

## A NEW EVAPORATION SYSTEM FOR CHEMICAL VAPOUR DEPOSITION

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### ABSTRACT

*In this paper, a new evaporation system is presented, allowing the injection of viscous and/or sensitive precursors inside a CVD reactor chamber. The setup was originally developed for Titanium(IV) Isopropoxide (TTIP), which is known for its sensitivity toward air moisture, its high viscosity, and its ability to precipitate easily in undesirable conditions. This setup is adapted for the injection of all types of liquid and viscous precursors, and for the evaporation of solid precursors with the help of an adequate accessory. The major benefit of this system is a precise control and a high stability of evaporation temperature, and a homogeneous temperature gradient from the point of evaporation to the junction with reactor. This virtually eliminates all risks of re-condensation or deposition inside of the evaporator. The construction and the functioning of this device is explained in details, and compared to the usual evaporation methods.*

### 1. INTRODUCTION

Titanium(IV) isopropoxide (TTIP) and Titanium(IV) ethoxide ( $\text{Ti}(\text{OEt})_4$ ) are widely available commercially and used for CVD as well as in chemistry (Sol-gel processes). Titanium alkoxides such as TTIP and  $\text{Ti}(\text{OEt})_4$  are difficult to handle and sometime dangerous due to the high reactivity of unsaturated Ti centers toward air and moisture. They are also viscous and prone to pre-react in gas-phase before film deposition or interact with precursor of other components in multi-components systems. Under the effect of humidity or heat, transparent TTIP turns yellow/brown. A broad characterization of these precursors was carried out elsewhere [1, 2]. In the case of TTIP, thermogravimetric analysis shows a maximal evaporation rate at temperatures of 119.6°C. Moderate evaporation can already be observed at temperatures as low as 50°C. Thermal decomposition (generating the coating film) happens at temperatures above 220°C in a neutral low-pressure atmosphere, but the presence of oxygen in the reaction atmosphere decreases the decomposition temperature to a value of 70°C.

Since oxygen presence can modify the surface properties of obtained coating, or if a low deposition temperature is wished, TTIP deposition may have to be carried out with a low evaporation temperature (55°C for instance) and a low

deposition temperature (75°C for instance). This temperature gap is thin, and therefore any small in-homogeneity of temperatures along precursor path may lead to undesirable re-condensation or deposition of precursor. In our case, and for all the presented reasons, classic evaporation systems proved inefficient to produce a reproducible and measurable flow of precursor vapor at a constant and precise enough temperature, which affects negatively the quality of deposited films.

The supply of precursor in vapor phase is essential to the deposition of good quality coatings. As a result, various evaporation solutions were used and are presented in a first part. Experimentally the use of viscous precursors such as Titanium(IV) isopropoxide in classical industrial vacuum systems revealed their limits: Titanium(IV) isopropoxide tends to easily precipitate under the effect of humidity, react or condensate due to too high or too low temperature along the path of precursor, which not all evaporation system tolerate. A satisfactory system was obtained with the development of the *temperature gradient evaporator*, which is described in a second part.

### 2. COMMON EVAPORATION SYSTEMS

#### 2.1 Bubbling system with gas flow controller:

The simple and well known bubbling systems is a proven method of evaporation where a carrier gas simply goes through the liquid precursor. As pointed out in [3], it presents inherent problems such as poor stability and reproducibility, due to the extremely high sensitivity for changes in temperature. Figure 1 presents an improved version of this system, which was the first installed system on the experimental set-up. In such system, the precursor vapor is delivered with the use of an electronic device (a: Gas flow controller) which allows a precise control of the gas flow. The bubbling system (b) is heated to the evaporation temperature, and the bubbling of carrier gas inside of the precursor liquid ensures that the concentration of precursor in the gas reaches the saturated vapor pressure. However, in order to measure and control the gas-flow, the electronic controllers enclose a heated and extremely thin tube (c). Many precursors, such as TTIP react easily precisely there. As a result, deposition or condensation of precursors inside

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the measure instrument creates damages which can't be repaired except for a high cost.

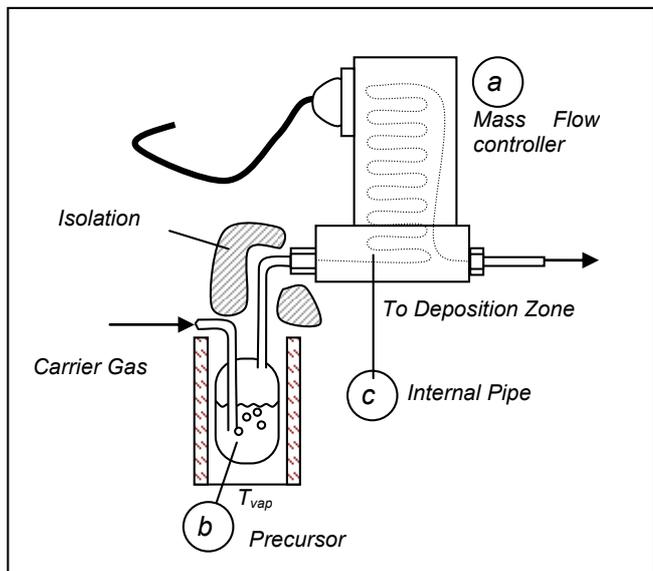


Figure 1 - Initial evaporator bubbling system.

**2.2 Classical evaporator for solid (powder) precursors:**

In Figure 2, a classical evaporator for powders is shown. In such configuration, the flux of sublimed substance depends on partial pressure and diffusion coefficient of evaporating substance and of Sherwood's number [4]. The powder is put in a mobile vessel (a), which can be moved from (b) the cold zone (room temperature, no evaporation) to (c) the heated zone, which is thermo-stated by the use of resistive heating system. Such systems are composed of resistive wires, either flexible, rolled against the walls of the evaporator, or directly welded on them. The heating system (brown wires representing the resistive elements) shall be divided into as many independent sections as possible (d1, d2, d3), in order to ensure a heating as homogeneous as possible, making heating regulation system relatively complex. This is a classic industrial solution for precursor transport, well adapted for the construction of industrial vacuum systems, made of massive metallic tubes. However, the accuracy of such a system is poor at the junction between construction elements (e: "potential cold point"). This is usually of no consequence when evaporation temperature and deposition temperature are very different. The transport tubes are simply heated well above the evaporation temperature, in that case the risk of cold points is insignificant. For other precursors, when evaporation and deposition temperatures are close to each other, it may to a significant extend trigger deposition and/or re-condensation along the transport tubes.

**2.3 Delivery of liquid precursor with Liquid flow controllers**

In order to introduce the liquid precursor into the evaporator, typical liquid dosing system (liqui-Flow controllers) may be used. Such systems, as described in [3, 5], are based

on a dynamic measure of liquid velocity by calorimetry, very similar to the gas-flow controllers described before. The liquid flow goes through a very thin heated capillary, which presents the same drawbacks for sensitive precursors (such as TTIP). Under the effect of temperature, precipitation or degradation of precursor occurs, which obstruct the capillary and may ultimately damages the whole dosing system in a definitive way.

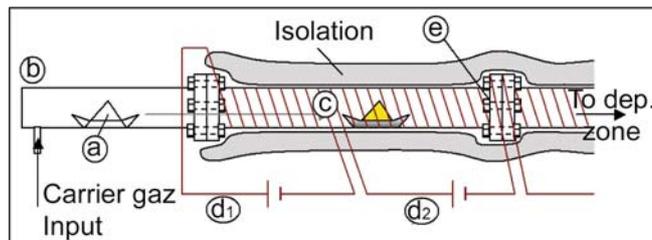


Figure 2 - Classic evaporator for powder precursors.

**2.4 Delivery by micro peristaltic pump**

A working system based on the system described in Figure 2, and adapted for the delivery of liquid or viscous precursors is presented in Figure 3. The main benefit of this system is the absence of contact between the liquid and any moving parts thanks to the use of a micro rotative pump (peristaltic pump). The precursor goes through a thin flexible tube, which is pressed between a fixed cage and the moving pallets. This system allows to control flows as small as 50µL per minute. Compared to the first bubbling system, this system presents important advantages because it allows a direct control of the quantity of precursor delivered to the evaporator. However, the length of the path between evaporation and deposition zones is long due to the construction method (Massive metal tubes), and the temperature control is complex (5 independent zones).

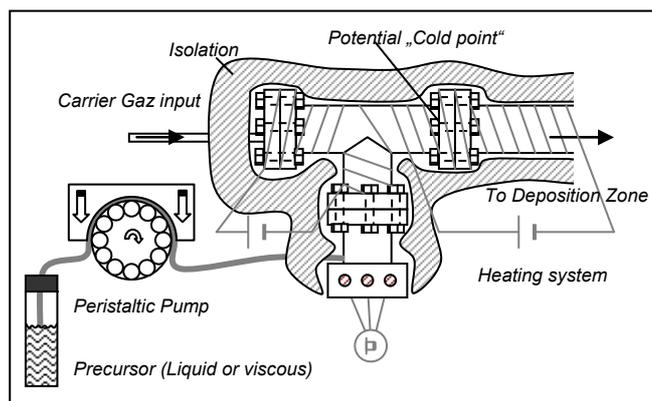


Figure 3 - Evaporator with delivery of liquid precursor by peristaltic pump.

This system suffers from the same problems as the classical evaporator for solid precursors does. Deposition or condensation can be observed between the evaporator and the theoretical deposition zone, due to the variations of temperature, and the presence of cold points.

## 2.5 Simple glass system:

In the system presented in Figure 4, the precursor, liquid or solid, is introduced in a glass recipient (a) prior to experiment. When Vacuum is reached, the recipient is heated to evaporation temperature in a Liquid bath (b) thermo-stated and stirred with a dedicated piece of equipment (c). The tubing between (a) the recipient (evaporation zone) and (d) the substrate, (reactor, deposition zone), is isolated in order to reduce risks of re-condensation. The drawbacks of this system are not linked to the quality of evaporation, but of practical nature since the system must be dismantled between each experiment and is limited in size and in the vacuum it can sustain. However, it appears robust chemically and allows the use of sensitive chemicals. It was decided to adapt and use such an evaporation system.

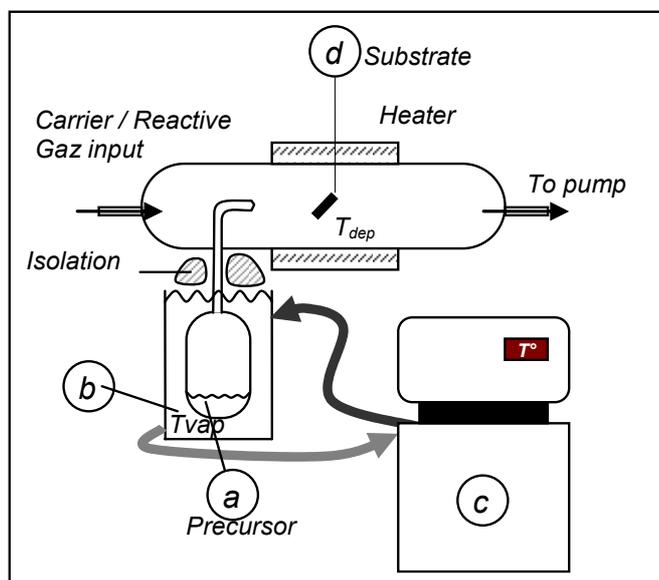


Figure 4 - Simple glass evaporator system.

## 3. DEVELOPMENT OF FINAL APPARATUS

### 3.1 Temperature gradient evaporator

Observation and use of several other evaporation systems, considerations on advantages and drawbacks of each, allowed the conception of a system combining most of observed advantages and avoiding most of known drawbacks. Technical drawings were achieved, realization was carried out at a subcontractor company, final assembly, adjustments, sealing and calibration were achieved in laboratory. The invention is an evaporation system based on the classical glass system presented in figure 4, with several improvements allowing its use in connection with an industrial vacuum system. First, the use of a peristaltic micro pump makes it possible to refill the evaporator with precursor without dismantling the whole system. It is possible to refill the evaporator during the experiment, allowing the deposition of unlimited amount of precursor. The whole system, including the glass vessel where precursor is evaporated, the pipe from evaporation point to deposition point, and gas pipes are immersed into a heat-conducting fluid, thermo re-

gulated and stirred by a dedicated instrument. The fluid is introduced in the device in a fashion which removes the risk of hot or cold points along the way of precursor vapor. The temperature of the system is very precisely controlled in multiple points. Several accessories allow the use of liquid, viscous, or solid precursors, the calibration of pressure and dynamic load losses, and the control of precursor temperature.

### 3.2 Operation of the apparatus:

As presented in Figure 5, the precursor is supplied from the precursor container (a) with the peristaltic pump (b) into the evaporation vessel (c). There, it evaporates and diffuses into the carrier gas (d). The vessel can be connected to a variety of accessories through a stopper (e). A valve (f) isolates the evaporation vessel from the vacuum chamber. When open, the precursor vapor is introduced in the vacuum chamber, meets the reactive gas (g) and goes through the thermo-stated tube (h) to reach the deposition zone, where it reacts on the substrate (i). The heating device (j) sends heating fluid with pressure at the tip of the thermo-stated tube (k). The fluid goes then up, decreasing in temperature (from a few Kelvin) and is evacuated at the top of the system (l). In Figure 5, the system is represented with a third thermocouple measuring directly the temperature of the liquid precursor inside the vessel, and connected through the accessory connector (m). Two other thermocouples (n) measure the temperature of oil at the tip of thermo-stated tube, and in the zone around vessel. The accessory connector is absent from Figure 6.

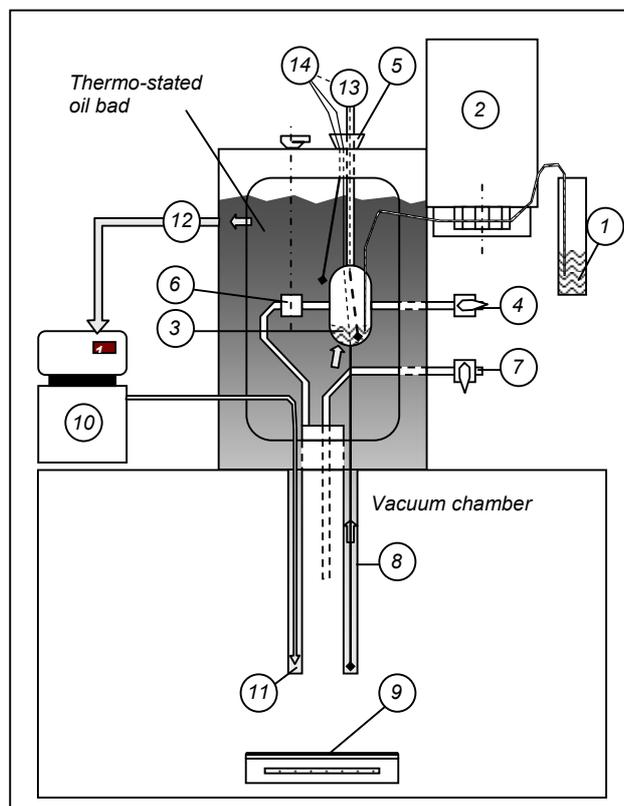


Figure 5 - Temperature gradient evaporator.

It is possible to refill the precursor vessel with the peristaltic pump. It is also possible to use solid precursor (filled through the accessory connection.). The second advantage is the extremely accurate control of temperature between evaporation zone (vessel) and deposition zone (substrate). This advantage is given by 4 innovations:

- The short distance between evaporation and deposition zone minimize potential problems.
- The configuration of heating pipes is the main innovation of this system, because the heating fluid is introduced at the tip of pipe, at a close distance to the substrate. The fluid moves then upward to evaporation zone and is pumped out to the heating system. Therefore, thermal losses create a small temperature gradient, the lowest temperature being at the evaporation zone. This eliminates all risk of cold point. That temperature gradient is illustrated in Figure 5 by the color gradient (hot=pale grey, a few Kelvin colder=dark grey), and can be controlled by the speed of the fluid movement.
- The integration of several temperature control elements in different parts of the apparatus allows an extremely accurate control of temperature and temperature gradient. Two thermo-couple are fixed in the apparatus, disposed in the heating fluid at the tip of the thermo-stated tube and next to the vessel. A third thermocouple can be inserted in the accessory connector in order to monitor the real temperature of the precursor inside the evaporation vessel.
- The large double-walls tube situated exactly at the vertical of deposition zone presents several advantages: The first is the isotropy of deposition, because the system presents an axial symmetry. The second is a laminar flow of precursor vapor (for a sufficiently low evaporation flow), which prevents irregularities of depositions rate which may happen in a turbulent flow.

This evaporation system was mounted on a plasma CVD reactor, tested and calibrated. General information on transport concepts such as flow regimes and boundary layers may be found in [6-8]:

The experimental CVD device works with Substrate temperature up to 700°C (Usually between 100 and 200°C), pressure: from  $10^{-1}$  to  $10^{-6}$  mbar and gas flow rates: from 1 to 100 sccm. Calculations of Knudsen number were performed using temperatures of 300K for gas without plasma and 1000K for gas with plasma, at a pressure of  $1 \times 10^{-4}$  mbar, and with molecule radius of 75 to  $800 \times 10^{-12}$ m, estimated from the radius and the geometry of ions and molecules. The pressure at which  $Kn = 1$  and at which the flow regime in evaporator turns molecular lies between  $1 \times 10^{-3}$  and  $4 \times 10^{-3}$  mBars, depending on precursor,  $1 \times 10^{-2}$  and  $3 \times 10^{-3}$  mBars in the case of Ar and O<sub>2</sub>. In the reactor zone,  $Kn \approx 10$  to  $Kn \approx 10^{-1}$  for ions and molecules, respectively (mixed regime), and  $Kn \approx 10^2$  and  $Kn \approx 1$ , considering the plasma only, for ions and molecules, respectively (molecular flow regime).

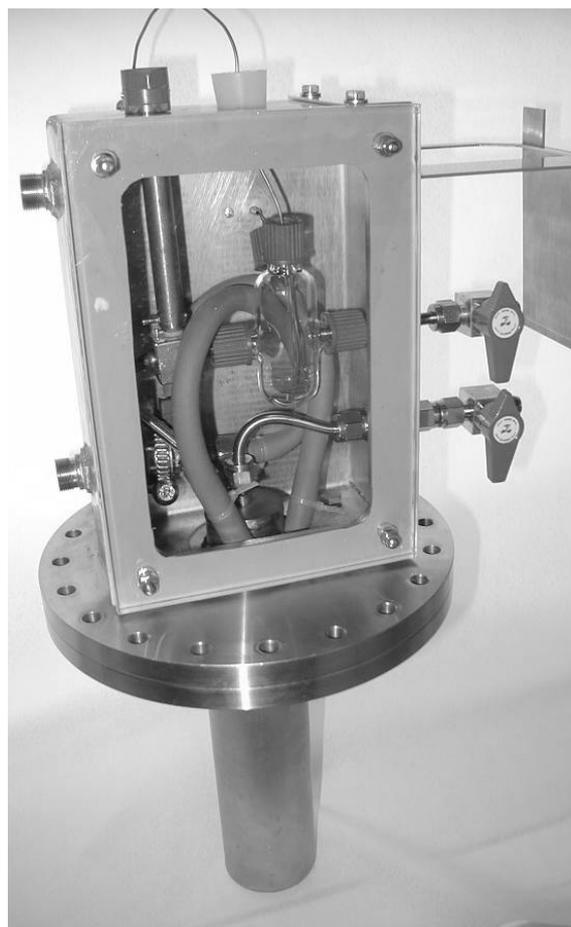


Figure 6 - Temperature gradient evaporator.

Pumping rates estimated from pressure-versus-time curves were: For the primary pump  $10.8 \text{ L.s}^{-1}$  at an end-pressure of 2.1 Pa (Leak Rate:  $9.5 \times 10^{-6} \text{ mol.s}^{-1}$ ). For the Turbo-molecular pump  $10 \text{ L.s}^{-1}$  at an end-pressure of  $7.5 \times 10^{-5}$  Pa (Leak Rate:  $3.1 \times 10^{-10} \text{ mol.s}^{-1}$ ).

The junction between the evaporator (glass) and the pipes of the set-up (metal) is made with a non-toric silicone-PTFE joint and is immersed in Oil. It allows a connection between glass and metal. This is however a point where leak occur. The leak rate was computed and reaches  $5.15 \times 10^{-8} \text{ Mol.s}^{-1}$  (0.07 sccm) in Oil. This value shall be reduced in the future with known technical solutions (toric joint).

The calibration of the apparatus allows the calculation of the flow rate of precursor vapor entering the reactor. The modeling of both reactor pressure, and of pressure inside the glass vessel as functions of pumping power and gas flows are carried out without chemicals (Ar and O<sub>2</sub>). Figure 7 presents the obtained curves: the variation of evaporator pressure as a function of carrier gas the flows through evaporator (a), the variation of evaporator pressure as a function of plasma gas flow (Ar) to reactor (b), and  $P_{Re}$ , as a function of  $F_{Ev}$  for several values of pumping power (c).

In figure 7c, three regimes can be observed with threshold pressures corresponding to the limits between molecular and continuum flows for Ar in the evaporator and in the reactor ( $1 \times 10^{-2}$  mbars and  $1 \times 10^{-4}$  mbars, respectively). With known values of carrier and reactive gas flows, the measure

of reactor pressure allows the calculation of incoming precursor flow and of the pressure inside the vessel, which allows a precise control of evaporation process. The evaporation rate can also be verified or estimated from the graduations of the evaporator vessel.

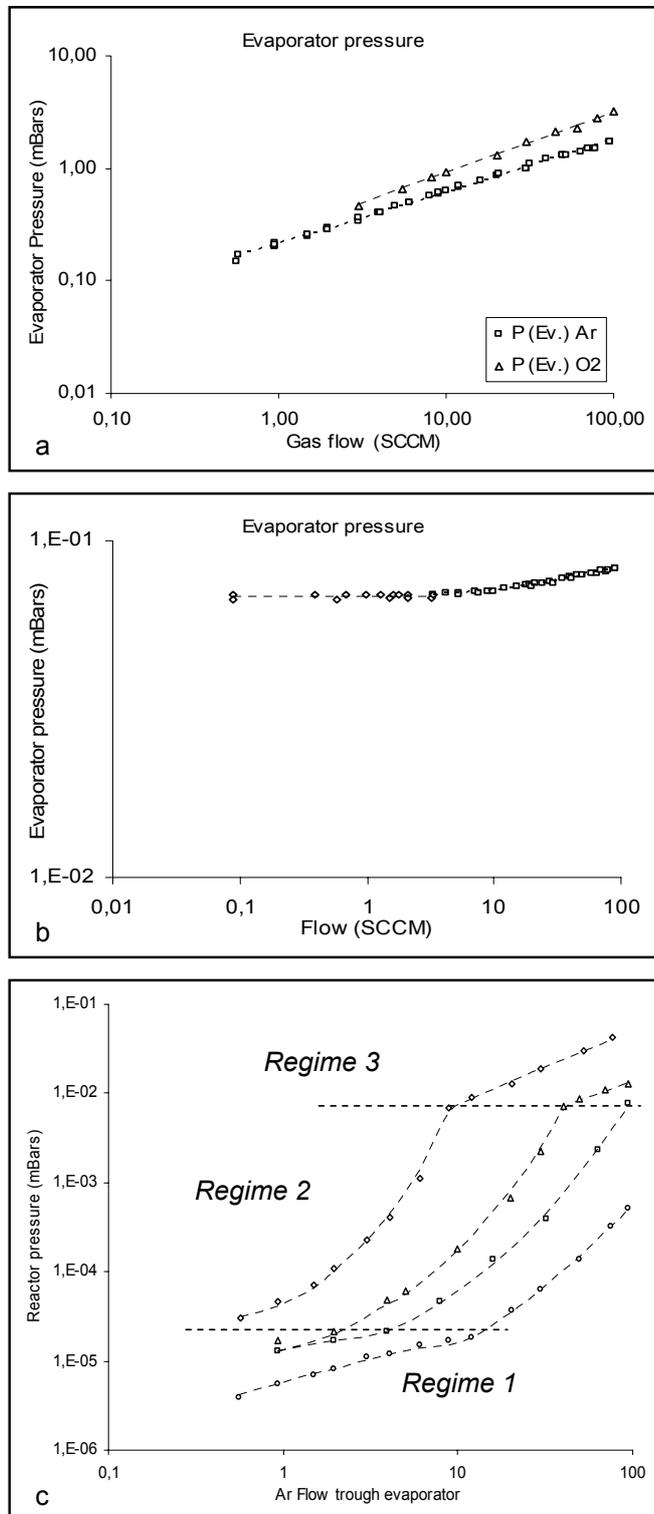


Figure 7 – Calibration curves.

#### 4. DISCUSSION AND CONCLUSION

The presented setup allowed the deposition of homogenous coatings with good quality, which had not been obtained with previous systems. The coating displayed in Fig. 8 presents an homogeneous aspect and a good surface quality. The surface of obtained coatings is smooth ( $R_a < 60\text{nm}$ ) and thickness ranges from 0.1 to 6 $\mu\text{m}$ . Experimental parameters are presented in [9]. These observations suggest that the attainable quality of the deposited coatings benefits from the precise control and the high stability of evaporation temperature provided by the *Temperature Gradient Evaporator*.

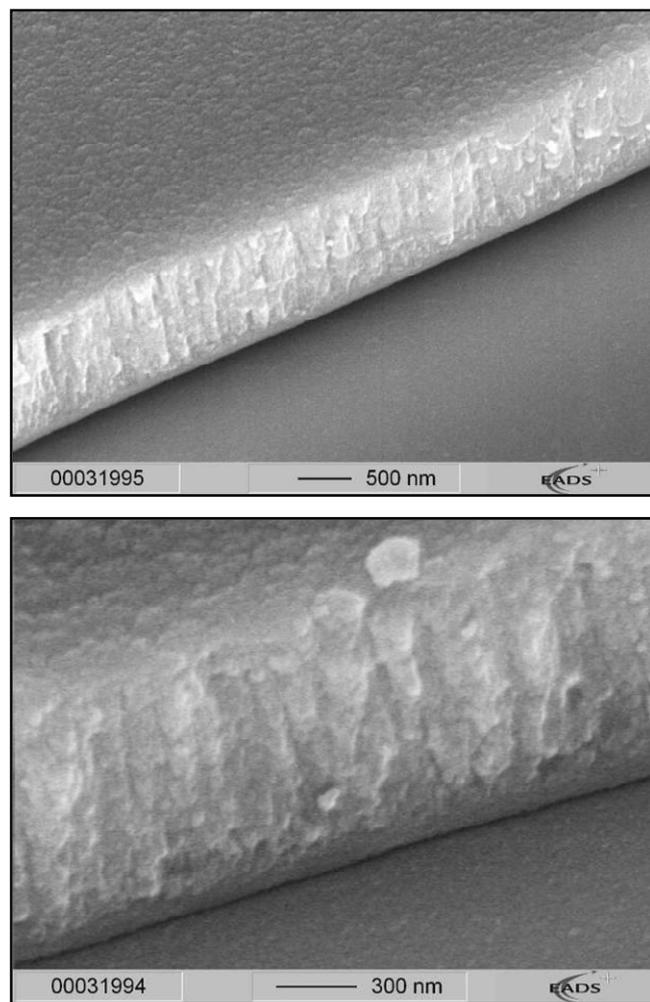


Figure 8 – Aspect of TiO<sub>2</sub> coatings obtained with temperature gradient evaporator (SEM).

In this work, a new evaporation system was presented and compared to other common evaporation systems. After calibration, this new *Temperature Gradient Evaporator* allows the injection of viscous and/or sensitive precursors inside a CVD reactor chamber in a reproducible and quantifiable way. While the developed prototype is functioning in a satisfactory fashion, performances could be increased by improving the connection of the vessel with a toric joint. The major benefit of this system is a precise control and a high stability of evaporation temperature, and a homogeneous temperature gradient from the point of evaporation to the junction with reactor. This virtually eliminates all risks

of re-condensation or deposition inside of the evaporator. Moreover, this system provides the ability to control the temperature of precursor vapor inside the reactor, up to several centimeters only away from the substrate surface with the thermo-stated double-walls tube.

The setup was originally developed for Titanium(IV) Iso-propoxide, a chemical which is difficult to handle due to its sensitivity, its viscosity, and its ability to precipitate or re-condensate. Therefore, the presented system shall present a solution for the evaporation of most chemicals (presenting the same difficulties or not), and is adapted for the injection of all types of liquid and viscous precursors. The evaporation of solid precursors is as well possible.

The construction and the functioning of this device was explained in details, and it is hoped that scientists in the field of CVD be able to improve their set-up by building similar apparatus. Commercial applications can refer to the pending Patent [10].

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