Gas contamination control in photovoltaic applications

Chemical purity is important to the manufacture of photovoltaic cells for many critical process steps, and acknowledging this, the Semiconductor Equipment and Materials International Corporation (SEMI) PV Group has established standards for gases specifically for the photovoltaic industry. PES investigates.

The standards outlined by SEMI include PV6-1110 for bulk argon, PV7-1110 for bulk hydrogen and many others. Impurities in the gas can have various negative effects on photovoltaic cells, such as causing inclusions during the ingoting process, or reducing the effectiveness of the antireflective coating deposited using plasma enhanced chemical vapor deposition (PECVD). The impact of impurities is dependent upon the cell design and the stage at which the impurities are introduced. Due to this, the benefit of using improved gas purity is typically measured for a specific process.

Gas purity can be achieved by purchasing high purity gas from gas suppliers and implementing best practices for gas delivery to ensure integrity of the gas supply. Higher purity gases are more expensive; and often, it is more cost effective to buy industrial grade gas and then use point-of-use purifiers to improve the gas quality for contamination-sensitive applications.

To further reduce the cost of gas consumption, there is the option to recycle or reclaim used gases in some applications. The largest application for this in the photovoltaic industry is for the argon purge gas used during the ingoting process. In this article, we will review the technology used for gas purification, the major applications within the photovoltaic industry, and cost effective solutions for gas contamination challenges.

Technology

Gases are purified using a variety of methods. Strictly speaking, most of these techniques are gas separations in which one gas is separated from other gases based upon specific gas molecular properties. The most prevalent method for gas separation is distillation. This technique is used to produce bulk gases like nitrogen, oxygen and argon from the atmosphere. In this method, the gases are separated by employing cryogenic traps which capture the molecules based on their boiling point. This is an energy intensive technique which is typically only economical at larger scales and where the majority of by-products are sold.

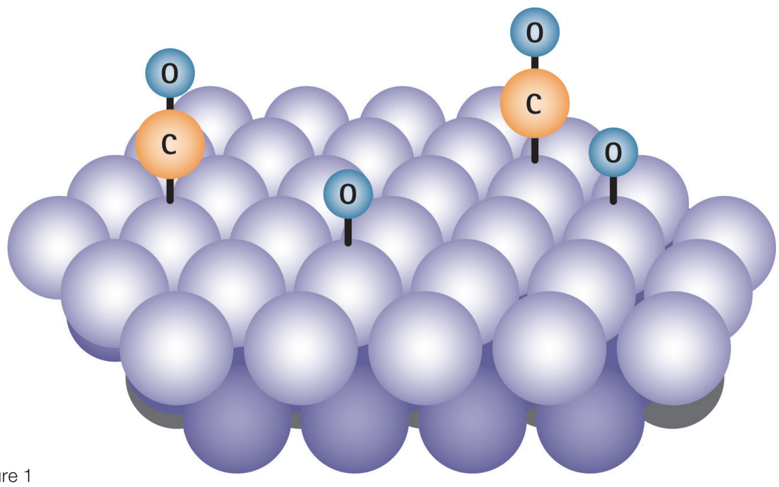

Figure 1

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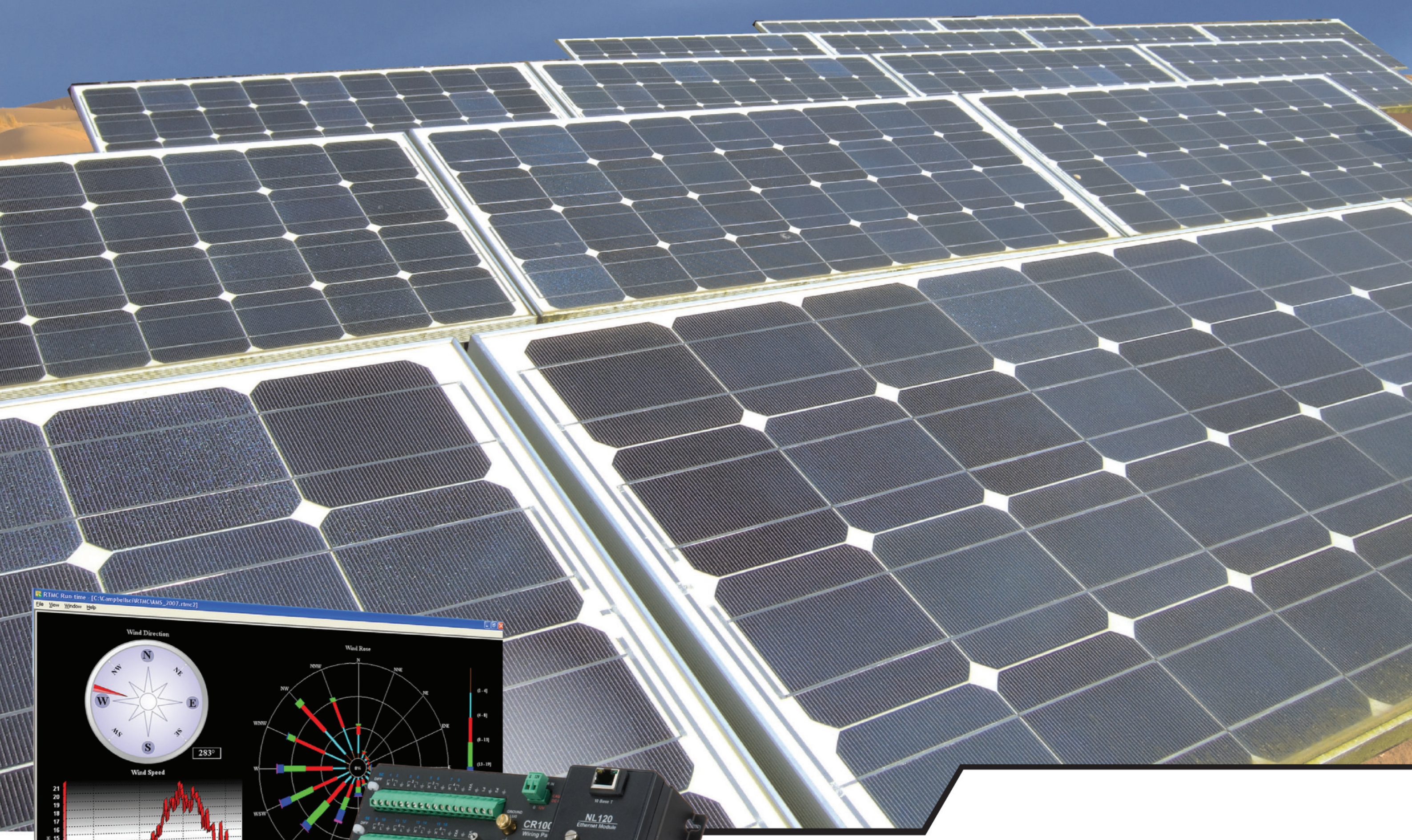

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Figure 2

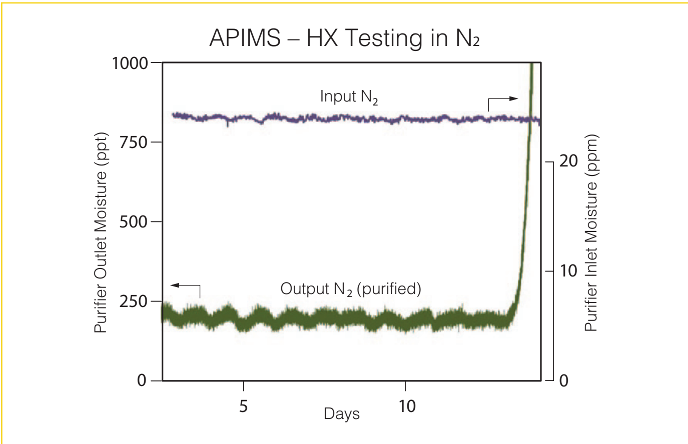

Figure 3

The other major technique can be broken into three major categories: membrane separation, physical adsorption and chemical adsorption. Membrane separation techniques use the differences in the relative molecular sizes to separate molecules. Smaller molecules pass through the membrane while the larger ones are excluded. This is also most effective at larger scales and for higher impurity concentrations.

Physical adsorption is used extensively for gas purification and can remove contaminants from gases to levels of less than 1 ppm under the correct usage conditions. In physical adsorption, the molecule is retained on the surface of the adsorbent via weak molecular forces – van der Waal forces.

A special class of adsorbents, called molecular sieves, selectively adsorbs gases based on their molecular size due to their crystal structure. Since the molecules are physically adsorbed on the surface, purifiers based on this technology can typically be regenerated when they become saturated by using a pressure, temperature, flow protocol to restore the molecular sieve to their original state. While molecular sieves are very useful, they have limitations in the efficiency of contamination removal and selectivity.

The most versatile class of purifiers is based on chemical adsorption. The contaminant first physically adsorbs and then chemically bonds to the purification media as shown in Figure 1. The composition of the purifier can be modified to selectively adsorb specific contaminants, while not affecting the process gas. Chemical adsorption purifiers can be single-use or in some cases they can be regenerated by using a protocol which reverses the chemical adsorption process.

An example of a self-regenerating system using this technology is shown in Figure 2. This system incorporates an inorganic regenerable media which purifies gases at ambient temperatures down to parts-per-trillion (ppt) levels. Typical impurities removed from an inert gas stream include hydrocarbons, amines, siloxanes, alcohols, NH_3, SO_2, NO_2, NO_x, SO_x, CO, CO_2, H_2O and O_2 to levels less than 1 ppb.

Purifiers come in all shapes and sizes to cover flows in excess of 10,000 slpm to as low as a few cc/minute. The lifetime, or time between regeneration cycles, is a function of the purifier media's surface area that is available to react with contaminants, and the reactivity with a given contaminant. The lifetime is also determined by reaction kinetics and flow rates that affect capacity and efficiency by increasing impurity load and reducing residence time. Large systems will typically have at least two purifiers that work in parallel so that one can continue to purify gas while the other is being regenerated.

An illustration of a purifier lifetime is given in Figure 3. This figure shows what is termed 'a challenge test' in which an impure gas of known gas composition is continuously introduced into the purifier and the output of the purifier is monitored to measure the contamination level. In this particular case, 20 ppm of water in nitrogen is introduced into the purifier. The purifier continues to remove the water to less than 250 ppt until day 13 when the water signal begins to rise in the output gas.

This point is sometimes called the 'breakthrough point.' In real world applications, the input contamination level and composition will vary with time. The manufacturer of the purifier will recommend the appropriate regeneration cycle based on the most likely maximum contamination scenario. The larger purification systems may also be equipped with sensors to detect the 'breakthrough point' and may include the capability to switch the gas to the alternate purifier to maintain continuous operation. Ultimately, the optimum selection for a purifier is application dependent. Some examples of applications are discussed in the following sections.

Gas purity in cell manufacturing

The majority of process steps in silicon-based photovoltaic manufacturing utilise dry processes in a gaseous environment. One of the primary steps is the formation of the p-n junction through a doping process. This is typically accomplished with the deposition of a dopant on the surface followed by a thermal process step which distributes the dopant into the bulk with the desired concentration gradient.

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Contaminants which enter the gas stream during the doping process can be deposited on the wafer and then be driven into the bulk of the material, which may result in the formation of dislocations or ion traps which reduce the minority carrier lifetime. Film properties can also be adversely affected by contaminants. Passivation layers, anti-reflective coatings, and barrier layers are integral to many cell structures and contaminants can influence the electrical and optical properties.

Argon recycle application

One of the largest uses for high purity argon is in the manufacture of silicon ingots for the photovoltaic and semiconductor industries. In the production of silicon ingots, argon is used as a purge gas to remove contaminants during the ingot formation process . Gaseous impurities, if not removed, can react with the molten silicon to produce defects such as SiC, SiN and other compounds.

These systems typically employ a constant flow of argon from 10 to 40 slpm depending upon the equipment design and ingot size. An ingot facility producing an equivalent of 1GW of solar cells would use greater than two million m3 of argon, which represents a significant operational expense. Large savings could be realised if the waste argon is purified for reuse. The effluent argon is typically composed of argon and a few percent of contaminants, chiefly composed of hydrocarbons and COx. Purification of this gas stream is typically accomplished in multiple steps in order to achieve a purity level for photovoltaic grade gas of 10 ppm maximum (Figure 4).

The first purification step typically removes hydrocarbons. This is accomplished either through a catalytic or other chemical reaction cycle. The next step is typically designed to remove COx, H20 and residual oxygen via adsorption bed technology. To achieve purity levels lower than 10 ppm often requires subsequent specialised purification beds.

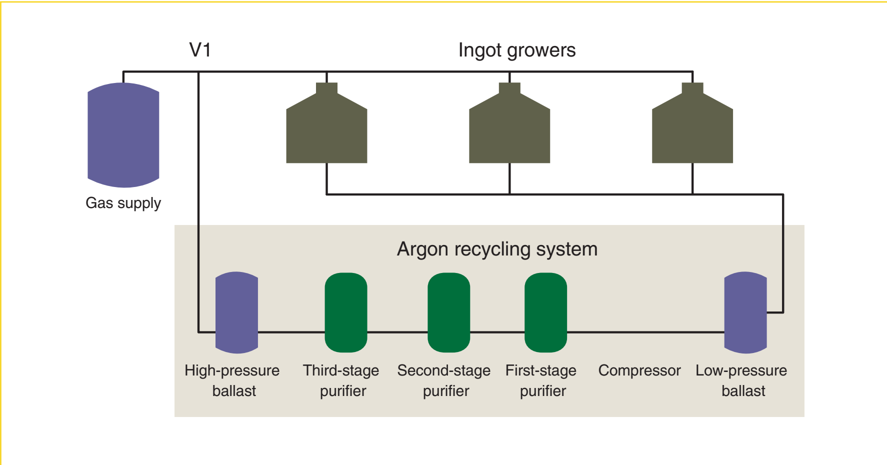

Figure 4

These systems are designed to operate continuously and remove contaminants to levels below 0.1 ppb for the most demanding applications.

The recycle systems are designed for continuous use and to maximise the amount of gas recovered. Recovery percentages range from 80% to greater than 90% depending upon the specific application. While the basic elements of the systems are common, each installation is customised for facility integration and optimisation for the specific contamination profile. Return on investment times for the systems vary but can be less than three years for many applications.

Conclusion

Research, development, process and production engineers strive to ensure their manufacturing lines function at their optimum. The manufacture of photovoltaic cells relies on chemical processes, and in turn on the purity of the chemical precursors. Gas impurities can lead to product excursions, variation in product yield, and worst case, product scrap.

In most cases, excursions are not easy to detect and can lead to long periods of downtime, with adjacent resources and equipment in a non-productive state. This is more inevitable on high volume production lines that have a fragile substrate and many variables; eliminating or minimising the risk is key to good manufacturing and continuous improvement practices.

As the photovoltaic industry continues to drive toward higher efficiency cells, critical processes will require improved contamination control. Selective addition of gas purification capabilities to these processes is an effective method to make process improvement without large capital investments in whole facility gas distribution upgrades or conversions of all processes to more expensive high purity gases. ■

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