FEATURE

Cheating Raoult's Law to Enable Delivery of Hydrogen Peroxide as a Stable Vapor

By Jeff Spiegelman and Dan Alvarez

Introduction

Check your home medicine cabinet and there is a good chance that you will find that familiar brown bottle of 3% hydrogen peroxide. Much stronger concentrations of hydrogen peroxide can be found in most hospitals and industrial facilities for use in sterilization. It is also a common component of most semiconductor wet cleaning processes, always as a liquid, but never as a gas.

Historically, volume usage of hydrogen peroxide, H_2O_2, has been in the liquid phase, with only a few applications for hydrogen peroxide vapor (HPV). These include low-temperature surface sterilization of medical instruments, and in next generation thin film processing research on selective oxidation, cleaning, and atomic layer deposition. Raoult's law has limited the widespread use of HPV. If the inherent limitations in Raoult's law could be overcome, HPV could potentially replace ozone, oxygen plasma, steam, and water vapor for a wide variety of oxidation and sterilization applications.

Raoult's law relates the ratio of components in a liquid to the ratio of the components in the vapor above the liquid headspace. For an ideal solution, the partial vapor pressure of each component above the liquid headspace is equal to the vapor pressure of each component multiplied by its mole fraction in the solution. See Figure 1.

Once the components in solution have reached equilibrium, total vapor pressure p of the solution is:

$$p = p^*_A x_A + p^*_B x_B + ... + p^*_i x_i$$

and the individual vapor pressure for each component is:

$$p_i = p^*_i x_i$$

where

p_i is the partial pressure of the component i in the gaseous mixture above the solution

p^*_i is the vapor pressure of pure component i

x_i is the mole fraction of component i in mixture (in solution)

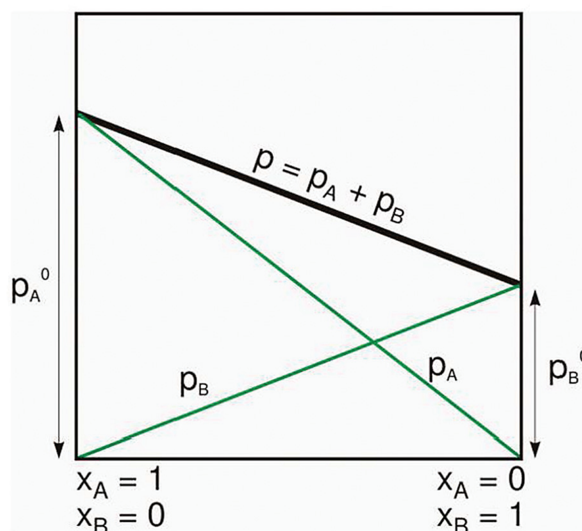

Figure 1. Raoult's Law under ideal conditions

For Example:
Ideal Solution 30% H_2O_2 at 30°C

$x_{H_2O_2} = 0.185$; $x_{water} = 0.815$

$p^*_{water} = 23$ Torr ; $p^*_{H_2O_2} = .208$ Torr

A 30% by weight solution of H_2O_2 at 30°C under ideal conditions is equal to 23*0.815 + 0.208*0.185 = 18.8 pressure total or a H_2O_2 to H_2O ratio of 487. Actual measured value is shown in Table 1 .

For a solution of hydrogen peroxide and water, water vapor has a much higher vapor pressure than hydrogen peroxide. The boiling point for water is 100°C while for pure H_2O_2 it is 150°C. Because the vapor pressure of water is much higher than H_2O_2, water vapor tends to dominate the headspace above the liquid. So even though water may make up only 70% of the liquid, it will be greater than 99% of the vapor for a 30% solution.

As vapor is drawn off or swept away from the headspace, water vapor preferentially evaporates to refill the headspace. As the vapor removal continues, the higher rate of water evaporation concentrates the solution for H_2O_2. This increases the H_2O_2 mole fraction in the solution, so the HPV starts to increase. As vapor is drawn off, there is a disproportionately large decrease in both water vapor in the headspace and water in solution and a small increase in HPV. This leads to an overall drop in vapor pressure above the liquid. Unless the vapor draw is halted, the solution will continue to concentrate. As it approaches greater than 90% H2O2 solution, it can become an unstable, explosive mixture.

Industrial Uses for Hydrogen Peroxide Vapor

Raoult's law describes how the vapor pressure of H_2O_2 and H_2O continuously change during vapor draw and how this can lead to a dangerous situation. This has prevented the widespread adoption of HPV delivery into large-scale applications in industries such as semiconductor, food service and health care.

Semiconductor and Microelectronic Processing Applications

The continuous miniaturization of semiconductor structures has created large challenges in wafer cleaning and surface preparation. New techniques are needed to avoid damage to the substrate and prepare a ready surface for follow-on processes. HPV can be used as an alternative oxidant to replace ozone, oxygen plasma or steam.

Wet cleaning processes that use hydrogen peroxide liquid are not viable for new, thin films. Too many defects and contaminants remain after processing, putting manufacturing yield at risk. Dry cleaning processes using HPV are being investigated under the assumption that they will be superior in penetrating structures, removing surface carbon deposits and forming a dense hydrophilic surface.

We realized that we had to control the process so that we preloaded only enough water vapor to stabilize the solution as defined by Raoult's law.

Cleaning and Surface Preparation Applications

HPV can address a wide variety of wet cleaning steps and improve throughput if used in situ prior to a deposition step. Hydrogen peroxide has been shown to readily remove carbon contaminants, is non-toxic and decomposes into water and oxygen gas when reacted.

As the active cleaning ingredient, HPV is superior to water vapor for cleaning and surface preparation for three key reasons. First, operations can be conducted at lower temperatures, reducing risk of damage to the semiconductor structure. Second, hydrogen peroxide is more reactive than water. Third, hydrogen peroxide is more acidic than water so can reduce reaction time in ALD processes.

Similar to HPV, ozone is also an oxidant, but ozone is more reactive toward metals than HPV. This can lead to corrosion of electrodes in the device structure. In addition, some carbon-based layers need to be cleaned without removing underlying material. Ozone can be overly aggressive, while HPV can be used to clean and hydrolyze the surface without significant etching.

Hydrogen peroxide has the further benefit of easy availability in safe and stable concentration. Semiconductor processes are already in place for handling 30 percent by weight hydrogen peroxide liquid. An HPV delivery system sourced from liquid hydrogen peroxide should require little or no change to chemical storage and handling policies within the fab.

Pharmaceutical and Medical Applications

As reported in 2009, approximately two million patients per year in the United States suffer with nosocomial or healthcare-associated infections (HAIs) while staying in a hospital. An estimated 90,000 of these patients die from HAIs, which makes this one the top five causes of death[1].

Hydrogen peroxide is in limited use in medical and pharmaceutical applications for the sterilization of instruments, buffer zones, patient rooms and surgical spaces. General adoption as a sterilant has been disappointing due to the difficulty in creating a consistent vapor stream. Current technology creates an atomized fog of peroxide droplets that land on the surface to be sterilized. This eliminates the need to wipe down surfaces with bleach. However, because the hydrogen peroxide is a fog and not a true gas phase vapor, it does not fully diffuse and leads to a high level of excess moisture on the surfaces being sterilized.

With heightened concern about Ebola and food-borne illnesses, a new approach is needed to reduce risk. A low temperature technique for sterilizing large public areas,

Concentration	Temperature (C)	H_2O_2 Out (PPM)	Water Out (PPM)	Ratio (Water/H_2O_2)
30	35.2	329	43434	132.0
	40	456	56411	123.7
	50	876	94527	108.0
	60	1629	152922	93.9
50	35.2	850	31024	36.5
	40	1240	40391	32.6
	50	2229	68009	30.5
	60	4093	110521	27.0
70	35.2	1806	16906	9.4
	40	2617	22118	8.5
	50	4651	37604	8.1
	60	8444	61670	7.3

Table 1. Relative water and hydrogen peroxide vapor ppm value dependency on temperature and concentration of the hydrogen peroxide solution by moles

instruments, and food surfaces without heating and with minimal space constraints could save countless lives and dramatically reduce legal fees associated with injury and wrongful death lawsuits.

HPV Delivery Challenges

Conventional delivery methods for HPV are inefficient and ineffective. The basic difficulty is that hydrogen peroxide is mixed with water and these components act differently in liquid versus gas phase. This leads to many different failure modes depending on the application and the vaporizer.

Historically, semiconductor researchers have not demonstrated a significant advantage of HPV over water vapor. Based on communication with these researchers, we believe this was due to the fact that the researchers assumed the vapor pressure ratio above the solution was equal to the mole fraction in the solution and did not understand that extremely dilute HPV was actually being delivered into the process. In medical applications, excess water led to mold growth on surfaces. Quantitative testing showed that in both cases the vaporization process was the problem.

In fact when starting with a 30 percent liquid concentration of hydrogen peroxide, less than one percent of vapor delivered to the process was actual HPV. At room temperature, a 30 percent by weight hydrogen peroxide solution generates a water vapor to HPV molar ratio of about 130:1. If delivered as vapor with carrier gas, only 0.03 percent hydrogen peroxide (or 300ppm) is delivered to process. This is generally not enough to show any noticeable effect.

While only 300ppm of HPV is picked up by the carrier gas, 39,000 ppm of water is also being removed from the liquid source headspace. The hydrogen peroxide liquid supply is increasing in concentration, creating a dangerous and potentially explosive condition. The net result is very dilute HPV delivery and an increasing hydrogen peroxide concentration in the source container. This is demonstrated in Table 1, where ratio increases with temperature and concentration. Continuous withdrawal from a H_2O_2 liquid source will convert 30% to 70%, increase HPV delivered, reduce water vapor delivered, and lower overall delivery pressure.

Another challenge springs from the relationship between temperature and the solution mix. There is a false assumption that the hydrogen peroxide to water ratio is constant with temperature. However, while both HPV and water vapor pressure increase with temperature, the relative ratio changes. In addition, overall head space pressure will continuously decrease unless bulk temperature is raised. This happens because water vapor pressure in the head space drops faster than it can be replaced by HPV, even though hydrogen peroxide concentration is increasing in both the vapor and liquid.

It is difficult for process engineers to control a process when the target molecule varies both with the changing concentration in the solution and changing ratio with temperature. Process recipes cannot be written around continuously changing mixtures. This prevents simple bubblers from being used to vaporize two-component solutions and deliver stable vapor concentrations.

Instead of bubbling, flash vaporizers are sometimes used to prevent the solution source from concentrating. However, it is difficult to deliver consistent, high purity HPV from vaporizers at medium to high flow rates. These vaporizers work by atomizing the hydrogen peroxide liquid into small micro-droplets and then converting the droplets into vapor using a heated plate. When applied to hydrogen peroxide and water droplets, the water preferentially boils off leaving behind concentrated

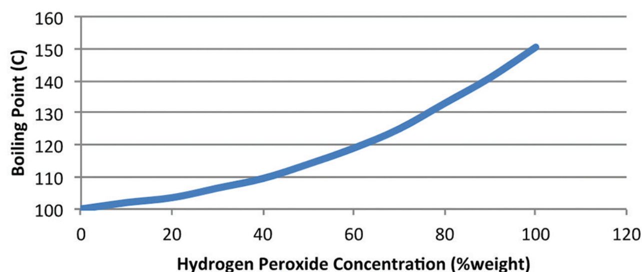

Figure 2. Comparison of H_2O_2 boiling points at different concentrations

hydrogen peroxide micro-droplets that tend to coalesce on the heater plate. To boil off the hydrogen peroxide, the temperature must exceed 150°C. See Figure 2. In fact, the vaporizer plate temperature must be significantly hotter to ensure that it does not dip below 150°C due to the thermal energy required to vaporize the mass.

An unfortunate side effect of the high heat is an increase in the hydrogen peroxide decomposition rate. As temperature approaches 200°C the decomposition rate can exceed 62 percent. The violent vaporization and decomposition leads to a continuous explosion on the vaporizer surface. The atomized droplets are now H_2O_2 concentrated, very difficult to further vaporize, and are then swept away by the carrier gas stream. This leads to spot and particle formation in the film. In addition, the metal vaporizer plate required to achieve rapid heat transfer to support several grams per minute delivery can contaminate the hydrogen peroxide with metals and increase the decomposition rate.

For all these reasons, conventional vaporizers and bubblers have not enabled commercial use of HPV at reasonable mass flow rates. This lack of success is due to the difficulty in providing stable hydrogen peroxide flow without particles, droplets and metal contaminants. They are also constrained by Raoult's law.

Overcoming Raoult's Law

Raoult's law explains physical limitations that cause basic deficiencies in performance of conventional bubblers and vaporizers. A novel technology is needed to overcome Raoult's Law. The solution needs to be safe, easy to use, stable and repeatable. It has to produce high vapor generation rates without overheating the hydrogen peroxide, which causes excessive decomposition. It also needs to be metal free in the liquid portion to prevent metal contamination and hydrogen peroxide decomposition. In addition, the HPV has to be 100% complete vapor to avoid droplet formation and the related particle formation and staining of the material to be exposed.

The problem with the delivery of HPV was first brought to our attention is 2006. For the next several years we continued to receive inquires for the delivery of HPV.

In 2010, came the "aha moment." Theoretically it should be possible to prehumidify a carrier gas before contact to the target solution. After several experiments it became apparent that we could add water vapor to our carrier gas before exposure to the H_2O_2 source, so that we would only remove HPV from the H_2O_2 solution. This led to a gradual depletion of the H_2O_2 from the solution and the related fall off in HPV. Yet Raoult's still held. Instead of concentrating the HPV, we

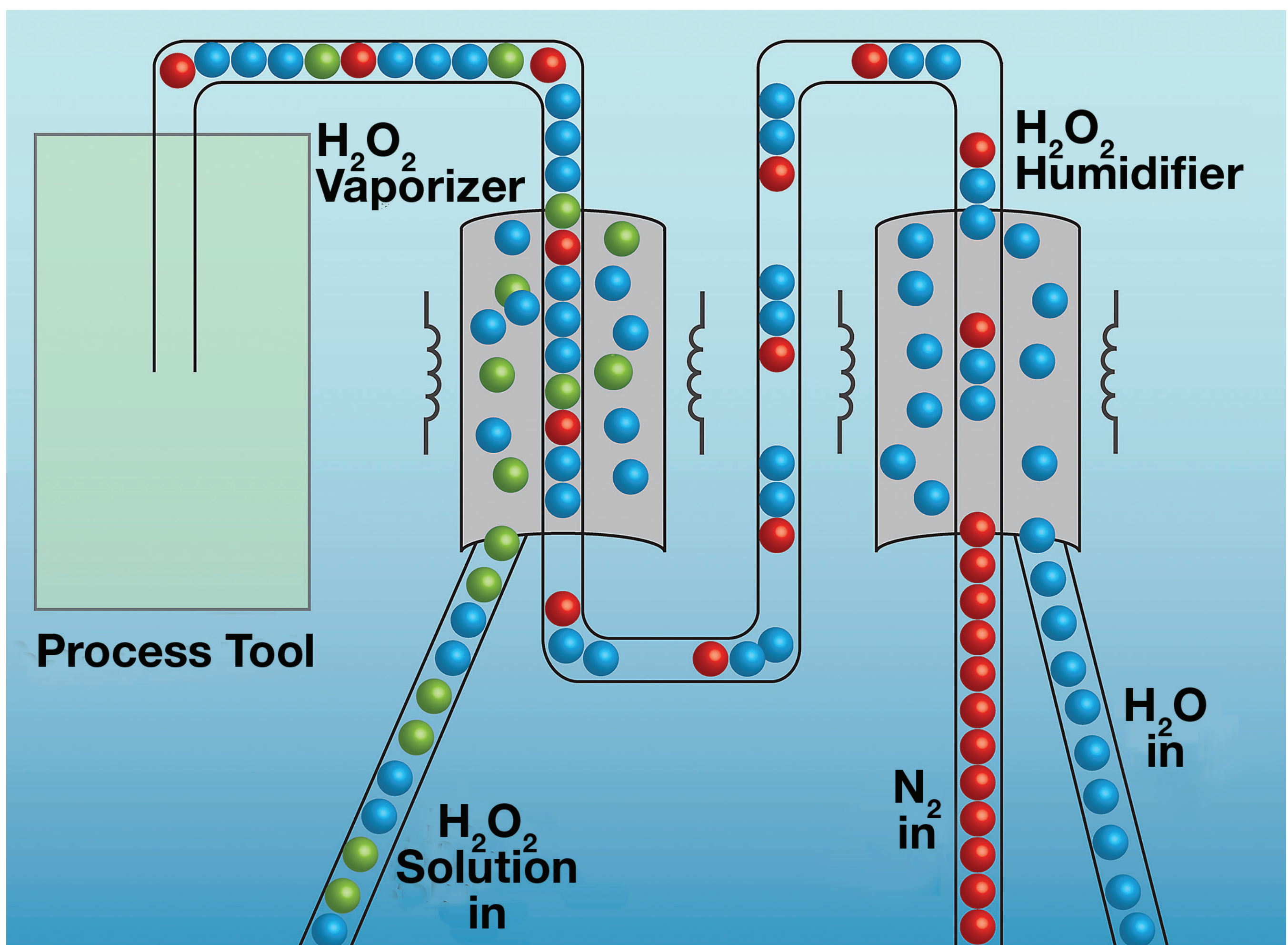

Figure 3: RASIRC SVD conceptual design.

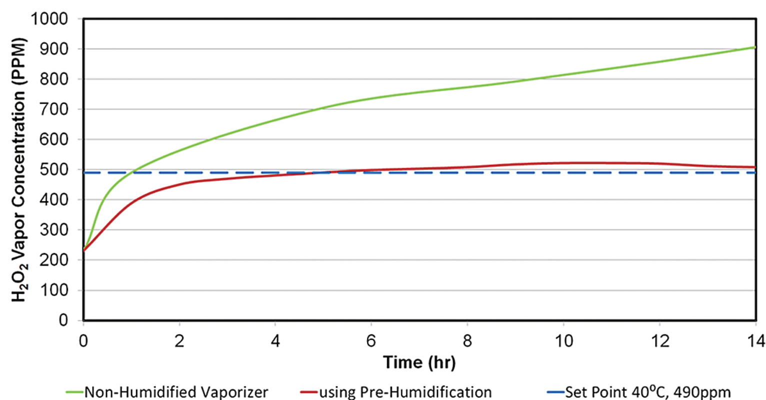

Figure 4. Output from a pre-humified and non-humidified HPV vaporizer at 40°C.

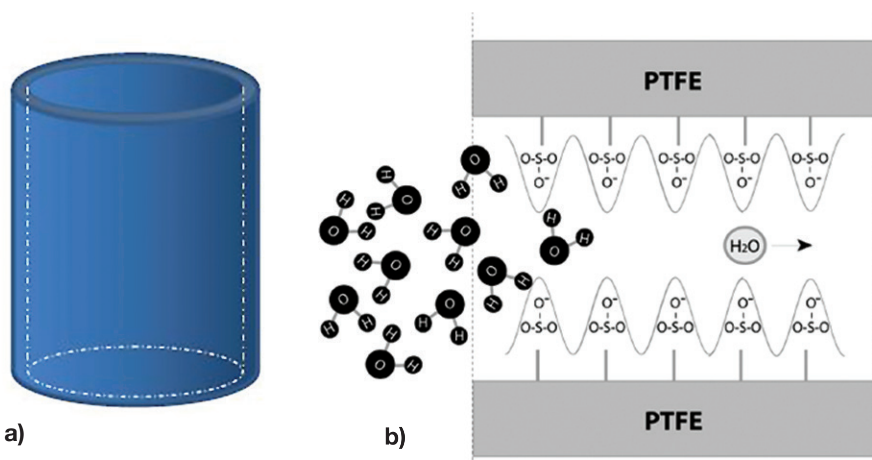

Figure 5a. Membrane in tubular form; liquid diffuses in a radial direction from the outside liquid into the center to be swept away be a carrier gas. Figure 5b. Membrane cross section showing water flow across the membrane

Figure 5b. Idealized membrane for showing the hydronium ion, water molecules, and radially symmetric axially periodic distribution of sulfonate (– $S0_3$ –) fixed sites

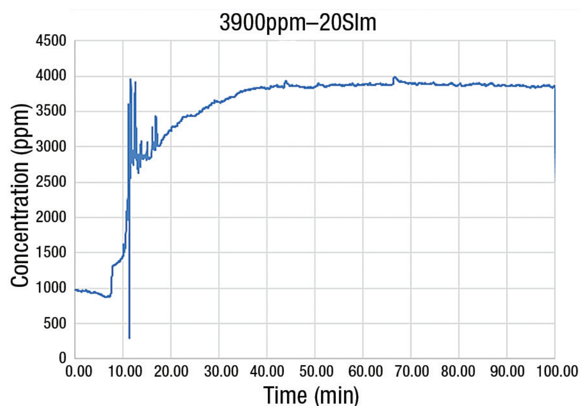

Figure 6. SVD output from a cold start with 30% H2O2 solution can deliver 3900ppm

were now diluting it.

We realized that we had to control the process by preloading only enough water vapor to stabilize the solution as defined by Raoult's law.

Because water preferentially evaporates from a hydrogen peroxide solution, the carrier gas stream must be preloaded with water vapor. By slowing the water evaporation rate, we could match the ratio of HPV to water vapor carried away in the gas phase with the hydrogen peroxide to water ratio in the liquid. For example, if the ratio in the liquid is 4 to 1 and the ratio in the headspace is 100 to 1, the carrier gas is preloaded with 96 parts, so that only 4 parts water and 1 part H_2O_2 are removed from the H_2O_2 solution in the vaporizer.

In theory, this seemed like a way around the limitation imposed by Raoult's law. It took us several years to build the necessary setup and find the correct instruments to measure the output. None of these instruments were or are commercially available yet.

The basic RASIRC SVD™ design is shown in Figure 3. The SVD uses two vaporizers. The first vaporizer pre-humidifies the carrier gas to a calculated dewpoint based on Raoult's law. The second vaporizer vaporizes hydrogen peroxide/water from hydrogen peroxide liquid solution. The controlled concentration of water vapor added to the carrier gas ensures that the peroxide solution remains at a safe and constant value with a stable and repeatable HPV output (Figure 4). Over 14 hours the concentration of the hydrogen peroxide solution in the non-humidified vaporizer rose from 30 percent to 42 percent, while the pre-humidified vaporizer changed by less than 1 percent, delivering controlled, steady state output.

The active component in the vaporizers is a non-porous tubular membrane assembly. Carrier gas flows into the membrane assemblies where water or H_2O_2/H_2O molecules diffuse across a membrane into the carrier gas (Figure 5a). On exiting the humidification vaporizer, the dewpoint is then measured and fed back to a temperature controller to adjust the water temperature. Internal pressure control maintains independence from variations in downstream process pressures allowing operation into atmospheric and vacuum pressure environments.

The non-porous membrane excludes particles, micro-droplets, and volatile gases from being transferred to the carrier gas and ensures only vapor is added. The membrane is highly selective, preventing most carrier gases from crossing over into the source (Figure 5b). Organic and metal contaminants in the liquid source are selectively excluded, preventing permeation across the membrane or entrainment in the carrier gas stream. The result is a chemical vapor saturated with water and

Figure 7. RASIRC SVD chemical cabinet where prehumidification and hydrogen peroxide vaporization take place.

H_2O_2 that is consistent and pure.

The carrier gas is saturated based on the temperature of the liquid, providing accurate delivery of both the water and hydrogen peroxide vapor. A process controller adjusts the humidification level based on the hydrogen peroxide solution concentration and HPV concentration set point.

After basic proof-of-concept testing, the pre-humidifier and the H_2O_2 vaporizer were then engineered into a commercial product known as the Stabilized Vapor Delivery System or SVD™. The SVD delivers stable HPV concentrations from 330-4500 ppm using 30 percent hydrogen peroxide solution at flows of up to 20 slm of carrier gas. (See Figure 6).

The SVD uses Raoult's law to first determine which temperature and vapor pressure of the H_2O_2 solution is needed to reach the desired HPV delivery rate in ppm. Again using Raoult's law, the SVD determines the necessary amount of water needed in the pre-humidification portion to keep the H_2O_2 solution constant as the solution is vaporized. Extensive testing of the SVD is on-going, with units now in field operation running 24 /7.

Next Steps

The present SVD design is able to deliver up to 4500 ppm of HPV from a 30 percent liquid source. However, users are requesting even higher concentrations of H_2O_2 in the vapor phase to improve performance and increase throughput. Higher concentrations are possible by starting with a higher concentrated liquid source, but EHS departments of most semiconductor fabs and hospitals discourage the usage and storage of bulk H_2O_2 above 30 percent concentration. Further development is needed to reach higher levels and is ongoing at RASIRC.

Conclusion

RASIRC has developed a new membrane vaporizer that commercializes stabilized vapor delivery of Hydrogen Peroxide. The RASIRC SVD also avoids problems that plague bubblers and flash vaporizers, including particles, HPV decomposition, and unstable flows. This new technology preloads the carrier gas with water vapor before it enters the hydrogen peroxide vaporizer. In this way the concentration of the aqueous hydrogen peroxide solution is maintained over time.

Hydrogen Peroxide Vapor, HPV, can now be delivered safely and consistently through the use of controlled pre-humidification. HPV can be used in the development of cleaning and surface preparation for next generation semiconductor processing as well as improved surface decontamination for medical applications. Conventional bubblers and vaporizers cannot meet these requirements.

The new technology from RASIRC described above does, proving in the end that Raoult's law cannot really be cheated but it can be the guide to stable delivery of hydrogen peroxide vapor. G&I

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