The Effects of Hydrogen On Device Reliability

…and Insights on Preventing These Effects

By Philipp wh Schuessler, IBM/SID and Diane Feliciano-Welpe, Oneida Research Services, Inc. Whitesboro, N.Y.

The potentially detrimental effects of outgassed hydrogen on device reliability have been substantiated in the trade press over the past several years. Non-specific to silicon or gallium arsenide technology, its negative impact is universal and can range from hydride formation with ensuing material deformation to oxide reduction followed by moisture-related failure mechanisms. In keeping with the microelectronics industry's move toward "building-in reliability," this article focuses on identifying one of the sources of outgassed hydrogen in hermetically sealed devices and offers some prospective alternatives to processing and assembly to aid in its prevention.

Introduction

As the microelectronic community has gained maturity in the last decade, it has also revealed unique materials and environmental stress failures that require a basic understanding of the chemistry and metallurgies before effective solutions can be implemented.

Of particular interest in recent years has been the unique problems that occur when hydrogen evolution into the cavity of a microelectronic device takes place. Hydride formation, oxide reduction, excessive moisture levels and, ultimately, device failure are now being attributed to this residual processing gas.

Several experiments employing residual gas analysis per the existing Method 1018 of Mil-Std-883 were designed to identify a primary source of this outgassed hydrogen and to provide some insights on controlling the effects of this gas.

Through these experiments, the ferrous alloy packaging materials used for the body and/or the cover of the device were identified as a primary source of outgassed hydrogen during and after standard manufacturing processes. Predevice manufacturing processes utilize this gas and although its presence is in the parts per million range for the base metal, hydrogen is readily detected at exponentially higher levels within the finished device. Neither nickel flash nor gold platings can prevent this diffusion of hydrogen into the cavity, but they can contribute to the problem.

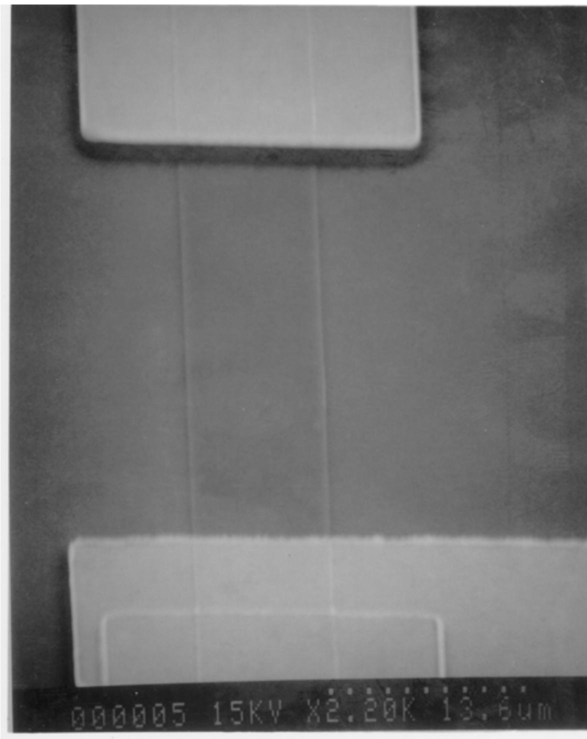

Figure 1, SEM at 2200X showing Titanium resistor.

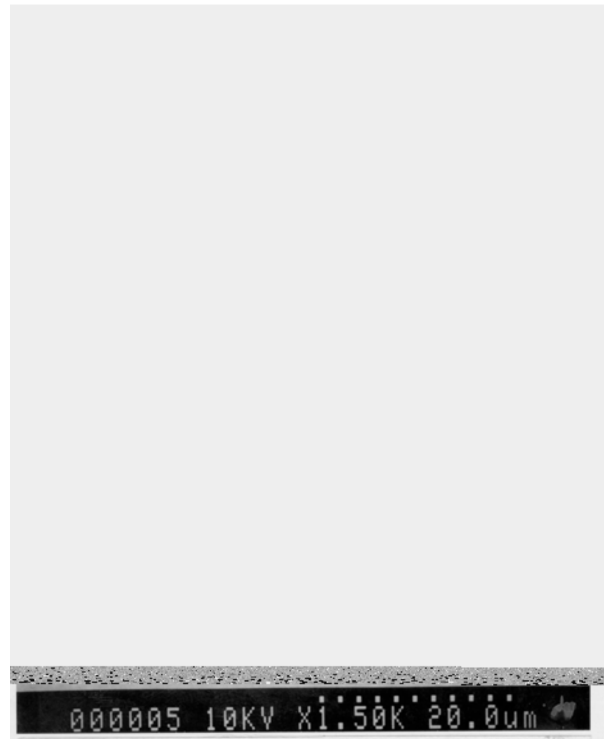

Figure 2, SEM at 1500X showing Titanium resistor forming the hydride.

Observations

A GaAs device, designed for use in a Radio Frequency (RF) application, had recently showed tendencies to lose performance as a function of time in test. Failure analysis of the devices showed that the titanium resistors used in the early designs had undergone physical change, as shown in figures 1 and 2. This series of photographs depicts how a normal thin film titanium resistor gradually degrades via hydride formation. The amount of material between the two leads becomes excessive as the H_2 is absorbed and the resistor begins to physically deform. In conjunction with the observed changes and loss of performance, a significant increase in hydrogen gas had been detected in the cavity of the device. This noted concentration of hydrogen was difficult to eliminate as shown in table 1 and it was, more importantly, shown to be directly associated with device failure. These data illustrate that prolonged preseal bake outs at temperatures of 125° C for longer that 336 hours was insufficient to desorb the H_2.

Non-hermetic devices, however, were not capable of retaining any H_2 and performed properly. Titanium hydride formation was subsequently identified as the cause of these particular failures as substantiated by the literature on titanium and its various compounds.[1,2] This particular hydride readily forms at the test and environmental conditions in effect for this hardware. Studies were also performed by other investigators and it was readily proven that gaseous hydrogen had the ability to degrade the GaAs devices.[3] In this particular study it was shown that H_2 was diffusing monoatomically into the platinum metallization, and thereby, effected doping compensation in the device.

The extended effect of this reactive gas on device reliability in general, whether gallium arsenide or silicon technology, was evidenced when a third series of device failures followed shortly thereafter. In this particular case, it was noted that standardized, mature, manufacturing processes had periodically yielded parts that could not meet the previously achieved quality levels. It also was noted that hydrogen concentrations were varying radically.

TABLE 1
RGA on Devices With Known Thermal History **

Sample ID		41*	43*	44*	41+°	43++°	44+++°
Nitrogen	%	98.2	99.3	99.4	97.7	97.5	97.0
Oxygen	%	ND	ND	ND	ND	ND	ND
Argon	%	0.04	0.04	0.04	0.04	0.04	0.04
CO_2	%	0.02	0.01	0.01	0.01	0.01	0.01
Moisture	%	0.12	0.09	0.08	1.39	1.50	1.56
Hydrogen	%	1.69	0.54	0.35	0.77	0.97	1.40

* 168 hour burn-in at 125°C
\+ Resealed and RGA after 48 hours at 125°C
\++ Resealed and RGA after 168 hours at 125°C
\+++ Resealed and RGA after 500 hours at 125°C
° Parts not prebaked
** Minor constituents deleted

TABLE 2
RGA Data From Six Date Codes*

Sample ID		1	2	3	4	5	6	7	8	9
Nitrogen	%	62.5	58.5	53.5	80.4	82.3	81.3	83.7	83.5	79.6
Argon	%	ND	ND	ND	ND	ND	ND	ND	ND	ND
CO_2	%	2.0	2.1	2.5	1.4	1.3	1.4	0.9	1.1	1.3
Moisture	%	0.43	0.42	0.4	0.58	0.55	0.52	0.14	0.2	0.19
Hydrogen	%	0.02	0.05	0.05	0.01	ND	ND	0.02	0.02	0.03
Helium	%	28.9	31.4	35.9	15.5	14.6	15.1	11.4	10.6	13.4

Sample ID		10	11	12	13	14	15	16	17	18
Nitrogen	%	82.4	84.3	89.2	70.8	74.0	60.9	75.5	67.1	70.3
Argon	%	ND	ND	ND	ND	0.01	0.02	0.02	0.01	0.01
CO_2	%	0.9	0.8	0.6	3.3	2.2	5.2	4.6	4.5	5.8
Moisture	%	0.22	0.21	0.15	0.26	0.18	0.31	0.27	0.18	0.15
Hydrogen	%	0.07	0.09	0.09	0.05	0.04	0.06	0.05	0.05	0.03
Helium	%	12	9.69	5.7	18.6	18.6	25.3	13.6	21.5	18.8

* Minor Constituents Deleted
0_2 Reported as "None Detected"

Sample History
Standard RGA data after 168 hours at 125° C (burn-in) for six representatives date codes of given product spanning over one year.

TABLE 3
Burn-Out Study: RGA Data For Empty Packages at 125°C*

Sample ID		48 Hours	168 Hours	500 Hours	1,000 Hours
Nitrogen	%	99.6	99.1	98.1	96.3
Oxygen	%	0.02	ND	ND	ND
Argon	%	0.05	0.04	0.04	0.04
CO2	%	0.01	0.01	0.01	0.01
Moisture	%	0.09	0.12	0.17	0.32
Hydrogen	%	0.15	0.67	1.7	3.3

* Minor constituents deleted

And, as shown in table 2, moisture levels within some of the devices were found to exceed the 5,000 ppmv limit permitted via the military specifications.[4,5]

Specifically, normally high hydrogen concentrations were lowered as reduction of surface oxides had occurred. This is evidenced by the abnormally and excessively high moisture levels in the other lots of devices.

Noteworthy in this data is the overall trend that hydrogen was maintained at a normal level until at one time within a specific date code (ref. sample ID's 4, 5, and 6) some aspect of the process had changed, causing the devices manufactured during this date code to fail lot qualification. Oxide reduction has been identified as the cause for the device failures because the only set of devices that failed moisture requirements were concurrently the only devices that had no discernible hydrogen gas.

Earlier articles in the trade press had provided indications that hydrogen within the cavities of microelectronic devices was becoming a common occurrence.[6] Literature again gave insights as to how hydrogen could be contributing to these failures[7,8], i.e., via oxide reduction. Yet, no source or root cause for this problem had been identified.

Experimental Results

With the potential that the performance and reliability for several major programs were at stake, an analytical scheme was developed wherein the cause for failure, i.e., the source for hydrogen was to be indentified and, if possible, eliminated.

Several outgassing studies on both standard microcircuits with welded seals and hermetically sealed glass ampules were subsequently designed. The chosen analytical technique for H_2 analysis in theses studies was Residual Gas Analysis (RGA) performed in accordance with Test Method 1018 of Mil-Std-883. Individual samples were loaded into a heated (100°C) test fixture that allowed the device lid or curved ampule surface to be firmly mounted against a small VitonR O-ring on the inlet of a quadruple mass spectrometer. Through a turbomolecular pumping system, the inlet and analyzer were pumped down to 1 x 10^{-8} torr and maintained until adequate back-ground levels were achieved. The samples were then punctured via a manually-driven, off-axis puncturing mechanism releasing the sample ambient gases into the mass spectrometer to be analyzed.

A cross-section of the RGA system used in these studies is illustrated in figure 3. In addition to the standard calibration requirements outlined in Test Method 1018, a more rigorous H_2 calibration schedule also was implemented to ensure the accuracy required in analyzing H_2 levels ranging from 100 ppmv to several percent. These extended calibration standards were prepared by an independent supply house and were traceable to NIST* standards.

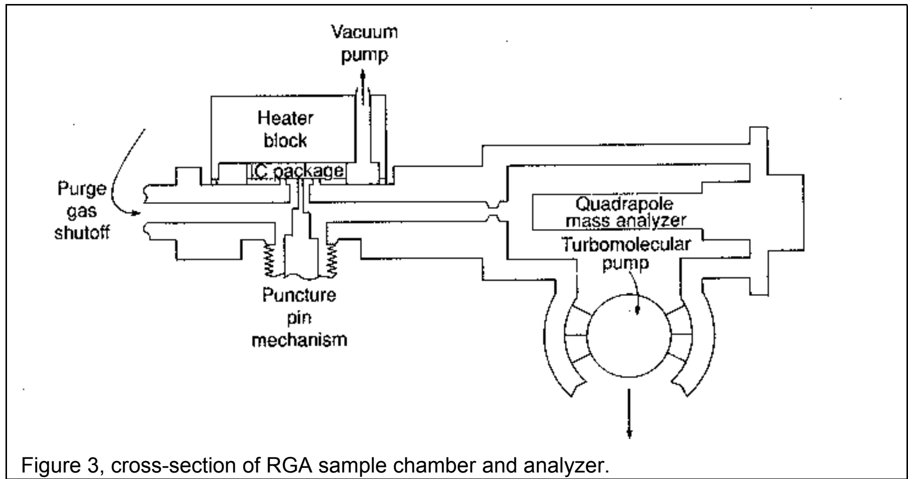

Figure 3, cross-section of RGA sample chamber and analyzer.

The first phase of outgassing studies were based on preliminary theories as to the source of the hydrogen which were essentially founded on the known fact that plating processes can entrap hydrogen within the plated metals. It was also believed that subsequent thermal stressing would force or diffuse the trapped hydrogen from the plating.

Several outgassing studies were subsequently designed in an attempt to rid the device package of hydrogen. The device package was a 1cm circular gold plated alloy with 0.2cc internal volume. As shown in table 3, attempts at desorbing the hydrogen for as long as

TABLE 4
RGA Afer 250° C/168 hr in Vacuum Preseal
Followed by 125° C/168 hr Post Seal*

Sample ID		1	2	3	4	5	6	7	8	9
Nitrogen	%	99.6	99.7	99.8	99.8	99.9	99.8	99.8	99.9	99.8
CO_2	%	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Moisture	%	0.12	0.08	0.1	0.1	0.04	0.08	0.09	0.05	0.11
Hydrogen	%	0.14	0.22	0.07	0.04	0.04	0.06	0.14	0.08	0.1
Fluorocarbons	%	0.09	ND	0.06	0.04	ND	0.05	ND	ND	ND

*Minor Constituents deleted
O_2 and Ar reported as "None Detected"

1,000 hours at 125° C proved to be unsuccessful. This particular study was actually repeated with a second set of four devices. Each gas analyses for each time period is a one time analysis only, i.e., after its particular time in test, each device was then removed from test. The repeated experiment was carried on in the same manner- hence eight separate devices contributed to the data in the table. As can be seen, this study was done in essentially pure nitrogen, no attempts were made to control moisture levels for these devices. A second series of samples were generated in which the devices were outgassed at higher temperatures, specifically 250° C for 168 hours (the nominal burn-in time). But subsequent RGA, after the standard burn-in (125°C/168hr) on these pretreated devices, again showed concentrations of hydrogen, albeit at a lesser level, as shown in table 4.

These data led to the conclusion that more than just the platings were the source for the hydrogen. Experiments were now devised that addressed the base alloy (a cobalt, nickel iron alloy) as well as the various platings.

Raw, as received base alloy, as well as base alloy processed up to, but not including plating, was submitted for analysis. However, a new means of sampling had to be developed that would ultimately reduce sample preparation time and costs. So far, only fully fabricated packages and lids were used for the analyses. These parts were processed per the standard manufacturing techniques and hermetically sealed via weld or solder sealing processes. Since raw and/or partially processed metals were to be analyzed, a means had to be devised for sampling that prevented any potential interferences from the "packaging." To accomplish this task, all subsequent experiments were performed by sealing the samples into pyrex glass ampules. These ampules were then evacuated to less than 1 mm and backfilled at least three times with dry, high-purity nitrogen. Once all traces of oxygen and other gases had been expelled, the ampules were sealed with a glass blower's torch, thereby providing a hermetic seal.

The "devices," i.e., base and processed metal samples sealed in ampules, were then subjected to various thermal profiles. An experiment was set up wherein gold plated/nickel flashed base metal samples were analyzed along with samples of the base metal with the gold and nickel mechanically abraded off. As shown in table 5, the hydrogen levels are essentially the same, indicating that the bulk of the H_2 derives its source from the base metal.

As shown in table 6, hydrogen was again detected desorbing from the base metal itself. The high levels of hydrogen, 0.5 to 0.9 percent, were again present even after preliminary heat treatments of 320°C for 100 hours.

These desorption parameters were beginning to reach the impractical limits for normal device manufacturers. Alternate means of desorbing, blocking, or preventing the effects of hydrogen had to be identified.

The oxide passivation approach was sought after, as it was known that some of the earlier GaAs devices with moderate to high levels of hydrogen had not failed. Auger analyses of those specific resistors had indicated a titanium oxide layer much thicker than in those devices that had failed. This observation is again substantiated by literature.[2,9] Two experiments were subsequently designed to ascertain if a passivating oxide barrier could be developed *insitu* which would prevent hydrogen desorption at the package level.

In the first of these two experiments, raw and annealed base metal were heat treated in air for 100 hours at 320° C. They were subsequently sealed in glass ampules and the heat treatment was continued for an additional 50 hours at 325° C. However, one sample of each had the surface base metal oxide abraded away with 800 grit emery prior to sealing in the N_2 atmosphere. As shown in table 7, hydrogen desorption had been effectively blocked for both the raw and the annealed metals. Only when the passivation (oxide) had been removed, was hydrogen capable of diffusing out of the base metal into the simulated device cavity (ampule).

A second experiment with nickel plated base metal was performed with less time for oxide passivation to occur,

TABLE 5
RGA Data for "Low Hydrogen" Products*

Sample ID		1	2	3	4	5	6	7	8	9	10	11	12
Nitrogen	%	98	97.7	97.9	98	98	97.9	97.9	97.7	97.8	98.2	97.4	98.3
CO2	%	0.11	0.14	0.16	0.17	0.07	0.06	0.17	0.21	0.12	0.07	0.21	0.14
Moisture	%	1.12	1.26	0.97	0.84	1.04	1.11	1.08	.097	1.19	0.94	0.93	0.6
Hydrogen	%	0.6	0.57	0.78	0.84	0.83	0.8	0.7	0.93	0.73	0.68	1.2	0.84

* Minor Constituents Deleted
O_2 and Ar Reported as "None Detected"

<u>Sample History</u>
1,2: Hydrogen Product #1, sealed in N_2, heated at 320° C for 168 hours.
3,4: Low Hyrogen Product, #1, Au and Ni abraded off, sample then sealed in N_2, heated at 320° C for 168 hours.
5,6: Standard Product, same as 1 and 2
7,8: Standard Product, same as 3 and 4
9,10: Low Hydrogen Product #2 – same as 1 and 2
11,12: Low Hydrogen Product #2 – same as 3 and 4

24 hours at 320° C versus the previous 100 hours. As shown in table 8, the nickel oxide is also an effective barrier to hydrogen diffusion with the amount of detectable hydrogen dropping radically from the 7,000 to 9,000 ppm range in non-passivated samples to nondetectable in passivated samples.

TABLE 6
RGA Results of Base Metal Degassing*

Sample ID		2	4	R2	R3	R4	R6	A2	A4	A6
Nitrogen	%	98.9	99.3	99.0	99.1	99.0	98.7	98.6	98.9	98.9
Co2	%	0.04	0.01	0.06	0.03	0.01	0.11	0.05	0.04	0.09
Moisture	%	1.08	0.69	0.41	0.37	0.29	0.63	0.35	0.23	0.4
Hydrogen	%	ND	ND	0.52	0.54	0.74	0.54	0.97	0.84	0.73

*Minor constituents deleted
O_2 and Ar reported as "None Detected"
Sample History
2,4: Blank Ampules
R2, R3: Raw Base Alloy – Heated 100 hours at 320° C in N_2
R4, R6: Raw Base Alloy – Heated 150 hours at 320° C in N_2
A2: Base Alloy annealed in partial H_2 atmosphere – heated 100 hours at 320° C in N_2
A4, A6: Base Alloy annealed in partial H_2 atmosphere – heated 150 hours at 320° C in N_2

TABLE 7
RGA Data on Base Metal After Passivation*

Sample ID		R7	R8	R9	A7	A8	A9
Nitrogen	%	98.8	99.0	99.4	98.6	98.9	99.2
Co2	%	0.13	0.09	0.02	0.14	0.01	0.01
Moisture	%	0.39	0.86	0.59	0.55	1.1	0.79
Hydrogen	%	ND	0.05	0.01	0.74	ND	ND

*Minor constituents deleted
O_2 and Ar reported as "None Detected"

Sample History
All samples, raw and annealed base alloy, were heated in oven at 320° C for 100 hours, then sealed in ampules with N_2 and heated again for 50 hours at 329° C. Samples R7 and A7 were mechanically abraded to remove surface oxides prior to sealing in N_2.

Discussion

The foregoing experiments have shown that the bulk of the hydrogen found within the cavity of a microelectronic device is the result of diffusion of the absorbed gas from the base metal.

Base metal package and lid suppliers reportedly perform their annealing processes in hydrogen atmospheres; this accounts for residual hydrogen concentrations in the base alloy. Some suppliers have also periodically claimed "Low Hydrogen" products as their product data sheets indicate a nominal residual of 0.5 ppm of hydrogen within the base metal. It should be noted that these suppliers are reporting H_2 in ppmw (parts per million by weight), whereas the microelectronic device manufacturer has to report cavity gases as ppmv (by volume).

As shown in table 9, making some general assumptions about a typical package size and device cavity, one can apply some general chemistry and recalculate the 0.5 ppmw hydrogen as equivalent to 17,000 ppmv hydrogen, i.e., package and cavity dimensions dependent. For base metal not considered to be a "Low Hydrogen" product, the outgassing potential can reach even more alarming levels.

These experiments also explain why gold-plated base metal continuously desorbs hydrogen, since no passivation can build up on the gold to block the diffusing gas. The net result is a clear diffusion path for H_2 in the base alloy, through the nickel flash and surface gold into the device cavity.

Alternatively, one can preheat the gold-plated base metal to diffuse the underlying nickel flash to the surface and subsequently oxidize that metal to form a barrier. Unfortunately, this process defeats the purpose of the underlying nickel flash per the military specifications. Furthermore, the oxide layer achieved prevents or inhibits the final sealing process.

What remains for a final solution to this problem is either of two approaches:

1. Have the base metal supplier perform the anneal processes in non-oxidizing atmosphere other than hydrogen, or
2. Develop an open-seal partial burn-in schedule that allows for oxide passivation of a non-gold plating to occur, but in such a manner that the final seal process is not effected. Future studies will concentrate on the validity of these proposed solutions.

Whether the effect of hydrogen outgassing is hydride formation or oxide reduction, the negative implications of such effects on device reliability extends to a substantial portion of the microelectronics industry. With an estimated 30 to 40 percent of the industry being effected, the design and process engineering communities are strongly encouraged to review their respective technologies to ascertain the potential impact of this previously unpublished phenomenon.

Attempts to desorb the hydrogen have failed to yield a viable base alloy with no discernible hydrogen. Yet hydrogen free alloy would eliminate the preventative steps such as passivation that are now required to assure that subsequent H_2 diffusion into the cavity of the device will not utimately effect performance and reliability.

**National Institute of Standards & Technology*

References

1. L.C. Covington, and R.W. Schultz, "Corrosion Resistance of Titanium," May 88, Timet Corp. Publication M2-5M-588.
2. G.G. Libowitz, "The Solid State Chemistry of Binary Metal Hydrides," W.A. Benjamin, Inc., 1965.
3. W.O. Camp. et. al "Hydrogen Effects On Reliability of GaAs MMICs," GaAs-IC Symposium Technical Digest, 1989.
4. Mil-M-38510 – Military Specification – General Specification for Microcircuits, March 31, 1989.
5. Mil-Std-883 – Military Standard Test Methods and Procedures for Microelectronics, November 29, 1989.
6. D. Epstein, "How to Test for One Way Leakers, " Hybrid Circuit Technology, March 1988.
7. J.W. Moellerm "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Volume III, Longmans, Green Co., 1923.
8. T. Ramsey, G. Heiner, "Controlling Moisture in Ceramic Packages," Semiconductor International, August 1988.
9. C. Canali, et. al, "Gate Metallization 'Sinking' Into the Active Channel in Ti/W/Au Metallized Power MESFETS," IEEE EDL Vol. 7, No.3, March 1986.

Contact author at:
Oneida Research Services
One Halsey Road
Whitesboro, N.Y. 13492
Telephone: 315/736-5480

TABLE 8
RGA Data on Nickel-Plated Base Metal*

Sample ID		**1**	**2**	**3**	**4**	**5**
Nitrogen	%	97.8	95.9	98.6	98.5	99.5
Oxygen	%	ND	2.41	0.09	ND	ND
Argon	%	0.01	0.11	0.01	ND	0.01
CO2	%	0.2	0.12	0.16	0.17	0.09
Moisture	%	0.93	0.63	0.33	1.38	0.37
Hydrogen	%	0.97	0.74	0.7	ND	ND
Sample ID		**6**	**7**	**8**	**9**	**10**
Nitrogen	%	97.6	99.6	99.4	99.1	96.3
Oxygen	%	0.12	0.08	ND	ND	ND
Argon	%	0.01	0.01	0.01	0.02	0.02
CO2	%	0.03	0.03	0.06	0.04	0.13
Moisture	%	2.23	0.32	0.51	0.89	3.53
Hydrogen	%	0.01	0.01	ND	0.01	0.01

* Minor Constituents Deleted

Sample History

1,2,3: Base metal sealed in N_2 and heated at 320° C for 140 hours.

4,5,6,7: Nickel-plated base metal, heated in air, 24 hours at 320° C; sealed in N_2 and heated for 115 hours at 320° C.

8,9,10: Nickel-plated base metal, heated in air 76 hours at 320° C; sealed in N_2 and heated for 65 hours at 320° C.

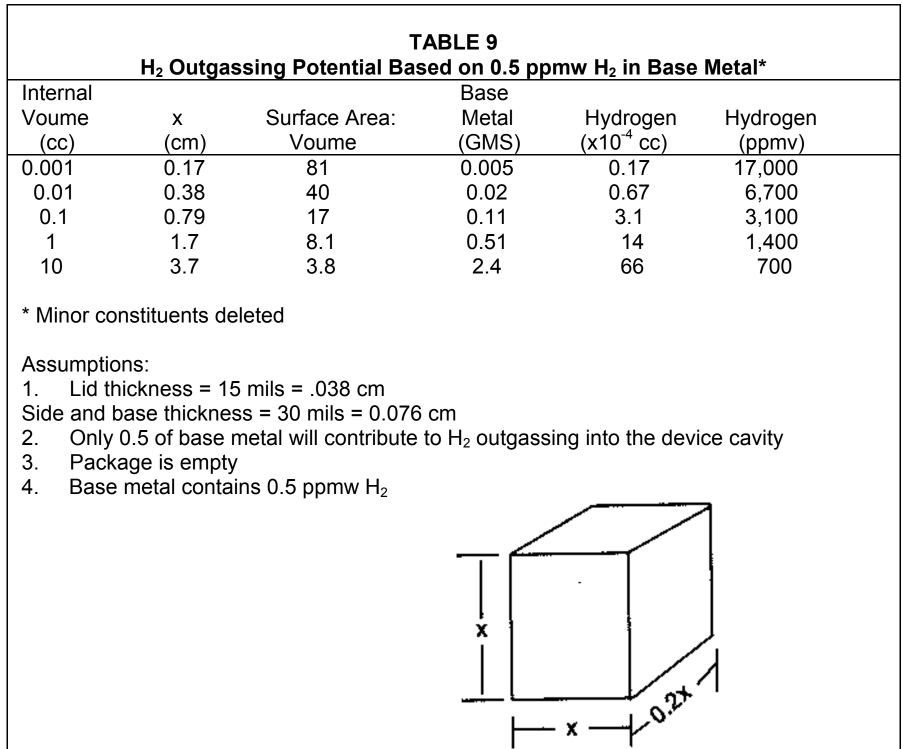

TABLE 9
H_2 Outgassing Potential Based on 0.5 ppmw H_2 in Base Metal*

Internal Voume (cc)	x (cm)	Surface Area: Voume	Base Metal (GMS)	Hydrogen ($x10^{-4}$ cc)	Hydrogen (ppmv)
0.001	0.17	81	0.005	0.17	17,000
0.01	0.38	40	0.02	0.67	6,700
0.1	0.79	17	0.11	3.1	3,100
1	1.7	8.1	0.51	14	1,400
10	3.7	3.8	2.4	66	700

* Minor constituents deleted

Assumptions:

1. Lid thickness = 15 mils = .038 cm
Side and base thickness = 30 mils = 0.076 cm
2. Only 0.5 of base metal will contribute to H_2 outgassing into the device cavity
3. Package is empty
4. Base metal contains 0.5 ppmw H_2