Manufacturing and Packaging of High Purity Chemicals

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INTRODUCTION

The need to control particulate and trace metallic and ionic impurities within semiconductor process chemicals has become a critical factor as the complexity of integrated circuit process technology continues to increase. Inherent in this trend toward process complexity comes smaller circuit feature sizes, thinner film materials, and larger die sizes. The process chemicals used to fabricate critical integrated circuit devices can easily become a limiting factor relative to device yield and reliability, hence the chemical purity at the wafer surface must continue to be a critical concern for wafer fabrication process engineers (1).

Process chemicals are also used for preparing surfaces other than silicon wafers prior to sputtering or depositing various metallic films. The presence of particles on a surface prior to metal deposition can create film integrity and adhesion problems. The size of a critical particle that can cause a film defect varies on the specific application and on such film properties as thickness, film composition, and surface contour. The presence of organic and ionic impurities on a surface prior to metal deposition can create film adhesion and surface roughness problems. The use of process chemicals can be effectively used for removing particulate, ionic, and organic contaminants as part of a surface preparation process.

Maximum concentration specifications for particles and a wide range of electrically active impurities have been incorporated by most process chemical suppliers in their high purity grades of chemical products. New manufacturing, material selection, and process control techniques incorporated in the past five years have been responsible for major improvements in the quality of process chemicals used in high purity processes. These improvements include reduction of metallic ions and particles in the 1.0 and 0.5 micron range (2).

One notable example of the improvements made in chemical purity is hydrogen peroxide (3). Hydrogen peroxide diluted to 30 percent with ultrapure water is used for several critical surface cleaning and photoresist removal steps (4). The decomposition of hydrogen peroxide into oxygen and water is accelerated by metallic impurities (such as iron and aluminum) introduced by various mixing, handling, and storage steps (5). This decomposition can cause rather severe product functionality and safety problems. To combat this problem, chemical manufacturers have historically added stabilizer compounds such as sodium or potassium stannate. Unfortunately, these stabilizers also introduce very significant quantities of ionic and metallic impurities. New processes have been developed to provide very pure hydrogen peroxide streams that do not require the addition of stabilizers to prevent rapid product decomposition. The use of such high purity hydrogen peroxide products require the employment of very careful storage and handling techniques so as to not introduce metallic impurities which would promote decomposition. Table 1 presents typical purity levels of a new grade of hydrogen peroxide without additional stabilizers as compared to a previous grade with a tin-based stabilizer. With some impurities, there is as much as a fifty-fold decrease in impurity concentration. The improved purity levels are a result of advances made in product distillation methods, material of construction of unit operations, and product distribution.

There are many other examples of chemical products where the purity has been significantly improved by upgrading chemical production and packaging facilities and by generally paying close attention to details. The sections following present the various aspects of synthesizing, purifying, packaging, and delivering high purity process chemicals to the wafer point-of-use.

RAW MATERIALS

In manufacturing high purity chemical products, very careful control of the entire chemical process must be established, from the selection and handling of the raw materials to the packaging of the final product. In considering the process of converting raw materials to a finished chemical product, one must pay close attention to the source of the raw material. For example, the raw material for aqueous HF is fluorspar ore, CaF_2. The particular mining site and method of ore removal will influence the purity of the HF product. This is true with other mineral acids as well. Fluorspar is converted to anhydrous HF by reaction with sulfuric acid by the reaction:

$$CaF_2 + H_2SO_4 \xrightarrow{\quad} CaSO_4 + 2HF\uparrow$$

The anhydrous HF material is stored and transported before being converted to aqueous HF. At the final manufacturing facility, anhydrous HF is distilled to remove certain impurities (e.g., arsenic, antimony, lead), then contacted with ultrapure water. Within this process, the materials used for all reaction vessels, storage tanks and transfer components have an important effect on the purity of the aqueous HF. Additionally, the purity of the ultrapure water is of critical importance.

Other examples of raw material processes include the reaction of ammonia gas with ultrapure water to form ammonium hydroxide, NH_4OH. Some chemical products are made by starting with lower grades of the same chemical and purifying to remove the impurities. For example, high purity hydrochloric acid is made by distillation of industrial grades of HCl. The distillation unit materials of construction as well as the process control procedures greatly influence the characteristics of the purified HCl.

SYSTEM DESIGN CONCEPT

In the detailed design of a chemical manufacturing facility, there are several key elements that significantly influence the purity and consistency of the chemical produced. The chemical manufacturing process can be broken into six major unit operations, as shown in Figure 1. The design, integration, and operation of these unit operations have changed dramatically in recent years to meet the requirements for semiconductor-quality chemical products. It should be noted that many of the criteria for a quality chemical manufacturing plant are also important criteria for a high purity chemical distribution system located within a semiconductor manufacturing facility. The chemical manufacturing process can be broken into several major design concepts. These are:

- System Materials of Construction
- Piping Connections
- Chemical Flow Velocity and Pressure
- Chemical Hydraulic Stability
- Design and Materials for Components such as Pumps, Valves, and Regulators

EFFECTS OF STORAGE AND SHIPPING CONTAINERS

Bulk storage tanks are used extensively by chemical manufacturers to store or stage process chemicals. These systems are dedicated by chemical and are constructed of materials suited to each particular chemical to maintain the purity of the chemical product. Selection of materials of construction, valve types, elastomer gaskets and other components is very important to maintain particulate and ionic stability of stored chemicals. Chemicals that are hygroscopic in nature require noncontaminating purge systems such as filtered nitrogen or clean dry air for bulk storage.

Transportation of chemicals in bulk quantities between the manufacturing and packaging facilities or to the end user's site is sometimes required. This is accomplished through the use of trailer tankers and rail cars varying in capacity from 3,000 to 20,000 gallons. Chemical contamination during the transportation process can represent a common contamination source which can be effectively eliminated by the following steps:

- Manufacture the tanker/rail car of materials suited to the chemical being transported.
- Employ proper tanker cleaning procedures between loads of chemical products.
- Isolate the tanker interior from the external environment.
- Select valves, gaskets, and seals which are made of materials that are compatible with the chemical.
- Carefully select and dedicate the chemical transfer hoses.

Bulk transfer systems (i.e. holding tanks) used to load and unload bulk chemicals are subject to the same factors affecting chemical purity in trailer tankers and rail cars. Personnel training is very important in chemical transfer and transportation operations. Maintaining the cleanliness of equipment and using proper techniques in transferring chemicals minimizes contamination from the outside environment. Additionally, it is important that bulk transfer stations be dedicated by product to ensure there are no chemical cross-contamination effects.

PACKAGING CONTAINERS

For many high purity chemical products, the package represents the rate limiting step relative to particulate and ionic impurity levels. The most common packaging container used today is the one-gallon bottle made of high density polyethylene. Bottles made of borosilicate glass are also used, but the cleanliness is inferior to optimized polyethylene bottles.

Significant improvements have been made in recent years in both the shape of the bottle and the materials of construction. The bottle shape must be optimized to enable cleanability and to prevent isolated areas where particles can accumulate. The polyethylene resin used must be carefully controlled with respect to additives such as mold-release agents and plasticizers which will leach out of the contained to contaminate the product. A well-organized quality control/testing program must be instituted for each batch of resin to be used for molding chemical containers.

Blow molding is the principle technique used in making containers for semiconductor chemicals. Containers ranging in size from one gallon to 55 gallons are commonly fabricated using the blow molding process. In most applications the quality of blow air is not important. However, in high purity chemi-

Impurity	Standard Semiconductor Quality	Megabit Purity Grade
Aluminum	35	5
Boron	5	1
Chromium	5	5
Copper	5	2
Gold	10	<5
Iron	10	8
Nickel	10	5
Potassium	400	8
Sodium	30	6
Tin	200	8
Zinc	10	4
Total	720 ppb	57 ppb

All units in parts per billion.

TABLE 1
Hydrogen Peroxide Purity Levels

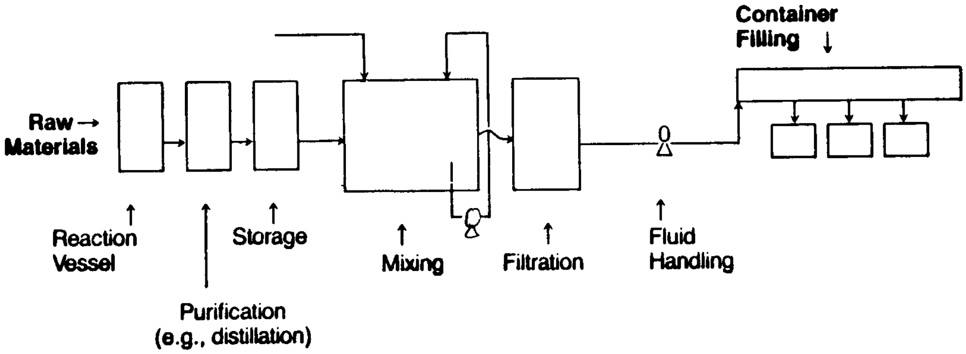

Figure 1
Major Unit Operations of the Chemical Manufacturing Process

cal products, the quality of the blow air can affect the purity of contained chemicals. Tests using sixteen 5-gallon containers were conducted to quantify container particulation as a function of quality of the blow air. Particulate filters can be used to remove shedding characteristics. Containers were made with and without the filter module in the blow air line. In this test the containers were filled with sulfuric acid and particle counts were taken over several months. Figure 2 shows the effect of removing particles greater than 0.02 microns from the blow air stream on particle counts seen in the sulfuric acid product. This figure represents the average number of particles within the sixteen containers over this time period. When no blow air filtration is used, particle levels in the sulfuric acid were initially three times greater than when air filtration was employed. Particle counts increase with time with no blow air filtration, indicating particle shedding from the containers; particle levels remain constant when air containing few particles and no oil residue is used.

There is a current trend to move away from gallon bottles to the use of a bulk-dispense chemical system within wafer fabrication areas (6,7). Larger container sizes are used within chemical distribution systems. The containers can be 55 gallon drums, 10 to 20 liter canisters, 200 gallon mobile “tote” tanks, or other configurations. These containers are made of high density polyethylene, PFA Teflon, and polyethylene or PFA liners with steel or fiberglass overpacks. The same container design and material selection procedures used for gallon bottles must also be implemented for the larger containers. With 55-gallon drums, the quality of the blow molding process has particular significance on the cleanliness of the container. Table 2 shows the particle levels at 0.5 and 1.0 microns of a newly developed drum using carefully controlled blow molding conditions versus a conventional polyethylene drum, using three common process chemicals.

The equipment and procedures used for cleaning packaging containers before filling or between fillings (i.e. for returnable drums) is a critical part of the chemical manufacturing process. Polyethylene and fluoropolymer containers collect particles on the interior surfaces through exposure to the ambient air used in blow molding and through subsequent handling steps (e.g., trimming, leak testing).

Washing and drying steps are commonly employed to remove cardboard and other particles from the interior and exterior bottle surfaces prior to filling. To clean bottles, the bottles are inverted and blown with filtered ionized air to remove gross contamination, then sprayed with filtered ultrapure water. The ultrapure water must be pressurized to reach all interior areas of the bottle with sufficient force to remove any remaining particles. The bottles are then dried with filtered, ionized air. The cleaning environment within the automatic packaging line must be controlled to ensure that the clean bottles are not contaminated prior to filling and capping.

Experience has found that cleaning of larger containers, in particular 55 gallon drums, can be more difficult than gallon bottles for several reasons. First, there is a much greater surface area that the high pressure cleaning solution must reach to remove particles. Secondly, the configuration of drums currently has isolated areas where it is very difficult to spray cleaning solution. Lastly, drum materials made of fluorinated polymers (e.g., PFA Teflon) are very difficult to clean with ultrapure water alone, due to the hydrophobic nature of the interior surfaces. The use of surfactant solutions can be effective here. Optimized drum cleaning techniques must overcome the various difficulties associated with larger chemical containers.

CONTAINER FILLING

The environment in which a clean package is filled with a clean process chemical is critical (2). These environments include open air, clean laminar flow hoods, and cleanrooms. Cleanroom chemical filling facilities can be manual or automated in operation. Automated clean room packaging facilities provide the best control of the packaging environment.

The particle level of the chemical emerging from a packaging system strongly depends on the amount of chemical that has been flowed through the system and particularly through the filtration modules. Filters that are new or that have been dormant release particles for some period from the membrane, support structure, and housing (8). The practice of initiating chemical flow in a stagnant piping system releases some particles from interior surfaces. It is therefore understandable that the particle concentration varies as a function of the batch size. An effective technique to reduce the variability in the particle level in a packaging line is to recirculate the chemical through the filter module to a desired level before packaging.

Chemical filling lines are critical in maintaining low particle levels in chemicals being transferred from filters to packages. The length of the filing lines, materials of construction, and the flow rate of material through the fill nozzles affect the particle level of the product entering the containers. Additionally, the degree to which the container filing line is automated will affect not only the average particle content but also the consistency of the chemical product. Control of the environmental quality around the filling operation also has an affect on chemical particle levels. While a Class 10 or better environment around a filling operation is not as important as other measures, the requirement for a consistent environment that is relatively clean is necessary. The procedure followed by personnel in and around a packaging line also can have a profound effect on product quality.

ULTRAPURE WATER

Ultrapure process water is used extensively in the manufacture of integrated circuits and other critical products (9,10).

Ultrapure water also plays a very key role in the production of high purity chemicals. The water purification process consists of several unit operations including ion exchange, reverse osmosis, and filtration. The water purification process is designed and maintained to strictly control particles, organic molecules and ionic impurities. The distribution of ultrapure water from the purification plant to wafer use point can provide numerous opportunities for further contaminating the water (11). Bacterial contaminants can exist and thrive within an ultrapure water system; the extent of this problem depends on flow conditions within the distribution system, organic nutrient levels within the water, and on other parameters.

A variety of process chemical products include ultrapure water as a key ingredient. For example, hydrogen peroxide that is commonly used in wafer processing is approximately 70 percent water, by volume. Ammonium hydroxide, NH_4OH is approximately 60 percent water; the process of synthesizing sulfuric acid relies heavily on ultrapure water as well. Additionally, ultrapure water is used for container cleaning, filter flushing, laboratory reagent preparation and other uses. Improvements in the quality of ultrapure water are important to improve the ionic and particulate quality of many of the process chemicals. Table 3 shows examples of ultrapure water problems encountered within water purification and distribution systems. An optimized ultrapure water purification system as well as monitoring and operational procedures and hydraulic flow conditions are extremely important parts of the chemical manufacturing process.

CHEMICAL FILTRATION

Filtration is the process by which particles are removed from a chemical product stream at various points within the chemical manufacturing process. Filter products most commonly used for process chemicals are of the membrane type, configured in a pleated arrangement around a 10 to 30 inch filter element (12). The materials that a filter device is made of and the methods of construction heavily influence its performance characteristics relative to particle capture efficiency and ionic extraction levels. All components of the filter device must be chemically compatible with the fluid being filtered; this includes the membrane, drainage layers, support structure, and o-ring seals.

The process used to manufacture a filter device will influence its cleanliness and efficiency. Manufacturing debris generated as the membrane is cut, folded, and welded to the filter structure can contribute to significant levels of particles released from the filter (8). The filter device must be thoroughly flushed with a clean fluid (e.g. ultrapure water or alcohol) to remove particles; this should be done at the filter manufacturing site. These and many other factors must be considered when selecting a filter product to be used in a chemical manufacturing process or distribution system.

An important feature of a filter cartridge is its ability to be integrity tested. An integrity test will detect a damaged membrane, ineffective seals, or other system leaks. Two kinds of integrity tests are commonly used — the bubble-point test and the forward diffusion flow test (2). Filter devices that use fluoropolymer membranes (such as PTFE) with aqueous-based chemicals must be wetted with a fluid that will lower the membrane surface tension before the filter is installed in its housing. High purity isopropyl alcohol is most commonly used as the wetting agent. The specific procedures for wetting the filter and flushing the alcohol from the cartridge (with ultrapure water) are critical; careful personnel training is paramount.

The surface area of the filter media is an important design parameter to consider when sizing a filtration system. Large filter surface area is required to maintain low differential pressure across the filter membrane and hence provide an acceptable chemical flow rate. Series and parallel filtration are often used together to maximize chemical flow rate and to minimize particle loading. Prefiltration using media with larger pore sizes (e.g., 1 to 2 μm) can be effective as well. The viscosity of the chemical to be filtered must be taken into account when designing a filtration module. For example, the flow characteristics of sulfuric acid (viscosity of 25.4 centipoise at 20°C) through a filter membrane are significantly different than those of water (viscosity of 1.0 centipoise).

CHEMICAL PRODUCT ANALYSIS

The determination of the purity and chemical concentration (i.e., assay) of a process chemical is a major part of the chemical manufacturing process. A variety of standard analytical techniques are recommended by the Semiconductor Equipment and Materials Institute (SEMI) (13). All of these techniques involve batch analysis of particulate and dissolved impurities; the sampling techniques are very critical to ensure that the sample to be analyzed is representative of the entire chemical batch. As the requirements for semiconductor process chemicals become more stringent, the analytical techniques and sampling procedures must also continue to be improved.

Trace metallic impurities in process chemicals are commonly measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES) (14). As impurities are excited within an argon plasma, return of the excited atomic species to the ground state produces photons of characteristic energy. These photons can be characterized by a high-resolution spectrophotometer. Sensitivity of the ICP-AES techniques is of the order of 1-10 ppb for most impurities in most process chemicals. At these levels, very careful sample preparation techniques (i.e., concentration via evaporation) are required. Another analytical technique commonly used for analyzing process chemicals is graphite furnace atomic absorbtion spectroscopy (GFAAS). This technique offers excellent detection limits for many elements (to 1 ppb) but it is a very slow, single-element technique and not often suited to a manufacturing

5 GALLON CONTAINERS FILLED WITH SULFURIC ACID

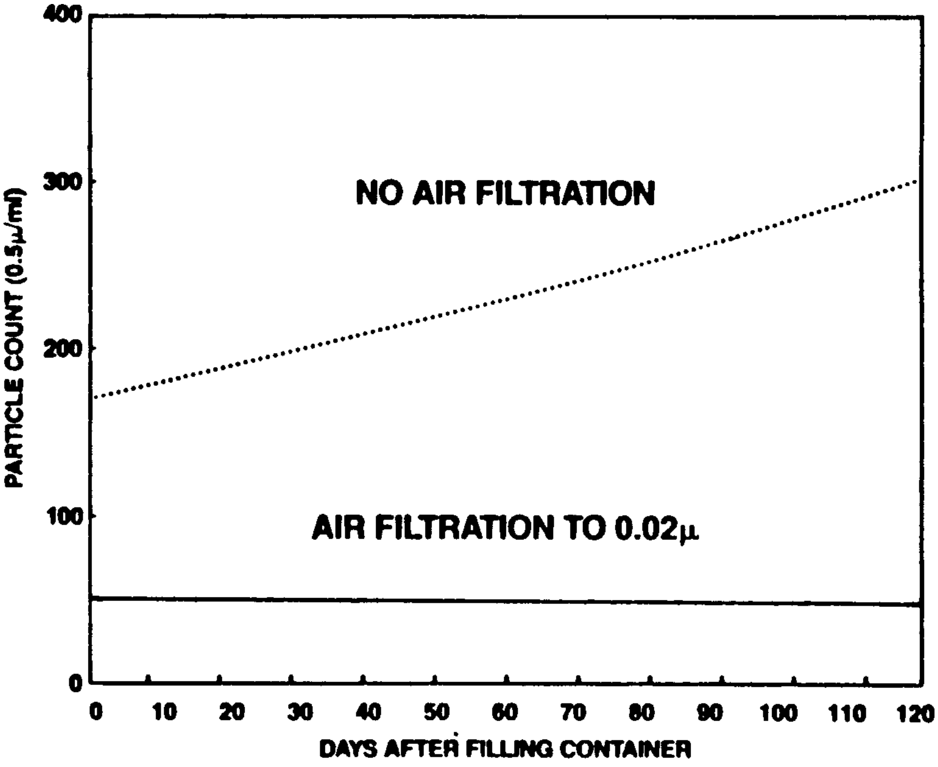

FIGURE 2
PARTICLE LEVELS OF SULFURIC ACID AS A
FUNCTION OF BLOW MOLDING AIR QUALITY

CHEMICAL	CONVENTIONAL DRUMS ≥ 0.5 μm	CONVENTIONAL DRUMS ≥ 1.0 μm	NEW CLEAN DRUMS ≥ 0.5 μm	NEW CLEAN DRUMS ≥ 1.0 μm
Sulfuric Acid	1063	21	49*	1.4*
Hydrogen Peroxide	2042	28	133*	2.8*
10:1 Dilute HF	3500	195	23*	1.5*
Hydrochloric Acid	450	22	31	9

*Simulated transportation operation.

Table 2
COMPARISON OF DRUM PARTICLE LEVELS

As purity requirements near the 1 ppb level and below (per impurity) appear, a new trace analysis tool becomes necessary. Inductively coupled plasma mass spectroscopy (ICP-MS) is a relatively new technique that provides slightly better than parts-per-billion sensitivity with little sample preparation required (3,15). Here samples are introduced into the inductively coupled plasma source and converted into singly-charged positive ions. The ions are extracted using a double-cone sampling apparatus into a quadrapole mass spectrometer where they are separated and detected based on their mass-to-charge ration. The ICP-MS technique has demonstrated very good impurity recovery characteristics for most impurities found within semiconductor process chemicals (3,15).

Particles in process chemicals are typically measured using particle counting instruments that utilize light scattering principles (16). For process chemicals, these instruments are most commonly operated in a batch-sampling mode. Current instruments have detection limits of 0.3 microns. With light scattering techniques, particles having a different index of refraction than the background fluid scatter light; this light is collected, focused, and detected via a photo diode or photomultiplier tube. The number of particles in a sample volume and their size as compared to calibration spheres of known size are recorded (17). Bubbles formed during chemical sampling will be detected as particles, and hence must be minimized during sampling. Procedures have been developed for readily detecting the presence of bubbles so that this faulty particle data can be discarded. New chemical pressurization sampling techniques have been developed to eliminate the presence of bubbles during sampling, thereby improving the integrity of the particle data (18).

Recent improvements have been made in the ability to reliably count particles significantly smaller than 0.5 μm with detection efficiency better than 50 percent. Batch sampling instruments with sensitivity of 0.2 microns have recently been introduced (19). Microscopic particle counting techniques providing the ability to count and characterize particles as small as 0.2 μm have been utilized in Japan for about five years. This manual technique is very time-intensive, but can enable particle identification with and without the use of a Secondary Electron Microscope (20).

In situ particle detection instruments are available for measuring particles within chemical process streams in a continuous fashion. Currently available instruments have a detection sensitivity of 0.2 μm but detect particles in only a small area of the chemical stream. Such continuous particle counting instruments can be used for characterizing chemical packaging and distribution systems (21).

CONCLUSION

Process chemicals used for manufacturing semiconductor devices represent a very critical process parameter; their use within a wafer fabrication facility must be carefully engineered. The chemical manufacturing process from the mining of the raw materials to the packaging of the ultrapure chemical product has certainly become more robust within the past five years due to much attention to details (11). The distribution and use of the chemicals within the wafer fabrication facility must be engineered and tested with equal care. The analysis of process chemicals often approaches the limits of the analytical instruments, and hence must be integrated into the entire chemical process. Specific improvements in analytical instruments and procedures are certainly needed for the next generation of process chemicals. In order for semiconductor process chemicals to meet the strict purity and functionality requirements for submicron device processing, the entire chemical manufacturing, packaging, and distribution process must be optimized as an integrated system.

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CONTAMINANT	SOURCE OF CONTAMINANT
PARTICLES	-MECHANICAL GENERATION FROM VALVES -SHEDDING FROM FILTERS -FILTER BREAKDOWN -PUMP IMPELLERS -SPALLING FROM PVC PIPE -BACTERIA
BACTERIA	-LOW VELOCITY IN PIPES AND TUBING -STAGNANT WATER AT NOZZLES
T.O.C.	-LEACHING FROM PIPES, FILTERS, ETC. -IMPROPER ION EXCHANGE MAINTENANCE -HIGH BACTERIA LEVELS
SILICA	-EXHAUSTION OF MIXED BED RESINS
DISSOLVED METALS	-EXHAUSTION OF RESINS -DEGRADATION OF STAINLESS STEEL COMPONENTS

Table 3
Examples of Ultrapure Water Problems at the Point-of-Use