We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

172,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Direct Liquid Injection Chemical Vapor Deposition

Vincent Astié, Cyril Millon,
Jean-Manuel Decams and Ausrine Bartasyte

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/intechopen.80244>

Abstract

Thin film technology, based on different chemical and physical methods, enabled miniaturization, co-integration, and amelioration of the performance of the devices. Chemical vapor deposition (CVD) systems ensure high productivity and demonstrate excellent film uniformity (up to 12 inch wafers) and repeatability with high throughput for a variety of different films of oxides, nitrides, metals, chalcogenides, etc. In the last two decades, direct liquid injection (DLI)-CVD enabling the usage of solid and liquid precursors has proven to be one of the most versatile CVD process to meet industrial requirements. In this chapter, the requirements to the precursors suitable for DLI-CVD, different classes of available precursors, and models used to describe the evaporation are overviewed. Then, different liquid delivery devices used in DLI-CVD such as capillary tubes, syringes, aerosol delivery systems, and valves are reviewed in detail.

Keywords: direct liquid injection, DLI-CVD, evaporation, precursors, injectors, thin films

1. Introduction

In the last decades, thin film technology has been integrated with many large area applications in electronics, information processing/storage, telecommunications, LED lighting/displays, solar energy harvesting, etc. Thin film technology enabled miniaturization, co-integration, and amelioration of the performance of the devices. Many different chemical and physical deposition methods were developed in order to satisfy industrial needs and requirements in different application fields. There is no universal technique for the processing of functional coatings. For each application, more than one technique is being considered at industrial level and the final choice depends on the specifications and on the maturity and readiness level of each one. The industry

prefers conservative approaches in terms of available subcontracting environment, which makes that process modification requires much higher performance, durability, and lower cost than actually implemented solutions, the safety/environmental issues are considered, as well.

There are two basic technologies, used for the synthesis of functional coatings: dry methods (depositions in vacuum conditions) and wet chemistry. The liquid-phase techniques, such as ink-jet printing, aerosol/spray deposition, sol-gel method, spin-coating, or dip-coating, are widely used in the coating technology due to their scalability and low cost [1, 2]. The usage of liquids/solvents in the wet techniques may induce degradation of the properties of the bottom layers and substrates and may introduce the impurities/defects in the heterostructure, which may be a critical limitation to device performance in the applications such as electronics [2]. Moreover, the drying of the solvent can also lead to the inhomogeneous distribution of the solute—"coffee stain" effect [3]. It is very challenging to grow the homogeneous coatings on 3D substrates with high aspect features by means of wet techniques due to dewetting and surface tension issues on the sidewalls and edges [2]. There is a considerable effort to be made to solve the strong drawbacks and limitations to the types of substrates of the wet techniques. Moreover, these methods usually provide poor reproducibility and non-uniform compositional distributions in the coatings. Thus, dry methods are highly preferred for the controlled synthesis of functional coatings. However, due to the strong advantages (low cost and easy up-scaling), wet techniques are able to meet actual specifications and thus take lead in "technology competition" with regard to dry techniques.

Different physical and chemical vapor deposition methods are used for the dry synthesis of the functional films at laboratory scale [4]. Physical vapor deposition techniques, such as pulsed laser deposition (PLD), magnetron sputtering, etc. offer in most cases a direct link between the composition of the gas phase and that of the coating [5], they may require less tuning and for this reason they are able to provide to the academia and the industry with "real samples" easier and faster than chemical vapor deposition techniques. However, these techniques will face issues in the stoichiometry adjustment in the case of multicomponent films if one of the deposited components is highly volatile (or presents very different evaporation characteristics). For instance, molecular beam epitaxy (MBE) is very powerful and essential tool in the semiconductor industry. Sputtering and evaporation techniques are widely applied for deposition of metal, oxide, and nitride films in the microfabrication of devices. Pulsed laser deposition (PLD) is broadly used by researchers for fundamental studies of new materials. However, physical methods, such as PLD, evaporation, and magnetron sputtering, are not compatible for depositions on non-planar surfaces and cannot offer precision control of the film thicknesses as required by some industries.

The industrial requirements (quality and reproducibility) for designed coatings and especially on 3D surfaces are more likely to be attained by chemical deposition methods, such as (metal organic) chemical vapor deposition (MOCVD) and atomic layer deposition (ALD) [6, 7]. ALD provides a tool for conformal coating on very high aspect-ratio nanostructures with excellent uniformity. It has become a technique for both template-directed nanofabrications and engineering of surface properties. For example, ALD is used to deposit HfO_2 layers with nanometer scale thickness in the complementary metal oxide semi-conductor (CMOS) fabrication. CVD systems

ensured high productivity and demonstrated excellent film uniformity (up to 12 inch wafers) and repeatability with high throughput for a variety of different films including semiconductors (Si, III–V, etc.), dielectrics (e.g. SiO_2 , AlN, etc.), rare-earth oxides, ceramic materials (e.g. TiN, ZrO_2 , etc.), ferroelectrics (e.g. PbTiO_3 , LaNiO_3 , etc.), superconductors (e.g. $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$), chalcogenides, and noble metals. Despite industrial success of CVD in the manufacture of thin films and its flexibility, offered by chemistry, CVD is still an expensive method compared to the wet chemistry techniques.

In the CVD process, gaseous or evaporated precursors are transported to the heated substrate where decompositions or other type of reactions take place. However, not all precursors are under gaseous form at atmospheric pressure and ambient temperature (see **Figure 1**). In fact, only about 10% of the industrially available precursors are gaseous (e.g., trimethylborane $\text{B}(\text{CH}_3)_3$, trimethylsilane $\text{Si}(\text{CH}_3)_3$, etc.). The vast majority of precursors are available in solid form (powders or crystals) (80%). About 45% of elements can be grown by using liquid precursors and the precursors of 5% elements are only liquid. Most available precursors exhibit safety hazards and must be carefully operated and stored. The main disadvantages of classical MOCVD systems are the difficulty to control the chemistry and the evaporation of the solid/liquid precursors and therefore the composition and structure of coating (especially those of multicomponents coatings), which affect the reproducibility. It makes difficult the control of the film thickness and growth rate, which affects crystalline orientation, surface morphology, and film density. Nevertheless, chemistry of deposition process might be a potential advantage for precision manufacturing of films, if used in a controlled manner.

Periodic Table of the Elements

																		<div>Atomic Number</div> <div>Valence Charge</div> <div>Symbol</div> <div>Name</div> <div>Atomic Mass</div>														
1 1A H Hydrogen 1.008																	2 2A He Helium 4.003															
3 Li Lithium 6.941	4 Be Beryllium 9.012																	5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180									
11 Na Sodium 22.990	12 Mg Magnesium 24.305																	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.065	17 Cl Chlorine 35.453	18 Ar Argon 39.948									
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.922	34 Se Selenium 78.972	35 Br Bromine 79.904	36 Kr Krypton 83.80															
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 98.906	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.905	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.757	52 Te Tellurium 127.6	53 I Iodine 126.905	54 Xe Xenon 131.29															
55 Cs Cesium 132.905	56 Ba Barium 137.327	57-71		72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.967	80 Hg Mercury 200.59	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [209]	85 At Astatine [210]	86 Rn Radon 222.018														
87 Fr Francium [223]	88 Ra Radium 226.025	89-103		104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [271]	111 Rg Roentgenium [272]	112 Cn Copernicium [285]	113 Uut Ununtrium [284]	114 Fl Flerovium [289]	115 Uup Ununpentium [288]	116 Lv Livermorium [293]	117 Uus Ununseptium [294]	118 Uuo Ununoctium [294]														
Lanthanide Series																		57 La Lanthanum 138.905	58 Ce Cerium 140.115	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.965	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.26	69 Tm Thulium 168.934	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
Actinide Series																		89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [252]	100 Fm Fermium 257.085	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

Figure 1. Physical states of commercially available precursors at ambient temperature for each element in the periodic table (gas in green, liquid in red, and solid in gold). www.sciencenotes.org

In the case of solid precursors, the sublimation rate is directly linked to its free surface, which in turn depends on the powder grain size and the amount of remaining precursor. Consequently, as sublimation occurs, its surface area in contact with the gas changes, thus changing the mass transport rate during the deposition. Due to the difficulty in precisely controlling the evaporation of a powder, depositions involving multiple solid precursors frequently were done by grinding optimized amounts of multiple precursors together to have a homogeneous single-source powder and rarely multiple evaporators were used. Various single-source powder precursors and techniques used to introduce powder in the evaporator were reviewed in Ref. [8]. In 1998, Gorbenko and Bosak [9] used a vibrating feeder to control the introduction of a mixture of β -diketonates precursors (see Section 2.1), namely $\text{La}(\text{thd})_3$ and $\text{Ni}(\text{acim})_2$ or $\text{Ni}(\text{thd})_3$, for the deposition of LaNiO_3 thin films and succeeded in growing oriented stoichiometric layers. However, as many precursor powders are moisture sensitive, another method was later proposed in which pellets were covered by an inert material [10]. An alternative way was a packaging of a mixture of precursor powders in a quartz tube, which was then slowly introduced into the vaporizer. The large thermal gradient in the evaporator combined with the slow entrainment of the tube ensured that the growth rate would only be dictated by the density of the powder [11]. Although it worked well in laboratories, it proved to be difficult a scaling-up to industrial requirements.

The term “direct liquid injection (DLI)-CVD” refers to reactors, which use liquid delivery units to feed the deposition zone in reactants. It is much easier to regulate precisely a liquid flow rate than that of powders. In some systems, the liquid goes through an evaporation unit where it is vaporized, and in other cases, the precursors reach the surface of a heated substrate in a liquid state and then they are vaporized prior to decomposition. If the precursor is still in liquid phase when it reaches the substrate, the deposition method is called spray or aerosol pyrolysis [12] depending on the generation method of the liquid droplets. Sometimes spray/aerosol pyrolysis is called atmospheric pressure CVD as usually the evaporation takes place in proximity of the substrate heated to high temperatures. The main advantage of DLI-CVD is that, in most cases, the solution is kept under pressure at room temperature, which makes it possible to use precursors with low thermal stability and low vapor pressure. Moreover, powder precursors may be dissolved in the solvent and used in DLI-CVD systems, as well.

A bubbler technology is well established as a liquid precursor delivery system since many years [13]. The principle is rather simple and robust: the liquid is stored inside a so-called bubbler, typically a stainless steel canister, and an inert carrier gas (usually Ar or N_2) is introduced inside the liquid to bubble. The precursor vapor saturates the atmosphere in the bubbler and the vapor is then entrained to the heated substrate surface. The delivery of reactants depends on three parameters: the temperature of the bubbler, the carrier gas flow rate, and the pressure over the surface of the liquid. This system works particularly well with liquid precursors which vapor pressures are not too low and not too high. In the case of precursors with low vapor pressure, the only solution is heating the bubbler to increase the equilibrium vapor pressure inside the canister. Yet, this has some major drawbacks as it restricts the usage to precursors that are stable at high temperature, and implies to heat the whole delivery line so that condensation does not occur before reaching the substrate. To overcome the problems of non-saturation of the carrier gas and fluctuation of the precursor flow rate, many different devices

were imagined, from two bubblers in series [14] to a self-metering reservoir [15]. Before 1990, the main research effort on the heretofore mentioned interesting materials were dedicated to physical deposition processes such as physical vapor deposition (PVD), as problems with vapor phase control and stoichiometry were not totally overcome in CVD.

In the 1990s, the growing interest in the thin films of superconducting materials, ferroelectrics, and high- κ dielectrics ($\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$, BaTiO_3 , SrTiO_3 , etc.) [16] leads to the development of more reliable and versatile delivery systems adapted to a wider range of precursors. The first generation of the IIA group solid precursors were thermally unstable at their sublimation temperature. They had a strong tendency to oligomerize and aging issues [17]. Much effort was made in precursor chemistry and in development of new liquid injection systems. In this chapter, we overview liquid delivery systems developed to date emphasizing on the problems it solved and the challenges it rose.

2. Precursors for DLI-CVD

2.1. Choice of the precursors

The injection devices have greatly enhanced the vaporization efficiency, thus the high volatility is not the main issue as it was with previous delivery systems. From a point of view for large-scale CVD applications, choosing the best precursors for a given application can sometimes be troublesome. As a matter of fact, a suitable precursor should meet several key requirements:

- i. High purity and high yield,
- ii. Stability at ambient temperature,
- iii. Easiness to handle and non-toxicity, and
- iv. Congruent volatilization with a significant temperature gap between evaporation and decomposition.

Additionally, it was shown that the molecular structure of the precursor had a significant impact on the growth dynamics and properties of the films, as well [18–20]. An *organometallic compound* should have a direct metal-carbon bond in their molecular structure, and it is admitted that precursors with a metal ion and a coordination complex (e.g. a metal ion is linked to a carbon chain through oxygen or nitrogen) are *metalorganic compounds*. Most of commercially available products belong to these five major classes of metalorganic compounds: metal β -diketonates, metal cyclopentadienyls, metal alkoxides, metal alkyls, and metal alkylamides depending on the organic complex associated to the metal.

Metal β -diketonates are the most used and common precursors for MOCVD and especially for depositions of oxide films. The ($\text{O}, \text{O}'-\eta^2$) chelating ligands of β -diketone usually form both thermally and hydrolytically stable complex with metal ion. Although it is mostly an advantage, it implies that the deposition temperature should be high enough to reach the precursor

decomposition temperature or that additional source of energy (plasma, UV light, etc.) is provided at low deposition temperatures. However, it can heavily increase the carbon contamination when working at low temperatures. Additionally, their low reactivity with water has proven to be a complication in ALD processes. Many derivatives of β -diketonates precursors and the abbreviations of their names are presented in **Figure 2**. The volatility of the precursor can be tuned by modifying R-groups of ligands. For instance, Schweitzer et al. have shown that the lead precursors with bulkier R-groups became more volatile ($\text{Pb}(\text{acac})_2 < \text{Pb}(\text{dhd})_2 < \text{Pb}(\text{thd})_2$) [21]. They explained this tendency by the increased shielding effect on the highly positive metal center and the reduced intermolecular oxygen-metal interactions in the solid state. Additionally, Fahlman et al. have reported that the increased fluorine substitution in the R-groups could improve significantly the volatility of zirconium β -diketonate precursors [22]. But on the other hand, fluorinated precursors often led to fluorine contamination in the deposited oxide layers. This contamination could be reduced by the introduction of excess H_2O vapor [23]. Another way to increase the volatility and/or the solubility in a solvent of the β -diketonate complex [24] is to add stoichiometric amount of a Lewis-base compound in the solution or directly on the complex in order to saturate the coordination sphere of the metal. The β -diketonates precursors have been successfully used to grow a large variety of films from pure metals, simple oxides, solid solutions, and composite materials (e.g., ruthenium and ruthenium oxide (RuO_2) [25], lanthanum-modified lead zirconate-titanate (PLZT) [26], yttria-stabilized zirconia (YSZ) [27], lithium niobate [27, 28], etc.).

Metal alkoxide ($\text{M}(\text{OR})_n$) precursors are the second type of the most used precursors in MOCVD processes. They are usually more volatile than β -diketonates and provide less carbon contamination even at low oxygen partial pressure. Their volatility is linked to the electron density on the metallic center and the saturation level by ligands as it will condition the tendency to form oligomeric ($\text{M}(\text{OR})_n$)_m clusters [29]. The oligomerization can however

Figure 2. Composition, names/abbreviations of β -diketonate ligands [31].

be attenuated, or even suppressed, by using bulky ligand (e.g. isopropoxide (O^iPr) or tert-butoxide (O^tBu)) [30]. For example, the volatility of zirconium precursor increases in the order $\text{Zr}(\text{OEt})_4 < \text{Zr}(\text{O}^i\text{Pr})_4 < \text{Zr}(\text{O}^t\text{Bu})_4$, the first being a trimer, the second a dimer, and the third a monomer. Another possible way is to use the alkoxides functionalized with a donor like dimethylaminoethoxide ($[\text{OCH}_2\text{CH}_2\text{NMe}_2]$ often referred to as (dmae)). However, metal alkoxide precursors can be hydrolyzed very easily [31] and some of them are highly toxic. These precursors too have been extensively used for the last two decades in the growth of oxide films like LiNbO_3 [32, 33], LaAlO_3 [34], YSZ [35], etc.

Metal cyclopentadienyl (Cp) precursors show good thermal stability and volatility. However, their η^5 -bonding mode makes them a considerable source of carbon contamination. They are reactive with water even at moderate temperature and this makes them suitable candidates for ALD processes [36, 37]. Metal alkyl precursors are usually very reactive, toxic, and/or pyrophoric, as well as being a source of heavy carbon contamination in oxide films [38]. Nevertheless, aluminum and zinc alkyls are successfully used in ALD processes to grow Al_2O_3 from trimethylaluminum ($\text{Al}_2(\text{CH}_3)_6$) [39] and ZnO from diethylzinc ($\text{Zn}(\text{C}_2\text{H}_5)_2$ or DEZ) [40]. On the other hand, metal alkylamides usually have medium volatility and some of them exhibit good stability to hydrolysis. Most of alkylamides can be easily aminolyzed. Thus, they are reliable precursor sources for the growth of metal nitrides. Although they do not have any metal-oxygen bond, high purity oxide films were grown under big oxygen partial pressures by MOCVD [41] and ALD [42].

As briefly presented, different types of metalorganic precursors have their own strengths and weaknesses and the operators should know the deposition temperature before choosing their precursors. Most of β -diketonates will show good yield at high growth temperatures and they will be more resistant to hydrolysis but a synthesis will be inefficient at low temperatures. The alkoxides could be more adapted to depositions at low temperature where the main issue is the carbon contamination. The cyclopentadienyls have shown good efficiency in ALD processes. To overcome limitations of different families of precursors, a number of scientific teams have tailored new precursors combining the good stability of β -diketonates with the high volatility of alkoxides and have shown that the precursors consisting of different types of ligands showed better performance than those with single type of ligands. In fact, Jones et al. [19] showed that $\text{Zr}_2(\text{O}^i\text{Pr})_6(\text{thd})_2$ was more suitable precursor for the growth of $\text{Pb}(\text{Zr,Ti})\text{O}_3$ at moderate temperatures than the commercially available $\text{Zr}(\text{thd})_4$. The influence of precursor structure on GaAs, ZnSe, and $\text{Al}_x\text{Ga}_{1-x}\text{N}$ film growth was described in detail by Jensen et al. [18].

2.2. Evaporation of liquid droplets

The theory describing the heat transfer between a gaseous medium and a droplet of liquid is well known and the basics of the evaporation process were given by Maxwell in 1877 [43]. His model for stationary state evaporation [44] assumed that:

- i. The droplet was spherical and without any relative motion with regards to the gas;
- ii. The vapor concentration at the surface of the droplet was equal to the saturation concentration; and

iii. The evaporation was an equilibrium process.

However, in the case of droplet evaporation with a low vapor pressure, this model is not sufficient. There are six different models, used to explain vaporizing process at low vapor pressure:

- i. The constant-droplet-temperature model (decreasing linearly as a function of the square of the droplet diameter, d , also called d^2 law);
- ii. The infinite-liquid-conductivity model;
- iii. The spherically symmetric transient droplet-heating (or conduction-limit) model;
- iv. The effective-conductivity model;
- v. The vortex model; and
- vi. The Navier-Stokes equation solution.

The infinite-liquid-conductivity model is commonly used in modeling of industrial spray processes. In order to simplify the description, this model is based on several assumptions:

- i. A single Lewis number in the gas phase surrounding the droplet and
- ii. A negligible transient liquid heating although it would appear to be a governing factor of the droplet vaporization rate [45].

Detailed description of fluid dynamics and transport of droplets and sprays can be found in Ref. [46]. This model was used to describe the fuel droplet vaporization in combustion processes [47, 48]. Although the description of evaporation phenomenon is complex and many assumptions are needed, basically it can be easily understood, that smaller droplets are more easily evaporated. In a heated environment at low vacuum, the heat is transferred through the exchange between the gas and the droplet. Two parameters have to be taken into account: the specific heat capacity, C_p , of the gas and the free surface of the droplet. The surface/volume ratio can be increased by minimizing the radius and evaporation at a given flow rate can be ameliorated by introducing more but smaller droplets. This possibility was not really considered in the first liquid delivery devices, but very quickly the atomization has become one of the major concerns of the injector industry and the key parameter, used to discriminate liquid delivery devices.

3. Liquid delivery systems

In this section, different liquid delivery devices used in DLI-CVD such as capillary tubes, syringes, aerosol delivery systems, and valves and their developments are reviewed in detail.

3.1. Capillary tubes and syringes

Capillary tubes are one of the simplest ways to introduce a flow of precursor with controlled rate into an evaporator. The liquid drops into a heated zone (either a quartz tube [49] or a

stainless steel “tee” [50]) with flowing a neutral gas, or more conventionally, a nebulizer. The principle of this method is based on the capillary effect. The flow inside the capillary is laminar, the liquid in contact with the walls is stationary and there is no radial flow. Thus, the pressure across the cross-section is constant. According to Hagen-Poiseuille law, the flow volume through the tube, Q , is governed by four parameters such as the viscosity of the precursor solution, μ ; the radius of tube, r ; the length of the cylindrical tube, d ; and lastly the pressure difference between the top (usually sealing to the bottle which contains the precursor) and the bottom “pressure drop”, ΔP :

$$Q = \frac{\pi r^4}{8\mu} * \frac{\Delta P}{d} \quad (1)$$

The main advantage of this liquid delivery system is an ability to provide a steady flow of precursors to the vaporizer. However, the substantial drawback is that the flow volume itself can only be tuned by varying the viscosity of the liquid. This means changing the solvent or the concentration of the precursor in the solution, which in turn could affect the quality of the deposition. Borgharkar et al. [50] have even reported that increasing the concentration of $\text{Cu}(\text{hfac})_2$, diluted in isopropanol (i-PrOH), led to an unstable flow rate through the capillary due to high viscosity.

To tune the injected flow itself, syringes were used as the precursor vessel, and the process was sometimes referred to as direct liquid evaporation-CVD (DLE-CVD) [51]. The syringe is placed into a syringe driver, or syringe pump, connected to the capillary tube. The liquid flow is controlled precisely by adjusting the rotational speed of a stepper motor. The multiple precursors can be introduced to the evaporator by means of either multiple syringes and their drivers, or by using their mixture in a single solution. However, this technology is well adapted only to the liquid precursors at ambient temperature and the usage of the precursor solutions may face several issues. Indeed, since the bottom of the capillary tube is in contact with a heated zone, the vapor pressure difference between the diluted solid precursor and the solvent may lead to the evaporation of the solvent with low vapor pressure prior to exiting the capillary. This in turn can introduce a partial/complete clogging of the tip with the precipitated solid precursor and disruption of the solution flow. The usage of heavy solvents may eliminate these issues but it can have a significant impact on the carbon contamination of the deposited layer. A possible solution to this problem was proposed by ASM International by an introduction a three-way valve in order to introduce a carrier gas together with the solution in the capillary system [16]. An example of such system using an advanced syringe-capillary system to control the precursor injection rate, adapted to the synthesis of carbon nanotubes, is presented in **Figure 3** [52]. Many different thin films of metals and binary oxides thin were grown using this technique: Cu [50], transparent amorphous Al_2O_3 [53], ZrO_2 [54], TiO_2 [55], La_2O_3 [56], VO_2 [57], etc.

3.2. Aerosol assisted-CVD and pulsed-pressure MOCVD

Some CVD processes rely on the nebulization, or the atomization of liquid precursors into a “mist”, or an aerosol, which is then brought to the heated substrate by carrier gases. The ultrasonic atomization process takes roots in the Lord Rayleigh’s “*The Theory of Sound*” [58], and Lang’s works on the absorption of energy by a liquid [59]. When a liquid is placed on a flat surface vibrating along the surface normal, some of the energy is absorbed and transformed

Figure 3. Schematic representation of a DLE-CVD reactor using a syringe pump associated with a 9" needle. Reproduced with permission [52]. Copyright 2018, MDPI.

into transverse standing waves called capillary waves in the liquid. As the amplitude of the vibration increases, the difference in height between the crests and troughs increases to the point where it compromises the stability of the wave. At this stage, the waves collapse and tiny droplets of liquid are ejected from the crests. If the vibrational frequency is too high, a cavitation can occur and large portions of liquid are sent [60].

Size of droplets, produced by industrial atomizers, follows a narrow Gaussian distribution and the mean size value depends entirely on the wavelength of the capillary wave, which in turn depends on the frequency of the transducer and the properties of the liquid [58, 59]:

$$\lambda_L = \sqrt[3]{\frac{8\pi\gamma}{\rho f^2}} \text{ and} \quad (2)$$

$$D_{N,0.5} = 0,34 \cdot \lambda_L \quad (3)$$

where λ_L is a wavelength of the liquid, γ is a surface tension, ρ is the density, f is a frequency of the actuator, and $D_{N,0.5}$ is the median diameter of droplets. Tsai et al. have demonstrated as expected that the drop size could be decreased by increasing the ultrasonic frequency [61]. However, it should be noted that the working frequency of some atomizers cannot be tuned. In fact, the working frequency of an ultrasonic spray nozzle is governed by its dimensions. The high-frequency nozzles work with small wavelength and are consequently smaller than low-frequency nozzles. The rate of liquid flow to atomizer can be calibrated and controlled accurately by means of liquid mass flow controller. Theoretically, a very large range of flow rates should be possible, but in fact, the ratio of maximum to minimum flow rates produced by the same atomizer is limited to 5 due to design constraints [62]. Usually, atomizer works with a piezoelectric transducer, which converts an electrical input into a mechanical

output. This transformation is accompanied by a heating of both the transducer and the precursor solution resulting in the shift in the resonance frequency and in the change of the liquid viscosity, respectively. This alters the flow rate of the liquid resulting in an unstable film growth. Thus, most deposition cycles to finish in a relatively short time (matter of minutes) [63]. Ultrasonic atomization in aerosol-assisted CVD (AACVD) has the benefit to allow a wider choice of precursors. In fact, a high volatility is not anymore a requirement and a solubility in solvent becomes the main selection criteria [64].

Different CVD systems based on aerosol delivery systems have been developed with customized vaporization zones. In the case of AACVD, also referred to as liquid source misted chemical deposition (LSMCD) [63] or liquid source chemical vapor deposition (LSCVD) [65, 66], the precursors or their solution are sent continuously to the reactor where they evaporate in the vicinity of the substrate surface due to high thermal gradient. Although McMillan et al. [67] have reported that in the case of LSCVD, an uniform film deposition could not be achieved on a rotating heated substrate unless a barrier plate was located in the vicinity of its surface, the homogeneous depositions were demonstrated by later developed AACVD systems. A possibility to grow thin films of a large variety of oxides and metals was studied by using an ultrasonic delivery systems. As illustrative examples of AACVD could be:

- i. The deposition of partially reduced tungsten oxide, WO_{3-x} , from polyoxotungstate anions $[n-Bu_4N]_2[W_6O_{19}]$ and $[n-Bu_4N]_4H_3[PW_{11}O_{39}]$ using a PIFCO ultrasonic humidifier [64] and
- ii. The growth of nanocomposite of VO_2 thin films with embedded cerium dioxide CeO_2 and titanium dioxide TiO_2 nanoparticles by means of a hybrid method combining the atmospheric pressure (AP)-AACVD using standard Vicks humidifier with a continuous hydrothermal flow synthesis (CHFS) [68].

In the case of pulsed-pressure CVD (PP-CVD) [69] or pulsed liquid injection with an ultrasonic nozzle [70], a small shot of liquid is pushed by an inert gas into the vaporizer through an ultrasonic nozzle (**Figure 4**), and quickly evaporates [71]. This produces a pressure pulse, and then the chamber is subsequently pumped back to the initial pressure in order to send another shot. High efficiency of deposition process has been achieved by means of PP-CVD [72]. Conventional nebulizer was employed in PP-MOCVD such as Sono-Tek ultrasonic nozzle. PP-MOCVD was used to grow sealing layers of yttria-stabilized zirconia on porous solid oxide fuel cell electrodes [35], tantalum oxide [73], epitaxial titanium dioxide [71, 74, 75], as well as lithium tantalate [76].

3.3. Valves

The liquid delivery systems in CVD, presented previously, were developed by implementing different industrially available valves. According to the operational mode, valves can be classified into ON/OFF valves and proportional valves. The proportional valve allows very precise control of the opening area via a piezoelectric material, which in return allows for an adjustable flow rate. The ON/OFF operating valve was typically used in the motor industry prior to the 2014 Euro 6 emission standards. In the 1980s, electromagnetic ON/OFF valves, in which a current is applied to the solenoid generating attraction force in order to pull the plunger below up, releasing the valve seat and letting the liquid flow out of the chamber through a very fine nozzle [77], are well known [78, 79] and used in many ON/OFF systems where the control of

Figure 4. Schematic representation of a PP-CVD reactor using an ultrasonic nozzle. Reproduced with permission [75]. Copyright 2001, Elsevier.

an injected volume is crucial. In 1993, Sénateur et al. have proposed to use them in a pulsed injection (PI)-MOCVD process [80]. A strong advantage of PI-MOCVD systems is a clear interface between the pressurized environment at ambient temperature where the precursor is stored safely and the low-vacuum atmosphere of the heated evaporator. Thus, the problems related to vapor pressure differences between the solvent and its solute could be mostly overlooked in the case of PI-MOCVD. The injector works as a valve, regulating the flow of liquid introduced in the evaporation chamber and as a nozzle atomizing the flow into tiny droplets.

As explained earlier (see Section 2.2), the dimensions of droplets have a fundamental impact on the evaporation efficiency of the liquid solution. Therefore, there are several key parameters of conventional solenoid injectors defining a quality of atomization: (i) the nozzle geometry (size, number of orifices, and degree of conicity), (ii) the flow regime inside the injector, and (iii) properties of the solution/liquid such as viscosity and concentration. The nozzle geometries and flow regimes have been extensively studied in the fuel injection industry [81–85]. Most commercially available injectors work in the frequency range between 0.1 and 200 Hz with very small opening times. These characteristics offer a very large working range in terms of injected flow rate and ultimately, in terms of film growth rate. In such injection system, the injection flow rate depends on the concentration and viscosity of the precursor solution, the opening frequency and time of the nozzle, and the pressure difference between the stored solution and the evaporator. Very small opening time ensures the fast evaporation process and helps to avoid the dissociation or premature decomposition of precursors before evaporation. However, it should be noted that the injector may produce instable flow at opening time below 1 ms. It is important to note, that injectors are commanded by

computer, which allows digital control of the injection frequency, number of injected droplets, opening time, and consequently thin film growth rate and thickness. As in the case of ultrasonic nozzles, there are usually no corrosion problems inside the injector with organic precursors/solvents, but some applications may require specially coated injectors.

It was shown that the precursors with low vapor pressure can be efficiently used in PI-MOCVD. PI-MOCVD reactors equipped with multiple injectors are used for the growth of multi-element films with controlled composition/stoichiometry, multilayers, nanocomposites and complex nanostructures of superconductors [16], high- κ dielectrics [86, 87], ferroelectrics, conductors [88], etc.

As the solvent can cause a carbon contamination in the films, Kaul and Seleznev [89] have proposed a method to remove the solvent of a solution prior to vaporizing the precursor. In this process, a fiberglass belt is wetted with a controlled amount of solution outside of the evaporation chamber. Then, the tape is brought into a warm zone of the reactor where only the solvent evaporates. The belt with solid precursor is then mechanically carried to a zone where flash evaporation of precursors occurs. Later, the same process has been applied with in situ wetting of the tape with sequential injection of micro-amounts of solution (illustrated in **Figure 5**) [90]. Although a solvent was introduced like in PI-MOCVD, only a mixture of precursor vapor and carrier gas reaches the substrate. This method may be particularly useful in the synthesis at low temperatures in order to solve carbon contamination issues.

An injection system was first commercialized under the JetPulse[®] name by Jipelec, a division of Qualiflow, and it was later acquired and further developed by AIXTRON[®] under the name TriJet[®] [91]. TriJet[®] evaporators are installed in the latest AIXTRON[®] ALD machines and have been used in MOCVD processes, called atomic vapor deposition (AVD). In fact, the reproducibility of the commercially available injectors was very poor. To face fluctuations in the partial pressure of the liquid, operators had either to dilute significantly the precursor solution or to lower the injection frequency. Additionally, since the nozzle of the injector is subjected to the heated environment, a premature evaporation of liquid solution trapped inside the injector may happen, which can significantly alter the injection flow rate of diluted

Figure 5. Schematic representation of a DLI-CVD furnace using solenoid electrovalves in combination with a moving tape. Reproduced with permission [90]. Copyright 1998, Elsevier.

solids and clog partially/completely the injector [92]. To overcome these issues, Kemstream® came up with the idea to have a two-stage injection process (**Figure 6**). The liquid injector introduces a precursor solution into the “mixing chamber”, where a controlled amount of carrier gas is mixed with the precursor solution. A few milliseconds later, the second injector opens and the mixture is injected and atomized into the evaporator. The operator must make sure that there is a short delay between the opening times of two injectors. The most important advantage of double injector is the formation of a homogeneous liquid-gas phase in the mixing chamber. This drastically diminishes the radius of the injected droplets, hence increasing the evaporation efficiency. This method offers a far better atomization of the precursor solution along with the possibility to use even lower vapor pressure precursors than in single-injection systems. Brooks® Instrument also proposes a multiple liquid inlet direct liquid vaporizer system (**Figure 6**), which injects the solution into a chamber where it is both atomized by sending a carrier gas perpendicularly to the stream and vaporized in contact with a hot gas [93]. Kemstream®’s injector (**Figure 7a**) can be found on Annealsys® CVD and ALD machines and process are called “direct liquid injection (DLI)-CVD and ALD” [94–96]. The Brooks® DLI Vaporizer Systems (**Figure 7b**) were successfully implemented in industrial CVD [97–99] and ALD [34, 100–105] processes, as well. The major part of the DLI-CVD industry is dedicated to the deposition of very well known III–V semiconductors, in which HORIBASTEC Liquid Vaporization Systems (**Figure 7c**) are broadly used [106]. It is also interesting to note that although the latest emission standards pushed the fuel industry to go toward piezoelectric injectors, the piezoelectrically driven injectors and piezo-valves are still very rare in DLI-CVD systems [107].

Figure 6. Schematic representation of Kemstream® two-stage injection process.

Figure 7. Kemstream DLI injector plugged into a vaporizing box (a), Brooks DLI vaporizer system (b), and HORIBASTEC liquid vaporization systems (c).

4. Conclusions and perspectives

Liquid mass flow controllers appear as a viable option for controlling a rate of a liquid flow, but they cannot be used as a direct liquid delivery unit in CVD systems. The main problem lies in the fact that it delivers a continuous flow of precursors in the evaporator. The process then depends entirely on the ability of the evaporator to vaporize the precursor, which is inefficient without any other atomizing system. The usage of a heated plate would be very unreliable in time. In the case of nebulizers or transducers, the progressive heating of the element leads to a drift in the aerosol flow. On the other hand, the ultrasonic nozzle shows a good reliability in evaporation and a good capability to handle “difficult” precursors. Each nozzle works at a certain frequency dictated by its dimension and it limits the tenability of the feeding rate. To regulate the amount of precursor sent to the substrate, the operator can either dilute/concentrate the solution or limit/increase the flow that comes to the nozzle.

Injection systems based on solenoid valves have reached very good performance and technological maturity. Major advantages brought by injection delivery systems are versatility, the digital control of the growth rate and the thickness of the film, and the storage of precursors at ambient conditions ensuring their stability in time. Advanced new-generation injection systems guarantee a controllable and stable feeding rate. DLI-CVD permits to vary and to control easily the composition of complex material film and doping level from sample to sample. Thus, it provides an excellent film composition control (<1%), has low cost, high efficiency, offers high uniformity on large area (<1.5%, up to 12 inch wafers), good conformal step coverage, high flexibility in precursors selection (solid or liquid), atomic control of film thickness (up to 10 Å), and possibility to deposit complex materials and multilayers. DLI-CVD is widely applied in industry of thin films fabrication ensuring high productivity and demonstrating excellent film uniformity and repeatability with high throughput in the CMOS era for a variety of different films including high-k dielectrics, rare-earth oxides, perovskite oxide and chalcogenide, and noble metals.

Although several solutions were proposed in the literature, the industrial DLI-CVD systems are still not well adapted to the depositions at low temperatures due to issues of carbon contamination originating from organic part of the precursors and the presence of the solvent. Thus,

further developments continue on the low-temperature CVD systems assisted by additional energy source such as plasma, UV, etc. Many research teams work on the molecular engineering of the precursor structure including combination of multiple ligands in order to ameliorate the decomposition of precursors at low deposition temperatures. CVD system efficiency and application at industrial scale remains highly dependent on the available precursor quality and reliability.

As described above, direct liquid delivery CVD has taken a profit from the developments in other fields, for example, chromatography, industrial spray coating, and automotive industry. The valves, transducers, liquid mass flow controllers, capillaries, etc. developed for other applications were successfully adapted to the liquid precursor/solution delivery in the CVD reactors. Thus, the advances in liquid delivery systems mainly used in large public applications determine the further developments of CVD systems, as well. The automotive industry has upgraded its fuel injection technology by implementing injectors with piezoelectric nozzles to adapt to the new emission standards. The piezoelectric nozzles react much faster, meaning a faster opening and closure of the valve assuring a better control of the injected flow, and the opening time can be tuned much easier by changing the allocated tension. Probably, all these improvements will be soon implemented in the next generation DLI-CVD systems, which will serve beyond CMOS Era.

Acknowledgements

The authors are grateful to the French National Research Agency for funding through the grants ANR LiLit (ANR-16-CE24-0022-011), Labex ACTION program (ANR-11-LABX-0001-01), and the EUR EIPHI program (contract no. ANR-17-EURE-0002). This work was partly supported by the French RENATECH network. The authors are also grateful to A. Almirall, S. Kuprenaite, and G. Clementi for the fruitful discussions and corrections.

Author details

Vincent Astié^{1*}, Cyril Millon¹, Jean-Manuel Decams² and Ausrine Bartasyte¹

*Address all correspondence to: vincent.astie@femto-st.fr

¹ FEMTO-ST Institute, University of Bourgogne Franche-Comté, CNRS UMR 6174, Besançon, France

² Annealsys, Montpellier, France

References

- [1] Braun D, Cherdrón H, Rehahn M, Ritter H, Voit B. Polymer Synthesis: Theory and Practice: Fundamentals, Methods, Experiments. 5th ed. Heidelberg: Springer-Verlag Berlin; 2013

- [2] Ozaydin-Ince G, Coclite AM, Gleason KK. CVD of polymeric thin films: Applications in sensors, biotechnology, microelectronics/organic electronics, microfluidics, MEMS, composites and membranes. *Reports on Progress in Physics*. 2012;**75**:016501
- [3] Deegan RD, Bakajin O, Dupont TF, Huber G, Nagel SR, Witten TA. Capillary flow as the cause of ring stains from dried liquid drops. *Nature*. 1997;**389**:827
- [4] Jensen KF, Kern W, Vossen JL. *Thin Film Processes II*. San Diego, California: Academic Press Inc.; 1991. p. 284
- [5] Reichelt K, Jiang X. The preparation of thin films by physical vapour deposition methods. *Thin Solid Films*. 1990;**191**:91
- [6] Choy KL. Chemical vapour deposition of coatings. *Progress in Materials Science*. 2003;**48**:57
- [7] Liu M, Li X, Karuturi SK, Tokb AIY, Fan HJ. Atomic layer deposition for nanofabrication and interface engineering. *Nanoscale*. 2012;**4**:1522
- [8] Choy KL. *Innovative Processing of Films and Nanocrystalline Powders*. Singapore: World Scientific; 2002
- [9] Gorbenko OY, Bosak AA. Growth of LaNiO_3 thin films on MgO by flash MOCVD. *Journal of Crystal Growth*. 1998;**186**(1-2):181-188
- [10] Chuprakov IS, Martin JD, Dahmen KH. New flash-evaporation feeder for chemical vapor deposition. *Le Journal de Physique IV*. 1999;**9**(PR8):Pr8-901-Pr8-908
- [11] Hiskes R et al. Single source MOCVD of epitaxial oxide thin films. *Journal of Crystal Growth*. 1993;**128**:781-787
- [12] Perednis D, Gauckler LJ. Thin film deposition using spray pyrolysis. *Journal of Electroceramics*. 2005;**14**:103-111
- [13] Manasevit HM, Simpson WI. The use of metal-organics in the preparation of semiconductor materials I. Epitaxial gallium-V compounds. *Journal of the Electrochemical Society*. 1969;**116**(12):1725-1732
- [14] Dickinson PH et al. Chemical vapor deposition of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconducting films. *Journal of Applied Physics*. 1989;**66**(1):444-447
- [15] Rodgers DB. *Self-metering Reservoir*. Rhinebeck, New York: Icon Dynamics LLC; 1997
- [16] Sénateur JP et al. Pulsed injection MOCVD of functional electronic oxides. *Advanced Materials for Optics and Electronics*. 2000;**10**:155-161
- [17] Sievers RE et al. Volatile barium β -diketonates for use as MOCVD precursors. *Coordination Chemistry Reviews*. 1993;**128**:285-291
- [18] Jensen KF et al. Metalorganic chemical vapor deposition: Examples of the influence of precursor structure on film properties. *Le Journal de Physique IV*. 1991;**02**(C2):C2-243-C2-252
- [19] Jones AC et al. Metalorganic chemical vapour deposition (MOCVD) of zirconia and lead zirconate titanate using a novel zirconium precursor. *Journal of the European Ceramic Society*. 1999;**19**:1431-1434

- [20] Loboda MJ. Low temperature PECVD growth and characterization of a-SiC: H films deposited from silacyclobutane and silane/methane precursor gases. In: Amorphous and Crystalline Silicon Carbide IV. Heidelberg: Springer, Berlin; 1992. pp. 271-280
- [21] Schweitzer GK, Pullen BP, Fang Y-H. The volatilities of some lead β -diketonates. *Analytica Chimica Acta*. 1968;**43**:332-334
- [22] Fahlman BD, Barron AR. Substituent effects on the volatility of metal β -diketonates. *Advanced Materials for Optics and Electronics*. 2000;**10**:223-232
- [23] Watson IM. Metal-organic CVD of the high-Tc superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. *Chemical Vapor Deposition*. 1997;**3**(1):9-26
- [24] Jodin L et al. Method for producing lithium-based layers by cvd. 2013. Google Patents
- [25] Lee D-J, Kang S-W, Rhee S-W. Chemical vapor deposition of ruthenium oxide thin films from $\text{Ru}(\text{tmhd})_3$ using direct liquid injection. *Thin Solid Films*. 2002;**413**:237-242
- [26] Tao W, Desu SB, Li TK. Direct liquid injection MOCVD of high quality PLZT films. *Materials Letters*. 1995;**23**:177-180
- [27] Matsuno S et al. $\text{YBa}_2\text{Cu}_3\text{O}_x$ thin films with yttria stabilized zirconia buffer layer on metal substrate by liquid source chemical vapor deposition using tetrahydrofuran solution of β -diketonates. *Japanese Journal of Applied Physics*. 1995;**34**:2293
- [28] Bartasyte A et al. Toward high-quality epitaxial LiNbO_3 and LiTaO_3 thin films for acoustic and optical applications. *Advanced Materials Interfaces*. 2017;**4**(8):1600998
- [29] Jones AC. Molecular design of improved precursors for the MOCVD of electroceramic oxides. *Journal of Materials Chemistry*. 2002;**12**(9):2576-2590
- [30] Bradley DC, Mehrotra RC, Gaur DP. *Alkoxides, Metal*. New York: Academic Press; 1978
- [31] El Eter M. Synthèse, caractérisation et évaluation de nouveaux précurseurs azotés pour dépôt de films d'oxydes métalliques MO_2 ($\text{M} = \text{Hf}, \text{Zr}$) par MOCVD à injection liquide. Lyon: Université Claude Bernard-Lyon I; 2008
- [32] Akiyama Y et al. Epitaxial growth of lithium niobate film using metalorganic chemical vapor deposition. *Thin Solid Films*. 2007;**515**(12):4975-4979
- [33] Tanaka A et al. Preparation of lithium niobate films by metalorganic chemical vapor deposition with a lithium alkoxide source. *Journal of Crystal Growth*. 1995;**148**:324-326
- [34] Gaskell JM et al. Liquid injection ALD and MOCVD of lanthanum aluminate using a bimetallic alkoxide precursor. *Journal of Materials Chemistry*. 2006;**16**(39):3854-3860
- [35] Krumdieck SP et al. Solid yttria-stabilized zirconia films by pulsed chemical vapor deposition from metal-organic precursors. *Journal of the American Ceramic Society*. 2002;**85**(11):2873-2875
- [36] Niinistö J et al. Advanced cyclopentadienyl precursors for atomic layer deposition of ZrO_2 thin films. *Journal of Materials Chemistry*. 2008;**18**(28):3385-3390

- [37] Niinistö J et al. Controlled growth of HfO_2 thin films by atomic layer deposition from cyclopentadienyl-type precursor and water. *Journal of Materials Chemistry*. 2005;**15**(23): 2271-2275
- [38] Freneck H et al. Low temperature remote plasma-enhanced deposition of thin metal oxide films by decomposition of metal alkoxides. *Materials Science and Engineering: A*. 1991;**139**:394-400
- [39] Goldstein DN, McCormick JA, George SM. Al_2O_3 atomic layer deposition with trimethylaluminum and ozone studied by in situ transmission FTIR spectroscopy and quadrupole mass spectrometry. *The Journal of Physical Chemistry C*. 2008;**112**:19530-11939
- [40] Lim SJ, Kwon S, Kim H. ZnO thin films prepared by atomic layer deposition and rf sputtering as an active layer for thin film transistor. *Thin Solid Films*. 2008;**516**(7):1523-1528
- [41] Williams PA et al. Growth of hafnium dioxide thin films by liquid-injection MOCVD using alkylamide and hydroxylamide precursors. *Chemical Vapor Deposition*. 2003;**9**(6): 309-314
- [42] Hausmann DM et al. Atomic layer deposition of hafnium and zirconium oxides using metal amide precursors. *Chemistry of Materials*. 2002;**14**(10):4350-4358
- [43] Maxwell JC. *Collected Scientific Papers*. Taken from Fuchs NA. *Evaporation and Droplet Growth in Gaseous Media*. Cambridge, New York: Pergamon Press; 1959;**11**:1877
- [44] Duguid HA. A study of the evaporation rates of small freely falling water droplets. Master Theses 5295, Rolla: University of Missouri; 1969
- [45] Sirignano WA. Fuel droplet vaporization and spray combustion theory. *Progress in Energy and Combustion Science*. 1983;**9**(4):291-322
- [46] Sirignano WA. *Fluid Dynamics and Transport of Droplets and Sprays*. Irvine: Cambridge University Press, University of California; 1999
- [47] Kuo KK. *Principles of Combustion*. New York: John Wiley and Sons; 1986
- [48] Williams FA. *Combustion Theory*, Benjamin Cummins. CA: Menlo Park; 1985
- [49] Sinnott SB et al. Model of carbon nanotube growth through chemical vapor deposition. *Chemical Physics Letters*. 1999;**315**:25-30
- [50] Borgharkar NS et al. Solution delivery of $\text{Cu}(\text{hfac})_2$ for alcohol-assisted chemical vapor deposition of copper. *Journal of the Electrochemical Society*. 1999;**146**(3):1041-1045
- [51] Li K. *Direct Liquid Evaporation Chemical Vapor Deposition (DLE-CVD) of Nickel, Manganese and Copper-Based Thin Films for Interconnects in Three-Dimensional Microelectronic Systems*. Cambridge: Harvard University; 2016. p. 127
- [52] Esquenazi GL, Brinson B, Barron AR. Catalytic growth of carbon nanotubes by direct liquid injection CVD using the nanocluster $[\text{H}_x\text{PMo}_{12}\text{O}_{40}\text{CH}_4\text{Mo}_{72}\text{Fe}_{30}(\text{O}_2\text{CMe})_{15}\text{O}_{254}(\text{H}_2\text{O})_{98-y}(\text{EtOH})_y]$. *C-Journal of Carbon Research*. 2018;**4**(1):17

- [53] Gordon RG, Kramer K, Liu X. Chemical vapor deposition and properties of amorphous aluminum oxide films. *MRS Proceedings*. 1996;**446**:383
- [54] Jones AC et al. MOCVD of zirconia thin films by direct liquid injection using a new class of zirconium precursor. *Chemical Vapor Deposition*. 1998;**4**(2):46-49
- [55] Awaluddin A et al. Direct liquid injection MOCVD growth of TiO_2 films using the precursor $\text{Ti}(\text{mpd})(\text{dmae})_2$. *Le Journal de Physique IV*. 2001;**11**(PR3):Pr3-531-Pr3-537
- [56] Kang S-W, Rhee S-W. Deposition of La_2O_3 films by direct liquid injection metallorganic chemical vapor deposition. *Journal of the Electrochemical Society*. 2002;**149**(6):C345-C348
- [57] Vernardou D, Pemble ME, Sheel DW. Vanadium oxides prepared by liquid injection MOCVD using vanadyl acetylacetonate. *Surface and Coatings Technology*. 2004;**188-189**: 250-254
- [58] Rayleigh JWS. *The Theory of Sound*. Vol. 2. London: MacMillan; 1896
- [59] Lang RJ. Ultrasonic atomization of liquids. *The Journal of the Acoustical Society of America*. 1962;**34**(1):6-8
- [60] Berger HL. *Ultrasonic Liquid Atomization: Theory and Application*. Hyde Park, New York: Partridge Hill Publishers; 1998
- [61] Tsai S, Childs P, Luu P. Correlation between droplet diameter and viscosity. *AIChE Journal*. 1996;**42**(120):3340
- [62] Engie R. Maximizing the use of platinum catalyst by ultrasonic spray application. In: *Proceedings of ASME 2011 5th International Conference on Energy Sustainability & 9th Fuel Cell Science, Engineering and Technology Conference*; Washington, DC, USA. 2011
- [63] Huffman M. Liquid source misted chemical deposition (LSMCD)—A critical review. *Integrated Ferroelectrics*. 1995;**10**(1-4):39-53
- [64] Cross WB, Parkin IP. Aerosol assisted chemical vapour deposition of tungsten oxide films from polyoxotungstate precursors: Active photocatalysts. *Chemical Communications*. 2003;**14**:1696-1697
- [65] McMillan LD, Paz de Araujo CA. U.S. Patent number 5.119.760. 1992
- [66] McMillan LD, Paz de Araujo CA. U.S. Patent number 5.138.520. 1992
- [67] McMillan LD et al. Liquid source CVD. *Integrated Ferroelectrics*. 1991;**2**:351-359
- [68] Warwick MEA et al. Hybrid chemical vapour and nanoceramic aerosol assisted deposition for multifunctional nanocomposite thin films. *Thin Solid Films*. 2011;**519**(18):5942-5948
- [69] Krumdieck SP. Pulsed-pressure MOCVD science. *Materials and Technology. ECS Transactions*. 2009;**25**(8):1209-1219
- [70] Versteeg VA, Avedisian CT, Raj R. *Method and Apparatus for CVD using Liquid Delivery System with an Ultrasonic Nozzle*. USA: Cornell Research Foundation, Inc.; 1995

- [71] Krumdieck SP, Raj R. Experimental characterization and modeling of pulsed MOCVD with ultrasonic atomization of liquid precursor. *Chemical Vapor Deposition*. 2001;**7**(2):85-90
- [72] Krumdieck SP, Raj R. Conversion efficiency of alkoxide precursor to oxide films grown by an ultrasonic-assisted, pulsed liquid injection, metalorganic chemical vapor deposition (pulsed-CVD) process. *Journal of the American Ceramic Society*. 1999;**82**(6):1605-1607
- [73] Porporati A, Roitti S, Sbaizero O. Metallorganic chemical vapor deposition of Ta₂O₅ films. *Journal of the European Ceramic Society*. 2003;**23**(2):247-251
- [74] Versteeg VA, Avedisian CT, Raj R. Metalorganic chemical vapor deposition by pulsed liquid injection using an ultrasonic nozzle: Titanium dioxide on sapphire from titanium(IV) isopropoxide. *Journal of the American Ceramic Society*. 1995;**78**(10):2763-2768
- [75] Krumdieck S, Raj R. Growth rate and morphology for ceramic films by pulsed-MOCVD. *Surface and Coatings Technology*. 2001;**141**(1):7-14
- [76] Xie H, Raj R. Epitaxial LiTaO₃ thin film by pulsed metalorganic chemical vapor deposition from a single precursor. *Applied Physics Letters*. 1993;**63**(23):3146-3148
- [77] Bosch Premium Fuel Injectors Trade Brochure. Robert Bosch LLC, Farmington Hills, Michigan. 17032145 RevA. 2017
- [78] Paule K. Fuel Injection System for Internal Combustion Engines with an Electromagnetic Injector. Stuttgart: Robert Bosch GmbH; 1957
- [79] Kennedy HE, Brooks W. Method and apparatus for the electromagnetic control of the fuel injection valves of an internal combustion engine. Patent no. DE655355C licenced to BROOKS WALKER. 1930
- [80] Sénateur JP et al. Procédé et Dispositif d'Introduction de Précurseur dans une Enceinte de Dépôt Chimique en Phase Vapeur. Patent no. 93/08838 licenced to J.I.P. Elec, 11 chemin du Vieux Chêne, 38240 Meylan, France. 1993
- [81] Reitz RD. Atomization and Other Breakup Regimes of a Liquid Jet. Princeton, New Jersey: Princeton University; 1978
- [82] Tennant PA et al. Simulation of flow through single orifice nozzles. In ICLASS-90, Hartford, Connecticut. 1990
- [83] Hiroyasu H, Arai M, Shimizu M. Break-up length of a liquid jet and internal flow in a nozzle. In ICLASS-91, Gaithersburg. 1991:275-292
- [84] Schmidt DP, Corradini ML. The internal flow of diesel fuel injector nozzles: A review. *International Journal of Engine Research*. 2005;**2**(1):1-22
- [85] Payri R et al. Diesel nozzle geometry influence on spray liquid-phase fuel penetration in evaporative conditions. *Fuel*. 2008;**87**(7):1165-1176
- [86] Dubourdieu C et al. Pulsed liquid-injection MOCVD of high-K oxides for advanced semiconductor technologies. *Materials Science and Engineering: B*. 2005;**118**(1-3):105-111

- [87] Dubourdieu C et al. Growth by liquid-injection MOCVD and properties of HfO₂ films for microelectronic applications. *Chemical Vapor Deposition*. 2006;**12**(2-3):187-192
- [88] Hušeková K et al. Growth of RuO₂ thin films by liquid injection atomic layer deposition. *Thin Solid Films*. 2010;**518**(16):4701-4704
- [89] Kaul AR, Seleznev BV. New principle of feeding for flash evaporation MOCVD devices. *Journal De Physique*. IV. 1993;**3**(3):375-378
- [90] Pignard S et al. Chemical vapor deposition and structural study of La_{0.8}MnO_{3-δ} thin films. *Thin Solid Films*. 1998;**347**:161-166
- [91] Senzaki Y et al. Atomic level solutions® for advanced microelectronic applications. In: *Solid-State and Integrated-Circuit Technology, ICSICT 2008*. IEEE. 2008:1308-1311
- [92] Guillon H et al. Device for Introducing, Injecting or Spraying a Mixture of a Carrier Gas and Liquid Compounds and Method for Implementing Said Device. Montpellier: KEMSTREAM; 2016
- [93] DS-VAP-DLI Systems-eng (0611) Data Sheet: Liquid Vaporizer Systems, Brooks Instrument, LLC, Hatfield, Pennsylvania. 2011
- [94] Avril L, Decams JM, Imhoff L. Pulsed direct liquid injection ALD of TiO₂ films using titanium tetraisopropoxide precursor. *Physics Procedia*. 2013;**46**:33-39
- [95] Avril L et al. Alumina particle reinforced TiO₂ composite films grown by direct liquid injection MOCVD. *Vacuum*. 2014;**107**:259-263
- [96] Boisselier G, Maury F, Schuster F. SiC coatings grown by liquid injection chemical vapor deposition using single source metal-organic precursors. *Surface and Coatings Technology*. 2013;**215**:152-160
- [97] Li N et al. Growth of atomically smooth epitaxial nickel ferrite films by direct liquid injection CVD. *Chemical Vapor Deposition*. 2011;**17**(7-9):261-269
- [98] Archana PS et al. Photocatalytic water oxidation at bismuth vanadate thin film electrodes grown by direct liquid injection chemical vapor deposition method. *International Journal of Hydrogen Energy*. 2017;**42**(12):8475-8485
- [99] Yengantiwar A et al. Direct liquid injection chemical vapor deposition of molybdenum-doped bismuth vanadate photoelectrodes for efficient solar water splitting. *The Journal of Physical Chemistry C*. 2017;**121**(11):5914-5924
- [100] Gaskell JM et al. Deposition of lanthanum zirconium oxide high-k films by liquid injection ALD and MOCVD. *Chemical Vapor Deposition*. 2007;**13**(12):684-690
- [101] O'Kane R et al. Growth of HfO₂ by liquid injection MOCVD and ALD using new hafnium-cyclopentadienyl precursors. *Chemical Vapor Deposition*. 2007;**13**(11):609-617
- [102] Black K et al. Deposition of ZrO₂ and HfO₂ thin films by liquid injection MOCVD and ALD using ansa-metallocene zirconium and hafnium precursors. *Journal of Materials Chemistry*. 2008;**18**:4561-4571

- [103] Chalker PR et al. Liquid injection atomic layer deposition of silver nanoparticles. *Nanotechnology*. 2010;**21**(40):405602
- [104] Karim Z et al. Advances in ALD equipment for sub-40nm memory capacitor dielectrics: Precursor delivery. *Materials and Processes. ECS Transactions*. 2008;**16**(4):125-134
- [105] Kim SK, Hoffmann-Eifert S, Waser R. Growth of noble metal Ru thin films by liquid injection atomic layer deposition. *The Journal of Physical Chemistry C*. 2009;**113**:11329-11335
- [106] PGV-CE23A, Liquid Source Vaporization System Datasheet. Kyoto: Horiba Stec, Co., Ltd.; 2018
- [107] Hemmer E et al. Nanostructured ZrO₂ membranes prepared by liquid-injection chemical vapor deposition. *Microporous and Mesoporous Materials*. 2012;**163**:229-236