Pd Material-based Getter for Removing H_2 from Microelectronic Package

Hua Xia, Jeffery Vriens, David DeWire
Ron Garcia, Brendan Fullam, and Joe Hale

Hermetic Solutions Group, LLC
4000 State Route 66, 1 Hovchild Plaza, Suite 310
Tinton Falls, NJ 07753, United States

***Abstract*— Palladium (Pd) based getter elements are considered to be one of the most promising solutions in removing H_2 gas from a microelectronic package because of no need for thermal activation. This paper has introduced the Sievert's method based manometry technique and internal vapour analysis to quantify H_2 uptake capacity, and uptake rate from Pd based getter elements. The analysed H_2 uptake capacities from different getter elements give a baseline for making decision on the down selection of an appropriate getter element for providing reliable protection to mitigate hydrogen induced microelectronic package performance degradation and reliability issues**.

***Keywords*— H_2 outgassing, Pd H_2 getter, uptake capacity, uptake rate, microelectronic package reliability.**

I. INTRODUCTION

Microelectronic assemblies for use in products at RF, microwave, millimetre-wave, and THz frequencies oftentimes are required to be hermetically sealed in order to protect the internal electronic devices with either metal, glass, or polymer material based containers. Such hermetically sealed microelectronic packages may contain microchips, circuits, and/or devices made from InP, GaN, and GaAs semiconductors, [1] and the performance is often degraded or failed during normal operation. It was found that H_2 gas can be present in packages sealed in forming gas environments, or from outgassing by gold and nickel package materials, or generated by other materials such as RF absorbers inside the package enclosure. H_2 outgassed from the microelectronic package materials can accumulate to 1-2% of the gas volume, which will degrade performance of microelectronic assemblies and devices in long-term operation.

To improve hermetically sealed package reliability against H_2 outgas induced failure modes, a thin-film like gettering element is often used in the package for removing H_2 gas by sorption. A getter is an active material engineered to remove the gas internal to a hermetically sealed volume by sorption process. [2-3] Sorption refers to the taking up of H_2 outgas by physisorption and chemisorption. [4] One method to determine the H_2 adsorption capacity of a reversible getter material is by its torr-liter per square centimeter (torr-liter/cm^2) characteristic, which is generally a measure of the amount of H_2 that a unit area getter element can hold and release. More specifically, it is a measure of the H_2 concentration or volume of the absorbption by a getter element. Being able to effectively absorb the required amount of H_2 from a hermetically sealed package one has to include the H_2 originally occurring at the time of sealing the package in addition to the amount of expected H_2 outgassing within the package over its lifetime. From the package design point of view, it is desirable for an engineer to know what the geometry and size, H_2 absorption capacity, and uptake rate of the getter material should be in order to reliably be used for maintaining the outgassed H_2 at least lower than 10 ppm.

This paper has provided a combined manometric measurement and internal vapour analysis on Pd based H_2 getter's sorption capacity and uptake rate analyses. It has solved practical challenges in precisely determining absorbed H_2 concentration and H_2 uptake capacity from a getter element. The analysed H_2 uptake capacities from different thickness getter elements could provide a baseline for making decision on the down selection of an appropriate getter element for maintaining lower than 10 ppm H_2 concentration in a microelectronic package for long-term reliable operation.

II. GETTER GAS SORPTION

A. *H_2 Gas Sorption Model*

To correlate the measured ΔP(t) data with getter gas uptake quantity and rate performances, especially in the case of H_2/Ar mixed testing gas, a gas sorption model has been developed. Figure 1 shows an imaginary H_2 gas adsorption, absorption and diffusion process surrounding a getter element that is attached to package interior wall. The H atoms adsorb

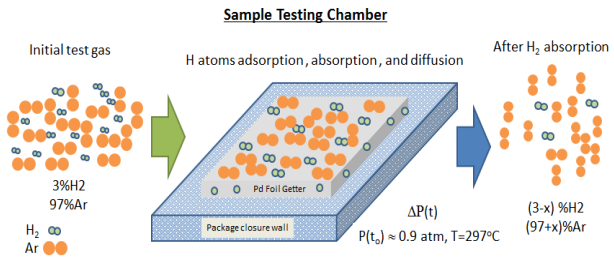

Fig.1 Gas sorption model from a Pd foil based H_2 getter with hydrogen and argon

onto the getter surface and diffuse into the Pd bulk volume, leaving Ar molecules in the testing chamber. At the static and non-gas-pumping testing condition, the chamber pressure is decreased by the H_2 absorption and diffusion kinetic processes of the getter element.

By using ideal gas *PV=nRT* law, the getter sorbed H_2 concentration at time, *t*, could be approximately obtained by measured testing chamber pressure variation by

$$C_H(t-t_o) \approx \frac{P(t_o)-P(t)}{P(t_o)}, \quad (1)$$

where $P(t_o)$ is initial testing chamber pressure before testing gas purge into the chamber. At the beginning of the test, the pressure shutoff valve controlled testing gas may take τ time for flowing through the getter element that leads to newly balanced pressure $P(t_o+\tau)$ and initial sorbed H_2 quantity, $C_H(\tau)$.

On the other hand, the 97% mixed Ar gas molecules won't be sorbed by the getter element but adversely act as "occupiers" for obstructing hydrogen molecules absorption at the getter surface, which likely reduces getter's H_2 uptake rate. Similar to gas outgas mechanism [5-10] the getter H_2 absorption quantity may be described as

$$C_H(t) = C_H(\tau)\cdot\left[\frac{t^{\nu}}{1-\nu}\right], \quad (2)$$

where ν is a time constant related to gas species. The obstruction effect of getter element surface H_2 absorption, produced by the argon gas molecules, may be written as

$$C_{Ar}(t) = -C_H(\tau)\cdot\mathrm{Ln}(t). \quad (3)$$

The absorbed H_2 gas in the getter element, at a specific testing time *t*, will be

$$C_H(t) = C_H(\tau)\cdot\left[\frac{t^{\nu}}{1-\nu} - \mathrm{Ln}(t)\right]. \quad (4)$$

Meanwhile, this time-dependent H_2 adsorbed quantity could give a so-called dynamic sorption or uptake rate by derivative of Eq. (2):

$$\gamma(t) = C_H(\tau)\cdot\left[\frac{\nu\cdot t^{\nu-1}}{1-\nu} - \frac{1}{t}\right] \quad (5)$$

where the ν has an estimated equivalent of 0.50 for pure H_2 gas and 0.55 for low hydrogen mixed gas. This rate actually includes both adsorption (surface accumulation) and absorption (diffusion into bulk Pd element) effects.

The up-limit of the H_2 gas absorbed concentration $C_H(t)$ is determined by non-stoichiometric ratio *x* or PdH[*x*]. If the density and mole weight of a rectangular shape (a×b×h) getter element are represented by ρ and M_o, the maximum molar hydrogen gas sorption is determined by

$$n_{max} = x\cdot\frac{\rho\cdot abh}{M_o}\times\frac{1}{2} \quad (6)$$

where the maximum stoichiometry *x* is about 0.70, representing 70% of the octahedral holes filled by H atoms with a completed β-phase getter structure. For electronic package industry, a getter element's gas sorption capacity is defined by

$$\Psi(T,P) = \left[\frac{P_0\cdot T(t)}{P(t)\cdot T_o}\right]\Psi_o = \eta(T,P)\cdot\frac{n_{max}\cdot RT_o}{a\cdot b}, \quad (7)$$

where *R* (8.314 J/K·mol) is the gas constant; H_2 capacity is Ψ_o with P_o=760 torr and T_o=298K; T(t) and P(t) are real-time temperature and pressure in the testing chamber. The unit of this H_2 capacity is in torr-liter/cm^2. On the other hand, the maximum absorbed gas volume also can give another expression of the H_2 capacity by

$$\Psi_v(T,P) = \eta(T,P)\cdot\Psi_\upsilon = 2.625\times10^3\cdot\eta(T,P)\cdot\frac{\rho\cdot RT_o}{\Delta P\cdot M_o}, \quad (8)$$

where the unit of this H_2 capacity is in cubic centimeter/cubic centimeter (cc/cc). As an example, H_2 capacity of a 1.0"×1.0"×0.006" getter element can be expressed either by 11.2 torr-liter/cm^2 or by 967 cc/cc at ambient pressure (760 torr) and temperature (298K) conditions.

III. EXPERIMENT

The characterization of the Pd getters has been conducted by the manometry method that measures pressure variation during the gas sorption process. The manometry technique is based on Sievert's method for measuring the sorption of hydrogen by materials, which uses an isothermal system with fixed volume, and the pressure drop amplitude is measured for estimating the absorbed H_2 quantity. The manometric measurements are conducted by observing pressure rate of drop in a static, non-pumped chamber either under ambient or elevated temperature conditions. On the other hand, internal vapour analysis is based on residual gas analysis that determines the concentration of hydrogen in the manometry testing chamber. By measuring pressure drop amplitude and residual gas analysis one can accurately obtain the absorbed H_2 quantity at a specific time. Figure 2 shows a diagram of the manometric testing system, with a computer based data acquisition unit.

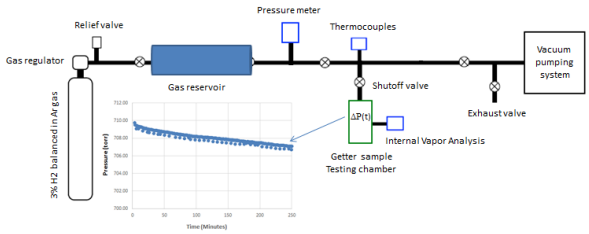

Fig.2. A diagram of the manometric testing system for H_2 getter performance quantification

The test was conducted under ambient 293K temperature where the pressure in the sample testing chamber, P(t), is recorded in one minute intervals. This manometry technique keeps the sample testing chamber under isothermal status with a liter volume for measuring pressure rate of drop statically without flowing test gas, while internal vapour analysis is used to determine residual gas composition in the testing chamber. For all tests, a test gas with 3%H_2, balanced in the argon gas is used, pre-certified for ±1% accuracy in gas compositions.

IV. RESULTS AND DISCUSSIONS

A. *Getter Kinetic Response*

Figure 3 is a typical pressure response from the getter H_2 sorption test, where the 1 liter volume testing chamber is under an initial temperature of about 292.7K. The observed

pressure amplitude drops as a function of time due to sorption of the H_2 in the getter element, accompanying about 2.5°C temperature decreases due to high heat capacity of the hydrogen gas during initial minutes. After testing chamber approaches quasi-equivalent, the gas pressure has dropped about 3 torr at the end of 300 min test.

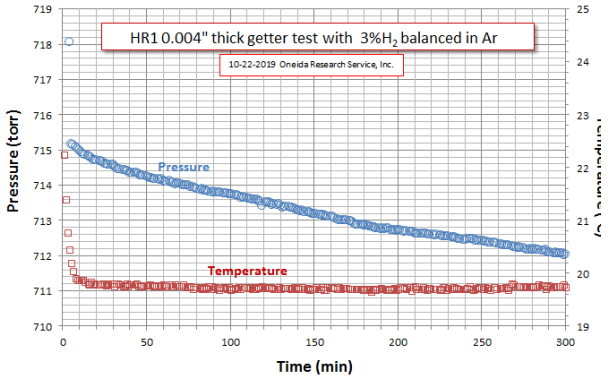

Fig.3. Measured pressure variation and the testing chamber temperature from a typical 0.004" thick Pd foil based getter element

The gas sorption model described by Eq. (2)-(5) has been applied for getter sorption analyses, as shown in Fig.4. First, the measured $\Delta P/P_o$ data are converted to the absorbed H_2 (□) using Eq. (1). The uptake rate (○) is simply obtained by $\Delta P/(P_o\Delta t)$ variation. Second, the calculated getter absorbed H_2 (red curve) and uptake rate (yellow curve) are compared with measured data with ν=0.55 and $C_H(\tau)$=(100±20) ppm.

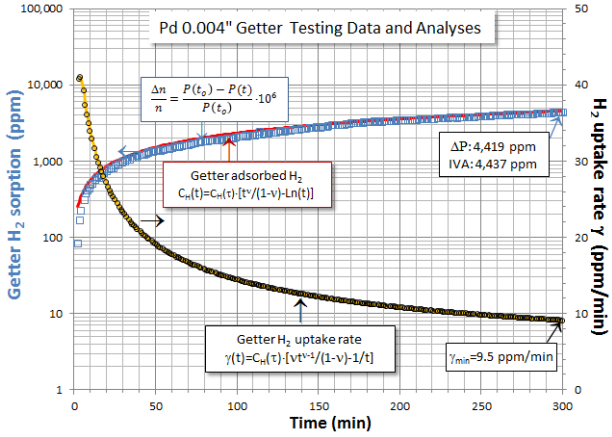

Fig.4. H_2 sorption concentration (open squares) from a typical 1.0"×1.0"×0.004" thick Pd based getter, where the red and yellow lines are from the gas sorption model analyses

To accurately measure how much H_2 is absorbed by a getter element, it will be ideal to measure real-time H_2 gas concentration from the testing chamber with a residual gas analysis during full measurement process. In fact, the taken away small amount of the testing gas will interrupt testing chamber quasi-equivalent gas pressure at least a few torr. Thus, the measurements in Fig. 4 were terminated at 300 min for testing chamber gas composition analyses. From the getter absorbed H_2 data the getter element may have adsorbed 4,419ppm H_2 after 300 min. The internal vapour analyses from a small portion of the gas sample, withdrawn from the sample testing chamber, show that the H_2 composition is about 25,563 ppm at 300 min, indicating a loss of the H_2 composition from 3%H_2 testing gas to be 4,437 ppm, which is consistent with the measured 4,419 ppm manometric data, within ±1% specified testing gas accuracy. Figure 5 further has extrapolated the H_2 kinetic responses from 0.002" thick getter to 0.004" and 0.006" thick getters, with maximum H_2 absorption quantities of 31,700ppm, 63,400 ppm, and 95,100 ppm and corresponding uptake rates of 2.9 ppm/min, 1.5ppm/min, and 1.0 ppm/min.

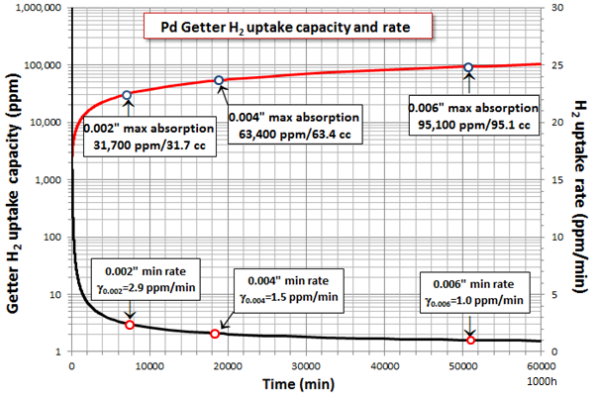

Fig.5. H_2 uptake capacity and uptake rate from Pd getter elements with different thicknesses

B. *Getter H_2 Absorption Capacity*

H_2 absorption capacity is one of critical parameters in characterizing a getter's performance. Figure 6 shows typical H_2 capacity measurements on a 0.004" thick Pd getter. The red curve is H_2 capacity at standard ambient condition of 760 torr and 25°C, while black curve corresponds to test at 22°C/800 torr. As gas sorption model has expected that both testing pressure and temperature can vary the measured H_2 capacity; for example, it is 1.59 torr-liter/cm^2 at 22°C/800 torr condition, but it is 2.02 torr-liter/cm^2 at 25°C/760 torr.

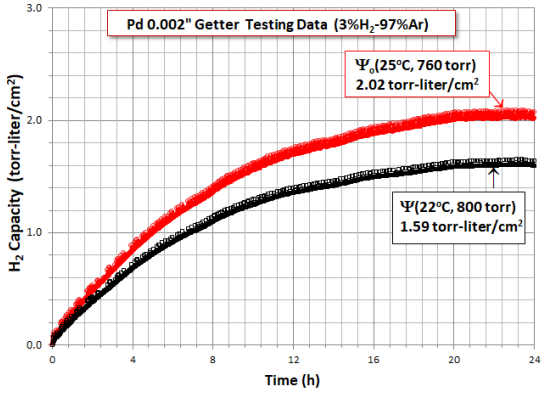

Fig.6. H_2 capacity from a 1.0"×1.0"×0.004" thick Pd getter element

C. *Package H_2 Outgassing and Removing*

To effectively ensure H_2 gas removal from a microelectronic package, including initial H_2 and outgassed H_2, another critical parameter is related to outgassing rate of the package materials. Metal materials (such as stainless steel and Ti-alloy) has its H_2 outgassing rate of typical 1.6×10^{-9} torr-liter/sec·cm^2, but polymeric materials may have 1.0×10^{-6} to 2.5×10^{-8} torr-liter/sec·cm^2 outgas rates. Table 1 has listed some of typical outgassing rates from some metal and polymeric materials for estimating what a Pd getter's uptake rate is sufficient to keep the package under 10ppm even 0 ppm during its operation lifetime. Since a microelectronic package is an integration of various package materials, including metal, glass, ceramic, polymer, and semiconductors, one can

Table 1. Typical H_2 outgassing rates from some metal and polymeric materials for references

Materials	Outgassing rate (torr-liter/sec-cm^2)
Stainless steel	1.4×10^{-9}
Ti-alloy	1.8×10^{-9}
Al-alloy	3.8×10^{-8}
PTFE (Teflon)	2.5×10^{-8}
PETP	4.0×10^{-7}
Viton	1.0×10^{-7}
Kapton	1.0×10^{-7}
Epoxy	1.0×10^{-6}

presume an averaged outgassing rate of 1.6×10^{-8} torr-liter/sec·cm^2, for estimate of averaged outgassing rate. The total hydrogen gas that has to be removed by a getter element should be the sum of the initial H_2 gas and outgas of all the package materials. Figure 7 has shown the predicted time for removing or pumping all the H_2 gas away from the package internal space with initial H_2 gas with its concentration from 1000 ppm, 2,500ppm, 4,000 ppm, and 5,000 ppm. As shown by Fig.7 that a Pd based getter, regardless its thickness, could

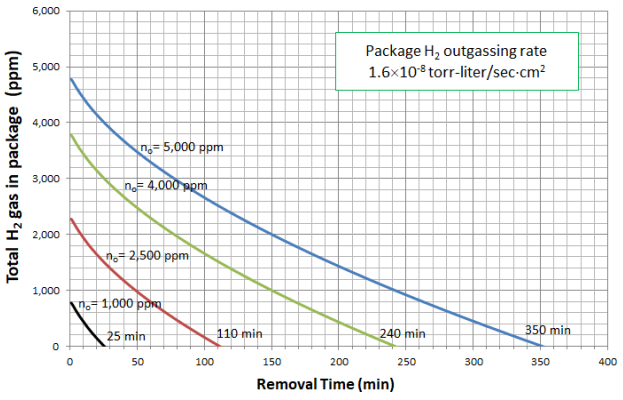

Fig.7. H_2 removal time from a getter element with initial H_2 after the package hermetically sealed, and the H_2 outgassing from package walls and various microelectronic devices sub-package materials

take 25 min, 110 min, 240 min and 350 min for fully removing or at least effectively reducing H_2 gas concentration to lower than 10 ppm, which is a critical level for ensuring long-term microelectronic package reliability. In fact, this absorption process could be accelerated by having package at a proper temperature or internal pressure if necessary.

After the getter has completely absorbed initial H_2 gas, it is also important to see how a getter acts to absorb or pump away the outgassed H_2. Figure 8 shows the Pd getter, regardless of thickness, has its H_2 uptake rate of $>1.0\times10^{0}$ ppm/min (red curve). While the outgassing rates of the metal and polymeric materials are 2-5 orders lower than the getter uptake rate. For example, the thermoplastic material's outgassing rate, such as Viton and Kapton, is close to 1.0×10^{-3}

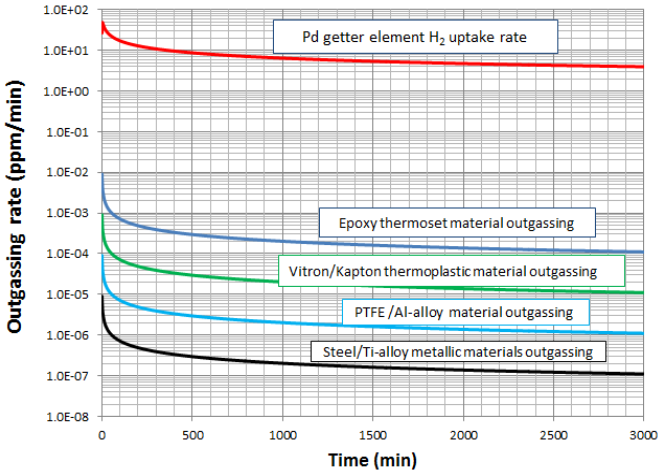

Fig.8. Comparison between H_2 outgassing rates of different package materials and H_2 getter uptake rate

ppm/min at the initial of H_2 outgassing, a 3-order lower than the getter's minimum uptake rate. It should be pointed out that the epoxy based material outgassing rate is only about two orders lower than the Pd getter's minimum uptake rate. It may be appropriate for selecting a getter element that has its H_2 uptake rate at least three-order higher than the averaged package outgassing rate. Such a 3-order selection rule could provide effective capability in pumping outgassed H_2 away from the package internal space.

V. CONCLUSION

This paper has presented a manometric method to quantify Pd based H_2 getter's adsorption capacity and uptake rate performances, and demonstrated how a Pd getter could be used to remove initial present H_2 gas during hermetic seal process and outgassed H_2 from the microelectronic package materials. The measured pressure drop is directly converted to loss of H_2 in the testing chamber, and the getter H_2 absorption can be directly verified by internal vapour analysis for the first time. A gas sorption model has been developed to simulate H_2 gas sorption kinetic process, which could provide fairly prediction on the gas absorption and uptake rate. Such a one-to-one correlation has solved practical challenges in precisely determining absorbed H_2 gas by a Pd getter element at a

specific time, and H_2 kinetic uptake capacity and rate, maximum H_2 capacity, and minimum uptake rate from the Pd based getter elements. These critical performance parameters could provide package engineers for down selecting an appropriate H_2 getter to mitigate outgassed H_2 induced reliability related failure modes.

ACKNOWLEDGEMENT

This work was conducted at Hi-Rel Alloy Division of Hermetic Solutions Group, LLC and the services on manometric tests and internal vapour analyses have been provided by Oneida Research Service, Inc. We appreciate Jeffrey T. Rossiter (ORS) and Daniel Rossiter (ORS) for their contribution in the testing system setup and conducted all tests.

REFERENCES

[1] D. Ragle and S. Kayali, Final Report on "Hydrogen effects on GaAs microwave semiconductors" IEEE 1997 GaAs Reliability Workshop. Proceedings (1997).

[2] R. Ramesham, "Getters for reliable hermetic packages", JPL Report D-17920 (1999).

[3] P. J. Nigrey, "An issue paper on the use of hydrogen getters in transportation packaging", Sandia National Laboratories Report, SAND2000-0483 (2000).

[4] Z. Zhao, Y. Sevryugina, M. A. Carpenter, D. Welch, and Hua Xia, "All-Optical Hydrogen-Sensing Materials Based on Tailored Palladium Alloy Thin Films", Anal. Chem. 76, 6321 (2004).

[5] R. Ramesham and R. C. Kullberg, "Review of vacuum packaging and maintenance of MEMS and the use of getters therein", J. Micro/Nanolith. MEMS MOEMS 8(3), 031307 (2009).

[6] R. K. Lowry, R. C. Kullberg, and D. J. Rossiter, "Harsh environments and volatiles in sealed enclosures", Proceedings of Surface mount technology association international technical conference, Orlando, FL, pp380 (2010).

[7] K. J. Gross, K. R. Carrington, S. Barcelo, A. Karkamkar, J. Purewal, S. Ma, H. C. Zhou, P. Dantzer, K. Ott, T. Burrell, T. Semeslberger, Y. Pivak, B. Dam, and D. Chandra, "Recommended best practices for the characterization of storage properties of hydrogen storage materials", National Renewable Energy Laboratory Contract No. 147388 (2012).

[8] K. M. Hubbard, C. W. Sandoval, "Characterization and testing of improved hydrogen getter materials -FY16 Annual Report", Los Alamos National Laboratories Report: LA-UR-16-28571 (2016).

[9] R. Grinham and A. Chew, "A review of outgassing and methods for its reduction", Appl. Sci. Converg. Technol. 26(5), 95 (2017).

[10] R. Ramesham, "Evaluation on non-evaporate getters for high vacuum hermetic packages", Final Report, JPL D-27440 (2017).

Author Contact Info

Hua Xia, hxia@pacaero.com, (509) 881-5420
Jeff Vriens, jeff@hi-rel.com, (289) 990-9296
David DeWire, ddewire@hermeticsolutions.com, (303) 921-2222
Ron Garcia, rgarcia@hermeticsolutions.com, (949) 241-3443
Brendan Fullam, bfullam@hermeticsolutions.com, (631) 807-2923
Joe Hale, jhale@hermeticsolutions.com, (508) 902-8699