



Prevention of Microbubbles During Filtration and Particle Counting of High Purity Chemicals in the Semiconductor Industry

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Abstract

High purity chemicals used in the semiconductor industry must contain minimal particulate and microbubble contamination. The presence of microbubbles in semiconductor chemicals can adversely affect the performance of a filter and other components in a chemical delivery system. Since the manufacturing area requires consistent delivery of chemicals, any restriction in the flow of chemicals has an adverse effect on the manufacturing process. The formation of microbubbles in a filter may lead to membrane blockage or restricted flow of chemicals through a filter.

This paper addresses the use of filters designed for different applications in the semiconductor industry. The proper design of a filter will diminish the formation of microbubbles that can interfere with many steps in IC fabrication. This paper also discusses particle counting procedures and the prevention of microbubbles in particle counting equipment. Prevention of these bubbles during particle counting will allow the end-user to get an accurate evaluation of the particles present in the processing fluid.

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Introduction

Proper selection of a filter for each application⁽¹⁾ will minimize the formation of microbubbles. The use of filters with hydrophilic or hydrophobic membranes may be warranted solely by compatibility factors. However, certain filters have been designed for applications to maximize performance and minimize problems.

The presence of microbubbles during particle counting may lead to incorrect determination of contamination present in chemicals prior to use in the manufacturing area. The presence of microbubbles will appear as particles in particle counters because of the tendency of bubbles to scatter light. The proper use of particle counting equipment will minimize the formation of microbubbles and eliminate “phantom particles” in the chemical. This will give a truer picture of the contamination levels in the chemical and thus meet the specifications of the customer.

Filtration of Aggressive Chemicals Involving Hydrophobic Membranes

The aggressiveness of some chemicals in the semiconductor industry requires components to be made from all-fluoropolymer materials to offer the compatibility required for long term exposure to the chemical. When the component is a filter, the membrane is usually made of PTFE (Polytetrafluoroethylene). PTFE is hydrophobic and spontaneously allows flow through its pores with fluids that have surface tensions of 28 dynes/cm or less. Several aggressive chemicals in the semiconductor industry have higher surface tensions (see Table 1), which makes it necessary to pre-wet the PTFE membrane with a low surface tension fluid [e.g. isopropanol (IPA) with surface tension of 21.7 dynes/cm] to facilitate flow of the higher surface tension chemical. Filter manufacturers supply their end-users with step by step procedures for pre-wetting and flushing hydrophobic filters⁽²⁾ prior to use in these high surface tension chemicals. Recent filter product innovations have led to the availability of prewet hydrophobic filters^(3,4) to eliminate the need for storage and usage of the prewetting solvents.

TABLE 1

The surface tension at 20°C of common chemicals used in the semiconductor industry

Chemical Name	Surface Tension (dynes/cm)
Water	73
Buffered Oxide Etch (BOE)	80-90
Sulfuric Acid (98%)	75
Nitric Acid (35%)	69
Hydrochloric Acid (37%)	65

Once the filter is prewet and the low surface tension fluid is flushed from the filter, the high surface tension fluid is slowly introduced into the filter housing. The filter housing must be vented to allow the air in the housing to be removed without passing through the filter pores and causing the filter membrane to be dewet. The venting must continue during use to prevent air buildup in the housing and possible dewetting of the filter membrane.

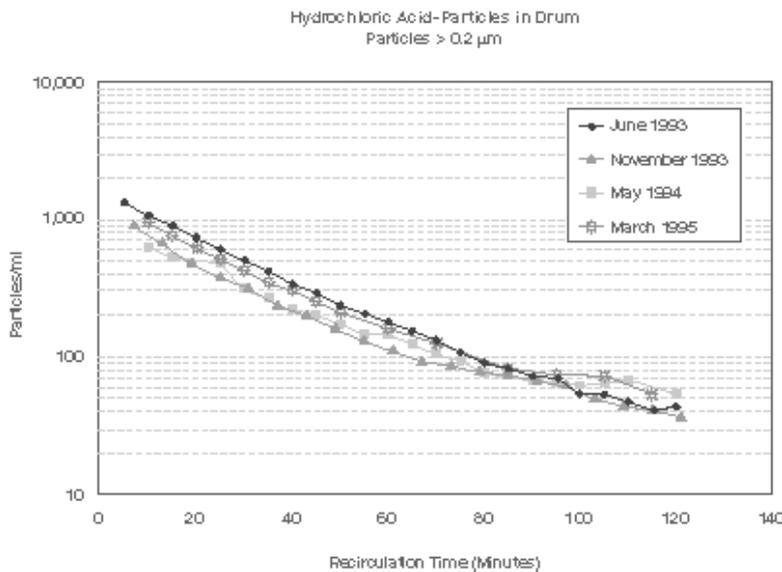
The long term use of the filter now depends not only on the proper venting of the housing but also on the filter design to prevent microbubbles from forming during the filtration process. Pall Corporation designs its filters with minimum differential pressure through the filter cartridge. This minimum differential pressure minimizes bubble formation from occurring in the actual pores of the membrane. The chemicals being filtered may contain a substantial amount of dissolved gases in them when they pass through the filters. If the chemical experiences a large pressure drop across the membrane, the cavitation will cause the formation of bubbles within the membrane. This bubble formation will partially or completely block off pores in the membrane eventually dewetting the pores. Once the pores dewet, flow is prevented because the high surface tension fluid will no longer wet the pores. If this is allowed to continue the filter will experience even higher pressure drops as portions of the membrane are no longer filtering the fluid.

Proper venting, good prewetting and proper filter design was demonstrated in a long term study⁽⁵⁾ using 0.1 and 0.05 μm Pall Emflon® PF Kleen-Change® filter assemblies on concentrated hydrochloric acid (HCl) in a chemical dispense cabinet. This study took place over a 22 month period at the facilities of a major semiconductor manufacturer.

The 0.1 μm assembly was used in a recirculation mode reducing particulates in 55 gallon drums prior to delivery to the FAB. The particle reduction performance ($0.2 \mu\text{m}$) of the 0.1 μm filter assembly over the 22 month period is shown in Figure 1.

FIGURE 1

The performance of a 0.1 μm Pall Emflon PF Kleen-Change Filter Assembly over a 22 month study



The 0.05 μm assembly was used at point-of-use (POU) before entering the FAB. Particle counting results on both assemblies showed consistent results over a 22 month period with no loss in particle removal efficiency or loss in fluid flow. These results were consistent with usage of the entire filter with no apparent loss due to microbubble formation. The performance of 0.05 μm Pall Emflon PF Kleen-Change filter assemblies in a variety of chemicals are shown in Table 2.

TABLE 2

The table summarizes the particle counting ($0.065 \mu\text{m}$) on the influent and effluent of the 0.05 μm Emflon PF Kleen-Change filter assemblies.

Chemical	Influent Particles (#/ml)	Effluent Particles (#/ml)
HCl (July 1993)	~ 150	11
HCl (May 1994)	~ 300	2.3
HCl (Mar. 1995)	~ 600	6.8
HF	~18,000	8
H2O2 (Cabinet #1)	~11,000	20
H2O2 (Cabinet #2)	~19,000	30

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Filtration of Buffered Oxide Etch in Recirculating Etch Baths

The filtration of buffered oxide etch (BOE) is generally performed in a bath specifically designed for rapid turnover of the etch solution via pumping through a filter cartridge. The bath, pump and filter housing are parts of a self contained unit. The filter must be compatible with the BOE and give rapid turnover rates of the bath using a low horsepower motor. The BOE may have a very high surface tension (see Table 1) which can be problematic in terms of dewetting a hydrophobic surface. Therefore, filters with hydrophilic surfaces are recommended for use in BOE. The Pall Ulti-Etch® filter⁽⁶⁾ is designed with a modified (hydrophilized) PVDF (polyvinylidene difluoride) membrane that accommodates the high surface tension of the BOE with a filter design that minimizes pressure drop for rapid bath turnover and thus exceptional particle reduction in the BOE bath⁽⁷⁾. The low pressure drop minimizes microbubble formation due to cavitation which may inhibit the turnover rate and add bubbles to the wafer surface.

Filtration of Photoresist at the Point-Of-Use Dispense

The generation of bubbles in photoresist can lead to defects on the wafer surface which are as damaging as particulates. The use of POU dispense filters for photoresist greatly reduces the chances of particle defects on the wafer surface. The dispense filter must be designed with a large surface area to decrease the pressure drop across the filter which can be realized with viscous photoresist products. The lower pressure drop minimizes the formation of bubbles during dispense. Proper venting of the filter housing will also allow the release of trapped bubbles in the photoresist and housing during priming. The Pall Falcon® Photoresist filter⁽⁸⁾ specifically utilizes Pall's patented Ultipleat® filter laid-over-pleat design to maximize filtration area and allow POU filtration down to 0.05 µm.

Prevention of Microbubbles During Particle Counting

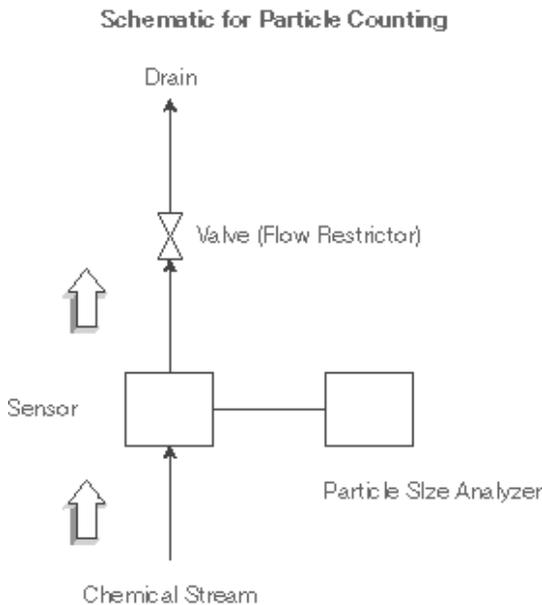
One of the major concerns in particle counting is being able to get an accurate picture of the particle contamination in the process chemical. The sensor and tubing needs to be thoroughly clean and flushed prior to attachment to the chemical stream. Since most particle counters are based on light scattering techniques to count and size particles, it is imperative that the system be free of bubbles. These particle counting techniques cannot differentiate between particles and bubbles in the liquid stream and are susceptible to "false" counts when a bubble passes through the sensor.⁽⁹⁾

Dissolved gas in the liquid will tend to come out of solution when there is a pressure drop across the sensor or the tubing leading to the sensor. This will result in the formation of bubbles that will lead to erroneous particle counts. The formation of bubbles in the sensor can be minimized by applying backpressure to the sensor (See Figure 2). This backpressure is usually on the order of 15 psi. This is best accomplished by using a flow meter or a flow restricting valve downstream of the sensor. The production of microbubbles on the membrane of a filter can be prevented by using filters that are properly designed for the application. In the case of filtration of aggressive fluids, a filter with a fluoropolymer membrane may be required for chemical resistance. These filters generally have hydrophobic membranes that need proper prewetting before they are introduced into high surface tension fluids. These filters must also be designed to have low differential pressure when the fluid is passing through the pores. This low differential pressure prevents the dissolved gases in the fluid to cavitate and form bubbles within the pore structure.

Formation of these microbubbles in the filter membrane that is hydrophobic can dewet the pore and cause fluid passage to be hindered.

FIGURE 2

Particle counting arrangement showing flow restricting valve after the sensor to prevent bubble formation in the sensor.



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Conclusions

The production of microbubbles on the membrane of a filter can be prevented by using filters that are properly designed for the application. In the case of filtration of aggressive fluids, a filter with a fluoropolymer membrane may be required for chemical resistance. These filters generally have hydrophobic membranes that need proper prewetting before they are introduced into high surface tension fluids. These filters must also be designed to have low differential pressure when the fluid is passing through the pores. This low differential pressure prevents the dissolved gases in the fluid to cavitate and form bubbles within the pore structure. Formation of these microbubbles in the filter membrane that is hydrophobic can dewet the pore and cause fluid passage to be hindered.

As previously discussed, proper prewetting of the membrane prior to the introduction of the chemical will reduce the chances of bubble formation during filtration. An especially effective method of reducing the differential pressure across a membrane is by the introduction of more membrane area of a filter. This, in fact, is accomplished by the patented Pall Ultipleat filter design.

The hydrophilic surface treatment of membrane, such as the PVDF membrane of the Pall Ulti-Etch filter, allows for use in a high surface tension fluid such as buffered oxide etch (BOE). The filter is designed for low differential pressure for rapid bath turnover and thus rapid removal of particulates in the bath without bubble formation within the pores.

The prevention of bubbles during particle counting is important to ascertain the particle cleanliness of the fluids used in IC fabrication. The fluid is susceptible to bubble formation when passing through the sensor on the particle counter. In performing particle counting on fluids, backpressure applied downstream of the sensor is important to prevent the cavitation of the fluid in the sensor. This will prevent the particle counter from seeing the bubbles and registering "false counts" during the particle counting process. This will allow an accurate determination of the particulate level in the processing fluid.

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