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Mist Deposition in Semiconductor Device Manufacturing

P. Mumbauer, M. Brubaker, P. Roman and R. Grant, Primaxx Inc., Allentown, Pa.; K. Chang, W. Mahoney, D.O. Lee, K. Shanmugasundaram and J. Ruzyllo, Department of Electrical Engineering and Nanofabrication Laboratory, Penn State University, University Park, -- 11/1/2004
Semiconductor International

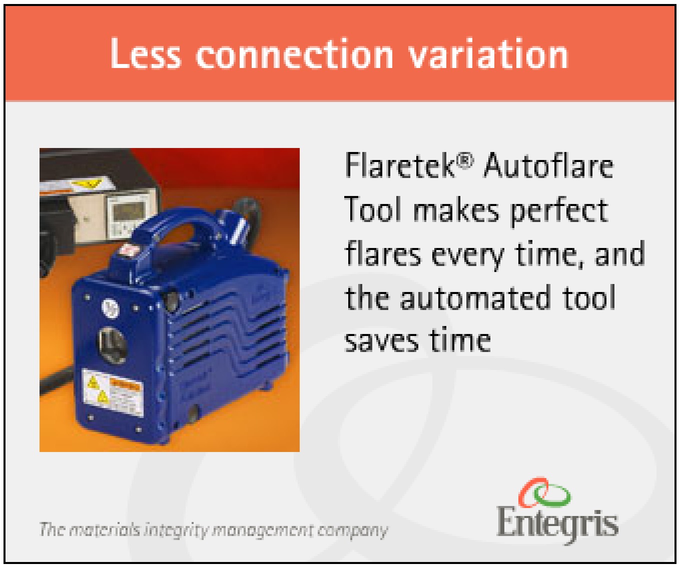
At a Glance

This article introduces mist deposition, a method that may extend the use of liquid precursors in semiconductor manufacturing in applications when spin-on processing will be of limited use. Principles of the method, as well as properties of mist-deposited films, are discussed, and two different mist deposition applications are considered based on experimental results.

Liquid precursors are commonly used in semiconductor processing. A liquid source can be converted into gas that will then act as a reactant in chemical vapor deposition processes such as metal organic chemical vapor deposition (MOCVD). Alternatively, viscous liquid precursors can be physically applied to the wafer surface and then solidified by thermal curing. Among the latter techniques, those that may be precise enough to manufacture electronic/photonic devices are briefly reviewed. Then a method of mist deposition that is free from several constraints of currently used techniques is introduced.

The most common method of physical liquid deposition (PLD) is a spin-on process in which a controlled amount of liquid is dispensed onto the substrate surface and distributed over it by centrifugal forces created by wafer rotation at thousands of revolutions per minute. The spin-on process is relatively simple to implement, and since the beginning of modern semiconductor manufacturing has successfully been used in photoresist deposition. More recently, it has also begun to play a prominent role in low-k dielectric technology. However, spin coating has inherent shortcomings that may limit its usefulness in the processing of nanoscale geometries on very large wafers, as well as eliminate it from the use in the processing of substrates much larger and heavier than a silicon wafer, such as those used in LCD manufacturing.

In the specific case of photoresist processing in high-end silicon manufacturing, the challenge is particularly severe, because two trends are playing against the capabilities of a spin-on process. First is a continued increase of the wafer diameter, and second is the need to keep reducing thickness of the imaging resist layer in response to the reduction of the wavelength of exposing radiation. Control of resist thickness uniformity for films thinner than 100 nm on wafers larger than 300 mm is difficult to accomplish by means of spin-on deposition. In addition, as the wafer diameter increases, so does the difference in linear velocity between points at the perimeter of the rotating wafer and in its center, and so does centrifugal force acting on the precursor at various points along the radius of the wafer. Hence, spin-on processing is likely to introduce radial inhomogeneities in very thin films deposited on very large-diameter wafers. Furthermore, spin-on processing has limited ability to uniformly coat surfaces featuring aggressive conformal geometries, such as those encountered in MEMS devices. It is also incompatible with flexible substrates, such as those that will be used in future-generation display technology. Finally, the spin-on process is not very efficient because only a very small part of the material dispensed on the surface as liquid stays there after spinning.[1]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Extrusion spin coating[2] was conceived and implemented with one goal in mind: to reduce the amount of photoresist wasted during spin-on processing by applying it to the surface in a spiral motion as a thin film by extrusion coating instead of dispensing it on the surface and distributing by a spin-up process. Other than reducing the amount of wasted photoresist, however, the extrusion spin coating is not free from the shortcoming of conventional spin coating previously outlined. It still requires a high-rpm spin-off cycle following extrusion coating. Also, it works best for final resist thickness ranges above 500 nm, and hence, it will not be an effective solution to the problems of advanced 193 nm and future 157 nm resist technology.

Yet another approach to PLD is to spray liquid on the surface of a slowly rotated substrate using a nozzle mounted on a swivel arm. The method of spray coating is free from the geometrical restrictions on the substrate inherent to spin-on processing, but with an average droplet diameter of ~20 µm, adequate thickness control can be best achieved in this case for films thicker than ~1 µm.[3]

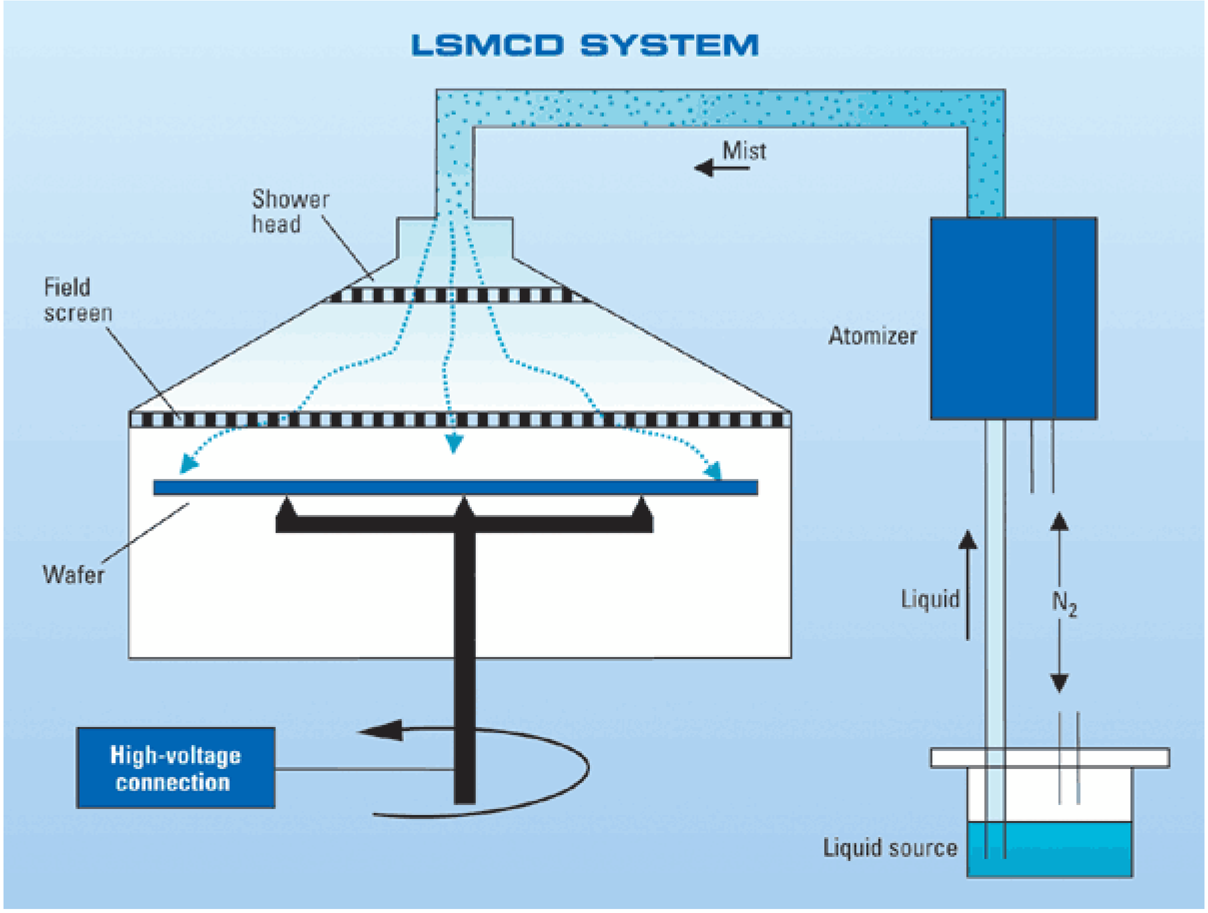
Finally, inkjet printing has been investigated as a method allowing direct patterning of liquid precursors on the surface of the substrate. However, this method lacks the resolution needed to create ultrasmall geometries and, in processes in which millions of features have to be individually printed, it would be prohibitively expensive and inefficient. All remaining physical liquid transfer methods, such as immersion or brush painting, are too crude to be considered for advanced semiconductor manufacturing.

Mist deposition is a method of covering solid surfaces with liquid precursor that is free from inherent limitations of spin coating and other techniques discussed. As the name indicates, the liquid in this case is slowly delivered to the substrate in the form of a very fine mist, which then uniformly coalesces on its surface. Just like in the case of spin-on processing, mist deposition is followed by thermal curing of the film. Mist deposition is independent of the shape of the substrate and does not have inherent limitations regarding its size. Also, it allows controlled deposition of films as thin as ~3 nm.

This paper first introduces principles of mist deposition, then illustrates workings of this method in applications involving deposition of high-k dielectrics and photoresist. The results discussed were obtained using a commercial 200 mm liquid source misted chemical deposition (LSMCD) tool.[4]

Principles of mist deposition

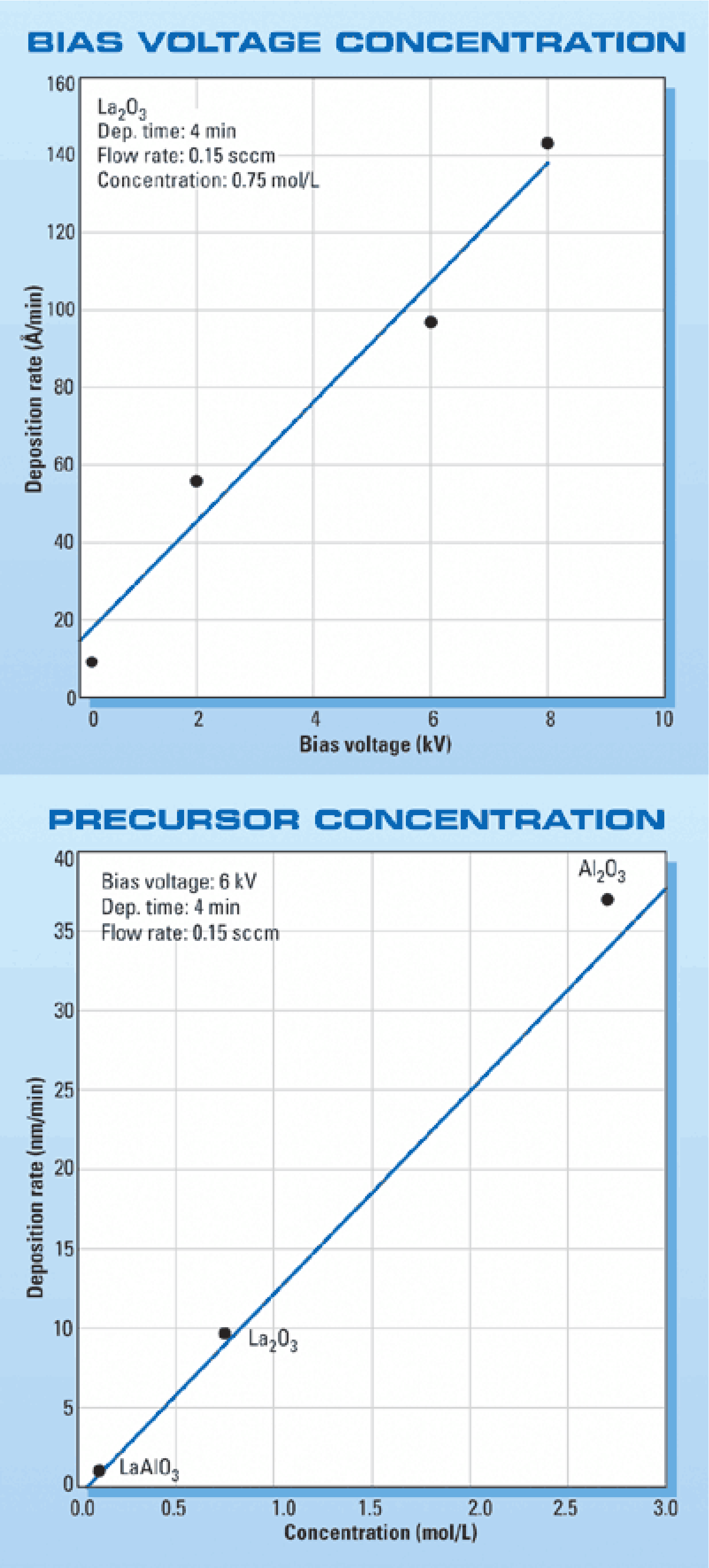
In general, the idea behind mist deposition is to convert liquid source material into a very fine mist, which is then carried by nitrogen to the deposition chamber where sub-micron droplets coalesce at room temperature on the wafer, covering its surface with a uniform film of viscous liquid. The film is then subjected to thermal curing during which the solvent evaporates, leaving on the surface a thin layer of solid. A schematic diagram of the commercial system implementing mist deposition is shown in Figure 1 . A liquid precursor is supplied in a stainless container from which it is flowed into the atomizer by nitrogen pressure. An atomizer liquid is converted into a very fine mist through interactions with a series of impactors. The average size of the droplet in the mist is ~0.25 µm, but can be smaller for a different impactor configuration. The mist is then carried by nitrogen into the deposition chamber where it coalesces on the surface of a slowly (10 rpm) rotating wafer at room temperature and a pressure very close to atmospheric.



1. Schematic diagram of the mist deposition module.

To control deposition rate beyond gravitational interactions, which in the case of submicron-sized droplets are very weak, an electric field is created between the grounded field screen and a wafer (Fig.1). After deposition, the film is thermally cured at a temperature of 160-300°C in ambient air or in the controlled ambient of either oxygen or nitrogen at atmospheric pressure. In the case of some inorganic materials, wafers may also be subjected to an additional anneal typically in the temperature range of 600-800°C either in nitrogen or in nitrogen with some oxygen added.

As indicated earlier, by controlling an electric field between the wafer and the field screen, the deposition rate can be controlled as shown in Figure 2a for the deposition of La_2O_3. Deposition rate also depends on the concentration of the precursor, regardless of its chemical composition (Fig. 2b). However, an increase in deposition rate by using high-concentration precursors may result in an inferior homogeneity of the deposited film. Consequently, a precursor concentration not exceeding ~1 mol/L is typically selected.



2. The rate of mist deposition as a function of bias voltage

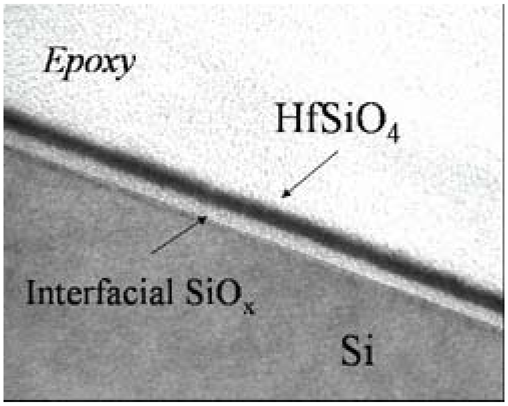
(top) and precursor concentration (bottom).

Examples of applications

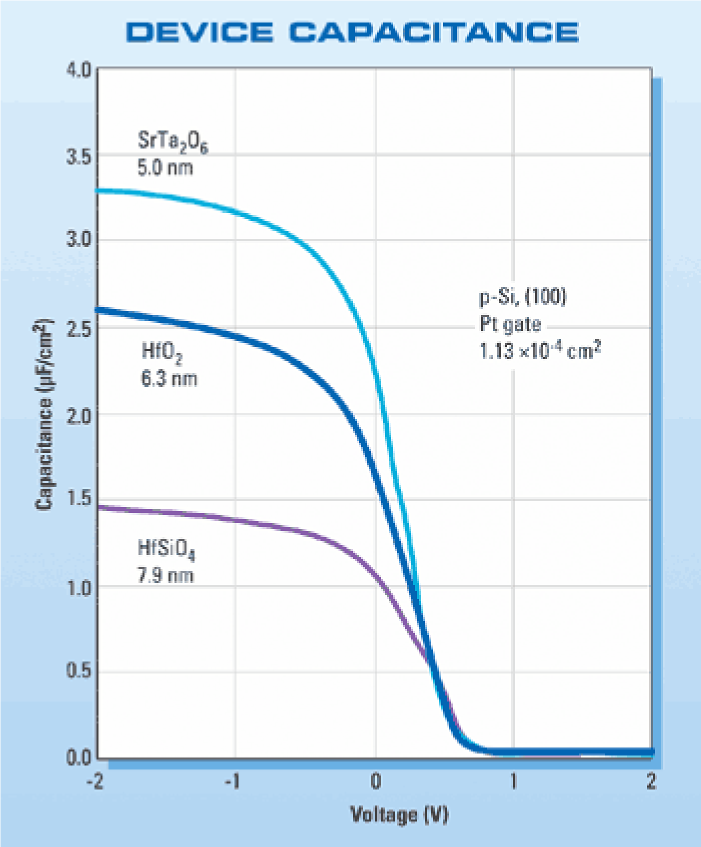
To define applications for mist deposition and prove its feasibility in advanced microelectronics manufacturing, the process was extensively explored in the deposition of a variety of materials. The LSMCD method was first successfully employed in the deposition of ferroelectric films in the thickness regime of ~80 nm.[5] Further experiments were focused on the deposition of significantly thinner films of high-k dielectrics for MOS gates, as well as deposition of photoresist.

High-k dielectrics for MOS gates The goal of this experiment was to test limits of mist deposition by attempting to form stable MOS gate structures comprising of compositionally modified interfacial SiO_x and uniform mist deposited high-k dielectric in the 3.0-8.0 nm thickness range, featuring low leakage current and a smooth interface with silicon. Liquid precursors used were commercially available solutions featuring desired composition. A series of screening experiments performed using several high-k dielectric compositions demonstrated effectiveness of the process in $SrTa_2O_6$,[6]$HfSiO_4$, and HfO_2 [7,8] depositions.

The results obtained demonstrated that mechanically coherent, uniform and smooth ultrathin films were formed by mist deposition on dilute HF-last treated silicon surfaces. Figure 3 shows a TEM cross-section of a ~3 nm thick $HfSiO_4$ film that was formed on a silicon surface with interfacial layer of SiO_x. Roughness of the film was determined by AFM to be 0.136 nm. Adequate integrity of the mist-deposited ultrathin films of high-k dielectrics was further verified through electrical characterization of platinum-gate MOS capacitors. As CV characteristics in Figure 4 show, device capacitance in accumulation scales with k-value of the film (k of ~16 for $HfSiO_4$, ~24 for HfO_2, and ~34 for $SrTa_2O_6$) and thickness of the dielectric film, which means that characteristics of the gate stack are controlled by high-k dielectric film. Current density-voltage measurements demonstrated leakage current of ~10^{-3} A/cm^2 at 1 V for effective oxide thickness (EOT) in the range of 1.5-2.0 nm, further confirming structural integrity of mist-deposited films.



3. TEM characterization of ~3 nm thick film of mist-deposited $HfSiO_4$.



4. Capacitance-voltage curves of Pt-MOS capacitors with three different mist-deposited high-k dielectrics.

These results demonstrate that, while the method of mist deposition may not be a solution to the problems of high-k dielectric MOS gate-stack manufacturing featuring EOT <1.0 nm, mist deposition of liquid precursors produces films that display structural, compositional and electrical integrity, even in the thickness regime below 5 nm.

Photoresist — This is the most widely used liquid precursor in semiconductor manufacturing. Consequently, photoresist deposition is considered to be the most obvious application for which the performance of mist deposition should be tested. Most likely, spin coating will remain a workhorse of photoresist technology in the future. However, in applications where its use may be limited, mist deposition may turn out to be an effective alternative. This modification of the resist processing is concerned solely with the way liquid resist of a given chemical composition is applied to the wafer surface, and does not require any changes in other aspects of resist technology.

Very promising early results of experiments with 1805 and UV-5 photoresists were presented earlier.[9] Mist deposition consistently produced smooth films of fully developable photoresist. A thickness variation of <2% across the 150 mm wafers was achieved with a resist thickness of ~100 nm. The deposition rate of diluted resists could be varied from ~10 to 50 nm/min, depending on the DC bias, and was weakly dependent on the resist dilution. Additional experiments carried out with 248 nm resist and a 248 nm stepper demonstrated that patterns down to 350 nm (which is likely the limit of the photolithography setup used) are sharply defined in the mist-deposited resist. Considering the fact that this experiment was performed without any extensive preparatory procedures, and the resist used was not an optimal choice for this particular process, the result is seen as very promising; further exploration of this deposition mode is warranted.

Other characteristics

Among other characteristics of mist deposition, the possibility of selective thin-film deposition should be emphasized. The concept of area-selective deposition using mist processes has been experimentally demonstrated in the deposition of Pt thin films using Pt nanoparticles suspended in solvent.[10] It is based on the selective changes of the surface energy of the substrate through localized predeposition surface treatments. Besides surface preconditioning, solvent selection plays a key role in the implementation of area-selective deposition through mist processing.

Compared with spin-on processing, mist deposition offers a certain degree of control over conformality of coating. The ability to cover surface features conformally is, in the case of mist deposition, a strong function of the precursor viscosity. On the other hand, mist deposition — in contrast to spin-on process — has a limited ability to planarize the surface, although surface smoothing or partial planarization is possible in the case of low-viscosity precursors. Moreover, because of the nature of the process, mist deposition is more sensitive than spin coating to the chemical condition of the surface, which determines surface energy, and hence, surface wetability.

Summary

The results discussed in this paper demonstrate the feasibility of mist deposition in the formation of very thin films in advanced nanoelectronic and photonic manufacturing using liquid precursors. In both cases of photoresist and high-k dielectric processing, deposition is well controlled and produces uniform, mechanically coherent films, even in the ultrathin thickness regime. The method is independent of the shape of the substrate, and hence, in the case of photoresist, can be used not only in standard wafer processing, but also in large display as well as large reticle manufacturing. Overall, mist deposition has the potential to supplement spin-on process in those applications in which effectiveness of the latter will be limited. By doing so, mist deposition may extend the use of liquid precursors in high-end IC, as well as LCD, manufacturing by supplementing spin-on processes in selected applications.

Author Information

Paul Mumbauer is a director of process engineering and technical services at Primaxx Inc. He obtained his Ph.D. in surface physical chemistry from Lehigh University in 1996. At Primaxx, his responsibilities include managing applications development for both additive and subtractive processes. He is also responsible for process equipment design and performance. E-mail: paulm@primaxxinc.com

Jerzy Ruzyllo is a professor of electrical engineering and materials science and engineering at Penn State University . He obtained his Ph.D. and served on the faculty at the Warsaw University of Technology in Poland. He does research, teaches, and extensively publishes in the area of semiconductor materials and device processing. He is a Fellow of IEEE and a Fellow of the Electrochemical Society.

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