Evolution of Getter Technology in Electronic Hermetic Packaging

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***Abstract*— Hermetic packaging is a well-established technology used for sealing electronic and optoelectronic devices. A reliable and enabling way to preserve the proper stable atmosphere conditions in hermetic packages is the integration of engineered getter solutions, specifically designed for the characteristics of different packaged systems. Getter solutions may vary from sintered, compressed or sputtered metallic alloys for vacuum sealed packages to dispensable hybrid organic-inorganic materials for gas back filled devices. The paper will present the main features of getter materials suitable for different type of packages and will show their efficiency in absorbing detrimental gases in the devices.**

Keywords*— *hermetic packaging, getter, gas sorption, gaseous contaminants.

I. Introduction

Hermetic packaging is a standard technology used for defense, aerospace and telecom applications. The main function of hermetic sealing is to protect the device from external atmosphere and harsh environments, ensuring higher performances and ensuring longer lifetime. The hermetic sealing can be obtained in vacuum or in gas back filling conditions, depending from applications and device features. Nevertheless, in both approaches, hermeticity alone is not always able to guarantee a stable and controlled internal atmosphere needed for proper operation of the devices over their lifetime. Indeed, the gas release inside the package due to internal outgassing or gas generation can significantly change the vacuum level or the back filled gas composition, leading to performance degradation or, in the worst cases, failures [1]. In order to manage such potential issues, a reliable and well proven solution can be the integration of getter materials, that can actively absorb the gaseous contaminants. There are different class of getters that can be integrated: Non Evaporable Getters (NEGs) or Dispensable Getters. NEGs are typically used in devices where vacuum is required. Vacuum level may vary in the range from $1 \cdot 10^{-7}$ mbar to 1.0 mbar. Typical devices that operate under vacuum conditions are X-Ray tubes, vacuum interrupters, cooled or uncooled bolometers, photomultipliers, MEMS (accelerometers, gyroscopes, microbolometers), microwave modules. Getter solutions specifically designed for these class of devices are based on metallic alloys that are milled in powders with different size and the powder can be compressed or sintered to constitute pills, or other structures, of different size: typically few millimeters in diameter and height.

Due to the miniaturization trend and shrinking of dimensions of devices in the electronic industry, new getter solutions have been developed that are based on 2D shapes: sintered powder onto metallic sheets to constitute strips or ribbons with height in the range of hundreds of microns.

MEMS sensors are even more challenging, as miniaturization is in the millimeter or sub-millimeter range, an entirely different type of getter has been designed to be integrated in such small, micron-level dimensions. The getter material is a thin sputtered metallic alloy with thickness in the range of few microns. All these types of getters are able to absorb many different gases like, H_2O, H_2, CO, CO_2, N_2, O_2 and hydrocarbons that are typically left inside the cavity of devices after the hermetic sealing process. The getter material gets rid of these contaminants allowing good vacuum levels inside the package and keeping it through the entire device lifetime, assuring not only the performances of the sensor, but also prolonging the stability and reliability over time [2, 3].

Inside opto and photonic devices, instead, gaseous contaminants present in the filling gas may be responsible of device malfunctioning and performance degradation. The main gaseous species that can be harmful for hermetic sealed devices are moisture, hydrogen and volatile organic compounds (VOCs).

In optical transceiver modules, hydrogen and moisture are the main gas contaminants to be removed. Critical levels of these gases are 1000 ppmv for H_2 and 5000 ppmv for H_2O.

There are several problems induced by the presence of harmful gases. For instance, H2 is responsible of electrical performance degradation, it can diffuse through metal layers of active components, causing shifts in currents and trans-conductance [4, 5], it can reacts with surface oxides inside hermetic packages promoting the formation of moisture [6].

Moisture, instead, can be responsible of electrical shorting or corrosion of solder joints. Photodetectors components may be affected by water from dark-current increase [7].

In laser diodes-based devices, like transmitters, the gases that are considered harmful are water and VOCs. The main issues are related to signal attenuation because of moisture or organic gas condensation.

SAES has been developing for many years engineered sorbing materials for optoelectronic and photonic packaging, combined with special polymeric matrixes and with solventless formulation, easy to be directly dispensed and cured on packaging components or sub-components.

The paper presents the functional performances of two classes of getter materials used in vacuum sealed electronic devices and in gas filled optoelectronic ones. The first class is the so-called "Non Evaporable Getters" family that can interact with many gaseous contaminants, the second one belonging to the ZeDry™ getter family is specifically engineered for sorption of H_2O+H_2, H_2O+VOCs or H_2O only, depending on the specific needs.

II. NON EVAPORABLE GETTERS

Metallic alloys-based getters have been developed in order to interact and absorb many different gas molecules that are generally present inside electronic devices that are hermetically sealed.

The getter surface chemically interact with molecules like O_2, CO_2, CO, N_2, H_2, CH_4 and HCs thus removing them from the inner volume of the package. The interaction is irreversible with all the previous gas species, but hydrogen. Indeed, H_2 gas is the only molecule that diffuses into the bulk of the material forming a solid solution. By heating the getter at elevated temperatures, like 600-900°C, H_2 can be released from the material. Typical operating temperatures of devices are well below such values and therefore the risk of H_2 release is negligible.

One of the main features of getter for electronic devices is the porous structure that allows the gases to diffuse into the inner parts of the getter body, thus optimizing the sorption performances of the material. Metallic alloy powder with selected grain size is compressed and eventually sintered in different size and shapes. Typical products are pills or disks like, 4-10 mm diameter and thickness in the range of 1-6 mm.

These bulky getters are integrated in devices where the available inner space is pretty large, like X-Ray tubes, uncooled bolometers or evacuated tube solar collectors.

In order to absorb gases, the getter material needs to be thermally activated. Heating at high temperature the alloy, the native oxides present on the material surface start diffusing into the bulk, leaving a metallic surface that is reactive and can effectively absorb molecules. Depending on the application and on the selected getter material, the activation temperatures range from 300°C up to 900°C. The activation of getters can take place directly during the vacuum sealing process of the device, if the sealing temperature is compatible and allows a proper activation of the material. In this approach, it is possible to manage both processes simultaneously, thus improving efficiency and reduce the overall manufacturing time. Getter configurations that can be integrated and activated directly during the sealing process are illustrated, as examples, in Fig 1.

Another possible approach to activate the getter is by electrical current. In this alternative solution, the material is not activated during the sealing, but afterwards. A metallic heater is integrated into the getter body in order to be used to heat, by Joule effect, the getter material at the desired temperature (Fig.2).

Fig. 1. Getter solutions that can be directly activated during the vacuum sealing process of the device.

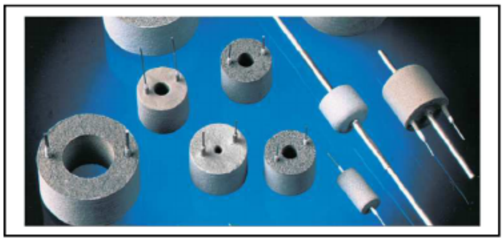

Fig. 2. Example of getter solutions that can be activated by electrical current.

Both options allow proper getter functionality and gas absorption capacity. The selection of the proper configuration is mainly related to the specific device architecture and manufacturing process.

MEMS devices require a completely different solutions from the getter point of view because of the miniaturized dimensions. In this case the getter material is integrated at wafer level. It is a thin film deposited by physical vapor deposition directly onto the cap wafer that is used to vacuum seal the opposite wafer where the sensors are manufactured.

The getter thickness is in the micrometer range and the material can be patterned and shaped according to the specific MEMS design (Fig.3).

The getter activation takes place during the hermetic vacuum sealing process of the wafers. The sketch below (fig.4) schematically shows the sealing process of MEMS with the simultaneous getter activation.

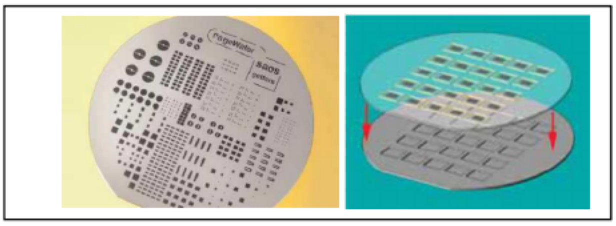

Fig. 3. Thin film getter deposited at wafer level.

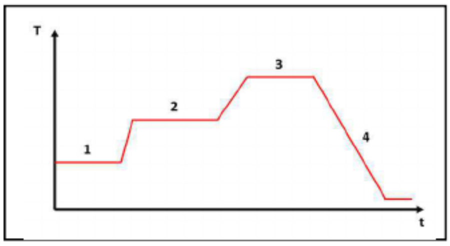

Fig. 4. Vacuum sealing process and getter activation procedure for MEMS: (1)outgassing, (2) getter activation, (3)wafers bonding, (4) cool down.

The first step is to heat the wafers at moderate temperature in order to promote the release of gases from the surfaces, cleaning up as much as possible the wafer before bonding (step 1). The second step is related to the getter activation: the temperature is increased in order to allow the diffusion of native oxides from the surface into the bulk of getter material.

Once the getter is active, the bonding process can take place leading to the hermetic sealing of the parts (sensors wafer and cap wafer).

Regardless the getter material, configuration, size and manufacturing process, the final purpose of the getter integration is the absorption of gases inside a hermetically vacuum sealed device. The following table highlights the residual gases inside an electronic device that integrates or not a getter material (Tab. 1).

This example refers to the residual atmosphere of two identical microbolometers, one without getter and one with getter inside. The getter solution is based on the thin film (about 2 µm thick getter film). The table shows that the getter is able to reduce the total pressure by 3 orders of magnitude or more, absorbing efficiently the active gases (H_2, CO, N_2, CO_2) and significantly reducing at very small levels the CH_4 and HCs partial pressures.

TABLE I. RESIDUAL GASES INSIDE MICROBOLOMETER, WITH AND WITHOUT GETTER (HCS=HYDROCARBONS, NGS=NOBLE GASES).

Gas	No Getter Residual Pressure (mbar)	With Getter Residual Pressure (mbar)
H_2	$4.9{\cdot}10^{-1}$	-
CO	$5.9{\cdot}10^{-1}$	-
N_2	-	-
CH_4	$2.8{\cdot}10^{-1}$	$3.0{\cdot}10^{-4}$
H_2O	-	-
O_2	-	-
CO_2	7.2	-
*HCs	$2.6{\cdot}10^{-1}$	$2.5{\cdot}10^{-6}$
**NGs	$1.1{\cdot}10^{-4}$	$7.7{\cdot}10^{-4}$
TOTAL	8.8	$1.1{\cdot}10^{-3}$

III. ZEDRY-FAMILY

A. Products description and main features

Dimensions of optoelectronic devices are typically small and the technological trend is always to get smaller and smaller footprint and volumes.

Consequently, the available space for integration of components and materials is always limited.

In order to accomplish to this trend, the engineered getters materials have been developed in the form of thick film that can be directly applied to the device lid, or eventually to a subcomponent of the package.

Integration can be effectively achieved by dispensing the getter materials on lids and patterning the shape according to specific geometrical requirements (Fig.5).

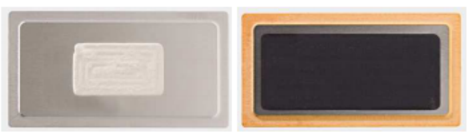

Fig. 5. Example of metal lids with ZeDry® getters coating.

In table 2 we reported the main characteristics and process information of ZeDry® family products.

After dispensation, a thermal treatment is necessary to cure and consolidate the material. The active getter material that reacts with the gas to be removed (H_2, VOC or H_2O) is dispersed into a polymeric matrix without the need of using solvents.

The solventless formulation ensures that no additional, undesirable gases are generated and released inside the device because of the getter formulation.

TABLE II. ZEDRY® FAMILY FEATURES

Formulation
• Solventless formulations: no outgassing issues • Getter coatings can be handled in ambient air • High thermal resistance: decomposition temperatures > 300 °C • Compatible with laser/seam welding sealing processes
Process Integration:
• Getter coatings applied on lids or other components • Thermally cured getter coating with high mechanical stability • Substrates: kovar lids, ceramic, glass
Getter activation conditions prior sealing
• Vacuum – nitrogen – dry air • Temperature range: 100 °C – 200 °C • Time: few hours

The getter composition is compatible with the typical temperatures of the hermetic sealing processes, like laser and seam welding or soldering with eutectic materials, i.e. AuSn preforms. Different substrates, like kovar, plated metals, ceramics and glass can be used: the getter coating has good adhesion and excellent mechanical stability.

To properly work, the getter must be activated by means of a thermal treatment that can be carried out in vacuum, nitrogen or dry air conditions, immediately before sealing the package. Usually, the baking process applied to degas the system components at 105-200°C for a few hours before the final sealing is sufficient to fully activate the getter.

Based on the hermetic package configuration and application, ZeDry® products can be selected in order to interact with the main detrimental gases that are present in the device. Tailored materials were developed for absorption of moisture and hydrogen, or moisture and VOCs, or moisture only if necessary. Depending on the gas species, the interaction can be reversible or irreversible: for H_2 gas the sorption is irreversible, while for VOCs and H_2O the adsorption occurs in a reversible way.

B. ZeDry®-H_2: Getter solution for H_2 and H_2O

ZeDry®/H_2 is a high capacity, solventless, thermally curable, dispensable hydrogen and moisture getter.

It has been designed for use in hermetically sealed optoelectronic devices, microelectronic devices and semi-hermetic packaging of optical and electronic modules. ZeDry®/H_2 works as an irreversible hydrogen getter and as a reversible moisture getter. This product has been engineered also to avoid bleeding tendency on metallic substrates, especially with Au-plated ones.

The specific sorption performances of the ZeDry®/H_2 getter material are reported in Figure 6. The left red graph shows the sorption curve for hydrogen measured at room temperature. Hydrogen uptake signal is followed in a continuous way for 24 hours. Most of the H2 quantity is absorbed after 6 hours of exposure.

The right blue graph highlights the water uptake at room temperature of the ZeDry®/H_2 getter. The kinetics in this case is even faster, since the most uptake of water takes place within 1.5 hours. The nominal hydrogen and moisture capacity are 40 Ncm^3/g and 13%wt, respectively.

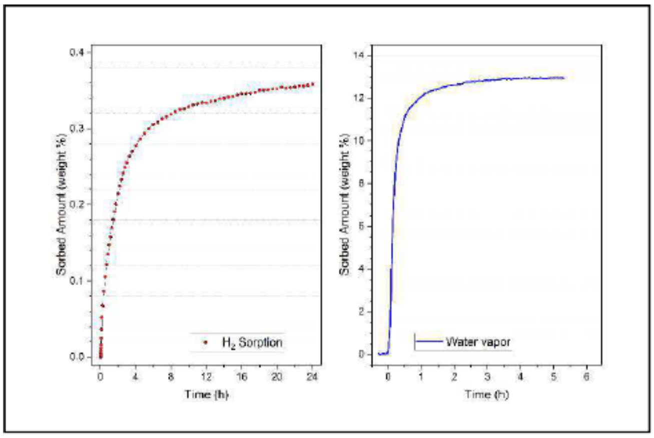

Fig. 6. Hydrogen (left) and water (right) uptake performances of ZeDry/H_2 getter.

C. Getter activation efficiency

In order to assess the efficiency and activation level of the getter material, in terms of water desorption, a series of experiments were performed to investigate different activation conditions and evaluate the performances of the product ZeDry®/H_2.

The water adsorption-desorption capacity and the overall performances were investigated using a digital microbalance (from Hiden) coupled to a temperature controlled vapor analyzer. A proper study of water desorption in isothermal conditions was set up to verify the achievable activation level in terms of recovered water sorption capacity.

TABLE III. RESULTS OF THE ACTIVATION EFFICIENCY-SCREENING PERFORMED ON ZEDRY®-H_2

	Low vacuum activation (<1mbar)		High vacuum activation (<$1\cdot10^{-4}$mbar)		Dry gas activation	
T(°C)	Efficiency (%)	Time (hr)	Efficiency (%)	Time (hr)	Efficiency (%)	Time (hr)
RT	75.6	27	86	26	48	24
50	90.5	8	93.6	7	70.2	10
100	100	4	100	3	100	8

The data reported in Tab.3 suggest that increasing the temperature is the best and rapid way to efficiently activate the getter material. Concerning the environmental conditions, dry atmospheric gas is the least effective procedure both in terms of time and efficiency. Scroll pump and turbo pump activation conditions improve significantly the efficiency, for each temperature, although at RT the activation time is very long and not exploitable for manufacturing purposes. As reported, green data are the most effective conditions for having a well-activated product, while the yellow ones are much less effective.

D. ZeDry®-H_2: Water Sorption uptake at different working temperature

Some demanding high temperatures (T≈100 °C) operating conditions for opto-electronic devices, suggested to set up specific tests in order to assess the performance of the getter in a pretty warm environment, since the getter could partially release the adsorbed water when heated.

In the below measurements (Fig.7), it is shown the moisture uptake at constant partial pressure of water (15 mbar) when the getter is heated at RT, 50°C, 80°C, 100°C and 120°C. The last one is considered the maximum temperature that opto-electronic devices can reach in operating conditions.

Water uptake at room temperature is 13%wt (corresponding to 100% efficiency). By heating the getter, we observed a weight decrease due to partial water desorption from the material. Despite this, the product still provides more than half of the full efficiency at 120°C (6.79% w/w corresponding to 52.1 % of max performance), guaranteeing good sorption properties even in tough working conditions of the device.

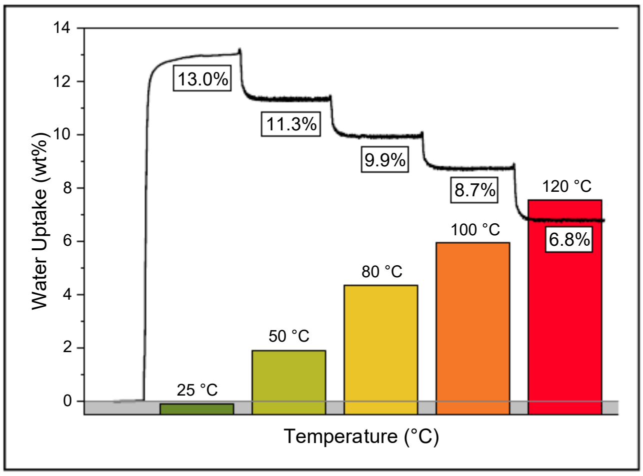

Fig. 7. Zedry®-H2 weight signal variation with exposure to different temperatures, simulating different operating conditions.

E. Water vapor pressure screening

The relative humidity inside devices plays an important role in terms of lifetime and reliability features. We carried out some measurements varying the water partial pressure at constant temperature (RT) in order to get indications about the H_2O uptake by lowering the humidity content and registering the corresponding adsorption signal for Zedry®-H_2.

The range of measured humidity were simulated by varying the operative partial pressure of water inside the microbalance chamber used for the test. In particular 1000, 5000 and 15000 ppmv were used as moisture levels for the test. The material has been activated under high vacuum conditions at 120°C, in order to get rid of all the absorbed moisture, and then the ZeDry®-H_2 lid has been exposed to humid nitrogen gas flow, according to the specific partial pressure of water. The sorption performances are reported in Figure 8.

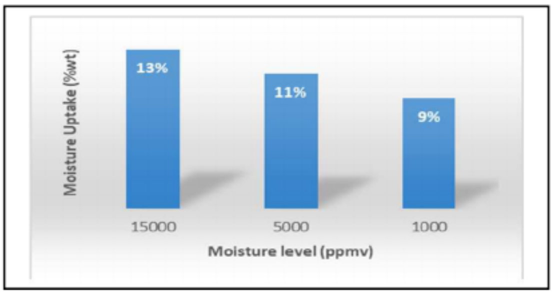

Fig. 8. H_2O uptake of ZeDry®-H_2 with different humidity level

The maximum water performance (13%wt) is reached at 15000 ppmv at room temperature, corresponding to approximately 50% relative humidity. By decreasing the relative partial pressure inside the microbalance chamber, the water absorption decreases to 11%wt and 9%wt, corresponding respectively to 5000 and 1000 ppmv (15% and 3% RH). The ZeDry®-H_2 sorption efficiency is still 70% even at very low moisture levels, demonstrating very good water uptake properties.

F. ZeDry®-VOC: Getter solution for H_2O and VOC

ZeDry®-VOC is a high capacity, solventless, thermally curable, dispensable getter for moisture and volatile organic compounds (VOC).

This product has also low bleed tendency on metallic substrates. It has been designed for use in optoelectronic devices, microelectronic devices and microelectronic devices.

ZeDry®-VOC works as a reversible getter for moisture and VOC (e.g. methyl-ethyl ketone or toluene). In Fig. 9, we reported the results of water and VOC adsorption test in order to highlight the quantity and kinetic of organic molecule uptake.

The sorption curve of Methyl Ethyl Ketone (MEK) is reported as an example of sorption test with VOC and is monitored for prolonged exposure (100 hr), until getter saturation is almost achieved.

For water uptake test ZeDry®-VOC is exposed to 15mbar of constant partial pressure until water saturation is achieved after the activation of the product (120°C for 4hrs).

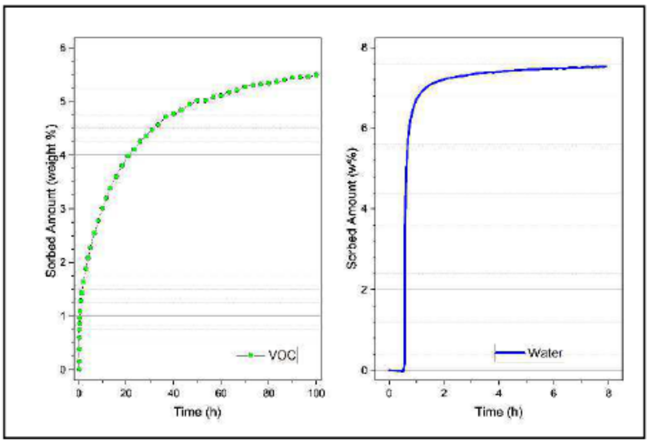

Fig. 9. VOC and Water uptake for ZeDry®/VOC.

The total amount of mix organic adsorption is up to 5.0%wt of cured getter paste recorded in the experimental test and almost 8%wt for water.

G. ZeDry®-VOC: Study of different VOCs adsorption test

The common VOCs can be classified into several groups on the basis of their different properties. Based on the boiling point, the VOCs can be divided into very volatile organic compounds (VVOCs), semivolatile organic compounds (SVOCs) and particulate organic matters (POMs). For the molecular structure, the VOCs include alkanes, alkenes, aromatic hydrocarbons, alcohols, aldehydes, ketones etc. Moreover, the polar and nonpolar VOCs are distinguished according to the degree of molecular polarity.

Taking into account this variety of molecules, we organized a series of experiment in order to highlight the quality of adsorption in terms of different VOC uptake for ZeDry®-VOC. The getter is preliminary activated to cleaning up its surface in order to adsorb the subsequent organic molecules exposed at constant pressure. As reported in Fig. 10 ZeDry®-VOC can face up with different molecules having different chemical features. Even though the kinetic observed was similar for all the compound on the first hour of exposure, on the other hand, the plateau of max adsorption registered was unlike depending on the type of compound.

In fact, for polar compound the maximum uptake recorded was 3.3%wt with a 2.0%wt after 10 hours of VOC exposure, explainable with a poor affinity towards the chemical composition of ZeDry®-VOC.

Linear molecular structure compounds (as ethylene, propane or MEK) resulted in high adsorption value (5.3%wt). Even better results are achieved for medium boiling point molecules showing very high sorption values, 7.4%wt.

This can be ascribed to the small structure of the molecules and easy flowing inside the getter structure, guarantying the best performance in terms of VOC adsorption.

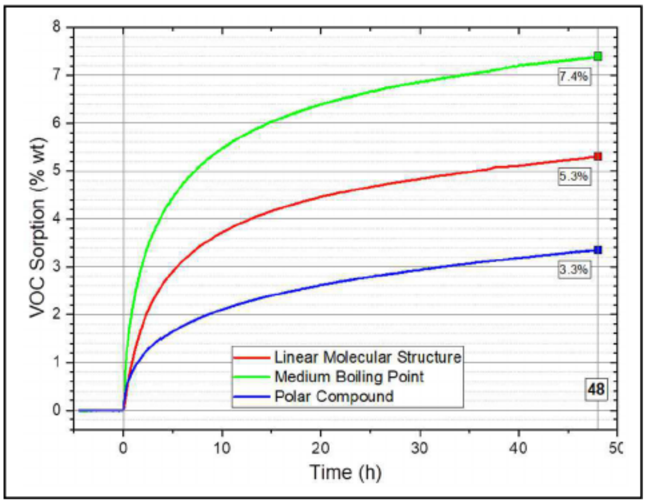

Fig. 10. VOCs adsorption results with different organic molecules families, for Zedry-VOC.

H. ZeDry®-M: High capacity getter solution for H_2O

ZeDry®/M is a high capacity, solventless, thermally curable, dispensable getter for moisture. It was designed to absorb high moisture levels for devices where the only concern is water.

ZeDry/M works as a reversible getter: it can be fully activated with a thermal process at 100°C-150°C, just before the device sealing.

The formulation is optimized for needle dispensing, with blading and die coating as alternate processing techniques.

ZeDry/M is a high capacity getter with a moisture capacity up to 15%wt, as reported in Fig. 11. The plateau is reached after only 1 hour of moisture exposure at 15 mbar, showing an outstanding adsorption kinetic.

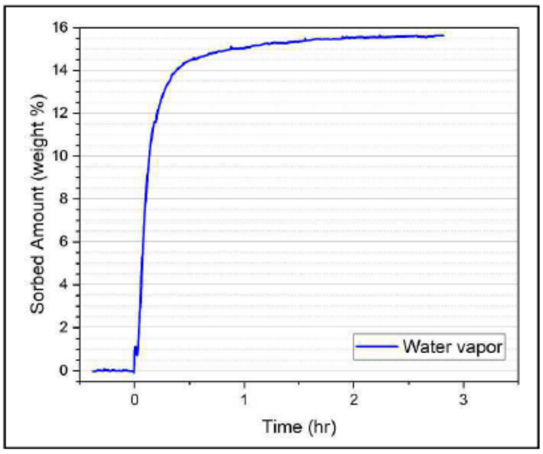

Fig. 11. Water uptake curve for ZeDry/M.

I. ZeDry®-M: Water Sorption uptake at different working temperature

As performed for ZeDry®-H_2, a series of test at different temperatures were carried out, demonstrating the performances of ZeDry®-M at different temperatures. In Fig. 12 is reported the value of water uptake registered with the microbalance, increasing the temperature in order to simulate different operating conditions of devices.

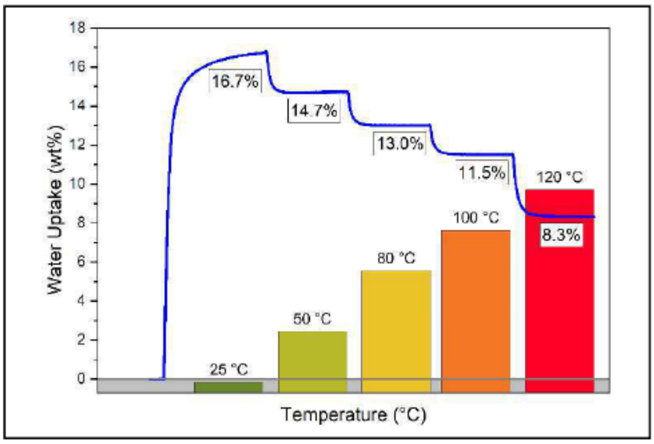

Fig. 12. Weight signal variation with exposure to different temperatures recorded on ZeDry®-M.

In the graph we outline the maximum water uptake at room temperature with an excellent 16.7%wt. As temperature increases, the performance of ZeDry® -M slightly decreases because of moisture partial desorption. At 120°C the water adsorption efficiency is still 50% of the one measured at RT, ensuring proper quality of the device and its reliability at high temperature. ZeDry®-M shows higher sorption performances for every investigated temperature compared to ZeDry®-H_2.

IV. CONCLUSIONS

In this paper, we have presented the evolutions, characteristics and performances of getter products used in hermetically sealed packages for vacuum operated devices and for gas back filled optoelectronic modules.

Hermetic vacuum packaging is achieved by the integration of non evaporable getters. Depending on the application, these materials can be integrated in the form of pills or as thin getter film, deposited by Physical Vapour Deposition, in the case of MEMS sensors. These getters are based on metallic alloy composition and can absorbs many different gases, like H_2, H_2O, CO, CO_2, N_2, Hydrocarbons, and O_2. The main feature of these products is the porous structure that allows the gases to diffuse into the inner parts of the getter body, thus optimizing the sorption performances of the material.

Hermetically sealed optoelectronic devices rely on gas back filling processes. The new products family developed by SAES for these applications, is based on engineered absorber materials with solvent-free formulation: the so called ZeDry® family. The main features are related to the ability to remove significant amounts of water even at elevated temperature conditions or at very low moisture levels; the materials can be easily activated at moderate temperatures in different environments (vacuum or dry gas). Furthermore, the developed products exhibit high sorption performances also for hydrogen and VOCs, ensuring the possibility to remove the detrimental contaminants and guaranteeing the proper operation of the devices along the entire lifetime.

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