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Advantages of a New V-Purge System* over Conventional Nitrogen Purge System for Pd Membrane Hydrogen Purifiers

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ABSTRACT

Palladium membrane hydrogen purifiers, a staple in the compound semiconductor industry, have been acknowledged as the purification technology of choice for MOVPE processes such as MOCVD. They are highly effective in removing impurities from hydrogen streams by effectively blocking out all impurities. Certain process changes and upset conditions, such as power interruptions or emergency shutdowns can affect the life of the palladium membrane. Under these conditions, the operating temperature of the membrane falls allowing the hydrogen that is absorbed in the crystal lattice of the palladium membrane to be trapped. The trapped hydrogen causes an expansion of the membrane and subsequently distortes and stresses the brazed joints. This condition results in decreased life of the membrane. Various methods of purging the membrane with nitrogen, or with other inert gases, have been employed to remove the hydrogen. A new and more effective purging design is presented and evaluated using SEMI guidelines. Significant benefits in rapid hydrogen purging and rapid return to full UPH flow were observed with the new design.

INTRODUCTION

It is imperative that the palladium membrane never cool down in the presence of hydrogen to insure long life of the hydrogen purifier. When the palladium (Pd) membrane cools in the presence of hydrogen, the Pd alloy may absorb hydrogen, increase in volume, and become distorted. The physical expansion of the palladium alloy causes stress on the membrane and the joints where the membrane is attached to the manifold. The result is reduced life of the membrane and possible leakage at the joints.

During normal operation, elimination of residual hydrogen from the Pd alloy is easily accomplished with a standard shutdown procedure. During a standard shut down, the membrane heater remains energized until all hydrogen has been removed from the purifier. Under emergency conditions or power failure situations when the heaters are off, a purge system must be incorporated to facilitate rapid removal of the hydrogen before the palladium membrane cools. Purge systems using nitrogen (or another inert gas) have found widespread use as a device for protecting the palladium membrane from sudden upsets. Conventional purge systems, although a relatively good solution to the problem, still do not provide adequate protection of the Pd membrane because conventional systems do not remove all of the hydrogen before the palladium membrane cools below 300°C during a power outage.

This paper discusses an alternative purging technology that combines an inert gas purge with a unique V-Purge system to rapidly remove residual hydrogen in a fraction of the time required by a conventional purge system.

THEORY

Palladium (Pd) membrane purifiers operate on the principle of diffusion to purify impure hydrogen. The Pd membrane absorbs hydrogen molecules onto its surface, where each hydrogen molecule dissociates into two hydrogen atoms. Each hydrogen atom loses its electron to the Pd alloy and diffuses through the Pd metal lattice as a proton. The protons recombine with two electrons on the far side of the lattice to form a hydrogen molecule that is desorbed from the Pd alloy membrane. The partial pressure of hydrogen on each side of the palladium membrane determines the direction and flow rate of hydrogen across the membrane. Hydrogen diffuses across the membrane from the process side with the higher hydrogen partial pressure to the low partial pressure side of the membrane. The diffusion process is maximized at a membrane temperature of 350°C and 200 psid. While a Pd membrane purifier is leak-free across the membrane, the total concentration of impurities has been shown to be less than 1 ppb. A leak across the Pd membrane significantly decreases the purification capability, therefore, periodic leak checks of Pd membrane purifiers is recommended to ensure the purifier is operating properly.

When a Pd membrane purifier is shut down, it is important to remove all of the hydrogen in the purifier before the palladium membrane cools below 300°C. When the Pd membrane temperature drops, the diffusion rate decreases and hydrogen can remain absorbed within the lattice of the palladium membrane. The diffusion rate decreases significantly when the temperature drops below 300°C and the lower diffusion rate causes a significant increase in the time required to remove all residual hydrogen. A palladium membrane that is saturated with hydrogen expands in volume and the increase in size causes significant mechanical stresses at the brazed joints. To preserve the integrity of the membrane it is critically important to remove all hydrogen from the purifier before the membrane cools below 300°C.

The conventional approach to removing hydrogen from a palladium purifier has been to purge the feed side with nitrogen. The objective of the nitrogen purge is to rapidly reduce the hydrogen partial pressure on the feed side and cause the ultra-high purity hydrogen to back-diffuse through the membrane in a phenomenon called uphill diffusion. All purge systems include a dedicated flow metering device to regulate the flow rate of nitrogen during the purge process. The nitrogen flow rate must be controlled to avoid the rapid cooling of the membrane by an excessive flow of unheated nitrogen.

DISCUSSION

In a conventional nitrogen purge design (Figure 1), nitrogen is introduced into the impure or feed side of the Pd membrane purifier and the nitrogen flow rate is controlled with a flow metering valve located downstream of the purifier in the bleed line. The purge rate in a conventional purge system is defined as the total combined flow rate of hydrogen and nitrogen exiting the purifier. During the purge process, the total flow rate of gases exiting the purifier is controlled to 10 slpm maximum. The composition of the gas stream exiting the purifier is mainly nitrogen therefore the actual flow rate of exiting hydrogen is restricted to less than 10 slpm. If the flow rate of exiting gas in a conventional purge system is increased to hasten the removal of hydrogen, the palladium membrane will be cooled faster by the increased flow of unheated nitrogen passing across the membrane in a power outage and the risk of trapping hydrogen in membrane increases.

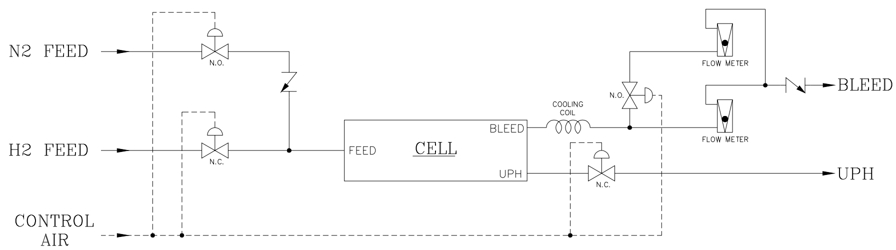

Figure 1 Conventional Purge System

In a conventional purge system, the total pressure on the feed side of the membrane during purging is 80 psig because the downstream flow metering device causes back pressure on the membrane. The high back pressure on the feed side results in a high partial pressure of hydrogen which inhibits the diffusion of hydrogen from the pure side to the feed side of the membrane. The low diffusion rate and the restricted bleed rate (<10 slpm) cause the total purge time to exceed 60 minutes. During this lengthy purge period the membrane will cool below 300^{o}C in a power outage. After the membrane cools below 300^{o}C, the diffusion rate decreases and the purge time is extended further. A conventional purge system can not adequately protect a membrane during a power outage.

In the new Johnson Matthey V-Purge design (Figure 2), nitrogen is also introduced to the feed side, but the flow rate of nitrogen is controlled by a flow control device located upstream of the purifier to avoid a high nitrogen back pressure on the membrane. Additionally, a vacuum generating device is located downstream of the purifier to assist in the rapid evacuation of the hydrogen. In the Johnson Matthey V-Purge design, the total pressure is on the feed side of the membrane while purging is only -11" Hg and the bleed rate is unrestricted. The partial vacuum on the feed side and the unrestricted flow path on the bleed line allow the hydrogen on the pure side to quickly diffuse across the membrane and exit the purifier. Within one minute, the pressure on the pure side of the membrane decreases to less than -24" Hg. The partial vacuum indicates that almost all of the hydrogen has been removed. In contrast, almost all of the hydrogen still remains in the conventional purge system after one minute. The pressure on the UPH side of a conventional purge system is more than 76 psig after the first minute of purging.

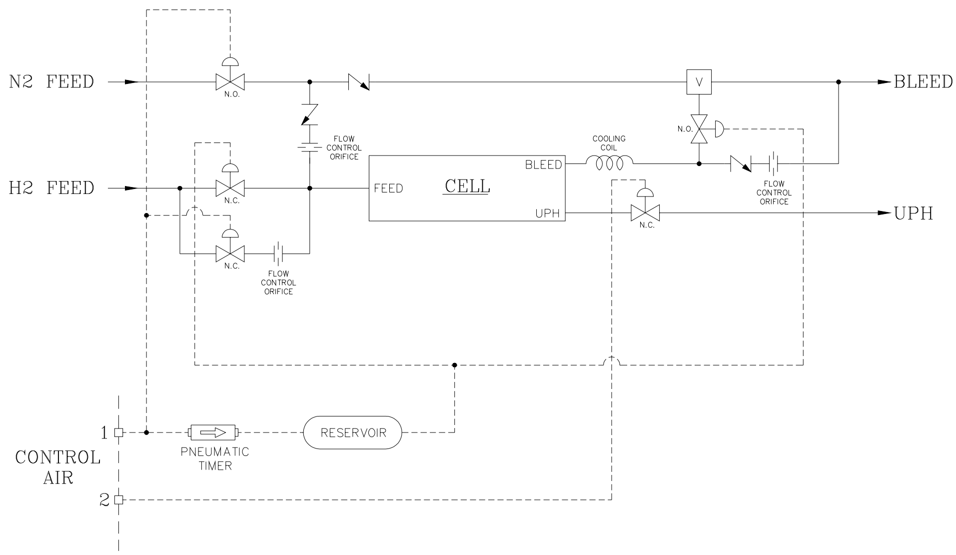

Figure 2 Johnson Matthey V-Purge System

The evacuation of hydrogen from the V-Purge system occurs very quickly and before the palladium membrane cools in a power outage. The V-Purge membrane decreases only 20 degrees to 340°C before all hydrogen is removed and the risk of damaging the membrane due to trapped hydrogen is very low. In contrast, the conventional purge system cools 115 degrees to 255°C and is well below the 300°C threshold for safe operation of the membrane. The temperatures in this study were measured at the palladium membrane. The temperatures were not measured at the heater or outer shell of the purifier where heater control thermocouples are typically located because the thermocouples do not accurately reflect the conditions at the membrane. It is important to monitor the membrane temperature and account for the effect that the cool nitrogen purge stream has on the palladium membrane.

ADDITIONAL PERFORMANCE BENEFITS

The Johnson Matthey V-Purge system provides additional improvements in performance and reliability. The V-Purge system eliminates the sudden pressure surge that occurs when the system is switched to the purification mode after purging. The feed side pressure in a conventional system immediately spikes to full feed pressure (typically 200 psig) when the feed valve is opened. The sudden pressure surge causes a spike in the thermal and mechanical stresses in the purifier that may lead to failure of the membrane. The Johnson Matthey V-Purge system eliminates this spike by providing an automatic 20 second ramp to full pressure. The V-Purge soft start function decreases the risk of membrane failure from pressure surges at start-up.

The Johnson Matthey V-Purge system enables full performance within the first minute of operation. In contrast, a conventional purge system takes over 35 minutes to achieve full performance after purging. When a conventional purge system switches to the purification mode, nitrogen is immediately trapped on the feed side of the purifier at 80 psig. The bleed rate in a conventional purifier allows only 4 slpm of the trapped nitrogen to be purged from the system by hydrogen. While the trapped nitrogen remains in the purifier, the purification rate is significantly reduced (Figure 5). The Johnson Matthey V-Purge system eliminates this problem by allowing the feed hydrogen to purge all nitrogen from the purifier through the unrestricted bleed line for approximately 20 seconds after switching to the purification mode.

The following table highlights performance differences between conventional purge systems and the Johnson Matthey V-Purge design. The V-Purge system outperformed the conventional system for each metric listed in the table.

Table 1

	Convention N2 Purge System	**Johnson Matthey V-Purge System**
Time to achieve full 29" Hg on UPH Side of membrane	>64 minutes	<10 minutes
Membrane temperature at 29" Hg UPH during power outage	255°C	340°C
Hydrogen Removal Rate	Bleed rate restricted to 10 slpm maximum	Unrestricted bleed flow rate
Nitrogen Purge Rate	Controlled to 10 slpm maximum (nitrogen and hydrogen)	Controlled to 6 slpm (pure nitrogen)
UPH Pressure after first minute of purge	76 psig	-14 psig
Time to reach 200 psig pressure on feed side at start-up	Instantaneous hard start pressure surge from 0 to 200 psig	20 second soft start ramp from 0 to 200 psig
Time to ramp to full hydrogen flow rate after purging purifier.	39 minutes	< 1 minute
Reliability in Power Outage	Some users have encountered membrane failure after first power failure.	Predicted MTBF 53 - 176 power failure cycles

EXPERIMENTAL METHOD

A laboratory test unit (Figure 3) was assembled to compare the performance of a conventional nitrogen purge design and a new Johnson Matthey V-Purge design.

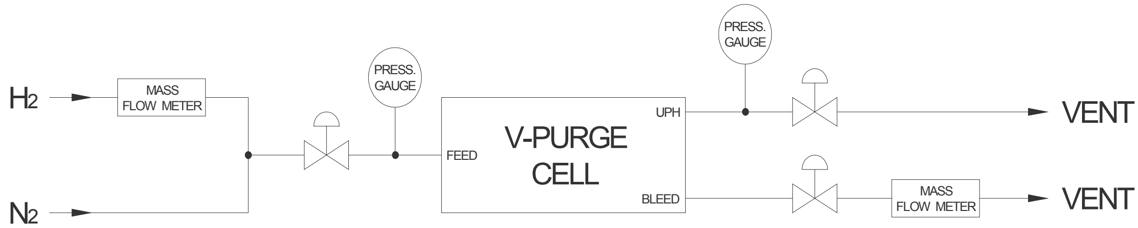

Figure 3 Test Fixture

Performance of each design was measured in the following experiments:

1. UPH Pressure ("Hg) vs. purge time
2. Time to achieve full purge (29"Hg vacuum)
3. Pd membrane temperature vs. purge time

Tests were conducted under the following conditions:

1. The cell heater set point was 400°C
2. The preheater set point was 450°C
3. The hydrogen feed pressure was 200 psig
4. The nitrogen feed pressure was 80 psig
5. The pure hydrogen (UPH) flow rate was 220 slpm
6. The hydrogen bleed rate was 8 slpm
7. The nitrogen purge rate was 6 slpm

Test procedure:
A standard JM HP-480 purifier was used for the experiments. The purifier was installed in a V-purge system and tested as described above. The same purifier was used for the conventional purge system test to eliminate any variability between palladium membranes. The V-Purge system was set up to operate as a conventional purge system by relocating the nitrogen purge metering device to the downstream side of the purifier and disabling the vacuum generating device. The same mass flow meters, pneumatic operating valves, and PLC control system were utilized for both designs during testing. A PLC control system was used to disable heater power, monitor process temperatures, and switch the operating valves from the purification mode to purge mode. Digital pressures gauges were installed on the feed side and pure side of the membrane to monitor pressures. For practical purposes, we stopped each pressure experiment after 29" Hg vacuum was achieved on the pure side of the membrane. We believe that the amount of residual hydrogen remaining in the Pd purifier at 29" Hg is insignificant and the time required to remove the very small quantity of residual hydrogen is approximately the same for either type of purge system.

RELIABILITY TESTING

The Johnson Matthey V-Purge system was tested to predict the reliability of the palladium purifier during power failures. The V-Purge system was operated on a test fixture for 146 power failure simulations. The heaters were turned off to simulate a power failure and the purifier was purged and allowed to cool to 250^{o}C which is well below the 300^{o}C threshold for safe operation of the purifier. A PLC was used to automatically control the operating valves, heaters, and monitor membrane temperature. Periodically during the testing the membrane was checked for leaks using a helium mass spectrometer. The acceptable leak rate was 1E-9 atm-cc/sec maximum. The V-Purge system was tested as follows:

Test Cycle:

1. The purifier was heated to 360°C membrane temperature and pressurized to 200 psig hydrogen feed pressure. The UPH valve was opened and hydrogen was purified at the full purification flow rate (220 slpm) for 5 minutes.
2. The heaters were turned off and the system was switched into the purge mode. The palladium membrane was allowed to cool from 360°C to 250°C while purging.
3. After the temperature reached 250°C, the heaters were turned on and the system was reheated to 360°C while purging.
4. When the temperature reached 360°C, the test cycle returned to Step #1.

Test Results and Conclusion:
The V-Purge system was operated through 146 power failures cycles. When the SEMI statistical guidelines for predicting equipment reliability are applied to the empirical data, the predicted mean time between failures is between 53 (lower statistical limit) and 176 (upper statistical limit) power failure cycles. The reliability prediction is based on the guidelines outlined in SEMI E-10-0699 “Standard for Definition and Measurement of Equipment Reliability, Availability, and Maintainability (RAM)” for failure censored data at 80% confidence level. The V-Purge system is very effective in reducing the risk of failure during power outages when the membrane cools in the presence of hydrogen.

DATA ANALYSIS

The results in Table 2 show that the JM V-Purge can achieve a complete purge or 29” Hg UPH vacuum in just 10 minutes, which is over 6 times faster than the conventional N_2 purge, and well before the Pd membrane cools to 300°C. The conventional purge, by contrast, takes 64 minutes to achieve a complete purge and the Pd membrane has cooled to 255°C, well below the desired 300°C threshold to eliminate the risk of mechanical stresses caused by hydrogen absorption.

Table 2
Comparison of time and temperature at 29”Hg vacuum (complete purge) for conventional N_2 purge vs. JM V-Purge

	JM V-Purge	Conventional N_2 Purge
Time to achieve full purge (29” Hg UPH vacuum)	10 minutes	64 minutes
Temperature at 29” Hg UPH vacuum	340°C	255°C

Purge Performance - Figure 4 shows Pd membrane temperature and UPH pressure as a function of time for the conventional N_2 purge vs. the V-Purge design. The Johnson Matthey V-Purge design has a sharp, rapid drop in the hydrogen pressure in the purifier, whereas the conventional N_2 purge design has a gradual pressure change. This implies that the purging in the V-Purge is more rapid and more efficient.

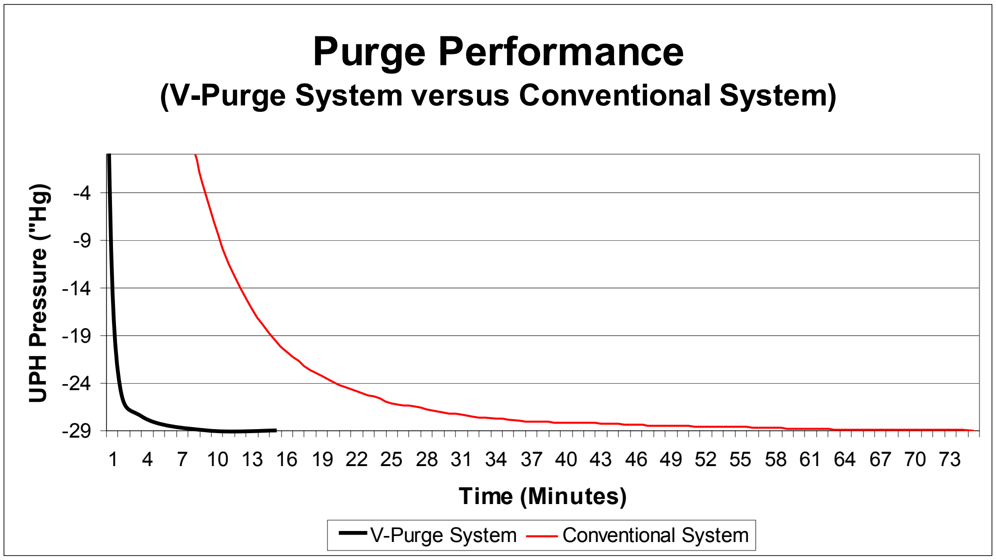

Figure 4 Purge Performance

UPH Flow Rate After Purging - Figure 5 shows that the V-Purge design achieves full flow of UPH hydrogen in just 1 minute, whereas the conventional N_2 purge design does not reach full flow for 39 minutes. The reason is that the V-Purge is much more efficient in the removal of residual N_2 purge gas, thus allowing the feed hydrogen to enter the purifier quicker and achieve high partial pressure sooner.

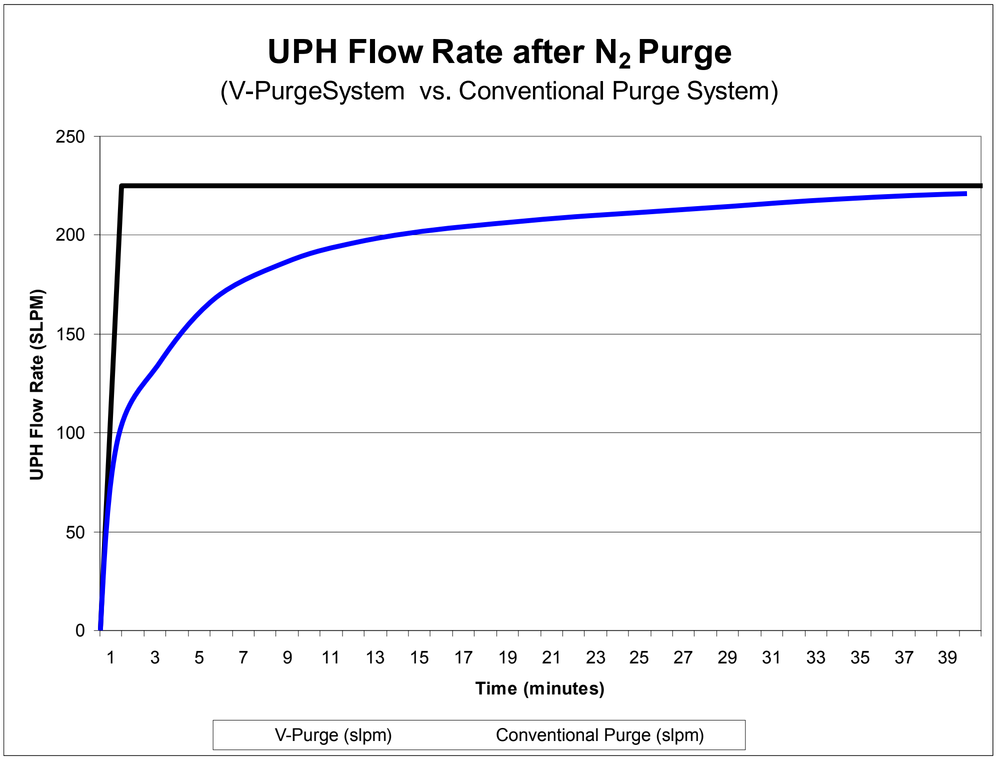

Figure 5 UPH Flow Rate after N_2 Purge

CONCLUSIONS

Johnson Matthey has demonstrated that a unique combination of valve placement, coupled with a vacuum generating device, can significantly improve the performance of the purging process in a Pd purifier purge system. A complete purge can be achieved in just 10 minutes at a Pd membrane temperature of 340°C, which is well above the recommended bottom limit of 300°C. This improved purge design will help extend the life of the Pd membrane and reduce cost-of-ownership. In addition, the V-Purge design allows the purifier user to go from full-purge to full-UPH-flow in just 1 minute to provide increased uptime.

* The Johnson Matthey V-Purge System is a patent-pending design.