EHD Basics with Emphasis on Semiconductor Process Applications

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Introduction

Electrohydrodynamics (EHD) has been used as a method of forming nanoscale droplets for a myriad of applications for the past three decades. By placing an electrical charge on a liquid, a unique spray mode can be used to generate and accelerate nanoscale droplets from an EHD nozzle. Applications range from the obscure to the routine, from micro thrusters for space vehicles[1] and particle beam fusion accelerators[2] to mass spectrometry ionizers[3] and aerosol drug dispensers[4]. Able to create uniquely small nanodroplets, the use of EHD technology to address advanced node (≤32nm) semiconductor manufacturing can lead to significant improvements in such diverse processes as low-k and high-k precursor vaporizers, sub-32 nm particle removal, and edge bead removal (EBR) for double patterning immersion photoresist processes.

EHD History

Electrohydrodynamic spray technology, often termed electrospray, has been used in numerous, diverse applications. The most commonly used electrospray devices can be found in laboratories where they are used to ionize large, complex, sensitive biological molecules such as peptides for analysis by mass spectrometry.

Figure 1 shows a diagram of such an ionizer for use in mass spectrometry. In the diagram a protein of molecular weight 47,342 is analyzed with electrospray ionization to yield over 50 peaks, the mass/charge ratio of which equals 1-2000 Th and therefore can be analyzed with a mass analyzer.[5] Work with electrospray ionization was awarded the Nobel Prize in Chemistry in 2002.

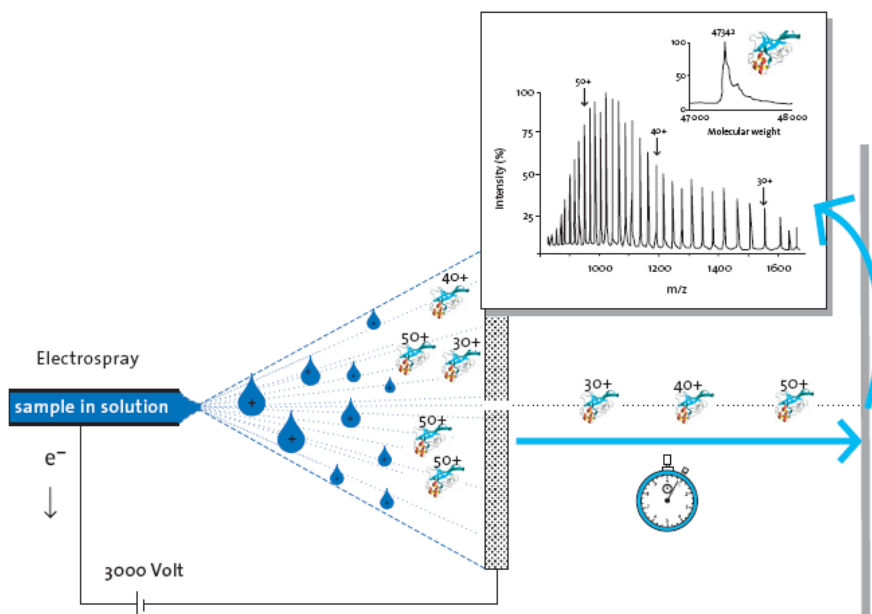


Figure 1: Diagram of a protein analyzed with electrospray ionization results in over 50 peaks of the corresponding charge pattern. [5]

Commercial versions of electrospray ionizer (ESI) sources are available from mass spectrometer suppliers. Figure 2 shows an ESI source from Agilent Technologies, Inc.[6] In addition to its use analysis of biological macromolecules such as proteins and peptides, EHD can also be especially useful for smaller polar molecules.

Figure 2: Agilent Technologies Electrospray Ionizer Source used for analysis by Liquid Chromatography Mass Spectrometry

Because of the success in spraying complex biological molecules, aerosolization of pharmacological preparations for therapeutic applications has been researched for a number of treatment studies. In one such study, comparison of EHD vs. Ultrasonic Nebulizers for lung

gene therapies using plasmid DNA demonstrated respirable aerosols of naked plasmid DNA can be generated without plasmid degradation.[7]

In one of the more exotic applications EHD spray has been applied to satellite thrusters. Ionic liquid salts with extremely low volatility, essentially non-volatile at room temperature, are applied to needle arrays and used to manipulate space vehicles. Because the needles are very tiny and therefore the thrust of the spray used for maneuvering very small, on the order of 0.05 μN to 0.12 μN, arrays are fabricated to increase thrust to useable ranges in practical applications.[8] Such a device is shown in Figure 3 wherein arrays are fabricated using micromachining processing methods: photolithography, chemical etching and thin film deposition. When a voltage is supplied, the salts vaporize. The needles determine the direction of the spray; manipulating the direction of the needle array can be used to steer the space vehicle.

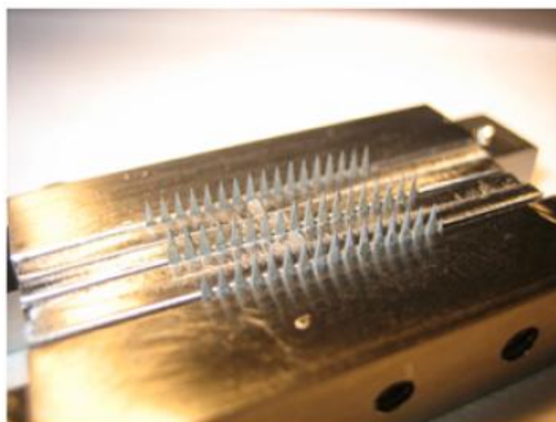


Figure 3: An electrochemically etched, 49 emitter tungsten electrospray thruster used with EMI-BF4, (3-ethyl-1-methylimidazolium tetrafluoroborate) a non-volatile ionic liquid salt at room temperature.[8]

How EHD Works

To generate nanodroplets using EHD, a pressurized reservoir of liquid is used. The liquid is then charged through a conducting wire or contact. One end of a capillary tube is placed in the reservoir, and the other end of the capillary is used as the EHD nozzle. An electric field is created at the nozzle end of the capillary, which breaks up the meniscus of the charged fluid and creates a stream charged nanodroplets. Electric fields further accelerate the nanodroplets and direct them toward the surface for particle removal. Figure 4 shows a typical EHD system.

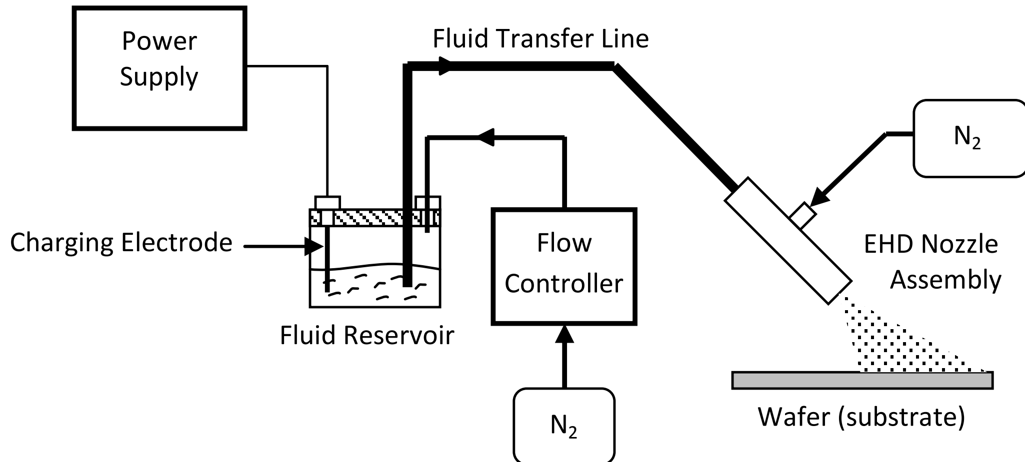


Figure 4: Atmospheric EHD System

EHD Processing Chambers

For demonstration purposes, multiple EHD processing chambers including ones that operate at atmosphere or in vacuum have been designed and installed in the cleanroom at the EHD Technology Group (EHDTG) facility in Duarte, California. One typical atmospheric EHD chamber is shown in Figure 5(a). This chamber is used to process 200mm and 300mm silicon wafers. Figure 5(b) shows a close-up of a typical EHD nozzle assembly.

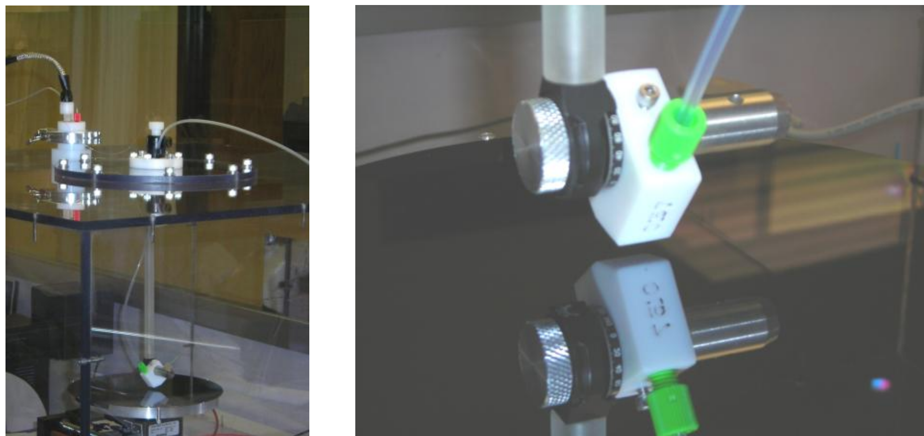


Figure 5: Atmospheric EHD nozzle assembly, (right: close up for detail) allows annular gas flow for special applications where needed.

Semiconductor Applications

At EHD Technology Group (EHDTG), EHD-assisted processing has focused on three primary areas:

1. Wafer Cleaning – At the ITRS Conference in 2008, Several issues were identified by the Yield Enhancement International Technical Working Group.[9] Among the challenges for the (<22 nm node included detection of killer defects, analysis and characterization of defects smaller than feature sizes, and lack of PWP (per wafer pass) data. The 2008 ITRS update showed significantly greater than 50% of the categories in the Yield Enhancement category with no known manufacturing solutions. While many of these are related to the difficulties of metrology at 22 nm and below, they stem from concerns about removal of killer defects at this node. EHD TG holds several patents related to substrate cleaning.[10] Efforts are currently focused on particle removal from silicon wafers at the 22 ηm node. The ability to generate nanometer scale droplets is believed to offer significant advantages in the removal of extremely small particles, particularly on patterned wafers with high aspect ratio features. In this application, aqueous solutions are directed toward the wafer at an angle to dislodge particles from the wafer surface. Recent work has been performed on Silicon Nitride (SiN) contaminated silicon wafers. Figures 6(a) and 6(b) show the results as measured by a KLA-Tencor defect mapping system. In this test 200mm bare silicon wafers are coated with a dilute slurry of <50nm silicon nitride particles. In this test Particle Removal Efficiency (PRE) was calculated to be 95%. Additional work is ongoing to further characterize and improve system performance as well as integrate the EHD nozzle into a production single wafer cleaning tool.

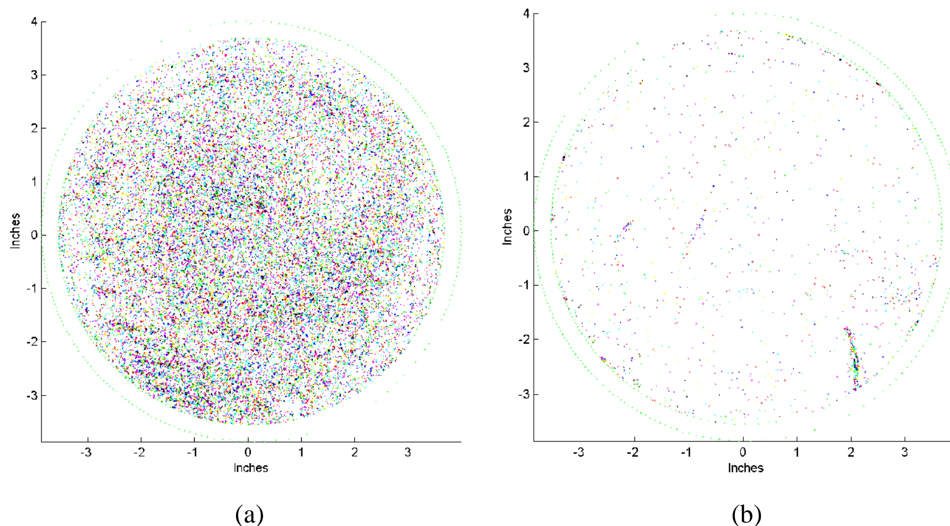


Figure 6: (a) SiN Particles Before EHD Processing, Count = 28,408 and (b) SiN Particles After EHD Processing, Count = 1,460

2. Edge Bead Removal (EBR) & Bevel Cleaning – Wafer edge (bevel) cleaning and film removal have been identified for their potential for significant defect reduction, particularly in leading edge lithography.. EHDTG has identified these applications and is undertaking experiments, beginning with EBR. This focus is driven by need for improved EBR for double patterning immersion lithography.[11, 12, 13]

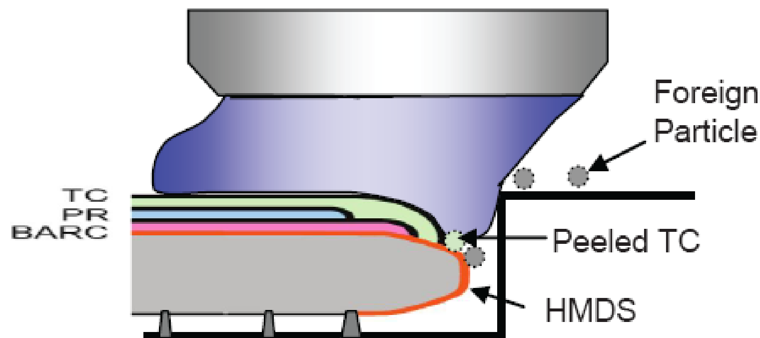
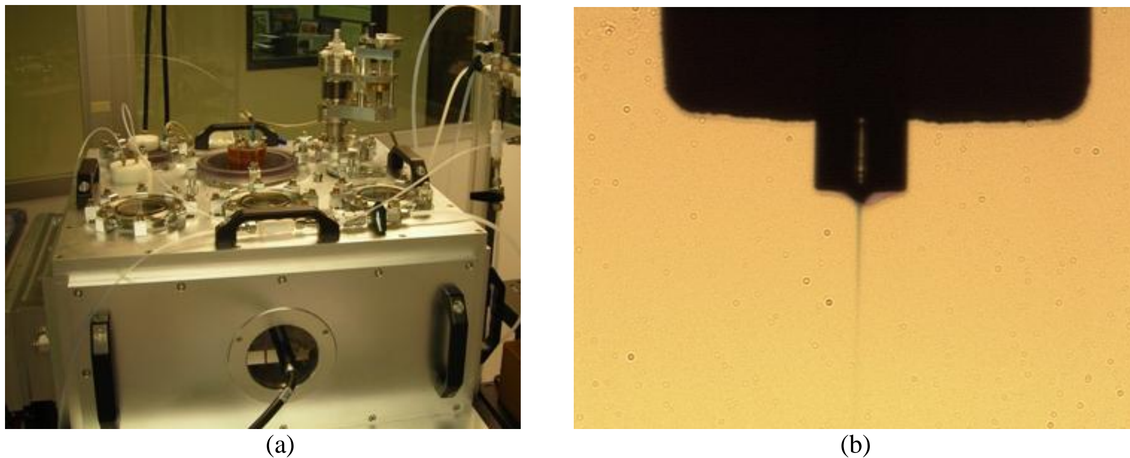


Figure 7: Particle contamination due to peeling, bevel or TCP (Top Cover Plate) contamination[13]

Immersion fluids can apply significant forces to the wafer surface, particularly at the wafer edge at the beginning of the scan. The multilayer ArF photoresist film stack used for double patterning processes is susceptible to debonding from the shear forces of the immersion fluid, especially at the edge of the wafer. Delamination and the resulting particle generation can result in particles on the wafer surface, often in the unexposed area, which can print as defects. The ability to direct a fine stream of liquid droplets at a small area has focused interest in EHD for edge cleaning applications. Whether for particle or film removal, the EHD spray offers the user a unique combination of variables to optimize process results, including aqueous, solvent or solution based chemistries, a range of energies, and extremely low liquid usage. The last item can have significant impact on reducing costly, potential harmful solvents and related chemistry usage and disposal costs, benefiting both the user's budget and the environment.

3. CVD Precursor Vaporizer – Low-k and high-k materials have been employed to overcome traditional silicon processing materials at the 65 nm node and below. To maintain the ability to reduce feature size to stay on the Moore's Law curve, these new materials have allowed chip makers to achieve even smaller features without sacrificing performance or reliability. As the industry strives to maintain it's desire for smaller and smaller features that enable faster and faster speeds and greater density, new materials are being considered to overcome

even greater material challenges. The latest round of low-k and high-k materials often requires the use of new processes and methods. Most significantly, where gaseous species have been the source of most thin films until recently, WF_6 and SiH_4 for example, the new precursors are often liquids or even solids at room temperature. Materials such as TEMAHf (tetrakis(ethylmethylamino)hafnium), OMCATS (octomethylcyclotetracyloxane), and DMDMOS (dimethoxydimethylsilane) have been in use for the past few years, and newer, more exotic materials are being tested. Vaporizing these materials has been a challenge, whether the compound is a liquid or solid. Often they can be sensitive to heat, therefore vaporizers that heat the liquid are prone to clogging at the nozzle or in some cases in the liquid reservoir. Because both the liquid material and the tool utilization are significant factors in wafer processing, either of these conditions can increase the cost of the process and ultimately the profitability of the finished wafer.



(a) (b)

Figure 8: (a) EHDTG's vacuum process chamber and (b) a close-up of a single nozzle successfully spraying TEMAHf into nanometer scale droplets for vaporization.

EHD's unique ability to apply energy only when the liquid leaves the nozzle offers significant advantages to heated vessel or heated tubing solutions.[14] The nanometer scale droplets produced by the EHD beam quickly vaporize at reduced pressure. EHD's use in ionizing complex, sensitive biological species provides additional evidence of the potential advantages of EHD's use in a vaporizer. EHDTG has successfully sprayed a number of high-k and low-k materials and is currently investigating integration into a production, plasma deposition tool.

In summary, EHD is applicable to a number of applications in the semiconductor industry. The clear benefits of EHD include its ability to generate nanodroplets smaller than other aerosolization techniques for cleaning at advanced nodes, it's localized and directed spray patterns for targeted cleaning such as wafer edges, and it's ability to add energy to a liquid just at the EHD nozzle to avoid precursor degradation and maintenance downtime.

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