Removal of 12 nm particles from UPW by a combination of Ultrafiltration and Microfiltration

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Introduction: The critical feature size of state-of-the-art semiconductor devices is on the order of 30 nm and expected to decrease to < 20 nm by 2015 [1]. Particles on the order of half this feature size in the ultrapure water (UPW) used during device manufacturing can reduce manufacturing yield and finished device reliability. Microfiltration (MF) and ultrafiltration (UF) devices with particle removal ratings below 50 nm are often utilized to control particle concentrations in the process water used in device manufacturing.

The ability of these filters to remove particles is typically measured using Optical Particle Counters (OPCs), which have reached a practical measurement limit of 40 nm with a counting efficiency of only a few percent at this size. This size detection is considerably above the critical size for current and future semiconductor device technologies. Therefore, this metrology is unable to confirm the presence of damaging particles and leaves the semiconductor manufacturers unaware of whether the filtration strategy used in the UPW systems is removing these small particles.

In addition, the small size of the particles to be controlled in UPW is approaching the capability of the particle removal technology used and it becomes increasingly difficult to characterize the filtration performance for the critical particle size of interest. Current methods of filter performance characterization using 50-200 nm PSL (polystyrene latex) spheres with OPCs and extrapolating performance to critical sizes below 20 nm is inadequate for guaranteeing filter performance at the extrapolated size.

This paper describes a new method that allows the measurement of filter retention efficiency for particles as small as 5 nm in diameter. A particle detection technique has been developed where the UPW is aerosolized and the particle size and concentrations are measured using conventional aerosol particle detection instrumentation. This detection technique was employed to evaluate the filtration performance of UF and MF devices like those used in many UPW systems today. In addition to characterizing the individual cartridges, the combination of UF and MF was tested to optimize particle retention performance.

Particle Counting Technique: In the particle counting instrument used in this study, called the Liquid Nanoparticle Sizer or LNS, a colloidal suspension undergoing analysis is injected into a nebulizer, which converts the suspension into ultrafine droplets dispersed in essentially particle-free air [2, 3]. The water in the droplets is then evaporated leaving the particles suspended in air, and the size and concentration of the aerosol particles are measured using conventional aerosol measurement techniques.

The key to making this measurement approach applicable for measurement of sub-50-nm particles is the nebulizer. The droplets produced by the nebulizer must be sufficiently small and uniformly sized so that particles formed from dissolved materials in the droplets do not form detectable “residue” particles when the liquid is evaporated. In addition, the particle suspension must be sufficiently dilute so that no more than one particle is present in each droplet. If more than one particle is present, the particles will be counted as one particle with a larger diameter. This results in a decrease in the measured total particle concentration and a shift in the particle size distribution (PSD) to larger particle sizes. A similar error occurs with optical particle counters when the coincidence limit of the sensor is exceeded. The droplets produced by the nebulizer in the LNS have a median diameter of approximately 300 nm and a geometric standard deviation of approximately 1.4.

Three different methods have been used to measure the size and concentration of the particles exiting the nebulizer/drier. All rely on convention aerosol measurement techniques. For example, total concentrations greater than a certain size can be measured using a condensation particle counter (CPC). If detailed information concerning the distribution of particle sizes is desired, a scanning mobility particle sizer (SMPS) is used. Also, particles of a single size can be measured using the SMPS.

CPCs are able to count very small particles by condensing a liquid onto the particles and thereby growing the particles (now droplets) to a size easily detected using relatively simple optics [4-6]. Condensation is achieved by subjecting the aerosol to conditions in which the aerosol is supersaturated with the

liquid vapor. Once condensation starts, the particles (droplets) increase in size as the liquid condenses. All particles larger than a certain size, regardless of their initial size, quickly form droplets that grow to > 2 µm in diameter. At this large size, the particles are easily counted by passing them through a laser beam where they scatter light onto a photodetector. By controlling the degree of supersaturation in the instrument, the minimum particle size on which condensation takes place can be controlled. The CPCs used in this study, described in Table 1, had detection efficiencies down to 5 nm.

The SMPS consists of an aerosol neutralizer, differential mobility analyzer (DMA), whose main component is an electrostatic classifier [7, 8], and a CPC. In the SMPS, the aerosol first passes through the aerosol neutralizer, which exposes the particles to a high concentration of bipolar ions generated by a low energy soft X-ray source. Through this bipolar diffusion charging process, any excess charges on the particles are neutralized resulting in a steady-state charge distribution – the Boltzmann equilibrium distribution [9]. The aerosol then passes through the electrostatic classifier in the DMA, which separates the particles according to their electrical mobility. Finally, the CPC counts the monodispersed particles exiting the DMA. The SMPS can be operated such that it measures a range of particle sizes or a single monodispersed particle size. The SMPS used in this study included a Model 3080 DMA with a Model 3081 classifier.

The LNS technique is capable of very accurate size measurements with 64 channels of size resolution per decade of size. The technique has been used to measure commercially available particles with narrow size distributions and NIST traceable sizes to verify the sizing accuracy of the technique. Both polystyrene latex (PSL) spheres and gold colloidal nanoparticles have been measured. Previous measurements of PSL spheres indicated diameters and diameter coefficients of variation (CVs) measured by the LNS that were very similar to those claimed by the manufacturer of the spheres for several PSL sizes [10].

Measurement of colloidal gold particles by the LNS is shown in Table 2 [11]. Sizing of three gold colloids (BBI Research, Madison, WI) measured individually is shown. The Table implies that the particles have narrow size distributions and that the LNS measurements correlate well with the manufacturer's sizing claims made using TEM.

Filtration Efficiency Test Procedure: Testing was performed to measure the retention efficiency of an ultrafiltration (UF) module commonly used in semiconductor high purity water systems and a high retention microfiltration (MF) cartridge. The UF module contained 150 ft^2 of a 10,000 molecular weight cutoff hollow fiber membrane and was rated to deliver approximately 50 liters/minute permeate at a differential pressure of 15 psi. The 30" MF cartridge contained 25.5 ft^2 of a high retention microfiltration media and was rated to deliver a flow rate of approximately 50 liters/minute at a differential pressure of 2 psi. Multiple filters of each type were included in the test sequence.

The filtration testing setup is shown schematically in Figure 1. The system allowed testing of each filter individually or in series. The series configuration with the MF cartridge following the UF module is shown. The filters were tested by pumping UPW through the filters at a flow rate of 32 liters/minute and injecting particles into the water upstream of the test filter. The retentate flow rate for the UF module was 1.6 liters/minute so that the recovery ratio was 95%. In order to maintain similar test conditions, the same flow rate of 1.6 liters/minute was bled to drain from the upstream side when MF cartridges were tested. In both cases, the 1.6 liters/minute was replaced by UPW. In all test cases, the final permeate or filtrate was returned to the inlet of the pump. This caused the challenge particle

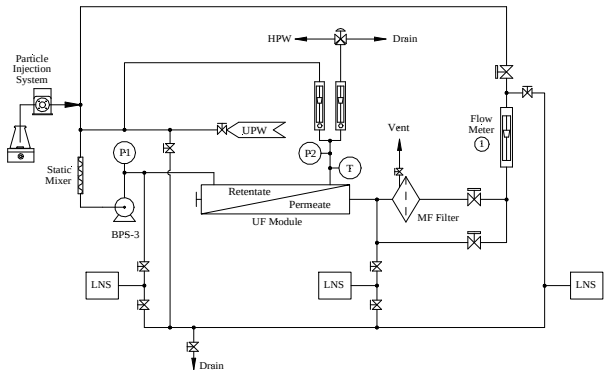
Table 1: Condensation Particle Counters used in this study

Manufacturer	Model Number	Inspection Flow rate, cm^3/min	Condensation Liquid	Minimum Detection Size, nm
TSI, Inc.	3772	1000	1-butanol	10
TSI, Inc.	3775	300	1-butanol	5
TSI, Inc.	3787	600	Water	5

Table 2. Gold nanoparticle size distributions claimed by the manufacturer and measured by the LNS technique

Nominal Size (nm)	Claimed size		Measured size	
	Mean (nm)	CV (%)	Mean (nm)	CV (%)
10	9.3	< 15	8.4	13
20	20.3	< 8	20.8	7.4
30	30.3	< 8	30.5	7.3

Figure 1: Test System Schematic

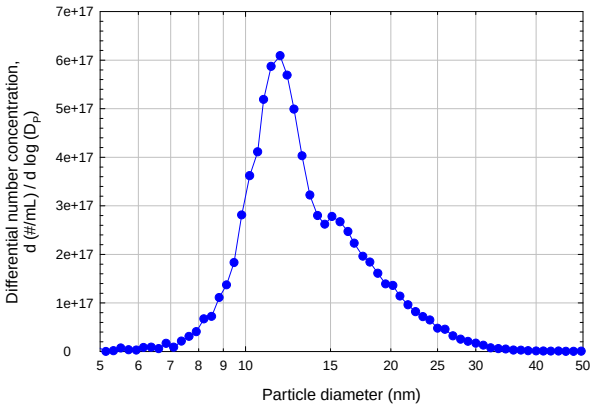


concentration to slowly increase during the course of a challenge test if there was significant passage through the test filter. Hence, it was necessary to measure the challenge concentration throughout the test. Cartridge retention and loading were calculated based on the measured challenge concentration.

The system was operated at 25-30°C with a pump outlet pressure of 35-50 psig. Valving and instrumentation were included in the system to maintain constant operating conditions throughout the test. A static mixer was used to ensure that the particles were uniformly mixed into the UPW during the challenges. The particle concentration could be measured at various locations throughout the system using multiple sample ports for the LNS as indicated in Figure 1.

All particle challenges were performed using Ludox SM30 silica particles (Grace Davison, Ltd.), which had been diafiltered prior to use to remove dissolved contaminants. The size distribution of the diafiltered particles as measured using the LNS technique is shown in Figure 2. The particles have a narrow size distribution with a peak near 12 nm. Thus, the particles will be referred to as 12 nm particles in the remainder of this paper.

Figure 2: Particle size distribution of Ludox SM30 Particles



Two types of challenge tests were performed – continuous and burst. In the continuous tests the particle concentration at the filter inlet was maintained at a constant concentration for an extended time (hours to days). In the burst tests the filters were challenged with short bursts (several minutes) of high particle concentrations. Challenge particle concentrations during the continuous tests ranged from 1E8/mL to 2E10/mL (equivalent to 0.2 – 35 ppb of particles). Particle burst concentrations ranged from 0.5 to 5.0 ppb.

Ultrafiltration particle retention: The retention of the 12nm particles by the UF modules with a constant challenge concentration is shown in Figure 3. Retention as a function of loading for 3 tests performed with one module and a fourth test performed with a second module is shown. Loading is depicted in terms of monolayer coverage calculated using the cross-sectional area of the particles. It was assumed that the particles removed by the module remained on the filter surface rather than exiting the module in the retentate stream, which represents a worst case scenario. Test 1 was run with two different inlet concentrations, 2E9/mL and 4E9/mL, while tests 2 and 3 were run with an inlet concentration of 2E10/mL. Test 4 had an inlet concentration of 2E9/mL.

Figure 3: UF module retention of 12 nm particles

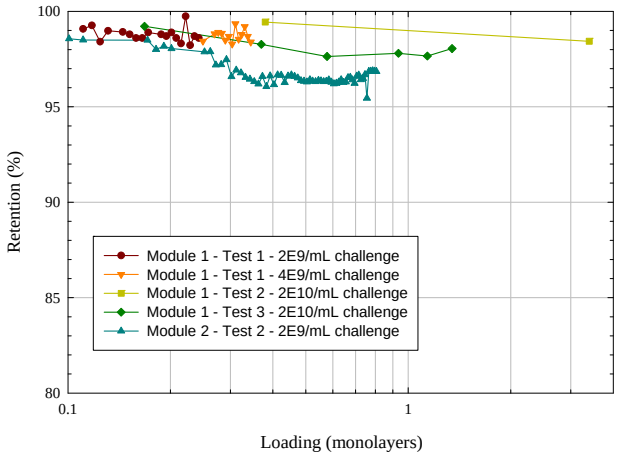
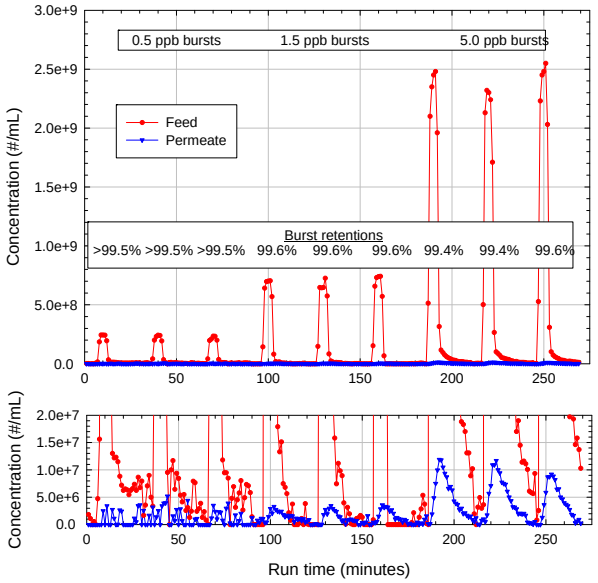


Figure 3 indicates that the modules retained 96-99.5% of the particles. Similar retentions were seen in each of the tests, and retention was not significantly affected by inlet particle concentration and decreased slightly with or was not affected by particle loading.

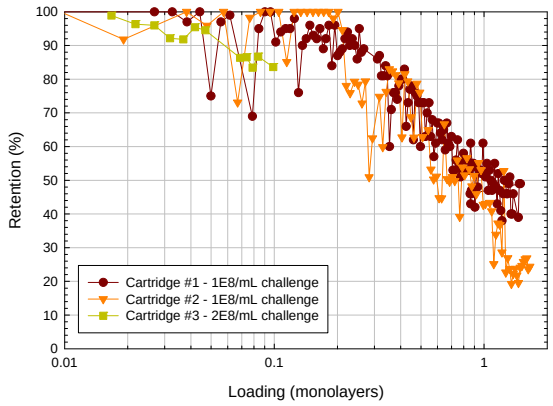
The retention of the 12 nm particles by a new UF module subjected to particle bursts is shown in Figure 4. Nine bursts were performed with concentrations ranging from 0.5 ppb to 5.0 ppb. The UF cartridge retained >99%, but not all, of the particles in each burst.

Figure 4: UF retention of 12 nm particle bursts



Microfiltration particle retention: The retention of the 12 nm particles by the MF cartridges with a constant challenge concentration is presented in Figure 5. Retention as a function of loading for 3 tests performed with three different cartridges is shown. Two tests were run with an inlet concentration of 1E8/mL; one with an inlet concentration of 2E8/mL.

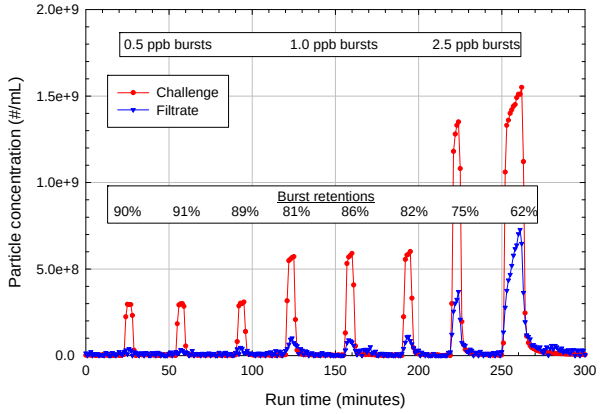
Figure 5: MF cartridge retention of 12 nm particles



The three cartridges demonstrated similar retention capabilities. The filters initially retained > 90% of the particles for all tests. The retention efficiency then decreased throughout the test as the filters were loaded with particles, as typically seen for microfiltration of small particles [12-14]. In all cases the filters retained > 80% of the particles until the coverage exceeded 0.1-0.2 monolayers, which is a loading in excess of typical UPW applications (also see the discussion section of this paper).

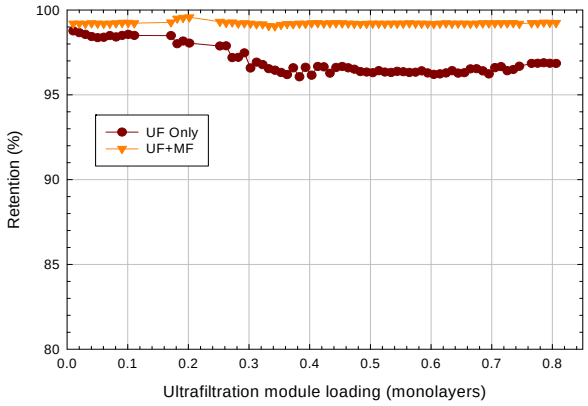
The retention of the 12nm particles by a new MF cartridge subjected to particle bursts is shown in Figure 6. Particle concentrations upstream and downstream of the filter during eight bursts with concentrations ranging from 0.5 ppb to 2.5 ppb are shown. All were 5 minutes in duration with the exception of the last burst which was 12.5 minutes long. The cartridge initially retained approximately 90% of the particles in each burst. Retention decreased as the filter was loaded and the concentration increased.

Figure 6: MF retention of 12 nm particle bursts



Ultrafiltration/Microfiltration particle retention: An example of the retention of 12nm particles by the series combination of a UF module followed by an MF cartridge with a constant challenge concentration is shown in Figure 7. The retention of the UF module was initially about 99% and decreased to less than 97% by the end of the test. Overall retention by the combination of UF and MF remained above 99% throughout the test.

Figure 7: Retention of 12nm particles by combined UF and MF



Two additional tests were performed with a combination of UF and MF and constant challenge concentration. Overall, 2 UF cartridges and 3 MF cartridges were used in these evaluations. Table 3 summarizes the retention efficiencies measured at the point in the tests when the UF loading was 0.5 monolayers. UF retention varied from 96.5% to 99.3% while the overall retention efficiency downstream of the MF was >99% in all cases.

Table 3: Cartridge retentions measured during the combined cartridge constant concentration challenge tests

Test	Cartridge		Challenge concentration, #/mL	Retention, %	
	UF	MF		UF Only	UF+MF
1	A	A	2.0E9	96.5%	99.2%
2	B	B	1.0E10	98.1%	99.4%
3	B	C	2.0E10	99.3%	99.6%

The retention of particle bursts by the UF/MF combination was also measured. Five 5-minute 5-ppb bursts were performed. The UF retention of the bursts varied from 99.2 to 99.6%. The MF cartridge retained some more (or most) of the particles passing through the UF cartridge. However, the total retention efficiency could not be quantified as the filtrate concentrations were so low that they were indistinguishable from the system particle background concentration.

Discussion: The UF modules tested in this study, a type commonly used in semiconductor UPW systems, retained 12 nm particles very well with retention efficiencies > 96% in all tests. The retention remained high even when the cartridges had been challenged with numerous particles; equivalent to more than 0.5 monolayers of coverage. However, some particles consistently passed through the UF module in all tests and were detected downstream. This low level particle passage has also been observed in previous studies [15-17].

The tested MF cartridges initially retained > 90% of the 12 nm particles. The retention efficiency was reproducible and remained high until the cartridges were loaded with 0.1-0.2 monolayers of particles, and then decreased with additional loading.

Combining the UF and MF filters with the MF cartridge downstream of the UF module was expected to provide better retention than either cartridge individually. This configuration was chosen so that the UF module, whose retention is largely independent of particle loading, would achieve the bulk of the particle removal, and the MF cartridge would act as a polishing filter to remove the particles passing through the UF module. The combination resulted in overall retention efficiencies > 99% up to loadings > 0.5 monolayers.

Filter loading in UPW filtration applications is expected to be a very slow process. Unfortunately, no metrology exists today to detect particles of the size utilized in this study in an actual UPW system. When using an extrapolation from measurable particle sizes above 50nm, it may be estimated that UPW contains up to 1.0E4 particles/mL of 12 nm size. When the filters tested in this study are operated in series at a flow rate of 50 Lit/min, then the loading of the UF module would be about 0.02 monolayers/year. If the UF module retains on average 98% of the particles, then the loading on the MF cartridge would be less than 0.003 monolayers/year. Hence, little change in retention due to loading effects would be expected for multiple years. Even if the MF cartridge were to be operated independently, its retention could be expected to remain high for more than a year.

Summary and conclusions: A new particle detection technique has been described that allows measurement of filter retention efficiency for particle sizes as small as 5 nm. This technique has been applied to measure particle retention by a commonly employed ultrafiltration module and a high retention microfiltration cartridge. The testing was performed with silica particles with an average diameter of 12 nm.

The testing demonstrated that the ultrafiltration module retains more than 96% of these small particles. In addition, the high retention microfiltration cartridge retained more than 90% of the 12 nm particles up to a loading well beyond what is commonly expected in UPW applications. While the ultrafiltration module showed high retention, some of the 12 nm particles consistently passed through the module and would pose a risk to semiconductor manufacturing. In order to minimize this risk, the series combination of the ultrafiltration module followed by the microfiltration cartridge was also tested. This combination resulted in optimal particle removal with removal efficiencies above 99% in all tests.

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