

The Use of Focused Aerosol Deposition in the Collection and Analysis of Nanoparticles from Ultrapure Water Systems Used in Semiconductor and Pharmaceutical Industry

Gary Van Schooneveld^{*}, Pat Keady^{**}, Derek Oberreit^{***}

^{*}CT Associates, Inc., Eden Prairie, MN 55344

^{**}Aerosol Devices, Inc., Fort Collins, CO 80524

^{***}Kanomax FMT, White Bear Lake, MN 55110

ABSTRACT

The reduction of particles in ultrapure water (UPW) systems is driven primarily by the semiconductor industry. Particles that can produce defects in chip manufacturing and potentially reduce yield, are now identified to be 10 nm and smaller. Isolating and collecting particles in this size range using the classical filtration technique of sieving is limited, time consuming and in many cases, ineffective. Additionally, locating 10 nm particles on a 25 mm filter with a total surface area of more than 500 mm² (500,000,000 nm²) is highly labor intensive.

Focused Aerosol Deposition (FAD) is a technique that combines extraction of nanoparticles from UPW via aerosolization with focused droplet deposition on an SEM-ready stub. This provides an extremely localized collection of particles as small as 5 nm. Improvements in aerosol focusing, evaporation management and direct deposition on scanning electron microscope ready media has resulted in a focal point as small as 0.04 mm² with repeatable positioning. By maintaining a tight collection area, the time required to collect sufficient particles for analysis is reduced 50 to 90% compared to traditional filtration methods and provides improved sizing analysis via Scanning Electron Microscopy (SEM) and elemental analysis using Energy Dispersive X-ray Spectroscopy (EDS).

This paper will review the enabling technologies associated with FAD, provide SEM/EDS analysis of collected UPW samples, and discuss the potential of the technology for particle characterization and identification, and risk mitigation in UPW systems.

Keywords: nebulization, ultrapure water, nanoparticle, bacteria, scanning electron microscopy

1 ENABLING TECHNOLOGIES

Extracting nanoparticles from a liquid and depositing them onto an analysis-ready substrate requires two enabling technologies. The first enabling technology is the conversion of a liquid-borne particle into a gas-borne particle, or aerosol, without particle agglomeration and minimal formation or growth of particles due to dissolved

residue in the liquid. The second is the deposition of the aerosol nanoparticles in a tight pattern with a precise and repeatable location onto an appropriate collection surface. Each technology will be discussed in detail in the following sections.

1.1 Aerosolization of Liquid Samples

Analysis of nanoparticles, within a colloid, using a deposition-evaporation-microscopy method is often inhibited by the presence of dissolved, non-volatile residue (DNVR) within the sample. The presence of DNVR causes two major measurement artifacts: surface precipitation and new particle formation. Surface precipitation is caused by the supersaturation of a solute in the presence of a thermodynamically favorable deposition surface. For colloids where the particle concentration is much higher than the concentration of dissolved residue, this effect is negligible. For dilute colloids (e.g. ultrapure water) where the particle concentration is significantly lower, the particles within the colloid act as precipitation sites for the residue. This deposition through precipitation leads to ambiguity in composition, shape, and size of native particles (Figure 1). New particle artifacts are caused by the homogeneous precipitation of a super-saturated solute where there is no thermodynamically favorable deposition surface present (e.g. in a particle-free droplet). Limiting this contribution by non-volatile residue in particle extraction improves the quality of the sample and subsequent analysis.

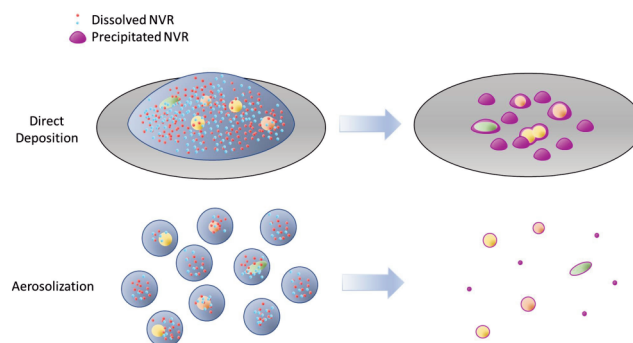


Figure 1. The effect of direct deposition versus nebulization on particle formation and collection.

A common method for reducing the contribution of non-volatile residue in a colloid is to process the sample using dialysis-filtration. In this process, a high purity solvent is introduced under pressure to a container with a semi-permeable membrane wall, where the non-volatile residue is transported through the membrane and the particles are retained. While this method is effective for some samples, it is ineffective for meta-stable particles where the concentration of the dissolved material affects the size and or composition of the particle. Additionally, for low concentration colloids the dialysis process may create a significant number artifact particles through mechanical generation. An alternate method for particle extraction, described here, is to extract the particles from the sample using aerosolization (Figure 1). In this process, energy is introduced into the sample causing breakup of the liquid into small droplets. These small droplets are then evaporated, which creates an aerosol (gas containing suspended solid material) that can be analyzed using conventional aerosol instrumentation. The principle advantage of the aerosolization step is that the artifacts described above are limited due to the small volume of dissolved, non-volatile residue present in these droplets. If the droplets are sufficiently small, the precipitated, non-volatile residue forms a negligible precipitate on native particles or for “empty” droplets, the precipitate forms an aerosol particle that is substantially smaller than the particles of interest.

Methods for nebulization include electrospray, ultrasonic, and fluidic. In the system described herein, aerosolization is accomplished through pneumatic nebulization (Figure 2). The nebulization device employed is engineered to generate sufficiently small droplets, as well as to remove any large droplets that may otherwise introduce artifacts in the aerosolized sample. Inspection of the shape and composition of the native particles using microscopy methods is then facilitated using focused aerosol deposition that selectively removes the particles of interest from the gas stream, and allows the smaller artifact particles to pass through the system.

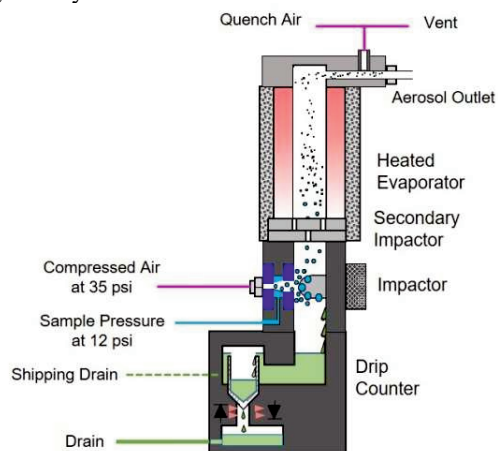


Figure 2. Precision nebulization system used in FAD

1.2 Concentrated Particle Deposition on an Analyzable Substrate

Nanometer-sized airborne particles that have been aerosolized from a liquid suspension are focused and deposited onto a flat substrate for subsequent microscopic and chemical analysis in the laboratory.

Impaction of dry aerosol particles onto a solid surface is a highly efficient method of collecting supermicron-sized particles, but becomes increasingly difficult for collecting smaller particles, and nearly impossible for sub-30nm particles. For inertial deposition of submicron particles, impaction jet velocities need to increase substantially as particle size decreases. To maintain a reasonable sample flow rate, aerosol impactors use multiple impaction nozzles of decreasing diameter having large pressure drops. This can cause particle breakup and bounce and decrease collection efficiency.

The approach used in FAD to collect nanometer-sized particles uses a method that physically enhances the size of the particles while still airborne so that they can be easily deposited onto a substrate using classical impaction. The aerosol sample flow is introduced into a region of supersaturated water-vapor to force water to condense on the tiny particles and form a fog of micro-droplets. A particle that was originally as small as 5 nm acts as the nucleus for condensation and becomes encapsulated into a droplet that grows to a relatively easy-to-capture 3 μm droplet. The droplets gently impact onto the collection substrate, without bounce or particle breakup (Figure 3). The substrate is warmed slightly to evaporate the water, leaving behind a highly concentrated, 0.04 mm², dry “spot” particle sample (Figure 4).

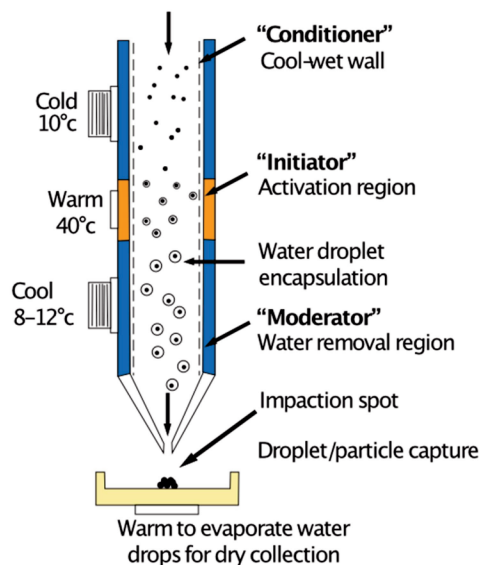


Figure 3. Nanoparticle collector schematic

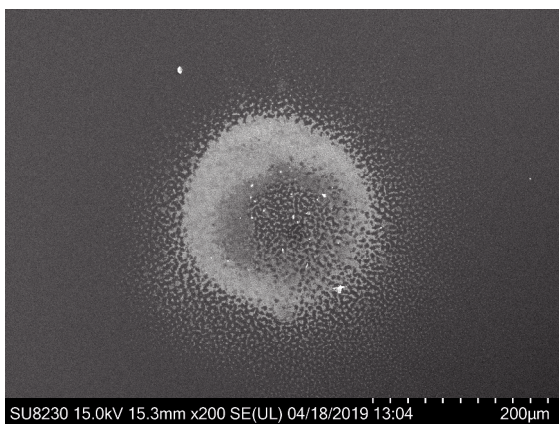


Figure 4. 36-hour collection of 5E5/mL 30 and 100 nm silicon dioxide mixture in UPW

The value of using the condensation growth tube capture (CGTC) method in this technique is that it is highly efficient at collecting particles from <10 nm to >2.5 µm independent of the particle's size, shape, or chemical composition. Hydrophobic and hydrophilic particles are collected equally well, with >95% collection efficiency of particles > 10 nm. A 1.5 L/min, laminar-flow CGTC is used with moderate temperatures that never expose the particles to temperatures greater than ~ 40 °C, so semi-volatile materials are preserved. Droplet collection uses a single impaction nozzle with low pressure drop (~0.05 atm). The tightly-focused, dry particle deposit reduces the sampling time needed for effective analysis. In the case of liquids with high particle concentrations, this time can be as little as ten minutes. A repositionable sample platen allows for unattended, time-resolved, sample collection onto silica wafer substrates adhered to an SEM post. Other collection substrates can be used to meet specific analysis requirements, for example, a surface-enhanced Raman spectroscopy (SERS) substrate or TEM grid.

2 APPLICATIONS

While the potential applications for FAD are broad, one of the early applications under active investigation is to better understand the morphology and composition of nanoparticles found in semiconductor manufacturing ultrapure water. The continuous shrinkage of semiconductor device features has driven the critical particle size, the size at which a particle could cause a compromised circuit, to smaller than 10 nanometers. The most common technique to collect these particles, filtration, is limited both in the size of particle that can be captured and the collection rate. When filtration is deployed, collection time can be as long as one month, and the captured particle size is typically 50 nm or larger. This is well above the critical particle size of 10 nm or smaller. In addition, the particles are distributed over a large area relative to the field of view of the SEM or other surface analysis instrument. Depending on the particle extraction

efficiency of the nebulizer and the size of the deposition spot, particle deposition rate as a function of analysis area is increased by a factor of 10 to 30 times. In addition, collecting at a precise location on an analysis-ready surface, while maintaining a small spot diameter, results in a significant reduction of the analysis time. Figure 5 is an example of a collection obtained from a semiconductor grade water system using FAD.

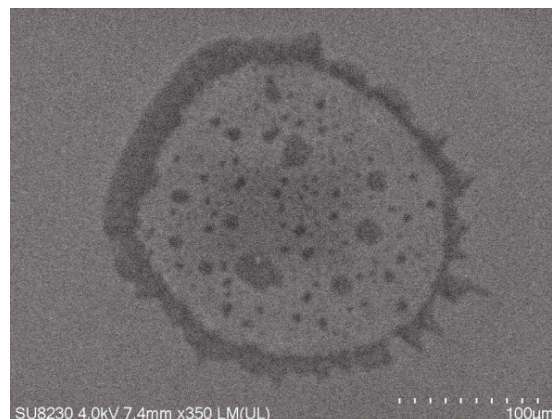


Figure 5. 37-hour collection from a semiconductor-grade UPW system on a silicon wafer

Another application being investigated is “fingerprinting” contamination sources within UPW systems. One of the critical components in a UPW system is the ion exchange (IX) resin, in particular the “final polish” resin. The surface area of an IX resin bed is very large, resulting in a high risk of nanoparticle shedding from these materials. If filters down-stream of the IX resins are compromised, or unable to capture the nanoparticles, these particles could deposit on the wafer surface. Figure 6 is an image of an IX resin effluent that was extracted with UPW from a virgin, semiconductor grade “final polish” resin and filtered using a 20 nm alumina filter. The filtered effluent was diluted online with UPW for collection with the FAD system. The resulting collection revealed pockets of gelatinous organic deposits as well as sub-20 nm particles that were released from this IX resin.

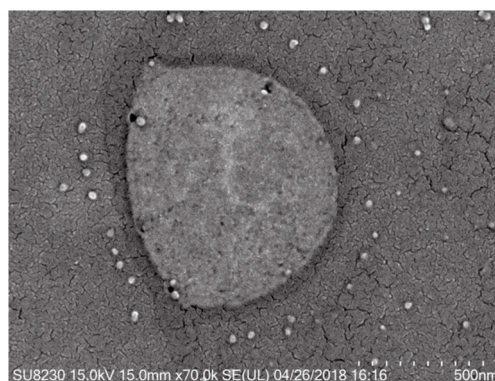


Figure 6. Ion exchange resin extraction FAD collection

An additional near-term application is the rapid collection of bacteria in pharmaceutical water (Figure 7). Taking advantage of the high deposition efficiency of the technique, bacteria can be collected rapidly on an SEM or SERS media for identification and analysis.

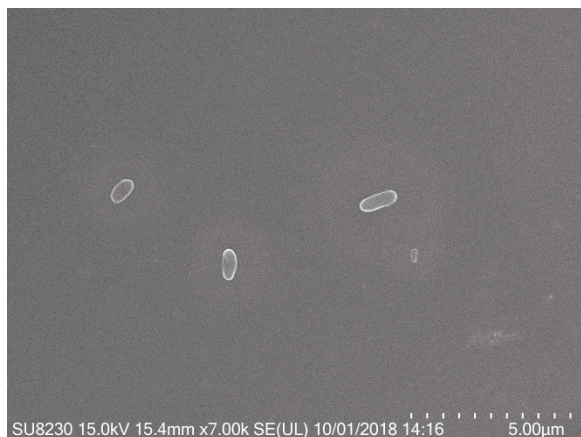


Figure 7. FAD bacteria collection from a UPW system

3 SUMMARY

The ability to extract nanoparticles from high-purity liquids, such as ultrapure water, and deposit them directly on an analysis-ready substrate provides enhanced and/or previously unavailable capabilities to measure the quality of ultrapure liquids. Liquid-borne particles as small as 5 nm have been extracted, deposited and examined using this technique. The unique capabilities and design of the instrument allows for interfacing with multiple analytical tools such SEM, TEM, and SERS. High particle collection efficiency provides the ability to quickly obtain analysis samples in the event of a water system excursion or bacteria release.

4 AUTHORS

Gary Van Schooneveld is President of CT Associates, Inc., a provider of contract research, development and testing services related to contamination measurement and control of ultrapure liquids, liquid filtration, colloid sizing and analysis, permeation, and chemical engineering since 1991. Gary has BS and MS degrees in Materials Engineering from Rensselaer Polytechnic Institute (Troy, NY) and an MBA from the University of Texas (Arlington, TX).

Pat Keady is an entrepreneur, co-founder, and CEO/President of Aerosol Devices Inc., an early-stage, rapidly growing company that is revolutionizing the science of airborne particle collection for physical, chemical and biological analysis. The Colorado-based corporation offers advanced instruments for collecting time-resolved, concentrated samples of nanometer- to micrometer-sized

particles to meet demanding applications in environmental science, bioaerosol sampling, and semiconductor contamination monitoring. Ms. Keady has a BSME and MSME degree from the University of Minnesota.

Derek Oberreit is the Vice President of Research and Development for Kanomax FMT. Kanomax FMT is a leading developer of particle measurement instrumentation solutions for the semiconductor and aerosol research communities. Kanomax FMT specialize in supplying online devices for detecting and measuring sub 20nm sized particles in ultrapure water systems and CMP slurries and has a growing list of innovative aerosol instrumentation used in basic aerosol research. Derek has a BSME, MSME, and PhD from the University of Minnesota.

5 RELATED MATERIALS

The following patents are relevant to the FAD technology and systems:

US 8,272,253 – Particle Concentration Measurement Technology (September 25, 2012)

US 8,573,034 – Residue Concentration Measurement Technology (November 5, 2013)

US 9,086,350 – Particle Concentration Measurement Technology (July 21, 2015)

US 9,513,198 – Residue Concentration Measurement Technology (December 6, 2016)

US 6,712,881 – Continuous, laminar flow water-based particle condensation device and method (March 30, 2004)

US 7,736,421 – High saturation ratio water condensation device and method (June 15, 2010)

US 8,801,838 - Advanced laminar flow water condensation technology for ultrafine particles (August 12, 2012)