FEATURE

Solvent-Free Method for Intense Vaporization of Solid Molecular and Inorganic Compounds

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New tools have been developed for vaporization of solid precursors to meet the demands of high feed rate for CVD, ALD and other deposition processes.

Chemical vapor deposition (CVD) processes have been extensively used in microelectronics for more than thirty years. Atomic layer deposition (ALD) has been more recently developed in the same field. The potential implementation of CVD and ALD techniques in other domains of industrial interest (cutting tools, aeronautics, optics, energy, etc.) has now been acknowledged; indeed, CVD coatings and films can be used in numerous applications targeting, for instance, thermal insulation, thermoabsorption and thermoelectricity, catalysis, magnetic, optical and electronic devices and high-density data storage, or efficient commutation related to the switching speed of electronic components such as CMOS transistors.

In order for CVD to successfully meet the high electrical potential of the above mentioned applications, a number of difficulties have to be resolved. Because numerous CVD reagents, commonly called precursors, are low vapor-pressure liquids or solids, one of these difficulties is the production of vapors from the reactive gases that are decomposed in the deposition chamber to provide the desired film. Such a production has to be supplied at high rate and must be reproducible and stable during the whole process. The development of new evaporation technologies called DLI (direct liquid injection) has allowed difficulties to be overcome in numerous cases [1]. Nevertheless, as it is necessary to dissolve solid precursors in an organic solvent when one wants to vaporize them with a DLI source, this process may yield low quality films (carbon contaminated) and may raise environmental concerns (organic vapors and/or carbon dioxide release). 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. These precursors are thus used as powders that are sublimated.

Three primary problems occur with sublimation of solid CVD precursors. The main problem encountered is the low saturating vapor pressure of most solids of interest (typically below 100 Pa at room temperature) compared to liquids. This problem is further complicated by the fact that it is often difficult to saturate the carrier gas with the precursor vapors. Raising the temperature of the precursor vessel/sublimator (and all lines and valves in contact with the carrier gas flow) increases the gas phase precursor concentration; this can lead to precursor degradation and limits the selection of gas line components. The second, often-encountered problem is maintaining a reproducible precursor vapor pressure. During a single run, especially if it is lengthy, the gas phase precursor concentration may decrease with time. From run-to-run similar changes are often observed. The third problem is particle contamination of the film. It occurs if suitable safeguards are not built into the precursor delivery line. Moreover, the low molar fraction of precursor in the gas phase often implies longer CVD runs and increases the risk of precursor thermal degradation in the delivery device.

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Inefficient mass and heat transport contribute to the first two of the above listed problems. In a typical solid precursor delivery system, the inability to saturate the carrier gas flow with the vapors of the solid is related in part to the inefficient mass transport away from the gas/solid surface interface. This would be a potential problem even if the surface transport of a precursor was completely

surrounded by the gas flow. The instability of the precursor delivery rate over time is caused by changes in the particle size (solids are usually used as powders) that affect the total solid surface area. Local variations in temperature can also alter the precursor vapor pressure.

The most commonly used delivery system for solid precursor vapors is the down stream fixed-bed saturator (Figure 1), which doesn't solve the above-mentioned problems. It is not able to saturate with vapors of a solid precursors carrier gas flows higher then a few slm (standard liter per minute). Such non-optimum operation of the process yields films and coatings with scattered, non reproducible characteristics and is therefore detrimental to the targeted properties of the material. A number of alternative solid precursor delivery methods have been published or patented. The simplest approach is to raise the precursor vessel temperature above the melting point of the solid, if it is thermally stable enough. For instance, the precursor, (MeCp)Ir(1-5 COD), heated above its melting point (≈ 40°C) is used as a liquid precursor in Ir MOCVD processes. However, that approach can be used for only a very limited number of precursors because most solid precursors start to decompose at a temperature that is very close to their melting point.

Alternative delivery systems that transport solid precursor directly to a hot zone (flash evaporator) before the reaction chamber have been proposed, but have encountered little success. This may be due, in some cases, to the complexity of the device and in other cases to the physical transport of powdery precursor to the vaporization zone. It appears that despite a number of solutions proposed in the literature to solve the problem of the controlled sublimation of solid precursors, none of them is satisfactory enough to leave the laboratory environment and to be integrated into a production line. There is thus a need for a simple solid precursor delivery device, which could deliver high, stable and reproductive molar fractions of precursor in the gas phase even with solids of low saturating vapor pressure. Such a device would allow the use of simple and cheap molecules, which are not yet commonly used in CVD and ALD processes.

A new sublimation process and system has been developed and patented [2] for solid precursors in the form of powders. It is based on gas-solid fluidization technology. A fluidized bed is formed in a vertical cylindrical tube with a perforated plate at its bottom, called a gas distributor. The powder is placed on this plate and gas is flowed upwards. At the appropriate gas flow rate, a fluidized bed is formed, i.e. powder behaves as a fluid due to the intense mixing of particles generated by the gas flow. In particular, high thermal and mass transfer rates

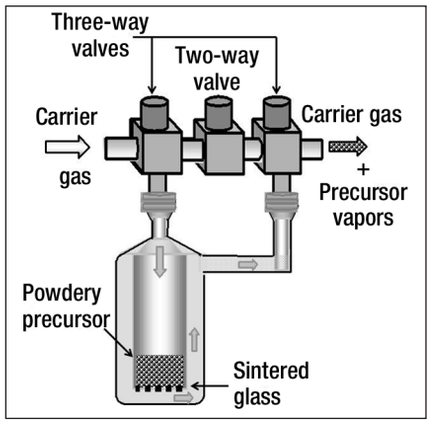

Figure 1. Down stream fixed-bed saturator

exist inside the fluidized bed, ensuring quasi-perfect isothermal conditions for the particles. These high transfer rates ensure that when heated at an appropriate temperature in a bed fluidized by an inert gas like nitrogen (N_2), the powder of the precursor is sublimated, providing high, stable and fully repro-

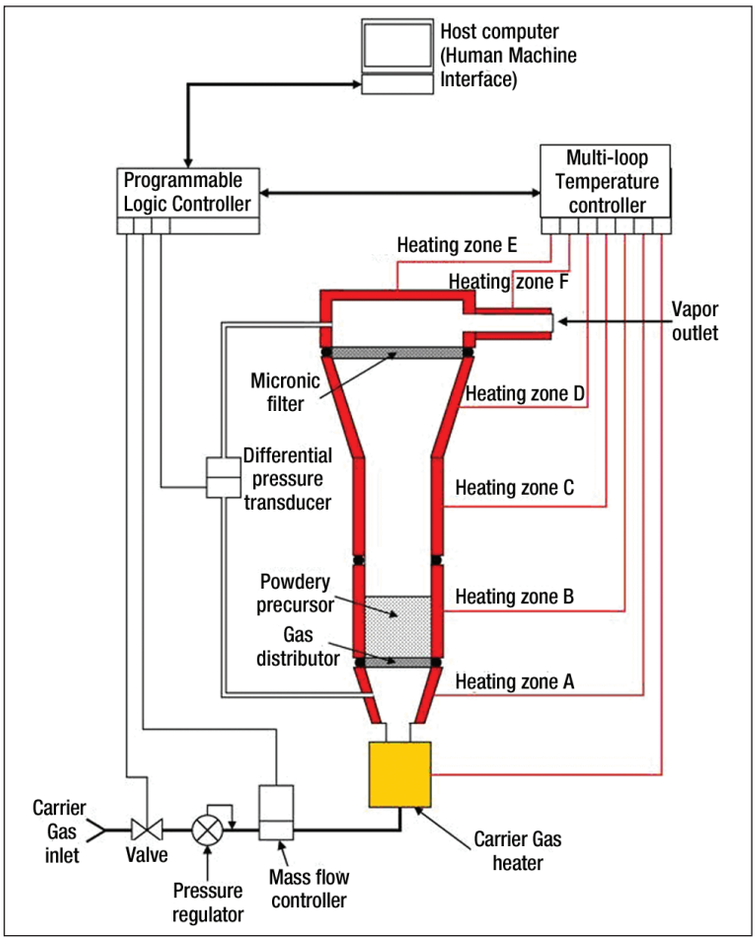

Figure 2. Schematic description of the fluidized bed sublimator.

ducible vapor concentration. With vapors of a solid precursor carrier gas, it is possible to saturate flows as high as a few tens of slm.

Figure 2 presents the schematic of the fluidized bed sublimator (FBS). It has been designed to follow the classical concepts of fluidization engineering. It is composed of a vertical stainless steel tube, connected at its lower part with an N_2 line. The top part corresponds to an expansion zone, to allow particles entrained by the gas flow to drop back into the bed. Its dimensions have been calculated using the concept of transport disengagement height (TDH) for a wide range of particle diameters. Indeed, since sublimation occurs into the fluidized bed, the diameter of particle always decreases with time. This mainly impacts the risk of particle elutriation and presents the possibility of distributor clogging. As a consequence, an appropriate gas distributor has been designed, positioned at the bottom of the reactor to keep the whole bed of particles at rest and to distribute the fluidization gas. A micronic filter has been placed near the exit in order to collect the finest particles and to avoid their transport to the CVD reactor. The FBS is fed with pure nitrogen. Mass flow controllers regulate its flow rate. Temperature is one of the most influential operating parameters for this sublimation process. It is precisely regulated for the whole set up, from the exit of the flow meters to the entrance of the upward CVD reactor. Another extremely important parameter is the fluidization quality of particles. Only optimum fluidization conditions will provide high and stable vapor concentration. When the powder is fluidized, the gas pressure drop across the bed (versus gas velocity), stabilizes on a plateau, corresponding to the particles' weight-per-unit surface area. The gas flow rate is then fixed using this criterion, by monitoring the pressure drop using a differential pressure transducer.

An initial prototype implementing the above-mentioned process has been developed by CIRIMAT and LGC. It has allowed for the validation of the new concept. Figure 3 shows some results obtained with this prototype. It can be seen that a fixed-bed sublimator can saturate up to approximately 1 slm of carrier gas with the vapors of Al(acac)3 while the prototype fluidized bed sublimator can do it up to around 7.5 slm.

From the initial prototype, KEMSTREAM has developed the first industrial fluidized bed sublimator Sublibox 50, shown in Figure 4. It features six independent heating zones and is able to handle up to 50 slm of carrier gas and to work up to 300°C. It has been designed so that it can saturate using the vapors of a solid precursor carrier gas, flows as high as a few tens of slm and to operate several hours without precursor refilling. Its design allows easy precursor powder filling and easy maintenance. For air sensitive precursors, precursor filling under inert atmosphere conditions can be done. Sublibox 50 is equipped with a programmable logic controller (PLC) and a gas panel. An industrial carrier gas heater heats the carrier gas before it enters the sublimation zone. All the electrical and pneumatical components of Sublibox 50 are connected to a PLC. It can be fully controlled from a host computer communicating with the PLC. PC control software is also provided. G&I

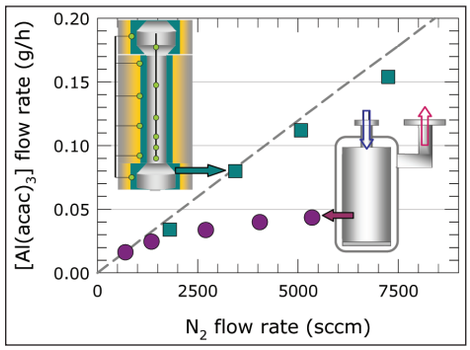

Figure 3: Flow rate of aluminum acetyl-acetonate [Al(acac)3], as a function of nitrogen flow rate. Sublimation in the fluidized bed (squares) and in the fixed bed (circles). Dashed line corresponds to the theoretical upper limit of the flow rate in the adopted operating conditions.

1. H. Guillon, S. Bonnafous. "Vaporization of Solid or Liquid Organic, Organometallic or Inorganic Compounds," Gases & Instrumentation, (May/June 2008) pp. 17-19.
2. C. Vahlas, B. Caussat, F. Senocq, W.L. Gladfelter, "Device For Providing Vapors Of A Solid Precursor To A Processing Device", US Patent Application, Publication number: US2008268143 (A1), Application number: US20050792020 20051130, Priority number(s): FR20040052817 20041130; WO2005EP56358 20051130

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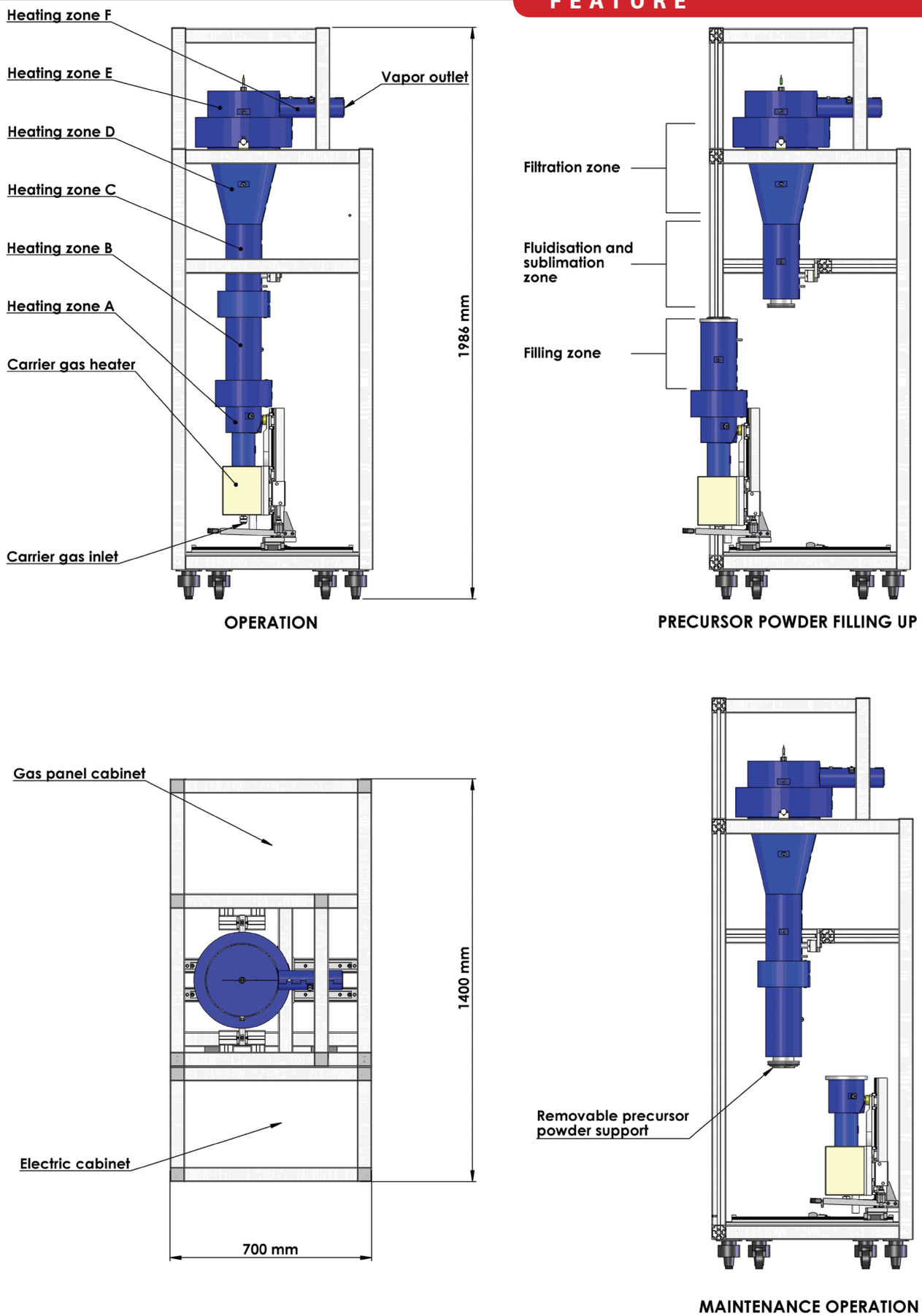

Figure 4: Schematic description of the first industrial fluidized bed sublimator.