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Liquid and Solid Precursor Delivery Systems in Gas Phase Processes

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Abstract: Due to attractive surface properties and to intrinsic brittleness of Complex Metallic Alloys (CMAs), most of their potential applications involve materials with high surface-to-volume ratios, including thin films and coatings. While physical vapor deposition techniques are efficient for the processing of CMA films on line-of-sight surfaces, chemical vapor deposition (CVD) is well positioned for their application on complex surfaces. However, for CVD process to be implemented efficiently in the processing of CMA films a number of challenges must be addressed. Because numerous CVD reagents, commonly called precursors, are low vapor pressure liquids or solids, one of these challenges is the production of vapors of such precursors, which are decomposed in the deposition chamber to provide the desired film. Such a production has to be ensured at high rate and must be reproducible and stable during the whole process. Actual solutions to this question involve (i) bubbling inert gas through thermally regulated liquid precursors, (ii) leaching the surface of fixed precursor powder beds, and (iii) in situ generating the precursor flow by passing a reactive gas through a thermally regulated bed of the metallic element to be transported. Such solutions neither may be satisfactory for actual R&D needs nor may be transferable to industrial environments. These reasons are in part responsible for the limited implementation of advanced materials (including CMA-based ones) in numerous industrial and hence societal needs. More recently, innovative solutions have been proposed to feed deposition systems based on vapor phase chemical techniques (CVD and Atomic Layer Deposition, ALD). Such solutions are Direct Liquid Injection (DLI) of dissolved solid precursors and also sublimation of the latter in fluidized beds or in elaborated fixed beds. Such technological responses show promise for industrial applications of CVD, especially for the deposition of metals and ceramic compounds for which the available molecular and inorganic precursors present low vapor pressures. This review provides an overview of the methods by which precursor vapors are transported to the deposition chamber. Early and recent patents dedicated to such technologies will be revisited and considered in the light of the deposition of multimetallic alloy coatings.

Keywords: CVD, chemical vapor deposition, CMA, coatings, complex metallic alloys, delivery system, fluidization, liquid precursor, solid precursor, sublimation, thin films, vaporization.

INTRODUCTION

Complex intermetallics, including Complex Metallic Alloys (CMAs) and quasicrystals, are a family of intermetallic compounds and phases which show excellent properties such as low adhesion (d-AlNiCo), catalysis (AlCuFeCr), hydrogen storage (TiCrV), and fretting (i-AlPdMn), friction (d-AlNiCo), oxidation (i-AlCuFeB) or wear (MgZnY) resistance (see [1] and references therein). For this reason, they can play a major role for the processing of innovative, advanced materials to face many societal challenges. Due to their brittleness in bulk form, however, there is a need for their processing as thin films and coatings.

Chemical Vapor Deposition (CVD) has been extensively used for preparation of films and coatings in semiconductor wafer processing [2]. CVD is a favored deposition process in many respects in comparison with Physical Vapor Deposition (PVD) technologies, in particular because of its ability to provide highly conformal and high quality films, at relatively fast processing times [3]. A variant of CVD being explored to deposit highly conformal nanometric films is Atomic Layer Deposition (ALD). ALD involves sequential steps of deposition from two reactive precursors alternatively injected.

Despite such generic advantages, tuning of CVD and ALD processes requires overcoming numerous difficulties, corresponding either to the complex involved chemistry, or to engineering aspects of the process. Among the latter there is the precise control of gaseous reactive precursors introduced into the process chamber, to produce the desired layer...
Various liquid precursors are successfully used in CVD/ALD applications by delivering the precursor vapor in a carrier gas. A common method is to bubble a carrier gas through the liquid at a controlled temperature in order to saturate the gas phase with the vaporized precursor. Such a bubbler requires that the involved compound has sufficient volatility at the bubbling temperature to enable compatible (high) flow rate of precursor vapors to the process chamber for a commercially viable process. In the early nineties Hersee and Ballingal proposed the well-known engineering formula allowing evaluation of the upper limit of the produced flow of the precursor in a bubbler [6]. According to this formula, the precursor flow rate is proportional to the carrier gas flow rate through the precursor and to the saturated vapor pressure of the precursor at the bubbler temperature, and it is inversely proportional to the difference between the total pressure in the bubbler (considered being the same as the one in the process chamber) and the saturated vapor pressure of the precursor at the bubbler temperature. At the same period Middleman explored the complex interaction among the thermodynamic and transport characteristics of such a bubbler in a steady-state analytical model, also considering the conductance of the flow path downstream of the evaporator [7, 8]. He focused on the operation of the bubbler at very low pressures where bubbles evolve, either from vapor or dissolved inert gases, may give rise to the entrainment of liquid droplets within the vapor stream. He analyzed the dynamics of mass transfer in such a situation and estimated the length of a tubing over which a droplet will evaporate. Ten years after, Mayer et al. developed a complementary analytical model to represent the liquid-gas interactions in the carrier gas bubbles formed in the precursor liquid during the time period from when the bubble pulls free of the sparger tube, to when the bubble breaks the liquid surface [9]. More recently, Senocq improved Hersee’s empirical model taking into account the bubbler efficiency [10, 11]. However, such mass transfer rate is difficult to control accurately [12]. Consequently, when different liquid precursors are vaporized, any uncontrolled variations in mass transport in the process streams may result in fluctuations in product stoichiometry.

Analogous attempts have been made to deliver vapors of solid powder reactants to a CVD reaction chamber using the sublimator/bubbler method. This procedure is often problematic because of the inability to deliver at a controlled rate a reproducible and stable flow of vaporized solid precursor [3]. Several factors including inefficient heat and mass transfer and the changing specific surface area of the powdered precursor decrease the efficiency of the sublimation process. A common problem encountered in CVD/ALD processing of films and coatings is a low deposition rate resulting either from a low vapor pressure of the liquid or solid precursor, or from transport issues associated with such low vapor pressures [11]. This relation is straightforward when reactor operation is in the diffusion limited regime, where growth rate is proportional to the availability of reactants in the gas phase. However, it may even impact operation in the kinetically limited regime and in ALD, if the availability of the reactants in the gas phase is lower than their consumption on the surface (starved reaction regime). This may be the case for high volume ALD reactors operating at short ALD cycles.

The relation between the saturated vapor pressure and temperature for pure components is described by the Antoine equations [13]. A low saturated vapor pressure of the precursor may be a thermodynamic consequence of the solid(liquid) - gas equilibrium. It can also be a consequence of premature, partial or complete decomposition of the precursor in the vaporization system upon heating, thereby limiting the vaporization temperature.

The development of new vaporization technologies based on DLI sources sought to overcome problems of uniform precursor delivery by dispensing a solution of the solid precursor into the reactor. Ideally the solvent will evaporate quickly upon entering the vaporization chamber leaving the gas phase precursor to deposit the desired film on the substrate. An advantage of this approach results from the fact that the precursor is maintained at a lower temperature (where it is stable) until it reaches the vaporization chamber. While one remains limited by the equilibrium vapor pressure, this is now higher due to the higher temperature of the vaporization chamber. Problems can develop if supersaturation leads to formation of precursor particles. In addition, introducing a large quantity of solvent into the reactor can lead to film contamination and raises environmental concerns. Furthermore, several low cost and potentially interesting solid CVD precursors cannot be vaporized by DLI sources because it is not easy and sometimes even impossible to dissolve them in an organic solvent [5].

Due to these reasons, a significant effort has been produced to tackle the question of robust, reliable, and reproducible introduction of precursor vapors in process chambers. This effort resulted in a series of patents rather than research articles due to the technological and commercial interest of the elaborated solutions. The golden age of this activity is centered in the last two decades of the 20th century and is compatible with the increased needs of the microelectronics, glass and steel industries for functional films with controlled characteristics. The present article provides an overview of early and recent patents dedicated to the various ways liquid and solid precursors can be vaporized and transported to CVD/ALD chambers. The liquid precursor delivery systems will be presented first, followed by solid precursor ones. The patents are organized in groups of similar technologies. Although many of the patents describe clever approaches to addressing the precursor delivery problem, they focus on product design and often present little in the way of quantitative measures of performance. Despite this, we believe this review will be valuable to groups seeking ways to improve the speed and reliability of vapor deposition proc-
ess for a variety of applications. Finally, we comment that throughout the review the figures were extracted directly from the patents and often include numbers identifying parts of the design that are not explained in the figure caption. Those interested in the details will need to go to the cited patents for a complete explanation.

LIQUID DELIVERY SYSTEMS

To improve the efficiency of heat and mass transport within the precursor system, the invention by Soubeyrand and McCurdy [14] incorporates a set of mixing blades that rotate inside the vaporization chamber, in order to distribute the liquid precursor as a uniform thin liquid film upon the walls. The chamber is flushed by an inert carrier gas with the aim to increase the precursor mass transfer, and the precursor vapor/gas mixture is evacuated through an outlet to the deposition chamber which can be suitable for CVD deposition. The examples of applications provided by the inventors reveal that this method is particularly devoted to the CVD glass coating in the float glass process.

The patent by McMillan et al. [15] describes an apparatus for generating fine mist of a stabilized liquid source or a stabilized solution of desired chemical compounds using one or more rotating turbine blades within a chamber. The turbine blades are fixed to the end of a rotating shaft, and rotate between 750 and 1500 revolutions per minute (rpm) in order to accommodate to various liquids. A mixture of a liquid and a carrier gas are flowed into this chamber; it impacts the blades and the resulting mist is withdrawn under vacuum to a deposition chamber. This turbine mist generator is to a large extent insensitive to parameters such as temperature and viscosity of the liquid, dilution, rate of volume of mist generation, etc. According to the inventors, it can reliably generate homogeneous fine mist over a wide range of conditions without adjusting the operating parameters. Alternatively, they also propose an ultrasonic mist generator: A constant level tank containing an ultrasonic transducer at its bottom. A carrier gas is flowed over the liquid surface and the resulting mist is transported under vacuum to the deposition chamber. The inventors claim that this device is more sensitive to experimental conditions than the turbine generator; for example it needs to be operated with more dilute solutions. In the given examples, precursors are isopropoxides of titanium, zirconium and yttrium, and lead and manganese acetates, and the solvent can be 2-methoxyethanol.

The invention by Ott and Kodas [16] aims at preparing films of multicomponent metal oxides. An aerosol of liquid droplets having diameters from about 0.1μm to about 10.0μm, is formed from solution(s) of suitable solvent and at least two precursors capable of volatilization below their decomposition point. Among suitable precursor molecules are substituted metal diketonates, halides or acetates. The metals can be rare-earth metals, barium or copper. No indication is given on the way to produce the aerosol. This is mixed with a suitable oxygen containing carrier gas (preferably an inert gas plus 1 to 10wt% oxygen), and the mixture is carried to a heated zone having a sufficient temperature to evaporate the solvent and volatilize the precursors. The resulting vapors are transported to the surface of the substrate to be coated. The temperature of the substrate is said to allow decomposition of the volatilized precursor(s) and to lead to the deposition of metal oxide. According to the inventors, this process is suitable for the in situ preparation of high critical temperature, multicomponent, superconductive metal oxide films. These are prepared on selected substrates (silicon, magnesium oxide, sapphire); they are uniform in thickness and predominantly C-axis oriented.

The patent by Ewing describes the use of several liquid pumps and automated valves to feed a vaporizer with a continuous and steady volumetric flow at a predetermined pressure, substantially independent of downstream pressure [17]. The vaporizer uses a stack of thin disks heated above the vaporization temperature of the liquid, to flash vaporize the liquid. The system is optimized by the use of one-way valves. Despite its mechanical complexity, the inventor claims that such a system is relatively simple and inexpensive, and that it can be connected to the processing chamber with no or few vapor flow lines and no additional inert gases lines. No indication is given about the use of solutions or pure liquid compounds. Comparison is given only with bubbler systems or pressurized heated vessels, and not with other pumping systems such as rotating pumps. This device can be used in a CVD process, as well in any process needing continuous and steady flow of vapors.

The patent by Kaloyeros et al. describes a process involving the use of liquid-source bubbler systems for the delivery of solid source precursors to a deposition chamber [18]. A precursor solution reservoir at room temperature is maintained at a preset pressure through an inlet of inert gas. The reservoir is connected to an atomizer through a dipping pipe, a micro pump and control valves. No precise information on the vaporizer is given, except that “A liquid delivery system flash vaporizer such as that manufactured by MKS Instruments may be used in the system to provide accurate and reproducible liquid flows”.

Versteeg et al. invented a liquid delivery system which involves one or more ultrasonic atomizing nozzles to inject
liquid precursor solution(s) directly into a CVD reactor chamber [19]. The delivery system operates either in a continuous or pulsed mode. The inventors claim that atomization in the deposition chamber allows complete vaporization of the liquid precursor and uniform deposition of the films on the substrates, and that the pulsed mode ensures control of the film deposition rates as fine as monolayers per pulse. The inventors describe the use of the system for the deposition of titanium dioxide from titanium tetra-isopropoxide dissolved in toluene delivered in a pulsed mode.

The invention by Boer is the first to introduce mixing and vaporization chambers between the metrology facility for the establishment of liquid precursor flow rate and the deposition area [20]. Such chambers are nowadays part of many liquid injection technologies. According to this invention, the supply of the liquid precursor is ensured through a passage (a chamber) positioned between an inlet and an outlet ports. A carrier gas is also supplied in the chamber at the outlet of the liquid passage, where thorough mixing of the liquid and the carrier gas is obtained. A dimensional variation of the inlet and outlet ports (the former being wider that the latter) and of the mixing space facilitates the complete vaporization of the mist. This is obtained in a heated vaporization space where the mixture is directed through to a second outlet, under pressure. Figure 1 shows a detailed sketch of a device according to the invention.

The invention by Klinedinst and Lester aims at providing an uninterrupted constant velocity flow of liquid precursor to a liquid vaporizer, and subsequently, to provide a controlled rate of the vaporized precursor to the deposition chamber [21]. The device consists of a restrictor element through which passes a flow of a liquid precursor containing dissolved inert gas. The dissolved gas is released and separated from the liquid precursor in a conduit at the downstream side of the restrictor element. In this way, a continuous flow of liquid precursor is created which is fed into an inlet of a vaporizer. The vaporized precursor is delivered into a low pressure CVD reactor. The efficiency of the invention is illustrated by a series of tests which consist in determining the flow of tantalum (V) ethoxide, [Ta(OEt)5]2 versus the pressure drop across the flow restrictor and the subsequent Ta2O5 deposition rate versus the pressure drop applied across the flow restrictor. In both cases the evolution of the measured parameter is linear with the pressure drop.

The invention by Li and Scott involves a modular vaporizing apparatus which is fed by a liquid precursor or solution of one or more precursors in a liquid solvent [22]. Upon introduction in the vaporizer, the precursor is first atomized by an ultrasonic nozzle. Then the created mist is vaporized through direct contact with a heated surface. This surface is provided by removable porous media disks, which may be varied according to the desired operating pressure and precursors. The vaporization takes place in a chamber whose inner walls are protected by an unheated curtain gas that prevents the atomized mist from contacting the inner walls. This prevents vaporization of the mist prior to contact with the heated surface, and transports the mist to the heated contact surface. Figure 2 is a schematic representation of the vaporizer system. The vaporized precursor is then mixed with a carrier gas and forced into a CVD reaction chamber.

The basic idea of the invention by Senateur et al. involves the pulsed injection of liquid precursor or a solution into a reactor that has a mechanism (e.g. two zones) to first evaporate the solution and precursor and, second, to transport them into the high temperature reactor where deposition may occur on the heated substrate [23]. The invention by Klinedinst and Lester aims at providing an uninterrupted constant velocity flow of liquid precursor to a liquid vaporizer, and subsequently, to provide a controlled rate of the vaporized precursor to the deposition chamber [21]. The device consists of a restrictor element through which passes a flow of a liquid precursor containing dissolved inert gas. The dissolved gas is released and separated from the liquid precursor in a conduit at the downstream side of the restrictor element. In this way, a continuous flow of liquid precursor is created which is fed into an inlet of a vaporizer. The vaporized precursor is delivered into a low pressure CVD reactor. The efficiency of the invention is illustrated by a series of tests which consist in determining the flow of tantalum (V) ethoxide, [Ta(OEt)5]2 versus the pressure drop across the flow restrictor and the subsequent Ta2O5 deposition rate versus the pressure drop applied across the flow restrictor. In both cases the evolution of the measured parameter is linear with the pressure drop.

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Yu et al. note that in many liquid delivery systems the liquid contains a low vapor pressure precursor (solid or liquid) dissolved in a high vapor pressure solvent [24]. Upon pumping this solution into a heated vaporizer, the more volatile solvent is rapidly vaporized. If the remaining mass of the low volatility precursor is such that its equilibrium vapor pressure is exceeded, condensation can occur leading to difficulties in maintaining a uniform feed rate into the deposition chamber. The solution proposed in this invention involves adding an independent feed of pure solvent to the vaporizer to maintain a higher solvent partial pressure. The inventors provide evidence that this serves to reduce the formation of residues with the system. In the particular set of precursors studied, Sr(dpm)2, where dpm = dipivaloylmethane, the solvent was isopropylamine. At the elevated temperatures reached in the vaporizer, it is possible
Fig. (2). Liquid vaporizer system (40) invented by Li and Scott [22]. It contains an ultrasonic nozzle 24 which receives liquid precursor from feed tube 22 mounted in an atomizer housing 12. A cooling jacket 26 surrounds the vaporizer apparatus segment for temperature control of nozzle 24. A curtain jack inlet port 28 is positioned adjacent the cooling jacket and creates a curtain of gas descending along the walls of the vaporizer as shown by the arrows. An expansion chamber 34 extends from the nozzle to the front face of a heated contact surface 48 in the form of a series of three porous disks 52, 54 and 56. The carrier gas heating chamber 72 surrounds the heating element 62 before passing into the contact surface where it mixes with the vaporized precursor.

that the solvent may also react with the precursor, which may also serve to reduce the formation of residue.

The patent by Loan and Salerno describes a delivery system that can be used with either solid or liquid precursors although the former requires minor changes to the design shown in Fig. (4) [25]. A primary goal of this design is to avoid the use of a carrier gas and to use mass flow controllers coupled with pressure measurement by capacitance manometers to deliver a uniform precursor flux to the reactor. The liquid precursor is loaded into chamber 20 (see Fig. (4), which is thermally insulated from the high temperature vaporization chamber [26]. As needed, precursor is dispensed through valve 24 onto the conical, heated surface [27, 28]. The precursor vapor is then pulled through port 32 into a gas-flow control subsystem that delivers a controlled, uniform flow into the reactor.

By generating an aerosol of charged droplets of a precursor solution, Solayappan et al. designed a delivery system in which the charged droplets can be size selected and accelerated to the substrate [26]. During operation the liquid precursor solution is pumped at a uniform rate through a venturi to create the aerosol. The aerosol droplets then flow past a corona wire in an atmosphere of an inert gas and oxygen, which induces a charge on the droplets. Size selection is accomplished using a particle inertial separator. Particles of uniform size provide better control of their velocities as they travel to the substrate. The negatively charged particles are accelerated towards a positively charged perforated plate to allow a portion of the particles to pass through to the substrate. Ideally, the charged plate is slightly larger than the substrate to allow uniform coverage over the entire surface. The substrate itself is grounded to minimize the effect of charge buildup.
The invention of Paz de Araujo involves venturi mist generators, one for each incoming liquid flow. This system is formed of various liquid precursors through liquid flow controllers to a vaporization zone, a vaporizer plate or a diffuser, which are based on an adiabatic expansion through the decrease of the atomized precursor met in traditional atomization processes. This setup avoids the drawback of temperature concentration along the substrate holder and the nebulizer. According to the inventors, this setup avoids the drawback of temperature concentration along the wafer, a vaporization zone, a vaporizer plate or a diffuser, which may be provided around the ultrasonic nebulizer. According to the inventors, this setup avoids the drawback of temperature concentration along the substrate holder and the nebulizer. This ring discharges a directionally situated, heated, "swiping gas" into the atomized precursor with the purpose assisting in the evaporation of the precursor droplets and directing them toward the substrate. This gas should have a high heat capacity and low molecular weight allowing for high binary diffusivity, which generally reduces evaporation time. To further ensure that the entire atomized precursor vaporizes before reaching the wafer, a vaporization zone, a vaporizer plate or a diffuser, may be provided around the ultrasonic nebulizer. According to the inventors, this setup avoids the drawback of temperature decrease of the atomized precursor met in traditional atomizers which are based on an adiabatic expansion through the use of a carrier gas pressure differential in the vaporization process.

The invention of Paz de Araujo et al. involves flowing various liquid precursors through liquid flow controllers to a mister/gasification system [12]. This system is formed of venturi mist generators, one for each incoming liquid flow stream. Each venturi mist generator has a liquid inlet, a carrier gas inlet and a mist outlet. Mist generators create a mist of small liquid droplets of liquid precursors in the carrier gas. If multiple liquid precursors are being atomized, then each venturi mister produces a mass flow rate of liquid equal to the liquid mass flow rate in the liquid inlet stream in order to control the overall stoichiometry. The mist streams containing the nebulized liquid precursors combine in a mist mixer containing baffles or other means to enhance mixing. The combined stream flows to a vaporizer to gasify the droplets at low temperature to avoid decomposition of the precursors. The gasified precursor stream flows to deposition reactor. If other than liquid vapor sources are used, they are combined after the gasifier to the gasified precursor stream. The mister/gasification system preferentially operates at atmospheric pressure. The CVD processes being preferably conducted at low pressure, at least two step-down stage valves are placed after the gasifier. Figure 5 presents a schematic view according to a preferred embodiment of the invention.

The invention of Brutti et al. concerns an apparatus for delivery of liquid precursor or precursors in solution into a CVD reactor [28]. The equipment is composed of an inlet head connected to an evaporation chamber, which is itself connected to a CVD chamber. The inlet head is equipped with at least one injector connected to an external tank filled with liquid precursor or precursor in solution. Each injector periodically sends predetermined quantities of droplets into the evaporation chamber in which the liquid/vapor state change takes place. The injector is formed by a solenoid valve, which allows accurate reproducible control of the volume injected. The injector can also be replaced by a spray nozzle delivering a continuous or pulsed aerosol flow of precursor. In this case, a liquid regulating flow meter is fitted between the tank and the nozzle. The evaporation chamber is designed with internal channels and porous sintered glass plates to reduce the size of droplets and increase the heated surface with the aim to vaporize all the liquid before the outlet. To prevent any condensation of the evaporated products on cold zones of the evaporation chamber, a carrier gas is injected into the chamber simultaneously with the liquid injection to enable optimum evaporation and efficient transportation of the vapors of precursor to the CVD reactor. Figure 6 presents a longitudinal sectional view of the evaporator apparatus according to this invention, which is equipped with two injectors.

The invention of Hillman et al. concerns a precursor vapor delivery system including a diffuser preferably conical in shape, whose larger bottom open end communicates with an opening at the top of a CVD reactor, possibly by a shower head [29]. The diffuser has a smaller top upper part to which is connected a high conductance vaporizer. The vaporizer has a precursor temperature control including an isothermal heat source and a temperature control to vaporize liquid precursor droplets. The top of the vaporizer is connected to an atomizer through which droplets are delivered to the vaporizer. A source of liquid precursor is connected through a liquid delivery line to a flow control device at the top of the atomizer. A source of inert sweep gas such as argon is connected to an inlet port of the atomizer. The sweep gas is

Fig. (4). Cross sectional illustration of a vaporization subsystem of the invention by Loan and Salerno [25].
Fig. (6). Longitudinal sectional view of the evaporator apparatus 10 for liquid delivery of reactants into a CVD chamber, according to the invention by Brutti et al. [28]. It comprises an inlet head 12 connected to an outlet tube 14 via an evaporation chamber 16. The inlet head is equipped in this illustration with two injectors 18 having an inlet 20 connected to an external tank filled with liquid precursors or precursors in solution. Each injector 18 periodically sends predetermined quantities of liquid into the evaporation chamber 16, in which the liquid/vapor state change takes place.

Introduced at a temperature between 60 and 90°C. The atomizer is provided with an exhaust port, which can be connected to a vacuum pump to allow the flow of sweep gas to bypass the CVD chamber during transient operations. The vaporizer can be formed of a series of concentric cylinders of progressively increasing diameters so that the cross-sectional area of passage into the reaction chamber increases along the flow path, in order to increase the amount of vaporized droplets; i.e. the conductance of the vaporizer. The novelty of this system is the presence of a vaporizer in integral communication with the CVD reactor, the vaporizer having a high flow conductance path of progressively increasing volume for atomized precursor to the CVD chamber.

The invention of Sun and Liu is based on the transformation of the liquid precursor or precursor solution into an aerosol composed of small and larger liquid droplets [30]. The aerosol generator operates at room temperature to avoid thermal degradation of the precursor. According to this invention, a compressed carrier gas enters a passageway having an orifice or nozzle at the inner end to form a jet that aspirates the liquid precursor arriving by another passageway. The liquid is broken into droplets to form a high velocity aerosol stream. This stream, in the form of a spray moves into a vaporizer having heated interior walls so that the carrier gas is heated rapidly in order to “flash vaporize” droplets of the aerosol. By this way, very few aerosol droplets directly contact the interior wall surfaces to minimize the precursor decomposition and crust formation and clogging. The
The resultant gas/vapor mixture is finally introduced into a downstream CVD reactor by passing through a restriction causing turbulent mixing of the gas/vapor mixture and a heated gas filter to collect any particulate contaminant. The carrier gas and the liquid precursor can also be introduced into an ultrasonic aerosol generator that provides vibrational energy at high frequency to break up the liquid into droplets. The vaporizer is capable of providing a stable source of vapor of uniform composition at high vaporization rate to the CVD reactor to obtain uniform coatings.

The invention by Westmoreland and Sandhu deals with the management of a nonvolatile CVD precursor through the dissolution in a solvent of moderate to high vapor pressure at room temperature [31]. In contrast to commonly admitted organic solvents, inorganic ones are used here, in order to avoid large carbon residue when processing temperature is high. These can be liquid ammonia, liquid NO₂, SO₂, TiCl₄, SF₆, or SiH₂Cl₂, depending on the materials to be deposited, on the involved chemistry and on the processing conditions. Also, instead of involving a vaporization chamber, the solution is transported at an elevated pressure and/or reduced temperature directly to the CVD chamber. The solution can be either evaporated upon introduction in the processing chamber or, in contrast it can be in contact with the heated substrate (wafer). The expected result in the latter case is the vaporization of the solvent and the formation of the targeted thin film. Typical precursors mentioned for the processing of such films are bis(cyclopentadienyl)titanium dichloride, cyclopentadienyltris(diethylamido)titanium, zirconium tetra-chloride, indenyltris(dimethylamido)zirconium or tungsten carbonyl.

The invention of Liu et al. concerns an apparatus forming an aerosol from a liquid source for vaporization and subsequent thin film deposition on a substrate [32]. A piezoelectric actuator allows adjusting the rate of the liquid flow from the liquid source. A compressed gas source containing a carrier gas is used for atomizing the liquid. When the gas source conjoins with the liquid, an aerosol is formed in a heated vaporization chamber. The resulting gas/vapor mixture then flows out of the vaporization chamber into a deposition chamber. The atomizing system consists of a small metal capillary tube through which the liquid flows and the gas source flows are organized outside the tube to form a high velocity gas jet (between 30 and 350m/s) at the exit of the capillary tube forming a spray of fine droplets in the heated vaporization chamber. As is the case for other inventions, solid precursors having a high vaporization temperature (in the present case the inventors mention 350°C) must be dissolved into a solvent and then atomized to form droplets to vaporize both the solvent and the precursor.

The invention of Marsh and Atwell relates to a vaporizer including a liquid precursor injector and a heater that is connected to a reaction chamber [33]. Precursor storage, solvent storage and optional carrier gas storage are connected by supply lines and inlet valves respectively to the injector, to a solvent port and to a carrier gas port of the vaporizer. The system can include a flow sensor in the precursor supply line and/or a precursor concentration sensor at the vaporizer or at the reaction chamber. A schematic diagram of the system during normal operation, in accordance with an embodiment of the disclosure is presented in Fig. (7). It is worth noting that to start a maintenance procedure, the controller can stop

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**Fig. (7).** Chemical vaporizer for material deposition systems by Matsh and Atwell [33]. Schematic diagram of the system during normal operation, in accordance with an embodiment of the disclosure. The system 10 includes a reaction chamber 20 and a vaporizer 30 for vaporizing precursor 11. 20 and 30 are connected by a delivery line 21. The latter contains an inlet valve 54 to regulate precursor flow to 20. The vaporizer includes a heater 31 and a heater control 35. The diagram illustrates the precursor (38), the solvent (40), the carrier gas (44) and the waste (50) storages.
all material flow into the vaporizer, command the heater to
reach a maintenance temperature and open the solvent inlet
valve to remove the residue from the injector and vaporizer.
By tuning this procedure, the authors discovered that vapor-
ized solvent better removes residue from the injector than
liquid solvent. It is believed that this is due to the existence
of solvent reflux (i.e. evaporation/condensation cycles) in the
vaporizer. This cleaning process is cost-effective because the
injector can be efficiently cleaned without removing it from
the vaporizer. It is worth noting that servicing of injector
technology may be frequent, necessary and significant due to
undesirable reactions or phase transitions in the vaporization
chamber, which often affects process reproducibility and
reliability.

SOLID DELIVERY SYSTEMS

Shenai-Khatkhate points out the problems of delivering
steady feed of precursor vapors to the processing chamber.
The unsteady precursor flow rate is attributed, among other
factors, to the progressive reduction of the exchange surface
of the precursor, inefficient and non-uniform carrier gas flow
through the precursor bed and channeling through it, leading
to preferential flows and reduced contact of the carrier gas
and precursor [34]. To circumvent this problem, the inventor
proposes a setup which looks equivalent to a conventional
bubbler for the vaporization of liquid precursors, but pres-
ts significant differences. A cross sectional illustration of
such a delivery device is presented in Fig. (8). The invention
involves a downstream flow of carrier gas through a layer of
packing material (0.25mm to 1mm particle size) displayed
over the precursor bed, the exhaust outlet of the precursor
plus carrier gas flow being at the bottom of the precursor
bed. The author claims a reduced formation of channel for-
mation in the precursor bed, and a consistent and stable con-
centration of precursor in the vapor phase without the need
to overheat it.

The invention described in another patent of Shenai-
Khatkhate et al. involves modification of the interior of a
traditional precursor vessel such that two chambers are pre-
sent within the vessel [35]. One chamber contains solid pre-
cursor along with a layer of packing material. In most em-
bedments the packing material is located on top of the pre-
cursor layer, and the carrier gas flows first through the pack-
ing layer then through the precursor layer. The packing layer
may be inert beads or other shapes of various diameters. An
unusual component of the invention is the conversion of the
particulate precursor into a porous frit. This is accomplished
by heating the precursor to the point where adjacent particles
fuse to one another, at most 5°C below its decomposition
temperature. The porous frit creates a tortuous path for the
carrier gas that can assist in saturating the gas with precursor
vapor. The precursor chamber is separated from the collection
chamber by an inert porous element. In a separate em-
bedment of this design the composition of the packing layer
may be modified to include a material that removes water
and/or oxygen from the carrier gas, thus improving the sta-
bility of the precursor. The packing layer can be separated
from the precursor layer as described above or mixed with
the precursor layer.

Suzuki et al. invented a method for preparing a solid pre-
cursor for use in an adapted evaporation system [36]. The
method consists in sintering or stamping the precursor pow-
der to form solid tablets. The tablets are placed in a solid
precursor evaporation container, which is composed of a
number of horizontally positioned annular trays with an axial
opening. Their diameter can be as high as 99 % of the inner
one of the container, with typical dimensions being 20cm
diameter, 2cm inter-tray spacing. Precursor vapors are pro-
duced by heating the evaporation system while flowing a
carrier gas radially, at different heights, from the inner walls
of the container towards the center of the container over the
trays and then axially upwards through the central opening
which is connected with the film process chamber via high
conductance tubing. Typical examples concern metal deposi-
tion from solid metal carbonyl compounds.

The invention of Chaubey and Xu [37] is comparable
with the one by Suzuki et al. [36]. It is schematically pre-

Fig. (8). Cross sectional view illustrative of a delivery device pat-
ented by Shenai-Khatkhate [34]. It presents a dip-tube 21 connected
to the gas outlet and having a porous frit 22 disposed at its lower
end. The solid precursor 27 is stacked at the bottom of the cylinder
with a packing material 26 disposed thereon. The carrier gas enters
the container, being saturated with the precursor vapors and exits
the container through the gas outlet opening 20.

sent within the vessel [35]. One chamber contains solid pre-
cursor along with a layer of packing material. In most em-
bedments the packing material is located on top of the pre-
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from the precursor layer as described above or mixed with
the precursor layer.
Similar to Chaubey’s one, the invention of Cleary load equal or better than 90% at constant output. A successful design typically ensures yield of the original which attains 100% utilization of the precursor load. A sufficient time/surface to saturate the carrier gas. Precursor upstream trays vanished, the downstream trays may not have stream trays deplete first. With the contribution from the beginning of operation, the entire vessel is evacuated and are evacuated to a process chamber. This system prevents the formation of channeling in the stacked powder during sublimation and thus ensures high and constant exchange area. Monitoring of the consumption of the precursor is ensured by various technical solutions such as weighing the vessel or infrared sensors.

In the invention of Sandhu et al., a temperature-controlled precursor vessel is charged both with solid precursor and with inert solid particles such as ceramic beads that are approximately 1 to 2 mm in diameter [42]. The size of the beads is chosen to facilitate circulation of the carrier gas through the mixture. An impeller serves to mix the inert beads and the precursor and helps to distribute the heat evenly. The mechanical action also serves to create fresh surfaces for sublimation throughout the process. At the beginning of operation, the entire vessel is evacuated and sealed. Applying heat to the closed system promotes sublimation of the precursor particles and condensation onto the ceramic beads (as well as the vessel walls). Spreading the precursor evenly over the surfaces promotes a more uniform sublimation rate.

Tasaki et al. based their patent on the concept that sublimation of a precursor film distributed evenly over an inert surface (as opposed to a powder) would produce a more uniform flux of gaseous precursor because the precursor surface
area would remain constant [43]. In one example, 10mm diameter glass spheres were dipped into molten precursor, removed and placed within a precursor vessel or packed into a tube through which flowed the carrier gas. Increasing the surface area of the inert spheres by the addition of a large number of smooth, hemispherical protuberances on their surface produced the expected effect of increasing the precursor flux. In a separate embodiment, the inventors coated precursor onto the surface of smooth steel discs, which were then stacked into a chamber that allowed a flow of carrier gas to entrain the gaseous precursor during operation. In addition to addressing the problem of a continuous change in the surface area of a precursor in powdered form, the embodiments of this patent in part help to address the problem of temperature non-uniformity because the precursor itself constitutes only a small portion of the mass within the precursor vessel.

In a design made to minimize the heat transport non-uniformity often encountered within a precursor vessel, Lei added heated baffles, rods, gratings or meshes to the interior of the precursor vessel onto which the precursor was coated [44]. This increases the surface area of the precursor, which will increase the rate at which the equilibrium vapor pressure is reached. By distributing the precursor in a layer over the heated surfaces a more uniform temperature may be maintained. The precursor can be applied to the surface by any one of a number of methods including dip-coating from solution or a melt or by compressing the precursor onto the surface. The patent notes that use of a rough surface of the heating element aids in precursor adhesion. In addition, by avoiding the use of a free-flowing powdered precursor, particle transport into the deposition zone is minimized.

In this invention of Derderian an intermediate, collection/delivery chamber is placed between a traditional, heated precursor vessel and the reactor [45]. At the start of the process the main precursor storage vessel is heated to sublime precursor, which is then condensed on the initially cooler surfaces within the intermediate chamber. After collection of sufficient precursor is complete, the collection/delivery chamber is heated and valves are opened to direct the flow of carrier gas and precursor vapor into the deposition chamber. The interior of the collection/delivery chamber is equipped with fins to increase the surface area. This has two effects. First, for a given thickness of precursor deposited, it both increases the amount that can be deposited and creates a greater flux of precursor vapor during the subsequent sublimation stage. Second, by maintaining a relatively thin precursor film, the precursor mass will be small allowing more effective control of the temperature. By providing a source of freshly sublimed precursor this invention will improve the uniformity of the precursor mass flow into the reactor compared to a traditional, heated precursor vessel because the portion of degradation products deposited within the collection/delivery chamber will be minimized. The inventors describe a modification of the design that incorporates multiple collection/delivery chambers connected in parallel so that one chamber can be filled while the other is being used to deliver precursor to the reactor.

The invention of Wang et al. describes a vapor delivery system comprising a vaporization vessel enclosing an interior volume that can be heated to vaporize the precursor, an inlet port for introducing the precursor, and an outlet port for discharging the precursor [3]. A process chamber is connected downstream the outlet port. A mass flow controller or a constant flow control valve can be placed in the vapor line to provide a controlled flow of vaporized source material. The vaporization vessel has a shape to facilitate the easy mixing of a carrier gas with the vaporized source material, i.e. a sphere, ellipsoid, barrel, cylinder, cone or combination of these shapes. It can also be a Knudsen cell in order to provide a controlled and constant flow of vaporized source material to the deposition reactor.
in a patent by Brcka the precursor is placed in a heating chamber containing a collection of concentric solid precursor cylinders supported on a gas distribution plate and configured in order to deliver a constant surface area to the carrier gas as the precursor is sublimed [46]. Figure 12 presents in cross-sectional view this system. The cylindrical solid precursor can be prepared by numerous processes, including sintering, stamping, dipping or spin coating process on cylindrical bodies, as these bodies can be heating elements. The flux of precursor out of the vaporization system is directly proportional to the exposed exchange surface, and when the inner and outer surfaces of the cylinders sublimate at the same rate, the evolving surface area of each cylindrical body remains constant. In such conditions, a constant flux of precursor vapors can be achieved.

In the six patents previously mentioned, the inventors shape the precursor powders by applying them on the surface of foreign supports or shape the vaporization vessel with the main objective to increase and maintain unchanged the surface area of the solid precursor. In the next three patents, the inventors deal with the low lifetime of the precursor at the face area of the solid precursor. In the next three patents, the main objective to increase and maintain unchanged the surface area of the solid precursor. In this way, the surface is vaporized without heating the entire volume of the precursor such that substantially no thermal decomposition of the remaining compound occurs. The vaporized portion of the precursor is then transported to a CVD or ALD chamber.

The invention of Dando et al. also concerns the management of the thermal stability of thermally sensitive solid or liquid precursors during their exposure to elevated temperatures [39]. This is often the case when a chemical ampoule or other vessel is continuously heated to maintain an elevated vapor pressure of the precursor. Such long term exposure of the entire quantity of the precursor to elevated temperatures may result in its decomposition. The inventors tackle this problem by controlling the rate of vaporization exclusively at the surface of a precursor bed. To achieve this, they propose a method in which a precursor vaporizer in the form of an energy source; i.e. a gas, a radio frequency coupling device, or an infrared irradiation source, interacts with the surface of the precursor. In this way, the surface is vaporized without heating the entire volume of the precursor that substantially no thermal decomposition of the remaining compound occurs. The vaporized portion of the precursor is then transported to a CVD or ALD chamber.

The invention of Leusink is based on the need to reduce or eliminate maintaining the solid precursor at a high temperature in order to provide the desired supply of the precursor vapor [48]. The patent describes a process based on light-induced vaporization of a solid precursor. The vaporization system is configured to hold a solid precursor that is irradiated by a light source through an easily replaceable window. In general, the desired frequency of the light depends on the type of precursor to vaporize. If the energy of the light is too high; i.e. wavelength too low, premature dissociation of the precursor can take place in the precursor vaporization system instead of the desired vaporization of the precursor. The precursor vapors are flushed to the deposition chamber, through a distribution plate, by an optional carrier gas line, as the deposition chamber is maintained at reduced pressure. According to this invention, the solid precursor may be main-
tained at a temperature lower than what is needed for conventional thermal vaporization. This reduces premature decomposition and possible recrystallization of the precursor in the precursor vaporization system while providing the desired supply of the precursor.

The patent of Tuominen et al. describes a method to improve the efficiency of a sublimation chamber fed by a carrier gas [49]. Chemically inert and thermally conductive elements (powder, rods, fibers) are inserted in the solid precursor bed and enhance the thermal exchange surface and the temperature homogeneity in the bed. A microwave heating device can be used. This configuration decreases the overheating of the precursor, the crust formation over its surface and enhances its sublimation. The precursor sublimation rate uniformity is improved, and the amount of unused precursor is minimized.

The invention of Atwell and Vaartstra concerns a dispensing device for providing an electrically charged precursor spray into a vaporization zone. Once in the vaporization zone, a heated element having a second electrical charge opposite of the first attracts the charged precursor droplets or particles towards the hot surface whereupon vaporization occurs [50]. The aim is to have little unvaporized spray in the vaporization zone and on the walls. Figure 13 schematically illustrates this invention. The dispersing device is an electrostatic spray device that converts a liquid or solid (powder) precursor into an aerosol. The vaporization of the precursor can be controlled by adjusting the temperature or pressure of the vaporization zone. A detection device detecting the concentration of unvaporized precursor spray can be placed in the vaporizing apparatus. A CVD chamber receives the vaporized precursor. This process provides highly reproducible vaporization of precursors for CVD processes. Precursors sensitive to decomposition near the vaporization temperature can be used. However, it is worth recalling that suggested commercially available electrostatic sprayers may use voltages as high as 100 kV DC.

Efficient ways to feed process chambers with stable precursor flow also include minimizing the distance between the vaporization and the process chambers and establishing a regulation loop on the precursors flow. This approach was adopted in the next four patents. Brcka invented a CVD system in which the precursor sublimation unit is integrated with the process chamber [51]. This unit comprises a housing positioned above the process chamber and supports a precursor tray. The tray is coupled to a carrier gas supply system configured to flow the gas through the precursor, through the annular space between the tray and the housing, and through the opening in the bottom of the housing, which is aligned with an opening at the top of the process chamber. The invention also includes a precursor valve system disposed in the annular space configured to open up or to close off the flow of the precursor vapor to the deposition chamber. In addition, a baffle plate may be positioned between the sublimation system and the process chamber to ensure homogeneous distribution of the precursor gas above the substrate. Figure 14 schematically illustrates this invention. The provided example concerns sublimation of ruthenium carbonyl Ru₆(CO)₁₂ for the deposition of Ru to serve as a barrier layer in Cu integration schemes in microelectronics.

The invention of Sandhu mostly deals with monitoring a precursor gas flow rather than with generating precursor vapors itself [52]. It consists in a flow monitor to measure and regulate the flow of sublimed solid precursor from the sublimation to the deposition chambers. The flow monitor chokes the supply of vapor to the deposition chamber to regulate the vapor flow. To avoid condensation of the solid precursor in the delivery lines or the flow monitor, the vapor flow measured by the monitor is fed back to a microprocessor based controller arranged to adjust the supply of the vapor available at the inlet of the flow monitor. This is achieved by acting on a fast response heater in the sublimation chamber, and on a valve positioned upstream of the flow monitor. The former affects rapid changes to the sublimation temperature while the latter adjusts the amount of excess vapor siphoned by the valve.

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**Fig. (13).** Block diagram illustration of a vapor deposition system (10) including the CVD precursor vaporization apparatus (12) patented by Atwell and Vaartstra [50] that delivers a vaporized precursor to process chamber (14). The illustration includes an electrostatic dispensing device (16) which provides a charged precursor spray into the vaporization zone (20).
In the invention of Ganguli et al., the precursor initially stored in a vessel as a solid, is sublimed by heating and is delivered to a process chamber by flowing a carrier gas into the vessel [4]. In a similar way as in the patent of Sandhu [52], a solid precursor delivery monitor (SPDM) is disposed in-line between the vessel and the process chamber. It is composed of a gas analyzer (typically a FTIR spectrometer) giving the precursor gas density and of a flow meter giving the volume flow rate of the process gas. A controller calculates a mass flow rate of precursor based on these two signals. The vessel may be any suitable container capable of withstanding the pressure and temperature required to sublime the precursor.

The invention of Oosterlaken is based on the concept that metering precursors in a liquid state can be more accurate than in a vapor phase, and that liquid state injection allows for larger doses of precursor to be delivered to the reaction chamber [53]. The solid precursor is melted by heating in a storage container. The liquid precursor is flowed into an intermediate liquid holding container and then to an intermediate, evaporation chamber in order to vaporize and finally delivered into a reaction chamber. This process requires precursors having a melting point lower than their decomposition temperature. To prevent long-term heating and reduce thermal degradation of the precursor, only the lower part of the storage container can be heated or multiple storage containers can be used among which only a part of them are heated.

Bauch and Gudgel claimed for their invention maximum simplicity and reliability while avoiding precursor condensation [54]. According to this invention, a storage vessel for a solid and/or liquid precursor, at room temperature is connected through a line to a mass flow controller and then to the inlet of a vacuum pump, the precursor being admitted in the pump at a pressure $P_m$. A carrier gas is admitted in the pump, through a second mass flow controller, and the compressed gaseous mixture at a pressure $P_{out} > P_m$ is evacuated to the process chamber. The entire process is computer monitored by pressure sensors and valves inserted downstream of the pump output, in order to keep the precursor partial pressure below its saturation point. In order to assist the precursor, one development of the invention could be to heat the connecting lines and the storage vessel, and the temperature of these devices could be computer monitored. The inventors do not elaborate on the stability of fragile precursors in pumps environment, especially in the high pressure stages and in the presence of lubricants.

A recent delivery system patented by Woelk and co-workers [55] involves dividing the carrier gas flow into two separate streams. One of the streams is heated and flows through a chamber containing the solid precursor. The second stream bypasses the precursor chamber and is combined with the first stream as the first stream emerges from the precursor chamber. This split carrier gas flow design is claimed to offer some important advantages. First, the mass flow rates of the two streams can be independently controlled allowing a lower flow rate through the solid precursor. The lower flow rate can minimize the formation of channels within the precursor bed and thereby lead to the generation of more uniform concentrations of precursor in the gas phase. The second advantage of working with two separate carrier gas streams results from mixing the two streams after one has been saturated with the precursor. The resulting dilution of the precursor reduces the likelihood that solid precursor will condense on the hardware leading to the reactor.

Atomic layer deposition (ALD) reactors require rapid (often fractions of a second) switching among the two (or more) precursors and the purge gas. When low vapor pressure solid precursors are used, they must be volatilized using elevated temperatures and mechanical valves can provide a site for unwanted condensation leading to clogging. As part of their design of an atomic layer deposition (ALD) reactor, Suntola et al. invented a solid precursor delivery system that has no mechanical valves placed between the precursor and the deposition zone [56]. During the delivery pulse, inert gas valving is used to flow the carrier gas over the solid precursor (located at “M” in Fig. (15)) and into the reactor. The precursor delivery pulse is halted by discontinuing the flow of carrier gas through the valve labeled 44 and initiating a carrier gas through the inlet labeled 49. The reverse flow exits the system through the vacuum pump labeled 50. Cooling coils (labeled 48) are added to condense the gaseous precursor before the carrier gas enters the pump.

Fig. (14). Schematic illustration of an embodiment of the invention of Brcka [51]. The precursor delivery system 105 above the process chamber 110 contains the precursor bed 175. The introduction of the precursor vapor to the process chamber is ensured through the openings 136 and 137. A vapor distribution system 130, including the baffle plate 134 is positioned between the precursor delivery and the process chambers, which can be isolated from each other by a valve system 180.
One of the most efficient ways to improve the transport phenomena in gas-particle systems is the use of fluidized bed (FB) technology. In the invention of Henery fluidization is dissociated from sublimation [57]. According to this invention, a fluidization chamber at a temperature below the vaporization temperature of the precursor allows heating the powder precursor by flowing a gas. An outlet conduit allows the fluidizing gas and suspended or dispersed particulate solid precursor to be drawn from the fluidization chamber. Connected to this conduit, a vacuum ejector (aspirator) allows a mixture of the fluidizing gas and particulate solid precursor to be withdrawn from the chamber and mixed with an additional volume of diluent gas at a second, higher temperature but lower than the precursor decomposition temperature. This particle/gas mixture is admitted to a vaporization chamber from which the diluted precursor vapors are distributed through nozzles to the substrate to be coated by CVD. This is one of the very early patents on sublimation involving fluidization of precursor powders. It does not deal with the question of particle elimination from the feeding gas prior to introduction to the process chamber.

The first who adapted this technology for the simultaneous sublimation of solid precursors and the transport of their vapors to a process chamber are Vahlas et al. [58] in this invention, the traditional precursor vessel is replaced by a fluidized bed system in which the solid precursor or a mixture of the solid precursor and inert particles are subjected to a carrier gas flow sufficient to fluidize the entire mixture. Fluidized bed reactors are renowned for their ability to maintain uniform mass and heat transfer behavior throughout a reactor comprising solid particles and gaseous components. This overcomes many of the problems associated with traditional precursor vessels and leads to a uniform precursor mass flow into the CVD/ALD reactor. Figure 16 schematically illustrates this invention.

In appropriate conditions of gas flow rate, a fluidized bed is obtained; i.e. powder behaves as a fluid, due to intense mixing of particles generated by the gas flow. In particular, high thermal and mass transfer rates exist inside the fluidized bed, ensuring quasi-perfect isothermal conditions to the particles. These high transfer rates explain that when heated at an appropriate temperature in a bed fluidized by an inert gas like nitrogen N₂, the precursor powder is sublimed providing high, stable and fully reproducible vapor concentration. Even with carrier gas flows as high as a few tens of standard liters per minute (slm), it is possible to maintain precursor concentrations at saturation.

Precursor transport efficiency measurements were performed using aluminum acetylacetonate (Al(acac)₃), a low vapor pressure compound used as a precursor for the CVD of alumina films. Inert corundum (alumina oxide) particles and Al(acac)₃ powder were charged to the fluidized bed sublimator Fig. (16), which was maintained at 120°C throughout the measurements. The results are presented in the two diagrams of Fig. (17). Figure (17a) presents the evolution of the flow rate of Al(acac)₃ in g/h as a function of the carrier gas, N₂ flow rate in slm. A linear evolution is observed, revealing precursor saturation of the gas phase, even at very high N₂ flow rates, namely 14 slm. Figure (17b) presents the evolution of the mass flow rate of Al(acac)₃ as a function of working time for a flow rate of N₂ equal to 10slm. A constant flow rate is observed for more than 80 h of operation, corresponding to a compound consumption of 28g, to be compared with the initial mass of 52g. The reported uncertainty in this diagram is due to the adopted technique for the determination of the quantity of the sublimed vapors. This consists in condensing them at the exit of the sublimator in a series of cold traps, which present a high, but not perfect trapping efficiency. In Fig. (17b), the evolution of the flow rate of Al(acac)₃ as a function of working time is also presented for a classic, fixed bed sublimator operating in the same conditions as the fluidized bed one except that the initial precursor mass is in this case 10g. It can be observed that the flow of the sublimed Al(acac)₃ at the exit of the fixed bed sublimator rapidly decreases with time due to the formation of channels in the packed powder where the carrier gas preferential passes through.
A particularly similar invention has recently been reported by Snijders and Raaijmakers [59].

In the later diagram, diamonds and squares correspond to sublimation in a fluidized bed and in a fixed bed, respectively.

A particularly similar invention has recently been reported by Snijders and Raaijmakers [59].

Despite the strong potential of fluidized bed sublimators, there are but few chemical compounds which can be fluidized in the as received state. While mixing with inert, easily fluidizable powders is a convenient solution to overcome this drawback, a complementary one could be the interaction with chemicals suppliers with the aim to provide powders of such compounds whose characteristics are compatible with the fluidization requirements.

CURRENT & FUTURE DEVELOPMENTS

A fundamental review of technical approaches to generate vapor phases form liquid or solid precursors was presented. This issue is important for gas phase chemical deposition processed such as chemical vapor deposition or atomic layer deposition. The selected technical developments cover main solutions proposed since nineties. Progress is continuing in this field with new inventions being patented every year.

The patents reviewed in this article provide details about invention designs, but few provide quantitative transport measurements and information on the organic precursors tested. This lack of data makes it difficult to compare and proceed to the selection of the most appropriate device for a given precursor and overall to the design of CVD systems or other processes that require precursor delivery. At the core of many of the designs, the inventors focus on a common set of issues. First, the design should maximize the precursor mass flow rate into the deposition zone. Second, the design should allow the precursor delivery rate to be uniform over the length of the deposition process. Third, the design should allow the precursor delivery rate to be reproducible from one run to the other, operated in the same conditions. Fourth, the design should maximize the precursor stability by storing it well below the temperature that is ultimately needed to vaporize it. Finally, the precursor delivery process should minimize the introduction of impurities into the film, including particles.

For high vapor pressure liquids, such as trimethylaluminum, traditional bubblers work well. For low vapor pressure liquids many of the patents describe methods to store the precursor at lower temperature, then pump the liquid as needed into a vaporization chamber and transport the vapor into the deposition zone. A variety of methods convert the liquid flow into an aerosol as it enters the vaporization chamber. The small aerosol droplets evaporate quickly leading to a carrier gas saturated with precursor. Precursor delivery rates can be controlled and sustained by regulation of the liquid flow.

Solid precursor delivery creates special challenges associated with constantly changing precursor surface area, undesirable temperature gradients and channeling of the carrier gas within the precursor powder. A common solution to this problem involves dissolving the solid in a suitable solvent and using one of the liquid precursor delivery systems to dispense the solution into the vaporization chamber. As long as the solid is stable in solution and the solvent does not introduce impurities, this is a reasonable approach. Here, the question arises as to whether vaporization is congruent or it mainly concerns the solvent. In the latter case, part or the entire precursor is re-condensed in the vaporization volume, leading to inefficient yield of the process and to frequent and time consuming maintenance of the vaporization equipment. An alternative approach to make the solid behave like a liquid is, by definition the use of fluidized bed technology. In such a way, a uniform precursor flux is directly created from the solid. Between these two cases, some of the designs describe methods to spread the solid precursor over a larger area either as a fixed powder bed or a thin coating. The common objective of all sublimation based technologies is to increase the surface area, to maintain it constant, and either to ensure uniform heating or, alternatively, to minimize the thermal load of the precursor by local or temporary heating.

Last but not least, the more the apparatus is complex, the more the requirements for servicing are high. Such servicing may include frequent interruption of the operation and/or replacement of sensitive parts, such as filters or injectors. It is critical in the case of change of the nature of the precursor.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.
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