Processing in a Hydrogen Rich Ambient

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Abstract

Hydrogen rich ambient are useful for processing when a thermal heat treatment needs to be achieved without oxidizing the surfaces of materials being processed. However, the reactivity of hydrogen with air poses safety concerns and requires the use of measures in system design and operation to manage the hazards.

Introduction

Semiconductor processing, MEMS fabrication, and solar cell fabrication utilize processing steps done at elevated temperature. In some steps the objective is to oxidize materials in a process chamber. However, often a step needs to be carried out without forming a surface oxide or even reducing an existing surface oxide. In that case, it may be desirable to process in a neutral or inert gas, mildly reducing or strongly reducing atmosphere. Argon, nitrogen or helium are common choices for inert gas environment and hydrogen containing atmospheres are the most common for reducing atmospheres.

Levels of hydrogen concentration

Inert ambient supplied by using gases such as nitrogen, argon, or helium will limit oxidation of surfaces during processing and are sufficient for many applications. However, for better suppression of surface oxidation, mildly reducing atmospheres is commonly used in metal working anneal furnaces to reduce and remove surface oxide from copper alloy parts. The commonly used atmosphere is a mixture of 5% hydrogen in nitrogen and is known as “forming gas”. Copper or brass parts annealed in such an ambient are free of surface oxide and the process is also commonly known as a “bright anneal”.

Reducing ambients are commonly composed of inert gases plus higher percentages of hydrogen. The upper limit is a fully reducing or 100% hydrogen ambient. For many cases, that full hydrogen ambient not only suppresses surface oxidation but also reduces existing oxide on surfaces and removes the oxygen, which is carried away in the exhaust stream.

Hydrogen Safety

When using hydrogen as a process ambient, there is always concern for following procedures that result in safe use and disposal of the hydrogen. Safety is managed by avoiding the conditions in and around the equipment in which the gas mixtures are flammable or explosive. Safety guidelines[1,2] indicate hydrogen is flammable when it is mixed with air in concentrations of 4% to 75% by volume. Explosive limits for hydrogen in air are generally given as 18.3 to 59% by volume. This means that low percentages of hydrogen (<4%) which may be readily detectable, are still safe as they are not rich enough to support a flame or explode. Similarly, at high concentrations (>75%) there is not enough oxidizer to support a flame or produce an explosion. It is the mid-range concentration that presents the greatest hazard and so interlocks are designed to eliminate having mid-range concentration of hydrogen and oxidizer present in the process chamber.

Pre-purging

For batch thin film process reactors, the hydrogen hazard is generally managed by loading a batch reactor at low temperature, allowing air atmosphere into the chamber. Loading is followed by sealing the chamber and performing what is known as a pre-purge step. This pre-purge step flows inert gas (usually nitrogen) at a flow rate and time designed to purge the air and its oxygen from the tube. If the chamber flow were ideal plug flow, one change of gas would remove all the oxygen. However, since there is some gas mixing, more than one gas change is provided during this step. In the worst case of full gas mixing, the oxygen, which in air is about 20%, is reduced by dilution by half for each gas change of the chamber. So after N changes of gas the oxygen level is expected to be below $(20\%) \times (0.5)^N$. For a pre-purge that provides three gas changes, the oxygen level is reduced to near 2.5%, below the flammability range for hydrogen. Typically a system's firmware interlocks will impose six or more gas changes before flow of hydrogen is enabled.

Ramp up to process temperature may begin during the pre-purge step to reduce cycle time of the pre-purge step. It is safe to begin to flow partial or full hydrogen and continue to ramp up to the desired anneal process temperature. During the ramp up of temperature, the hydrogen purge flow will complete purging any remaining air and establish an ambient low level of oxidizer (typically < 2 ppm) determined by the purity of the inlet hydrogen, any inert gas mixed with the hydrogen and any seal leakage of the chamber (including a very low level of diffusion through o-ring seals).

Post-purging

It is the usual practice for hydrogen anneal systems to ramp the temperature down while maintaining the hydrogen ambient purge until the temperature is near the unload temperature for the reactor. The hydrogen ambient then is removed by a post-purge step in which inert gas is used to displace the hydrogen. For the worst case of full mixing, the initial hydrogen level (which is up to 100%) is reduced by half for each volume change of the chamber. Since the objective is to reduce the hydrogen, which may be as high as 100%, to below the lower flammability level of 4%, more gas volume changes are required in the post-purge than for the pre-purge. For full mixing, five changes of gas should reduce the level to near 3%, below the lower flammability limit. Most systems will have interlocks that force an 8 to 10 volume change of the chamber to assure the hydrogen is reduced to below the flammability limit.

Additional Safety Interlocks

Any thin film processing system using hydrogen should be equipped with additional interlocks to guard against an unexpected opening of the chamber during a process cycle. It is typical to equip such systems with interlocks that perform the following functions:

1. A method of sensing closure of the process chamber door. For hydrogen anneal systems sensing should not rely on mechanical flags, magnetic switches or optical sensors as these can go out of adjustment and provide a false door closure signal. Instead it is better to seal the door with a double o-ring seal and pull a vacuum in the space between the seal o-rings. Not only does that vacuum provide added closure force for the door, sensing the vacuum level between the two o-rings verifies the door closure and also checks the seals for leakage.

2. When the door closure is detected, the pre-purge step is started. An interlock should remove power to the loading mechanism to prevent the loader from moving to extract the load until completion of the post-purge step.

3. An interlock should verify readiness of the hydrogen abatement system before initiation of the pre-purge step of the recipe.

Hydrogen Abatement:

Systems using hydrogen require an abatement system to provide for safe handling of the hydrogen once it has passed through the process chamber. While this might be accomplished by rapid dilution with air to below the lower flammability limit, that method is subject to unexpected ignition of the gas during dilution. A better method is to conduct the process exhaust into a chamber that provides both for mixing with some air and a source of ignition for a controlled burn of the hydrogen. The module for this task is commonly referred to as a "burn box" or a "CDO" (controlled decomposition oxidation) system and is located near where the gas exits from the process chamber. The ignition source is typically an electrically heated wire filament monitored by a temperature sensor to verify operation above the ignition temperature. The hot wire filament is located in the mixing zone where the process chamber exhaust is combined with air drawn into the enclosure. The exhaust from the "burn box" which contains some steam from the burned hydrogen is diluted with more air and conducted to a house exhaust duct for removal.

Abatement System Interlocks:

In addition to a temperature sensor for the ignition source, system interlocks should provide a flame sensor or other means to detect when the hydrogen is being oxidized. This is usually a UV sensor with a band pass optical filter designed to pass the strong UV lines of a hydrogen flame. The sensor provides assurance the hydrogen is actually being oxidized and not passed untreated into the exhaust ducts.

When a system has passed the pre-purge step and starts to flow hydrogen, initially the exhaust gas will be the inert ambient and no flame signal will result from the flame sensor. Interlocks need to provide a delay time and then begin to monitor for the flame signal after the expected lag time to purge out the tube. Once the flame signal has been acquired, if the signal is lost for more than a short tolerance time, interlocks activate shut off of hydrogen flow.

Summary:

Although there are hazards in using high concentrations of hydrogen in thermal processing, the hazards are managed by system design and interlocks that permit these hydrogen anneal systems to operate routinely in a safe manner.

Expertech diffusion furnaces have the following system design for hydrogen processing: proprietary flange design utilizing a stainless steel door with double o-rings to ensure a safe and proper seal at the tube opening; factory pre-programmed interlock of nitrogen purge to allow for complete hydrogen evacuation once process is completed; the hydrogen has to be purged before the wafers can be extracted – it's not recipe driven, it's part of the tool design; the facility is made safe with a burn box on the exhaust duct with a safety shroud as a part of the tool. Both hardware and software interlocks insure safe hydrogen processing in Expertech furnaces. For more details on all of the safety features with 100% hydrogen processing, contact Expertech.

References:

1. Material Safety Data Sheet for Hydrogen, from www.praxair.com/praxair.nsf/0/.../$FILE/p4604g.pdf

2. SEMI S2 Environmental, Health and Safety Guideline for Semiconductor Manufacturing Equipment, Revision 10D (March 2010).