EUV Lithography adds to increasing hydrogen demand at leading-edge fabs

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On-site production an option for supply

Hydrogen usage at leading-edge logic and foundry fabs has steadily increased over the past 20 years. What was supplied in individual cylinders is now frequently delivered by specialized bulk trucks carrying over one ton of hydrogen per vehicle; some fabs require multiple deliveries per day. With EUV (extreme ultraviolet) lithography nearing commercial, high-volume use, the demand for hydrogen will experience another inflection. In this article, we explain the current and future applications driving this demand, the geographical variation in supply, and on-site production solutions for high-volume customers.

Existing process applications

Hydrogen has been adopted as a material in processes throughout the fab. Its unique chemical properties continue to expand its usefulness. These applications typically use flows of 100s to 1,000s of sccm (standard cubic centimeter per minute):

- **Epitaxy:** Hydrogen is used as a reducing agent during the epitaxial growth of crystalline thin-films. This is often used to make a starting silicon surface for semiconductor manufacturing by reacting newly cut and polished silicon wafers with trichlorosilane ($SiHCl_3$) in an epi-house or end-user fab. The hydrogen reduces the gas-phase chlorine atoms, and the HCl product is removed from the reactor as a gas. Leading-edge channel materials like strained silicon, silicon-germanium, and germanium are also grown using hydrogen-mediated epitaxy.

- **Deposition:** Hydrogen can also be incorporated directly into thin-films to disrupt crystal lattices to make them less crystalline, more amorphous. This is often used with silicon thin-films, which need to be made more electrically insulating.

- **Plasma etch:** Hydrogen and hydrogen-containing plasmas are used to directly react with the surface of the wafer in order to clean or remove unwanted thin films, especially for removing unwanted fluorocarbon deposits on silicon oxides.

- **Anneal:** Silicon wafers are heated to temperatures over 1,000 C, often at elevated pressure, in order to repair their crystal structures. Hydrogen assists by transferring heat uniformly over the surface of the wafer, and also by penetrating into the crystal lattice to react with atomic impurities.

- **Passivation:** Hydrogen is used to react and remove native oxides on silicon surfaces and to mediate the reconstruction of silicon-silicon bonds in the final layers of the crystal.

- **Ion implantation:** With more precision than bulk annealing and passivation, protons produced from hydrogen gas can be implanted to specific depths and concentrations in a thin film using ion implanters. Not only can hydrogen atoms be inserted to modify a thin film, but in higher doses and implantation energies, it can be used to cleave slivers of silicon and sapphire wafers.

- **Carrier gas:** Hydrogen is used as a carrier gas to entrain (entrap) and transport less volatile chemicals—ordinarily liquids at atmospheric pressure and room temperature—into the reaction chamber. The hydrogen is heated and bubbled through the liquid chemicals. Because the mass of hydrogen is very light compared to entrained chemical vapor, specialized mass flow controllers can then be used to sense, measure, and precisely control the amount of chemical vapor dispensed.

- **Material stabilization:** The addition of hydrogen extends the shelf life of important electronic materials like diborane (B_2H_6) and digermane (Ge_2H_6), which otherwise slowly decompose.

- **Polysilicon manufacturing:** Although not part of the process flow in semiconductor fabs, hydrogen is used in large quantities in the upstream process of manufacturing polysilicon: thousands of Nm^3 per hour hydrogen are used, and typically an on-site hydrogen plant is required. Polysilicon is the starting material for making crystallized silicon, from which silicon wafers are sliced.

Application for EUV

Extreme ultraviolet (EUV) lithography is the much-anticipated new application expected to simplify the process patterning complexity for critical dimensions in leading-edge devices. While it has taken a long time for this technology to come close to commercialization, top-tier manufacturers are coalescing their predictions for volume manufacturing adoption in the 2018-2020 window. Whereas other hydrogen-consuming applications have a usage rate of 100s of sccm, EUV will require much larger flows of 100s of slm (standard liters per minute), or roughly 100 to 1,000x more per individual tool.

Deep ultraviolet (DUV) lithography, the current workhorse of the patterning tools, uses an electrical discharge in neon or krypton mixed with halogen gases like fluorine to produce UV light at 193 nm and 248 nm; EUV light production is much more complicated. Tin metal is heated above its melting point of 232 C, and small droplets of tin (~25 µm diameter) are rapidly (50,000 droplets per second) produced. These droplets are first vaporized and then excited with high-power CO_2 lasers. The excited tin atoms emit EUV light at 13.5 nm, which is more than 14 times shorter than the DUV tools.

The light is emitted in all directions and is collected and collimated (aligned) by an array of mirrors. The light is then passed to the primary lithography tool for focusing and image transfer before illuminating the photoresist on the wafer. All materials heavily absorb EUV light. Absorption losses are minimized by using multi-layer reflective optics instead of the transmissive lenses used in DUV lithography, and the entire light source and patterning systems are housed in vacuum chambers. These highly complex tools are expected to cost end users around $100 million USD each, and when fully adopted, a leading-edge fab could require 20 or more of these tools.

Scattered tin debris from the vaporization of droplets is a major potential source of contamination of both the collector and focusing optics. Unmitigated, the lifetimes of these expensive components would be unacceptable. Hydrogen gas is used to shroud the tin excitation region, and tin vapor and aberrant droplets are reacted to form stannane (SnH_4), which is then removed from that section of the housing by means of the vacuum line. Higher flows of hydrogen can be used in periodic plasma-based cleaning to remove tin that deposits on the collector optics.

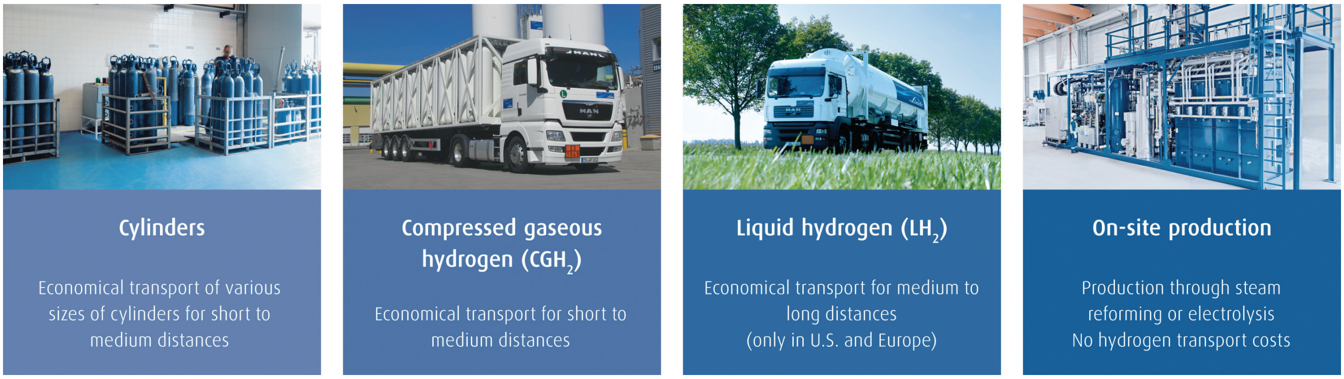
Demand and supply

Even before the adoption of EUV technology, leading-edge logic and foundry processes have begun consuming several normal cubic meters (1,000 liters) of hydrogen per wafer processed. This usage trend is expected to continue increasing in the 10 nm and 7 nm nodes commercialized before wide-spread EUV use. Consequently, major fabs now use hundreds of Nm^3 per hour. EUV, when fully extended to all of the critical layers, will roughly double the amount of hydrogen used in these fabs. In a related application, the largest LED fabs also use hundreds of Nm^3 of hydrogen per hour, primarily as a carrier gas and diluent for the gallium, arsine, and phosphorus precursors used to make the light-emitting devices.

Supply of hydrogen to electronics customers has been historically driven by regional source types, engineering and transportation codes, and by end user preferences and process qualification. However, steep demand curves are causing users to consider new supply schemes for access to larger volumes, greater supply chain security, and lessening of local fab logistics.

Over 60 million metric tons of hydrogen are produced globally, almost exclusively from hydrocarbon feedstocks: natural gas, oil, and coal. Most of this is used as a chemical intermediate to make ammonia, methanol, and transportation fuels. Electronics uses much less than 1% of hydrogen, yet relies on industrial technologies and sources as supply origins.

Hydrogen is supplied in the following modes (**FIGURES 1 and 2**):



Cylinders

Economical transport of various sizes of cylinders for short to medium distances

Compressed gaseous hydrogen (CGH_2)

Economical transport for short to medium distances

Liquid hydrogen (LH_2)

Economical transport for medium to long distances (only in U.S. and Europe)

On-site production

Production through steam reforming or electrolysis
No hydrogen transport costs

FIGURE 1.

Package	Volume [m^3]
Cylinder	7
Compressed gas trailer	10,000
Liquid trailer	40,000

FIGURE 2.

- **Cylinders:** In smaller volumes, hydrogen is supplied in standard-sized gas cylinders, which hold about 7 m^3 of gas pressurized at approximately 175 bar (250 cu ft at 2,500 psi). The largest fabs now consume this amount in less than one minute. Individual cylinders can be manifolded together to create larger packs of cylinders, which are typically mounted into metal pallets for easier handling. These packs can even be arrayed into full truck trailers of connected cylinders. Despite the increased volume, there is a limitation on the level of mass flow that can be safely achieved from this configuration.

- **Compressed gaseous hydrogen (CGH) trailers:** To improve on both mass distribution and packaging/handling costs, specialized trailers with much larger, pressurizable vessels are used. These CGH (compressed gaseous hydrogen) trailers can hold 10,000 Nm^3 at pressures similar to smaller packages, yet are the distribution equivalent to over 1,400 individual cylinders. Just as importantly, fewer, larger vessels are faster to fill, and easier to maintain quality to the very high standards required by the semiconductor industry. Fewer components and human interactions also reduce safety risks.

- **Liquefied hydrogen transport:** In North America and much of Europe, liquefied hydrogen transport is allowed. This further increases the amount of hydrogen per truck to 40,000 Nm^3 gas, or the equivalent of around 6,000 cylinders. In addition to increasing the volume, liquefication of hydrogen is also an added purification step. By cooling the material down to the boiling point of 21 K (-252 C), most impurities are solidified and can be reduced in concentration by absorption.

These benefits come with a trade-off, however. Liquefying hydrogen to the very low required temperatures consumes a lot of energy, and mandates additional safety protocols. Moreover, there are fewer liquid hydrogen production sources versus gaseous facilities, and transportation distances and supply logistics can be substantially increased. It is important to note that liquid hydrogen transport is not allowed in the primary semiconductor producing countries of Asia (China[1], Japan, Singapore, South Korea, and Taiwan), and therefore not a consideration for users in that region.

On-site hydrogen production

A solution that is becoming appropriate for some fabs is on-site hydrogen production (**FIGURES 3 and 4**). All major fabs already have either direct on-site production of gaseous nitrogen, or are supplied via pipeline by local plants. On-site hydrogen production has similar considerations of planning, footprint, redundancy, and back-up.

- **Planning and footprint:** On-site gas production should be planned at the outset of the entire fab concept. Like on-site nitrogen production, construction of the hydrogen facility usually begins at the same time as groundbreaking for the fab. The footprint of the plant and auxiliary equipment needs to be accounted for, either on the user's property, or on an adjacent parcel reserved for the gas supplier.

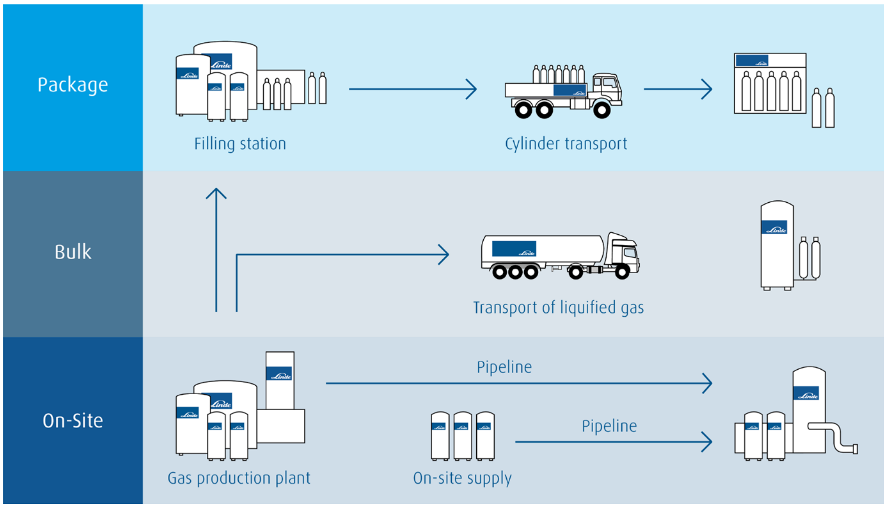


FIGURE 3.

FIGURE 4.

Pipeline delivery needs to be routed. And importantly for hydrogen, permits must be applied for which differ according to location.

- **Redundancy and back-up:** Continuous supply is essential for all semiconductor material supply chains. On-site production must ensure continuous supply for planned and unplanned equipment downtime, or in the case that fab demand grows past the on-site generating capacity. This can be accomplished by choosing from among three alternatives. If liquefication of on-site generated hydrogen is part of the production and purification scheme, excess hydrogen can be liquefied and stored in cryogenic tanks. Hydrogen generators appropriate to produce semiconductor-grade material are often modular, meaning that several will be used in parallel to make the full requirement of a fab. By installing an additional or redundant module, excess capacity is available in the event of planned maintenance or other event. Finally, off-site hydrogen is usually qualified as a supplement or temporary replacement. Often, this is the original source for the process of record for the manufacturer.

On-site hydrogen technologies suitable for semiconductor processes are either electrolysis of water, or so-called "reforming" and "shifting" of hydrocarbon feedstocks.

- **Electrolysis:** Electrolysis uses direct current electricity to split a water molecule into elemental hydrogen and oxygen. Actually, the reaction takes place in two physically distinct electrical poles of the equipment – the anode and the cathode – as two separate half-reactions. The net reaction is

  $$2\,H_2O_{(\ell)} \rightarrow 2\,H_{2\,(g)} + O_{2\,(g)}$$

  Electrolysis is relatively expensive at volume because of the energy needed to break water molecule bonds even though achieving purity in the feedstock water is relatively simple.

- **Steam Reforming and Shifting:** More economical are the industrial steam reforming and shifting processes, using hydrocarbon feedstocks like natural gas, LPG (liquefied petroleum gas – mostly propane and butane), and methanol. In fact, this is the process which produces most of the bulk hydrogen already used by existing semiconductor fabs, and is responsible for 95% of global hydrogen production. Natural gas (CH_4) and steam are heated over a catalyst to form syngas (a mixture of hydrogen and carbon monoxide).

  $$CH_4 + H_2O \rightarrow CO + 3\,H_2$$

  The syngas is then separated to give hydrogen. The carbon monoxide can then be further reacted (shifted) with the steam to yield additional hydrogen.

  $$CO + H_2O \rightarrow CO_2 + H_2$$

  Taken together, these process plants are known as steam methane reformers, or SMR plants.

Choices for the exact plant technology depend upon the local feedstocks available and the customer quality profile requirements.

Regardless of whether the hydrogen is supplied in gaseous or liquefied containers or made on-site, semiconductor hydrogen supply schemes incorporate on-site, and often additional point-of-use, purification using various technologies: adsorption, gettering, and application of the unique property of hydrogen to diffuse through palladium metal membranes, which are impervious to most other molecules. In addition, hydrogen purity is monitored at several points in the distribution by multiple types of detectors.

Safety

As with all chemical supplies, safety is paramount. With hydrogen, the main safety risk is associated with its wide range of flammability and explosivity. Throughout production and packaging, multiple types of redundant protocols are used to ensure that no oxidizers are contacted or incorporated into the hydrogen and plant designs minimize the risk for leaks. Specialized clothing resistant to fire and static is worn in some hydrogen producing and using environments. Materials of construction and component qualification are also important to guard against a phenomenon known as hydrogen embrittlement, where at elevated temperatures and/or pressures, hydrogen can permeate and weaken certain metals and alloys. Finally, liquefied hydrogen introduces the additional risk associated with cryogenic materials and the need to use insulating vessels and personal protection.

Conclusion

Semiconductor manufacturing has long used hydrogen in an essential and expanding portfolio of applications. Already, hydrogen supply is considered a bulk material scheme, with source, transport, and logistic considerations. The adoption of EUV at leading-edge fabs in the next few years will accelerate the pace of hydrogen consumption, and drive the consideration of new supply schemes. End users should evaluate hydrogen supply options for future fabs as part of their advanced planning to ensure that their quality, supply and process integrity requirements will be met.

References

1. China is in the process of approving liquefied hydrogen transport at the time of this publication. The details are not yet defined. ◆