Setting a new benchmark for **hydrogen delivery**

Purified hydrogen is an essential ingredient in the MOCVD processes used to manufacture LEDs, power devices and photovoltaics. Moves toward larger reactors and bigger wafers are increasing the demand for more and more ultra-pure hydrogen from increasingly reliable, compact sources. Fulfilling this need is a novel palladium technology developed by **Power and Energy, says the company's Stuart Bestrom.**

Sales of MOCVD tools have exploded over the last twenty years, leading to a vast increase in the number of chips produced by this technique. But the approach for purifying the hydrogen gas that supports this form of epitaxial growth – a palladium membrane purification technology – has stood still.

This lack of progress on the hydrogen front is a significant concern for LED chipmakers, who continue to migrate to more complex and demanding processes involving ever-larger chambers and ever-bigger wafers. Sensitivity to oxygen and carbon contamination goes up and up, hydrogen flow rates have recently tripled for the largest MOCVD reactors, and flow changes during the process recipe runs can surge from 0 to 300 standard litres per minute (slpm) with no transition period. The traditional palladium purifiers were never designed to handle these new process recipes and they have a number of inherent limitations in durability, quality and cost. This has prompted some users, particularly those in large fabs in China and Taiwan that are particularly keen to cut costs and work with higher flow rates, to consider alternative purification technologies.

These chipmakers are finding a solution to their needs in a palladium membrane technology developed by Power and Energy of Ivyland, PA, in cooperation with the US Department of Defense (DoD). The DoD pursued this development to serve its needs for pure hydrogen to power fuel cells (see box "Hydrogen fuel cells"), but the results of the project have proven successful in semiconductor applications as well.

The resulting palladium membrane technology that we have developed at P+E is the most significant innovation in gas purification in over 20 years. One of the biggest breakthroughs is a doubling-to-trebling of capacity per purifier compared to traditional palladium purifiers. This larger capacity means that a new LED fab requiring 12,000 (slpm) of hydrogen to support 50 MOCVD reactors needs only three of our gas cabinet-sized purifiers. If traditional purifiers were used, six would be needed, and each would have a much bigger footprint.

Reducing size also has additional benefits, because it cuts power consumption and other facility costs. What's more, the micro-channel palladium membrane technology at the heart of this new system has been proven to greatly improve durability: It provides uninterrupted purification for years of continuous operation. These advancements eliminate contamination, yield loss and downtime caused by hydrogen purity variability in compressed, cryogenic and generator sources.

Working with hydrogen

It is only possible to fully appreciate the benefits of our palladium technology after understanding how a conventional hydrogen purifier works, and the demands that are placed upon it. Conventional hydrogen purifiers have been widely used where hydrogen of the highest purity has been demanded, in order to yield MOCVD-grown wafers and crystal ingots of the highest possible material quality.

These conventional purifiers draw on palladium's unique properties to act as a catalyst (see Figure 1). Hydrogen gas molecules dissociate into atoms upon contacting the surface of the palladium membrane that is held, along with all the other parts of the purifier, at 400 °C. At this temperature, hydrogen atoms are small enough to readily diffuse through the membrane, driven by differential hydrogen pressure across the interface. No other material is small enough to diffuse through palladium, so impurities such as water, oxygen, nitrogen, carbon dioxide, carbon monoxide,

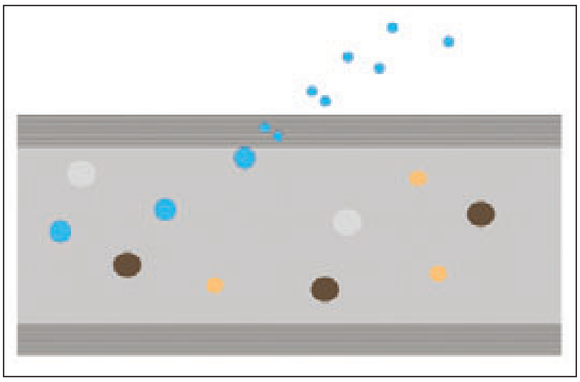

Figure 1: Palladium membrane tubes provide the unique ability to only allow hydrogen molecules to pass through to the pure side. When the feed gas is brought into contact with the inner wall of the palladium-silver membrane, molecular hydrogen (shown as blue spheres) dissociates into atomic hydrogen and is absorbed into the metal lattice. Other molecules, such as methane, nitrogen, water, carbon monoxide and carbon dioxide (shown as brown and grey spheres) are too large to pass through the membrane. While diffusing through the lattice, individual hydrogen atoms share their electron with the palladium in the metal

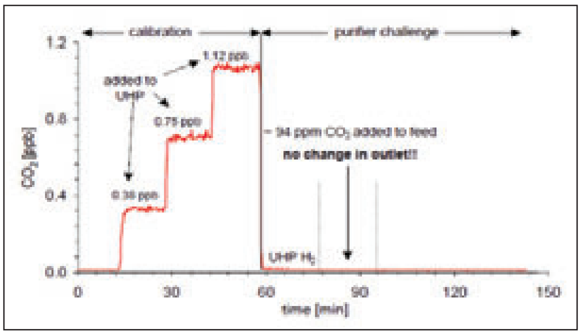

Figure 2: A palladium purifier is challenged with up to 94 ppm of CO_2 with no change in outlet purity. Outlet purity is below 50 ppt

hydrocarbons and rare gases remain on the inlet side of the membrane. The solid barrier provided by palladium results in no breakthroughs. This contrasts with catalysts and getters, which rely on chemical reactions on reactive surface areas under controlled conditions.

Palladium technology also offers the unique ability to remove high-ppm levels of impurities from a cylinder source gas without detriment to purifier lifetime or outlet H_2 purity (see Figure 2). Other methods of hydrogen purification, such as regenerable catalysts and heated zirconium getters, are intended for removal of low ppm impurities, and the purifier lifetime is directly dependent on the incoming impurity and flow rate. This robust capability makes palladium purifiers ideal for compressed cylinder and generator sources where the gas quality can vary significantly from day-to-day.

Hydrogen can be supplied as either a compressed gas, a liquefied (cryogenic) gas or it can be generated on site. The purity of gas varies widely, depending on the source and specific region. Liquid hydrogen is usually the most pure form of this gas, and it is typically between six and seven 'nines' purity – in other words, total impurities are 1,000-100 ppb.

However, liquid hydrogen is not available in Taiwan, Korea and China, the three countries where most new high-volume LED and photovoltaic fabs are located. In these fast-growing regions, fabs must rely on compressed and generator sources, which can include a great deal of variability in the purity of compressed and locally generated hydrogen. Typical sources are water, natural gas or propane, and costs associated with generating hydrogen in this manner are high, due to substantial power requirements.

Chipmakers that use high-purity hydrogen must have a contingency plan that can be brought into action when the primary source is unavailable due to maintenance or unforeseen downtime. One option is to use an industrial

Power and Energy's hydrogen purifier features a novel micro-channel membrane with an 'inside-out' flow path

or chemical plant in these emergencies, but that means a compromise in gas purity. For example, a facility with onsite storage of 99.999 percent hydrogen may be forced to use 99.99 percent backup hydrogen on rare occasions. Purification systems have to be designed to deal with these contingencies, so that the final gas purity is unaffected by changes in the quality of the sources. Palladium purifiers can ensure that all impurities are removed from the hydrogen, whether typically present or the result of an unusual event.

Innovative membranes

Through the support of a series of Navy, Army and DARPA research contracts over a period of eight years, we have developed hydrogen purifiers based on a unique micro-channel palladium-alloy membrane configuration. This technology is commercially available and highly reliable, thanks to automated membrane test and inspection methods and advanced manufacturing technologies.

Our unique membrane structure is based on an 'inside-out' design. It features a 'micro-channel', in which the hydrogen enters the inside of the membrane tube (see Figure 3). This palladium tube has an inner 'return tube' that is inside and concentric with the membrane. With this design, hydrogen diffuses out into a passivated stainless steel chamber while a small volume of hydrogen continuously sweeps all impurities to a bleed line.

Thanks to improvements in weld and brazing methods, quality inspection, and membrane assembly design, our micro-channel architecture can deliver a dramatic increase in durability compared to conventional designs. Stress on the membrane is reduced, eliminating the need for a supporting spring. In addition, hydrogen recovery is enhanced with the micro-channel. This enables efficient recovery, even with low concentrations of hydrogen from reformed fuel streams. We have been working with our vendors to improve the alloy and tube drawing processes. These efforts, which reduce impurities and physical defects, have yielded a more uniform alloy with fewer micro-defects. The upshot is more reliable membranes.

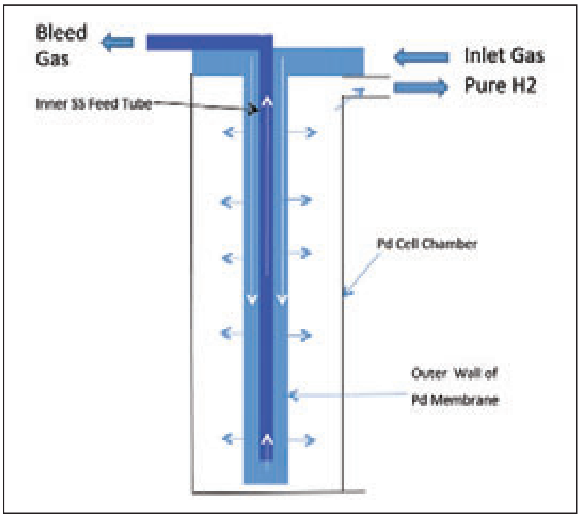

Figure 3: Power and Energy's inside-out micro-channel palladium purifier with vacuum brazing and laser weld improves durability over previous designs using traditional welding techniques. The welding of palladium to stainless steel will weaken the joint when performed with traditional weld methods. Using laser welding improves repeatability and long-term durability

The durability and lifetime of our palladium-based hydrogen purifier has been improved through more stringent quality control that pre-emptively screens out material defects. To realise this, we have developed a proprietary membrane inspection station for identifying and eliminating substandard membranes at the earliest possible stage. Each membrane is tested under extreme conditions, before being individually subjected to a helium leak-test prior to acceptance into inventory. With our configuration, the palladium membrane tubes undergo an advanced, computer-controlled vacuum braze process. This ensures precise, repeatable brazing of each membrane. The membrane assembly is then laser welded into an electropolished and passivated stainless steel manifold.

Using this design allows axial and radial expansion and contraction without restriction, reducing stress on the membrane tubes. Each membrane is held in an array that prevents it from ever contacting its neighbours. In contrast, traditional palladium purifiers allow

H_2 Source	Delivery	Typical Purity	Regional Availability	Large Volumes	Hydrogen Cost	Capital Cost
Compressed	Trailers, Cylinders	99.9%-99.999%	▲▲	▼	—	▼
Cryogenic Liquid	Tanker / Storage Tank	99.99999%	▼[1]	▲	—	—
Generator	Steam Methane Reformer (SMR)	99.9%-99.999%	▲▲	▲▲▲	▼[2]	▲▲
	Electrolysis of Water	99.999%	▲▲	▲	▲[3]	▲▲

1. Availability is limited to several regions including North America, northern Europe and Japan.
2. SMR requires availability of Natural Gas
3. Electrolytic H_2 generators consume large quantities of electricity

membranes to move freely against each other, thereby contributing to long-term stress of the tubes. Preventing membranes from coming into contact also leads to a free flow of gas and prevents tube damage.

To demonstrate the practical benefits of our palladium technology, we have developed automated, accelerated-life-testing systems to replicate extreme operating conditions. Membranes were pressure- and temperature-cycled to simulate the stresses possible from long-term operation. The goal was to confirm a minimum cycle lifetime of 10,000 – equivalent to 10 years with 3 on/off cycles per day. This benchmark, which is well above typical operating conditions, is always met with membranes that pass incoming inspection (see Figure 4). In fact, some membranes that failed inspection still show excellent lifetimes. This means that our inspection methods may eliminate 'good' membranes. However, they ensure that no accepted membranes fail the cycle test.

We subjected our sample membranes to thermal cycling to validate flow performance and stability over time. The result: Confirmation of the effectiveness of our membrane test methods to identify and remove membranes with micro-defects prior to assembly.

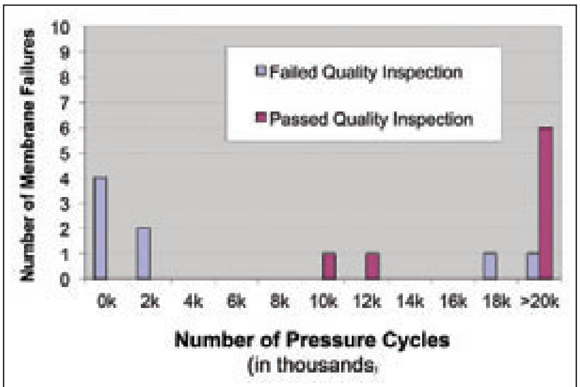

Figure 4: Membrane life cycle test confirms 10,000 cycle minimum lifetime for all membranes that passed new inspection procedures

Encouragingly, our test also showed that the new micro-channel membranes provide improved durability under the most hostile operating conditions. Our 9000MZ and 9000MS high-flow purification systems are now incorporating the new membrane. These purification systems have been manufactured with production and quality procedures that ensure a consistent operating environment with stable operation for many years. The compact array of membranes provides a high flow capacity in a very compact package. A single vessel measuring 6" x 24" that previously purified up to 200 slpm can now flow 600 slpm. The compact package also reduces power consumption, and in addition it allows savings in required floor space and HVAC sizing, important considerations for the larger semiconductor fabrication facilities in Asia.

Through analysis of raw materials, assembled systems and resulting outlet gas purity, it has been possible to improve the quality of the hydrogen supply so that impurities are consistently below 0.1 ppb (100 ppt). This exceptional level of purity predominantly stems from proprietary manufacturing processing for preparing and passivating stainless steel, which have reduced sources of carbon and moisture that can contribute impurities downstream of the palladium membranes. Thanks to this advance, we can now guarantee a start-up purity of less than 100 ppt for all impurities. In comparison, typical specifications from traditional palladium purifiers offer impurities of less than 1 ppb, and this is only assured after a lengthy start-up purging at a minimum 20 percent of rated flow.

Benefits associated with our micro-channel technology are by no means limited to LED chipmakers: They are also a great assistance to producers of photovoltaics, polysilicon devices and fuel cells. Improvements in the performance of all these devices are eagerly anticipated, and our hydrogen-purifying technology should help to unlock that promise throughout the remainder of this decade.

Hydrogen fuel cells

The Department of Defense is interested in developing high-quality hydrogen sources for fuel cells. These devices are incredibly energy efficient, and can generate twice as much energy per gallon of fuel as combustion-based generators. The challenge is that military fuel supplies are high in sulphur contamination, an impurity that drags down fuel cell performance. A better, more durable method for separating hydrogen for fuel cells is needed to unlock the door to auxiliary powering of vehicle, plane, ship, platoon and field installations.