metals or alloys.

The use of getters in vacuum technology and gas purification has gained increasing interest in recent years as advances in electronic technology have demanded cleaner ambients and gas feeds for success. New types of getter materials have been developed for these applications, exploiting advanced materials and technologies compatible with the production process of the specific applications.

In vacuum technology, the gettering capability of a material is defined by its gettering rate and capacity. The gettering rate represents the number of gaseous atoms or molecules which are removed from the gaseous phase by the getter per unit time. The gettering capacity is the number of atoms or molecules which can be captured by the getter before it stops sorbing gas. Hydrogen typically shows high solubility and diffusivity inside a getter material, which translates into a high sorption capacity for this gas.

**How to quantify the amount of Hydrogen present**

No means of controlling the amount of Hydrogen present in a sealed system or package can be engineered unless the size of the problem is quantified, allowing proper dimensioning of the getter solution. In order to determine the amount of getter necessary to remove the Hydrogen from a microelectronic package it is necessary to quantify the amount of Hydrogen originally present at the time of sealing the package and the amount expected from outgassing within the package over the lifetime of the package. A normal RGA test can be used to determine the concentration of Hydrogen in the package at the time of sealing. Special tests and equipment are required to determine the outgassing

*Figure 2 – ASTM sorption curve showing getter performance*
component of the total gas load over time. In order to determine the outgassing rate, two techniques are typically used. The first is the known conductance method, which is carried out in dynamic conditions, i.e. pumping away the gas flow coming from the sample. The second is the pressure rate of rise method, which is carried out in a static, non-pumped system. The choice between these two methods depends on the outgassing characteristics of the type of material being studied. The known conductance method is used to measure the outgassing rate from metals, glasses, ceramics, and other materials, which release a relatively low amount of gas. The pressure rate of rise is very useful to make measurements on plastics, foams and other materials that show a large amount of gas evolved, typically water vapour. Both methods can be applied to make measurements on single materials or complete devices. For measuring the outgassing rate of gases in microelectronic packages the known conductance method is typically used.

Hydrogen outgassing and getter dimensioning

Once the outgassing rate for Hydrogen in a system has been determined it can be inserted into a well understood model to estimate with a fair degree of accuracy the total amount of hydrogen expected to accumulate over the lifetime of the package. As we have already mentioned, the time dependency for outgassing is:

\[ q = q_o t^{-\nu} \]

By integrating the measured outgassing rates from typical packages it can be seen that the service life will be quite short if the outgassed species are not trapped in some manner.

Total gas load \((Q) = q_o (t^{1-\nu} - 1)/1-\nu\)

A combination of this total outgassed Hydrogen over the system service life plus the amount of Hydrogen originally present equates to the required getter capacity. There are great variations in Hydrogen outgassing rates from package to package depending on variability in plating and other production processes used by package suppliers. Good engineering practice takes this into account with rather large getter capacity safety factors ranging from 15x to 30x.

How getters work

The theory of bulk gettering of diatomic gases is highly evolved. In a traditional getter system the getter is activated by a thermal treatment in order to depassivate the surface of the getter material, thereby rendering it chemically active. Once the surface is chemically active two gettering mechanisms come into play depending on the gas to be pumped.

In the case of gases like Oxygen or Nitrogen, the gas molecules are first physisorbed onto the getter surface. If the physisorption occurs on a chemically active site the gas molecule will react with the getter material and be permanently captured. Hydrogen is pumped by a different mechanism. On a chemically active (or “activated”) getter surface, a Hydrogen molecule that is physisorbed cracks into monatomic Hydrogen. As protons, the Hydrogen easily diffuses into the lattice or bulk of the getter material. Another gettering mechanism commonly used to pump Hydrogen is to chemically react it with PdO.

\[ \text{PdO} + \text{H}_2 = \text{Pd} + \text{H}_2\text{O} \]

The downside to this means of pumping Hydrogen from a sealed system is that water is formed. This is not unbearable in a cryogenic system where the resulting water vapour can be frozen out on the cold wall of the inner vessel, but can present problems in microelectronic packages. To deal with this issue some vendors put a desiccant in with the PdO. Desiccants add their own problems to the mix by having a relative high vapour pressure of water over them and a tendency to generate particles within the package.

A getter solution for Hydrogen

A Hydrogen getter for microelectronic packages must meet several, competing and severe constraints. A getter must:

- have a high capacity for Hydrogen
- not generate particles
- not contaminate the package by generating water vapour, organics or ioniics
- be able to be integrated into the package
- not require activation at elevated temperatures.

Saes Getters has industrialised a new type of getter designed to meet these requirements. The getter selectively pumps Hydro-
gen and therefore can be used in package ambients (e.g. a package filled with dry Nitrogen) where earlier generation non-evaporable getters (NEGs) cannot work. Advanced Hydrogen getters based on Saes’ Rel-Hy technology take advantage of Palladium’s transparency to the passage of Hydrogen gas. A Palladium film is deposited on top of the Titanium layer in order to prevent its exposure to atmospheric gases that will repassivate it by the formation of oxides, carbides and nitrides.

Once the Hydrogen has passed through the Palladium film it is pumped in the normal fashion by the Titanium. This results in a Hydrogen getter that does not need activation, is insensitive to air and other normal getter contaminants and which does not generate water vapour or particulates. In fact Rel-Hy getters help reduce water concentrations in packages by eliminating Hydrogen that otherwise might react with metal oxides present to form water vapour. The Rel-Hy getter structure is formed by a proprietary process on common electronic industry substrate materials including Kovar, Silicon and other metallic or ceramic substrates up to 228 x 304 mm (Figures 3 and 4).

A common substrate for the Rel-Hy getter film is the package lid itself. The fabrication process allows the getter films to be patterned around ports, windows or sealing flanges on the lid. Figure 4 shows a typical Gold plated Kovar lid with a patterned Rel-Hy getter formed directly on the inside surface of the lid.

**H₂ getter performance and dynamic sorption test results**

Representative samples of the new Rel-Hy Hydrogen getter were tested for performance in a dynamic sorption test at 0.1 Torr of H₂. The test was performed per an ASTM method. The getter shows excellent and consistent pumping speed until the film has reached its capacity for Hydrogen. The fabrication process allows the getter capacity to be tailored to the requirements of the system to be gettered. Hydrogen sorption capacities for Rel-Hy Hydrogen getter films are around 200 cc-torr/cm² (Figure 2). In the laboratory we have also researched Hydrogen getter films with Hydrogen sorption capacities up to about 700 cc-torr/cm². Further developments are ongoing in our labs. In a typical microelectronic package covering the package lid with a getter film with a capacity of 200 cc-torr/cm² will solve the problem with a significant safety margin, while allowing more economical production for the end user.

**Comparison of Rel-Hy Hydrogen getter with a traditional H₂ getter**

Palladium metal is often used as a rough and ready Hydrogen getter. As the closest equivalent material to Rel-Hy it is interesting to compare the Hydrogen capacity of these two materials, particularly given that the gettering mechanism is similar.

The gettering process takes place with minor effect on physical and mechanical characteristics of Palladium, so long as Hydrogen concentrations are kept at low enough levels to prevent the formation of a hydride. The solid solution formed is usually named the α phase. The upper concentration limit for the α phase is called the solubility limit. Concentrations below the solubility limit do not cause changes to the crystalline structure of the Palladium metal grain.

Concentrations beyond the solubility limit create a new phase with a different crystal structure. This new phase, normally called the β phase, is a real hydride with a substantially fixed stoichiometry and very different physical and mechanical characteristics than the α phase. The transition from the α to the β phase induces significant stresses in the material. The lattice structure of the metal grains eventually fails, causing particulation.

Given the sensitivity of microelectronic systems to particulates, the practical capacity of Pd for Hydrogen is therefore that of the α phase. In common units used in the gettering field this capacity is 8.67 torr·l/g at 20°C. Of course it is possible to achieve higher Hydrogen concentrations in Palladium metal by entering the β phase, but, as previously noted, this causes stresses in the material with possible particulation. For ease of comparison between Rel-Hy, which is a thin film, engineered getter material, and bulk Palladium it is useful to norm the Hydrogen capacities of the getters to atm-cc/g of getter material. For Palladium metal it is 11.4 atm-cc/g, while for Rel-Hy the Hydrogen capacity is more than 11 times larger (Table 1). Rel-Hy’s larger Hydrogen sorption capacity provides a more flexible way to integrate a Hydrogen getter inside hermetic packages.

**Film adhesion and particulation**

A qualitative test of Rel-Hy getter film adhesion was performed per MIL-STD-977, Method 4500, Metallisation Adherence, on deposited films. In addition, a qualitative test for particulation using ASTM D 3359-97 was performed on both freshly deposited films and ones that had pumped Hydrogen up to saturation of sorption capacity. In both series of tests there was no evidence of loss of adhesion or particulation.

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<tr>
<th>Rel-Hy Capacity</th>
<th>Performance Factor 1 g Rel-Hy vs. 1 g Pd</th>
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<td>250 cc-torr/cm²</td>
<td>132 atm-cc/g</td>
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Table 1 – Comparison between Rel-Hy thin film and bulk Palladium