

EHD Vaporization of CVD, PECVD, and ALD Precursor Materials

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Introduction

CVD and related deposition methods have been used in semiconductor film deposition for many years. Most often gaseous precursors are employed such as WF₆. In some instances, liquid materials are used, the most well known being TEOS. Recently the need to deposit high-k and low-k materials has brought new emphasis to the use of liquid and in some case solid precursors. The need to vaporize these materials has ushered in a myriad of methods including bubblers, pressurized sprays, and in the case of solid materials, heated vessels. While all of these methods are useful, some difficulties are associated with each of these methods including degradation of source materials due to elevated temperatures, nozzle clogging, and droplet entrainment due to incomplete vaporization. EHD spray technology represents a vaporization approach which addresses each of these concerns in that it can produce submicron sized droplets (<1 μm diameter) of liquid and dissolved solid materials. We report here on an EHD spray approach to apply EHD spray beams used for liquid source vaporization applications. The paper describes how liquids are sprayed as nanometer scale charged droplets through a series of steps including, 1) initial droplet formation at Taylor cone meniscus, 2) progressive Rayleigh¹ breakup of the droplets, and 3) final vaporization of the droplets in a vacuum chamber. Application to current and future film deposition is also discussed.

Motivation

CVD and related deposition methods have been used in semiconductor film deposition for many years. Most often gaseous precursors are employed such as WF₆. In some instances, liquid materials are used, the most well known being TEOS. Recently the need to deposit high-k and low-k materials has brought new emphasis to the use of liquid and in some case solid precursors^{4,5,6}.

The need to vaporize these materials has ushered in a myriad of methods including bubblers, pressurized sprays, and in the case of solid materials, heated vessels. While all of these methods are useful, some difficulties are associated with each.

In a bubbler, the precursor delivery rate is directly related to the vapor pressure of the liquid. Vapor is produced by either heating the liquid to evaporate it, or by heating the liquid and bubbling a carrier gas through it. Therefore, precursor delivery is directly related to temperature. With the nature and complexity of some of these precursor materials, however, increased temperature can lead to material degradation, particularly when a heated vessel of liquid is maintained at process temperature for extended periods of time.⁷ These changes can cause variation in evaporation rates, and resulting instability in the deposition process. In both cases the goal is to obtain a vapor that is transported through delivery tubing to the process chamber. However, due to the condensable nature of the materials and their potential to be chemically

altered by elevated temperatures, problems such as microdroplet formation and delivery tube clogging can occur, leading to process equipment downtime.

Pressurized sprays are one method to try to overcome some of the challenges of dispensing precursor materials with bubblers. Appropriate solvents can be employed where the materials are solids, increasing the number of materials that can be used. Flow rate can be accurately controlled using micro-stepper motor driven metering pumps or liquid mass flow controllers. Delivery system designs, some employing a carrier gas mixing chamber to insure complete vaporization have been employed in some cases to overcome performance limitations sometimes found in mechanical spray systems. In all such systems, spray nozzle design is critical to controlling droplet size and therefore evaporation rates. Some designs utilize heated delivery lines or a heated target surface to insure complete volatilization of the precursor material. Non-contact evaporation is preferred as contact evaporation methods are prone to residual material build-up on heated surfaces, potentially causing particle generation and increased downtime for maintenance. Other systems employ heated carrier gases. While these systems improve performance of pressurized spray systems, they do not eliminate them.

The key factor to avoiding such problems is droplet size, smaller is better, and the mechanical nature of pressurized spray systems have a finite droplet size limit. EHD spray offers a means of reducing droplet size by a factor of 10, 100 or 1000 vs. current vaporization systems. Table 1 provides relative droplet size for various spray technologies. EHD spray is able to produce the smallest droplets, thereby providing the largest surface area and the resulting increased vapor pressure per volume of liquid. Work described below describes the methodology and initial results of the work.

Spray Method	Published Typical Droplet Size (μm)
Jet Spray Atomizer	100 – 200
Rotary Atomizer	50 – 1000
Ultrasonic Spray	30 – 90
Piezo-Assisted Spray	10 – 20
EHD Spray	0.01 – 0.5 (10 – 500 nm)

Table 1: Comparison of typical liquid droplet sizes produced by various spray methods

EHD Principles of Operation

EHD Technology Group employs a novel technique to produce energetic beams of submicron charged droplets, as described previously^{1,2}. Electrohydrodynamic, or EHD, atomization breaks up and disperses a wide range of liquids into an ensemble of charged droplets of sizes smaller than 1 micron. Application of high voltage to the conductive fluid causes atomization when the electrostatic stress at the liquid-gas interface exceeds the surface tension forces that oppose meniscus disruption. This is a dynamic process which proceeds in a progressive fashion, as droplets undergo evaporation, then size reduction bringing the charges closer to one another, and the resulting increased electric repulsion and further droplet breakup into smaller and smaller sizes. A breakthrough EHD spray application was pioneered by Nobel Laureate John B. Fenn², the widely used ESI (Electrospray Ionization) for molecular mass spectroscopy.

Apparatus

Fluid contained in a hermetically sealed reservoir is delivered through a capillary to the emitter tip of the droplet source, with a rate controlled by filtered nitrogen gas pressure. While EHD spray may be performed either at atmosphere or in vacuum, CVD vaporization applications are done in vacuum. The configuration of the apparatus and the associated high voltage power supplies are shown below in Figure 1.

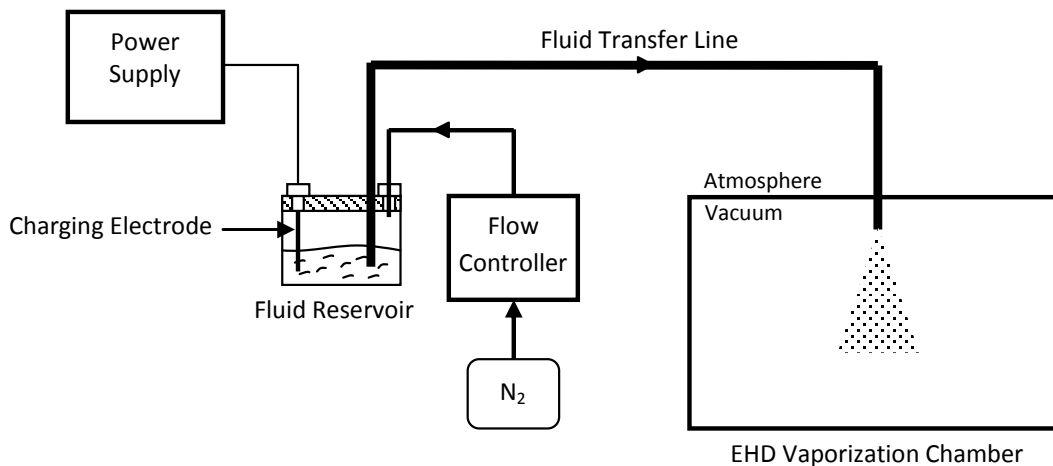


Figure 1: Schematic of EHD Atomization System.

Typical EHD beams consist of droplets emitted at a rate of 10^7 to 10^9 /s traveling at velocities which may be in the range 50 m/s to near sonic, depending on conditions.

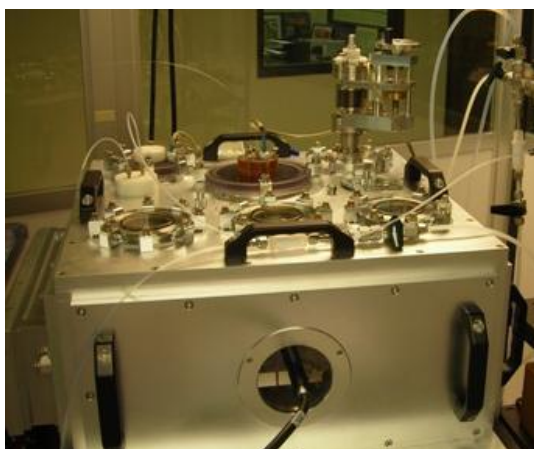


Figure 2. EHD Technology Group's Vacuum Chamber

Figure 2 shows a photograph of the vacuum process chamber used vaporization experiments. The chamber is evacuated by a turbo pump backed by a roughing pump. Typical base pressures

are in the range of 10^{-6} Torr. The chamber contains a rotational stage capable of handling up to 300 mm wafers. EHD spray is delivered through a vacuum compatible feed at the top center of the chamber. Various viewports and instrumentation feeds have been added to facilitate experimental data collection. The chamber is connected to a manual load lock for wafer loading and unloading. Figure 3 shows a close up of the EHD spray nozzle inside the vacuum chamber.



Figure 3 EHD Nozzle Inside Vacuum Process Chamber

In typical operating conditions, a pressurized conductive liquid is flowed through a narrow capillary tube to a nozzle tip, where it forms a meniscus known as a Taylor³ cone. Under certain conditions charged droplets are generated at the Taylor cone, whose size is determined by the balance between the force of surface tension and electrostatic repulsion on the droplet. The droplet radius r (first computed in 1882 by Lord Rayleigh) is given by:

$$r = \left(\frac{1}{4}\right)^{\frac{1}{3}} \sqrt[3]{\frac{q^2}{\pi^2 \epsilon_0 \gamma}} \quad (1)$$

where q is the bound surface charge of the droplet, ϵ_0 is the permittivity of the material surrounding the droplet, and γ is the surface tension of the conductive fluid.

The charge and mass of the droplets produced determine the trajectory and kinetic energy of droplet as it enters the vacuum chamber. The objective is to minimize droplet size to maximize evaporation rate, thereby achieving total vaporization of the liquid precursor material. In doing so material usage is maximized resulting in lower costly chemical usage, elimination of entrained droplets, and reduction or elimination of particle generated from drying of solid material containing droplets on process chamber surfaces. Figure 5 shows the droplet size, charge, and mass, as a function of reservoir supply voltage and beam current.

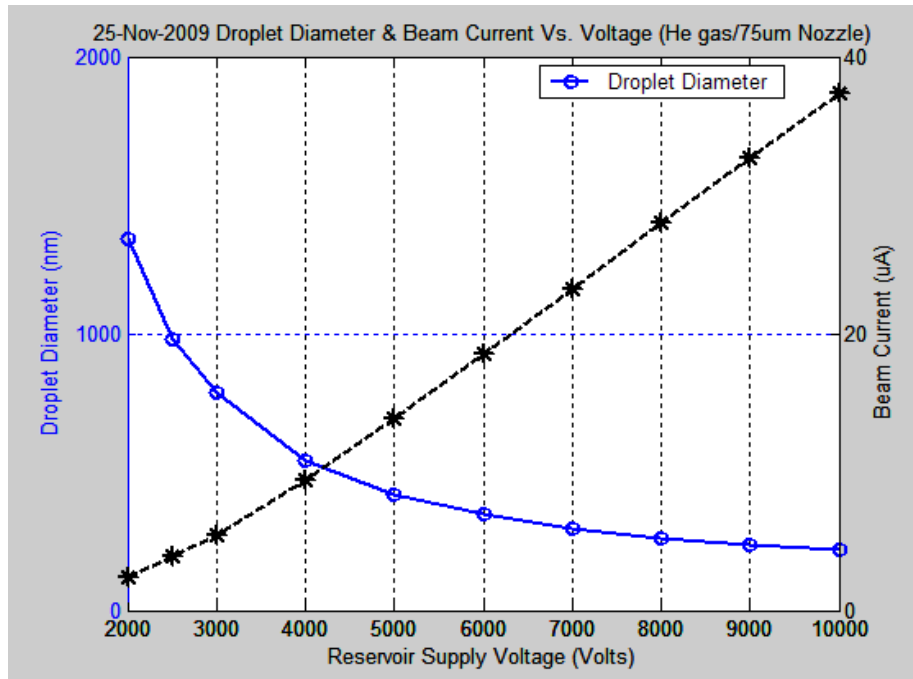


Figure 5: EHD is Capable of Generating Sub-micron Droplets

Complex physical processes are at work in EHD process including: 1) droplet formation of the Taylor cone, 2) droplet disintegration (into smaller droplets) as evaporation and successive breakup takes place, and 3) droplet motion in response to the forces acting upon it.

In the case of droplet motion in response to the forces acting upon it, actually contains further complexity, in that there are multiple forces acting on the droplet at various times in its journey from the nozzle, in vacuum being primarily the electric field forces.

Note also that the droplet flight from the nozzle is not necessarily that of a single droplet which stays intact from beginning to end. Rather the droplet can break up multiple times after leaving the nozzle, as evaporation takes place and the surface tension and electrostatic forces go out of balance, causing Rayleigh breakup. As each breakup occurs there may be multiple daughter droplets, each with a different value of size, charge, and mass. In the case of CVD liquid precursors, the process continues until the droplet is completely vaporized.

Experimental results

Several materials were tested to determine their suitability for EHD spray. Figure 6 is a photograph of the EHD nozzle during operation in vacuum. The material being sprayed is tetrakis(ethylmethanido)hafnium(IV), known in the industry by its acronym TEMAHf (CAS # 352535-01-4). In the photograph the TEMAHf is seen leaving the EHD nozzle and breaking up into droplets. Final droplet size is not possible to directly measure by known methods due to the small volume of material being sprayed and the extremely small, submicron droplet size. Figures 7, 8, and 9 show similar photographs for TOMCATS™ (tetramethylcyclotetrasiloxane), OMCTS (octamethylcyclotetrasiloxane, CAS # 566-67-2), and DMDMOS (dimethyldimethoxy-

silane, CAS# 1112-39-6) respectively. All were sprayed in their neat form. In all cases thin films were visually witnessed on silicon wafers placed into the process chamber.

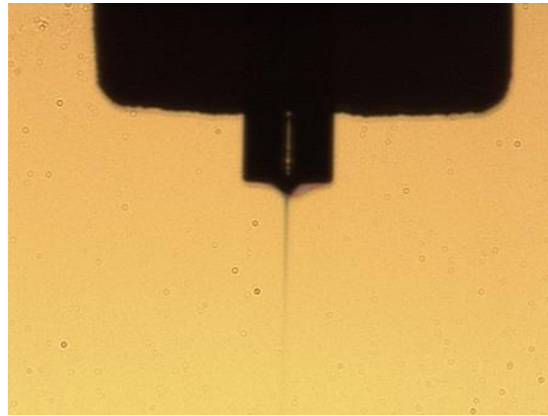


Figure 6: EHD electro spray of TEMAHF in EHD Technology Group's vacuum process chamber

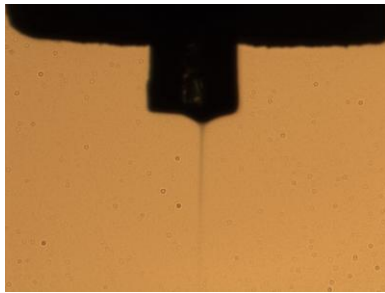


Figure 7: TOMCATS™ Spray

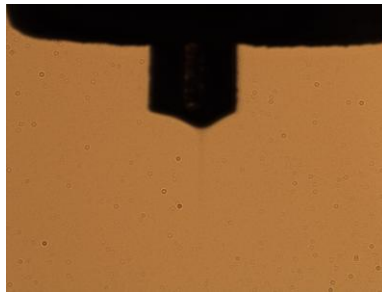


Figure 8: OMCTS Spray

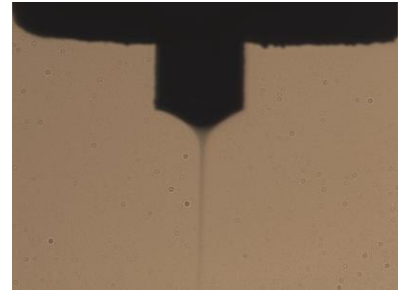


Figure 9: DMDMOS Spray

EHD advantages for vaporization of liquid CVD precursors

One key advantage of EHD spray as previously noted is the ability to spray thermally sensitive materials without heating them. In the case of bubblers in particular and pressurized sprays in general, heated reservoirs and delivery lines can lead to thermal degradation of the source materials. EHD spray does not require heated liquids to assist in vaporization, thereby eliminating thermal degradation as a source of concern.

Additionally, the method is extremely friendly to complex, chemically sensitive materials. EHD spray, as also noted above, is used in the delivery of such thermally sensitive materials as proteins for mass spectroscopy studies. The nature of EHD spray and the ability to form submicron droplets of nanoliters of liquids offer additional confidence the chemistry of the

precursor molecules is preserved until they enter the process chamber, assuring film properties are only those desired and not the result of thermal degradation byproduct contamination.

Finally, the ability to deliver and completely vaporize all of the liquid precursor material is seen as an advantage to reduce the cost of the precursor liquids, many of which can be relatively costly due to their complex nature and special handling requirements.

Next steps

Additional material testing is planned to provide data on a full range of materials. EHD Technology group is also in discussions with CVD tool suppliers and device makers to integrate the EHD spray head into a plasma process chamber to optimize film deposition and properties. Scaling of the EHD spray to achieve high volume manufacturing throughput rates will also be preformed to optimize material usage.

Summary

EHD spray has been demonstrated on several industry standard liquid precursors used in CVD of high-k and low-k films on silicon wafers. EHD spray offers the ability to achieve full vaporization of the precursor materials without the addition of heat, eliminating problems of thermal degradation found in alternative methods.

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