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Expanding Use of On-Site UHP Hydrogen Production Improves Safety, Quality and Productivity in Epitaxy Operations

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Abstract

Epitaxy and other semiconductor processes use active gases and a carrier gas stream containing high purity hydrogen to produce semiconductor devices. Expanding compound semiconductor and solar cell markets are improving operating environments at existing photonic manufacturing facilities, and creating opportunities for new academic and startup compound semiconductor facilities. All of these facilities must contend with the challenging safety issues presented by the active and carrier gases required for the epitaxy process. Process gases for epitaxy are subject to strict usage and storage limitations. Facility operators, whether an established photonics manufacturer, an academic facility, or a new startup, are looking for opportunities to reduce the hazards – every hazard reduction ultimately means a faster, less-expensive route to an operating permit. The need for storing significant quantities of flammable hydrogen carrier gas can be prevented through the use of onsite hydrogen generation. By reducing the inventory of hydrogen gas stored, the flammability hazard can be reduced, and with it the degree of the overall hazard.

Introduction

This paper will review hydrogen supply basics for the semiconductor industry, and introduce an on-site method of hydrogen carrier gas supply for manufacturing semiconductor devices, presently in use at 50+ semiconductor facilities worldwide. On-site hydrogen can provide:

- Ultra-pure gas for best process results
- Sufficient pressure for all reactor inlet purification methods
- Much lower pressure than stored hydrogen methods, eliminating self-ignition hazard
- True zero-inventory design – hydrogen is produced as it is used by the process
- No risk of introducing oxygen into piping during storage system change-out
- The ability to save money by reducing the cost of inlet gas purification

Hydrogen in Semiconductor Production

Epitaxy and other semiconductor processes use active gases and a carrier gas stream usually containing high purity hydrogen to produce semiconductor devices. The hydrogen in the carrier gas stream scavenges and reduces residual oxygen, preventing oxygen damage to the devices. Expanding compound semiconductor and solar cell markets are driving higher operating rates at existing photonic manufacturing facilities, and creating opportunities for new and expanded facilities. All of these facilities must contend with the challenging safety issues presented by the active and carrier gases required. Process gases for epitaxy present special challenges because of their highly hazardous characteristics. Many of these gases are toxic and some are pyrophoric. These substances are subject to strict usage and storage limitations. The storage of the poison process gases and flammable hydrogen together in a facility makes for great concern and delayed permits. Facility operators, whether an established photonics manufacturer, an academic facility, or a startup, are looking for opportunities to reduce the hazards – every hazard reduction ultimately means a faster, less-expensive route to an operating permit. Solutions such as gas cabinets, gas bunkers, and scrubbers are the usual solutions, and are an effective but expensive first step at reducing the hazards of a release. Little can be done about the need for aggressive process gases in epitaxy – the process gases are key components in the technology. But the need for storing significant quantities of flammable hydrogen carrier gas can be prevented. By reducing the inventory of hydrogen gas stored, the flammability hazard can be reduced, and with it the degree of the overall hazard. The customary method of supplying hydrogen for epitaxy is by use of stored hydrogen, typically cylinders or tube trailers, occasionally liquid hydrogen. All stored hydrogen methods make use of hydrogen that has been manufactured elsewhere, and hauled to the customer's location. Delivered hydrogen supply method requires that enough hydrogen be stored onsite to serve the process needs for two to four weeks between deliveries. The stored hydrogen, ranging from 3,000 to as much as 1,000,000 standard cubic feet, and generally stored in compressed to 2400 psig, creates a significant hazard in and of itself.

Why Hydrogen is Preferred over Alternative Gases in Semiconductor Processing

Hydrogen is used in many semiconductor processes, for applications from a cover gas for furnace processing to a carrier gas for transport of active doping gases. Semiconductor applications make use of several unique hydrogen properties:

- Reducing gas – oxygen removal
- Extremely high heat transfer capability
- Low density for low pressure drop
- Modest cost

Hydrogen's capabilities are important to many semiconductor operations such as semiconductor fabrication, semiconductor packaging, sintering, and wafer annealing. As compared to nitrogen, argon, helium or another inert gas, hydrogen provides a superior combination of oxygen removal properties, superior heat transfer properties, extremely low density, and relatively low price as compared with helium or a rare gas.

Issues with Stored Hydrogen

Hydrogen is a flammable gas, governed, like all other flammable gases, by a wide range of regulations and acceptable practices. Most guidance in the US for hydrogen safety is based on the National Fire Protection Association (www.nfpa.org), which publishes guidelines for industrial practice at hydrogen-using locations. The primary NFPA reference for hydrogen storage is NFPA Standard 55, Standard for the Storage, Use, and Handling of Compressed Gases and Cryogenic Fluids in Portable and Stationary Containers, Cylinders, and Tanks. This document describes the requirements for siting and operation of stored hydrogen systems, whether cylinders, gas storage tubes, or liquid hydrogen. Most governmental permit authorities and insurance providers will base their guidance and decisions on NFPA guidelines.

Any changes to, or operations within, your facility are likely to be subject to regulation of a local authority having jurisdiction (AHJ), usually a local governmental agency. Operation at major academic institutions or government facilities may additionally be regulated by an internal AHJ such as a fire marshal's office at a state university. The AHJ normally conducts periodic safety inspections to ensure that the operation complies with the permits granted and the local codes.

Many new or growing semiconductor hydrogen users find it difficult to obtain and comply with guidance regarding gas use and storage. Semiconductor manufacturing facilities employ hydrogen alongside other flammables, pyrophorics and poisons, in the form of the doping gases. The presence of additional hazards complicates understanding and practicing safe operational procedures. The local AHJ will not design your compliance practices for you – they will tell you if what you've developed is acceptable, but the design of the compliance procedures is your problem, not theirs. One of the challenges of hydrogen storage, especially for new, growing or academic facilities, is that there are multiple and sometimes contradictory sets of rules that apply. Ultimately, the local AHJ is "the Decider".

Until your operation is in compliance in the opinion of the local AHJ, you cannot operate. By eliminating the storage of large amounts of hydrogen, on-site hydrogen generation can reduce confusion and minimize the risk and cost of complying with applicable rules.

Where Hydrogen Comes From

Hydrogen is the most common element in the universe, but is normally chemically bound with other elements in molecules such as water and hydrocarbons. In order to provide pure hydrogen, suppliers split the hydrogen from water (electrolysis) or split the hydrogen from hydrocarbons mixed with steam (reforming). Regardless of the source, making pure hydrogen is a two step process, involving both making the hydrogen and purifying it for use.

Hydrogen is very efficiently produced in large, centralized plants, often located adjacent to major users, or next to large sources of byproduct hydrogen produced via brine electrolysis (for chlorine and caustic manufacture). Hydrogen from these plants can be used locally by pipeline, but hydrogen sent off-site is normally “packaged” in some way to be transported efficiently.

Hydrogen Supply Modes

Oil refineries use huge amounts of hydrogen, 24 by 7. To serve their needs, hydrogen is produced in a steam-methane reformer on-site, or adjacent, and supplied via a dedicated pipeline direct to the refinery. On-site production and a dedicated pipeline is by far the lowest cost supply approach for a major user, since product packaging and delivery costs are avoided.

Most hydrogen production facilities today are located at refineries. The operators of the hydrogen plants build them oversized for the refinery’s needs, and then make the excess hydrogen available to a hydrogen packager for truck shipment to customers. In order to ship the hydrogen, the gas is either compressed and packaged as a compressed gas, or it is liquefied and shipped as a cryogenic liquid.

Packaging and shipping hydrogen as a compressed gas or cryogenic liquid is relatively expensive. Gaseous hydrogen is relatively inexpensive to purify and compress, but very expensive to transport, because even highly compressed hydrogen has low density, and must be transported in heavy trailers or cylinders to contain the pressurized hydrogen gas. There are dozens of small gaseous hydrogen sources in the US where tube trailers may be filled. The largest (most efficient) road-legal hydrogen tube trailers carry over 120,000 scf (standard cubic feet) of hydrogen, weighing about 700 lbs. Thus a 40,000 lb. hydrogen tube trailer carries only 700 lbs of hydrogen. The situation for cylinder hydrogen is even more extreme, with the average 175 lbs hydrogen cylinder containing less than 1.5 lbs of hydrogen. A truck carrying 100 hydrogen cylinders would be transporting only 150 pounds of hydrogen. Normally, hydrogen cylinders are transported less than 100 miles from their fill depot, while hydrogen tube trailers may drive up to 300+ miles from their fill plant. Cost of hydrogen delivery is increasing more quickly than any other cost at this time.

By mass, most of the hydrogen transported in the US by road trailer is transported as a liquid. Liquid hydrogen is produced in 9 large plants in the US and eastern Canada (of which 8 are owned by only two suppliers), where gaseous hydrogen is liquefied to shrink its storage volume dramatically. Once liquefied, hydrogen may be shipped up to 1000 miles, relatively efficiently and with only minor losses.

The major challenge with liquid hydrogen is that all of the equipment used is esoteric and expensive – the plants, the trailers, and the liquid hydrogen storage at customers' sites. For example, each liquid hydrogen transport trailer costs about $1MM to purchase, and a liquid hydrogen tank for placement at a customer site would cost in the range of $500,000 to purchase and install, and would not be allowed in most urban areas.

With the exception of NASA and certain other mobile hydrogen applications, no users use hydrogen as a liquid. Unlike liquefied nitrogen, which is sometimes used as a liquid for its cooling power, hydrogen is used industrially as a gas only. Hydrogen liquefaction is done primarily for logistics efficiency – to move large quantities of hydrogen efficiently by trailer truck.

Hydrogen Purity Levels

Certain semiconductor processing operations demand extreme gas purity; others less so. It is critical that the exact purity and impurity needs of each operation be understood to avoid overbuying purity (at a penalty of paying too much for raw materials and impacting profitability), or underbuying purity (at a risk of manufacturing bad product). It is important to specify both assay (% purity) and to identity contaminates of concern. Hydrogen purity levels for commerce are defined for industry in the US by the Compressed Gas Association (www.cganet.com), in Europe by the European Industrial Gas Association (www.eiga.org), ISO (www.iso.org), and in Japan by the Japan Industrial and Medical Gases Association (www.jimga.or.jp). US standards define 7 industry-standard specifications for hydrogen quality – 4 standard quality levels for gaseous hydrogen, and 3 purity levels for liquefied hydrogen. Due to the specific production process, liquefied hydrogen tends to be much purer hydrogen than gaseous hydrogen because hydrogen impurities that are present in gaseous hydrogen are condensed out and removed in the liquid hydrogen liquefaction process.

In contrast to the CGA-defined standard industry production grades, gas suppliers often have their own marketing nomenclature for gas purity grades – terms such as ULSI, UHP, Prepurified, and Semi-grade. Each supplier has their own terminology, and the marketing grades are not directly comparable one with another. It is important to choose a grade of gas from your supplier that meets your needs for assay and also for specific contaminates. For example, fuel cell applications are essentially immune to nitrogen content, but the smallest amount of CO may be damaging. In contrast, some compound semiconductor applications require near-zero nitrogen content. It is important to understand that the type and species of contaminates may be as, or more important than the % assay. A complete requirement understanding requires a statement of both % assay requirement, and what impurities are not allowed to be present.

Due to current supply system logistics, most hydrogen delivered to customers in the US today is actually distributed from the hydrogen source to industrial gas depots as liquid hydrogen, then vaporized as a high-pressure gas into tube trailers and cylinders for local deliveries. Thus, most hydrogen users, most of the time, get gaseous hydrogen of nearly liquid quality.

Essentially, most users, most of the time, get extremely pure hydrogen, no matter what grade they ordered. This naturally suggests why pay extra for the good stuff if I can get the good stuff without the premium cost? The happy situation of something for nothing – liquid hydrogen purity for users of gaseous hydrogen, can become a problem if logistics change, or supply sources shift, and gaseous hydrogen produced from a gaseous hydrogen source is supplied to the customer. The product will meet the purchase specification, but may upset the production process. The customer got what they paid for.

Hydrogen is used for many applications industrially, but of all the major hydrogen applications, semiconductors impose the most rigorous purity requirements. It is critically important that semiconductor hydrogen users think about their purity requirements, and buy the grade of hydrogen that meets their needs. If they buy a lower grade of hydrogen, they might find that one day the “right” grade of gas is delivered, and their process is affected.

The Cost of Purity

Most semiconductor processes are developed by scientists working in a laboratory. During process development, technologists generally use the gases that serve their labs, often extremely high purity gases that are supplied to meet the highest purity needs that the lab might require. Once the process is developed, it is worthwhile to critically analyze the actual needs of the process, taking into account both process yield and gas cost considerations, to specify the most cost-effective gas that meets the process needs. It provides no advantage to supply purity in excess of the process needs.

Hydrogen gas provided for commercial sale in the US ranges from industrial grade (99.95% assay, -65C dewpoint, no other contaminant identifications) to semi or ULSI grade product, of 99.99999+% purity, with strict definition and limitation on every contaminant present. It is important to choose the grade that meets your process needs, and fits your budget. While prices vary widely depending on geographic location and monthly use rate, a useful rule of thumb is that the prices double for each additional “nine” of purity purchased. So if 99.95% purity costs ~$12/100 scf, then 99.99% costs $25/100 scf, 99.999% costs $50/100 scf, 99.9999% costs $100/100 scf, and 99.99999% costs ~$200/100 scf. Once a hydrogen-using process has been commercialized, it is crucial to take an aggressive stance toward hydrogen quality definition to avoid paying more than is necessary given the process requirements.

Hydrogen Purity Certification

It may not be entirely clear what is different when a customer buys higher purity hydrogen.

- Does it mean that the hydrogen is especially “cleaned” somehow to fit the process ?
- What does a certificate of analysis mean when applied to hydrogen cylinders ?
- How is the gas analysis determined ?
- What assurance does a certificate of analysis provide ?

In the filling process at the hydrogen source terminal, bulk, very high purity hydrogen (typically vaporized liquid hydrogen) is used to fill cylinders or tube trailers. While the hydrogen used to fill most cylinders is high purity, it is not electronics grade. Electronics-grade cylinders are often filled in specialized facilities, using electropolished liquid hydrogen tanks and gas cylinders, and high purity pumps, liquid and gas lines and fittings, and subjected to extra filling scrutiny. There are very few of these specialized facilities in the US, requiring that electronics grade hydrogen cylinders be shipped long distances for delivery. As a result, electronics grade hydrogen cylinders often cost $300 or more per cylinder.

There are several types of quality verification possible for cylinder hydrogen, and it is important to know what you are buying. Today, most hydrogen suppliers fill hydrogen cylinders in palletized fashion, and they assume that all of the cylinders are being filled with the same hydrogen. If all of the fill lines and fittings are tight and clean, and cylinders have been identically prepped (cleaned), then the hydrogen in each cylinder should be identical to all of the others. Hydrogen suppliers may sample and analyze the incoming gas used to fill the cylinders, and provide that analysis as a measure of the quality of the gas supplied. Alternatively, and more expensively, the supplier may analyze one of the cylinders from each group filled and provide that analysis as a typical of the batch. The most expensive option is to get a cylinder analysis that represents the contents of each and every cylinder supplied. Because each analysis may cost the supplier upwards of several hours to perform to electronics standards (the lower the detection level, the longer the analysis run), the price of every cylinder may be driven up depending on the type of analytical assurance demanded by the customer.

While tube trailer delivery reduces the number of containers to be cleaned, filled and quality-checked, it also introduces compromises. Tube banks and tube trailers are generally not available with electropolished internals, meaning that the porous mill finish internal of the tube assembly may harbor contamination. Additionally, the delivery of the gas from the delivery vehicle into the customer storage tubes requires very careful execution to eliminate the possibility of air or moisture ingress.

As compared to delivered hydrogen, onsite hydrogen eliminates the needs for hydrogen liquefaction or compression, delivery and storage. On-site hydrogen eliminates the need to attach and properly evacuate hydrogen gas lines, providing confidence that an on-site hydrogen supply generator will deliver consistent hydrogen to the process, at exactly the purity of hydrogen made in the generator.

Buy it Purer or Clean it Up?

The highest purity semiconductor applications may specify very high purity hydrogen, and also include purifiers in the facility hydrogen systems as guard beds to prevent impure hydrogen from contaminating the product. Facility operators prefer to think of these purifiers as guard beds rather than as purifiers – the difference being that a purifier is intended to regularly remove impurities from the gas, while a guard bed is intended to be a last resort insurance policy against bad gas reaching the process. A guard bed is employed after the proper quality gas is supplied to the process, to prevent the “one-in-a-million” situation from damaging the system.

The industry attitude to gas guard beds makes sense if the types or levels of impurities are unknown in the incoming hydrogen. For delivered hydrogen, the user must assume that that is the case, for there are many places in the packaging, shipping, transfer of custody, and house piping processes where the hydrogen can become contaminated. Users assume the worst and provide guard beds to protect the process and product from contaminated hydrogen.

But what if semiconductor users could be sure about the quality of the incoming hydrogen, and its precise composition, and if you didn’t have to worry about packaging, shipping or pipingrelated contamination issues? Then you might be willing to use a purifier as a cleanup approach – a polisher, used to consistently polish the supplied hydrogen to the exact hydrogen purity required, analogous to a water purification system, used to purify water of known composition to a higher Page 6 of 8 purity specification by removing known contamination. In both the hydrogen and water examples, the incoming stream must be relatively consistent and homogeneous so that the purification system can be configured for the specific duty needed.

Chemical Cartridge Gas Purification Systems Versus Palladium Purification

There are two main gas purification approaches for semiconductor use - chemical contaminate-removal cartridges and palladium alloy purifiers. The two approaches work differently:

- Chemical cartridges work by reacting with, and thus immobilizing, specific contaminants in the gas stream. Reactions that occur may be physical reactions, or they may be chemical reactions. Every contaminant in the gas stream requires an appropriate chemical "antagonist" in the chemical cartridge in order to remove it. You need to know what is going to be in the gas in order to use a chemical cartridge approach. If a chemical cartridge is challenged with an impurity that it was not designed for, it will let that impurity pass without removal, or the contaminate may rob the cartridge of needed capacity to remove another impurity. In general, chemical cartridges are low in initial price, and introduce little pressure drop in the hydrogen system, but costs can rise rapidly if poorly-chosen cartridges are exhausted cleaning impure gas streams.

- Palladium alloy purifiers are perfect hydrogen filters. Palladium metal's crystal lattice structure will expand when heated to 300 to 400°C, but just enough to allow hydrogen molecules to pass through the structure, while keeping all larger molecules behind. Palladium alloy purifiers can remove all hydrogen contaminants, whether known or unknown composition, and virtually irrespective of contamination level (some contaminants, if present, are best removed upstream of the palladium alloy purifier to avoid overheating). From the standpoint of versatility and process insurance, palladium alloy purifiers may be desirable, but they are expensive to buy, expensive to install, expensive to operate, subject to damage from process upsets and they introduce an average 50+ psig pressure drop in the hydrogen gas supply line they serve.

If you supply a gas system with hydrogen of known composition, and you know exactly the hydrogen purity required for your process, then the lowest cost approach would be to supply an engineered system of chemical hydrogen cleanup modules to remove the problem contaminates to below the concern level. This system design provides a rugged, low cost system, of predictable life, and which delivers hydrogen of required purity.

Stored Hydrogen Systems Versus On-Site Production

Generally, startup and small hydrogen users start with hydrogen delivered in cylinders, because that is the approach that they used when developing their process. Cylinder hydrogen is generally usable up to a use rate of 30,000 scf per month. From the standpoint of high purity users, cylinders have both advantages and disadvantages:

- The cylinders themselves can be specially constructed to enhance the purity of the gas contained within – electropolished cylinders are used for the highest purity gas grades.
- Cylinders can be processed specifically for the grade of gas they are to contain – for example, electronics grade gas cylinders are emptied, subjected to vacuum, and baked out before being refilled with gas, so that no gas from one customer will affect later customers to receive the cylinder. Lower grades often are filled on top of prior gas.
- Cylinders provide a nearly variable cost approach to hydrogen supply. Cylinders are a low cost storage mechanism, but offer relatively high cost hydrogen.

Onsite hydrogen production, regardless of the particular technology employed to make the hydrogen, eliminates many of possibilities of contaminating clean hydrogen accidentally. By eliminating the filling, containerization and delivery steps, onsite hydrogen sidesteps the most frequent sources of contamination. At the user location, onsite hydrogen is transmitted directly from the production equipment, through analytical equipment or purification/guard bed systems as appropriate, to the use process. By eliminating the Page 7 of 8 need to make and break connections, onsite hydrogen removes a major risk point for contamination.

Approaches to On-Site Production at Small Users' Locations

Until the mid 1990's, if you weren't running a refinery, it was difficult to find an onsite hydrogen supply approach that could meet your needs. As compared with delivered hydrogen supplies, onsite hydrogen generation had not matured to the point that it could be considered reliable, pure and cost-effective enough to meet users' needs in the US.

Beginning in the mid-1990's, efforts to commercialize onsite hydrogen technology to mature on two fronts - small electrolysis systems that split water to make hydrogen, and small steammethane reformers to make hydrogen from natural gas. Each of these efforts consumed many millions of dollars to commercialize. The objective of these efforts was not the relatively small market for industrial hydrogen, but the giant potential market for fuel cell hydrogen for use to power vehicles and provide electricity. Barring the potential fuel cell market, there would not have been enough potential in the hydrogen market to justify the hundreds of millions of dollars spent on technology commercialization for the onsite technologies. As a result of the development invested in onsite hydrogen, both compact steam-methane reforming hydrogen generators and water electrolysis hydrogen generators have been commercialized. These technologies work very differently, and have different cost structures.

Compact steam-methane reforming systems, like those made by H2Gen or HyRadix combine a relatively expensive equipment system with a relatively low-cost feedstock to costeffectively meet larger hydrogen requirements. In general, these systems are attempting to be competitive in terms of cost and volume range with liquid hydrogen delivered supply systems – monthly volume ranges starting at 500,000 scf/month.

Most of the marketing effort of the suppliers of compact steam methane reformers has been focused on materials processing, which is the larger volume, lower purity end of the small hydrogen market. These units generally need to be operated continuously, and function best with a flat (unvarying) load profile. Because they use a combustion process, steam-methane reforming systems may need an air permit and other environmental and operational regulations may apply.

Water electrolysis systems use a lower cost capital system, but use a higher cost feedstock in the form of electricity. In water electrolysis, electricity is used to break water into hydrogen and byproduct oxygen. The hydrogen is purified and dried, and may be compressed, before being supplied to the customer's process. The most modern type of water electrolysis uses Proton Exchange Membrane (PEM) electrolyte, a solid polymer which provides advantages such as improved hydrogen purity, higher hydrogen discharge pressure capability, a more compact system and enhanced safety. PEM water electrolysis hydrogen systems have been commercialized by Proton OnSite®; traditional caustic water electrolysis systems are built by Teledyne Energy, Hydrogenics, and Statoil Hydro. Water electrolysis systems are generally employed to make smaller quantities of hydrogen – usually less than 400,000 scf per month. Because of the technology employed and the pure water feedstock used, PEM water electrolysis systems make hydrogen which may be appropriate with little or no additional purification for many semiconductor applications. PEM electrolysis systems can adjust hydrogen production instantly from zero delivery to full delivery, and without any change in purity, so they can serve loads that vary up and down as needed. Because the only byproduct of electrolysis is oxygen gas, and because the systems contain near-zero hydrogen inventory, PEM electrolysis systems generally are welcomed by local authorities having jurisdiction.

Why Choose Onsite?

Onsite hydrogen production makes sense can be done cost-effectively, and if the resulting raw material quality is appropriate for the use. In these days of spiraling transportation costs, gas pricing volatility, limitations on storage volumes, and the desire of many producers to become more independent of outside influences on their business, onsite is increasingly preferred.

PEM electrolysis on-site supply is particularly advantageous for hydrogen supply to semiconductor processing, because of its high purity, and pressure capability. On-site supply eliminates the human factors that can result in leaky connections and air ingress, eliminates the need to Page 8 of 8 store large amounts of flammable hydrogen, produces among the highest purity hydrogen available, and allows users to eliminate the need to order, manage, manhandle, inventory, move and connect/disconnect flammable hydrogen cylinders.

Conclusions

- Understand your process needs, and buy hydrogen according to the assay and contaminates that are process-critical
- Minimize hydrogen inventory to reduce process hazards
- Consider onsite hydrogen if the cost and purity meet your process needs