Improvements in vaporization of liquid reagents and new precursor delivery methods

MCVD Process Today *(1)*

In any optical fiber fabrication process, the stability and repeatability of reagent vapor delivery is of extreme importance. Unstable reagent flows cause variation in layer thickness and refractive index, resulting in variations of both geometrical and optical quality of the final fiber.

In MCVD process these variations are more critical as preforms produced by this technology are smaller than preforms produced by VAD or OVD:

- same magnitude of variation on preform will cause larger change over shorter drawn fiber length, limiting yield and productivity and affecting production cost
- for MCVD process to stay competitive, better reproducibility of process and homogeneity of preforms have to be achieved:
  - better uniformity of deposition process from preform to preform on the same deposition system and as between different systems **(long-term repeatability)**
  - longitudinal and radial homogeneity on a single preform, to enable longer and thicker preform fabrication **(short-term repeatability)**
- While a number of parameters affect repeatability and homogeneity of MCVD produced preforms, reagent delivery is one of the most important and depends on
  - **precision and repeatability of gas flow controlling devices**
  - **design and process related parameters of precursor sources**
  - **design of the gas cabinet and quality of used components**
  - **production environment parameter**

Optacore's goal is to improve reagent delivery methods, making MCVD process more competitive and efficient, providing also solutions for specialty preforms and use of less common precursor materials !

MCVD Reagent Delivery *(2)*

In MCVD process the most common reagents (precursors) are:

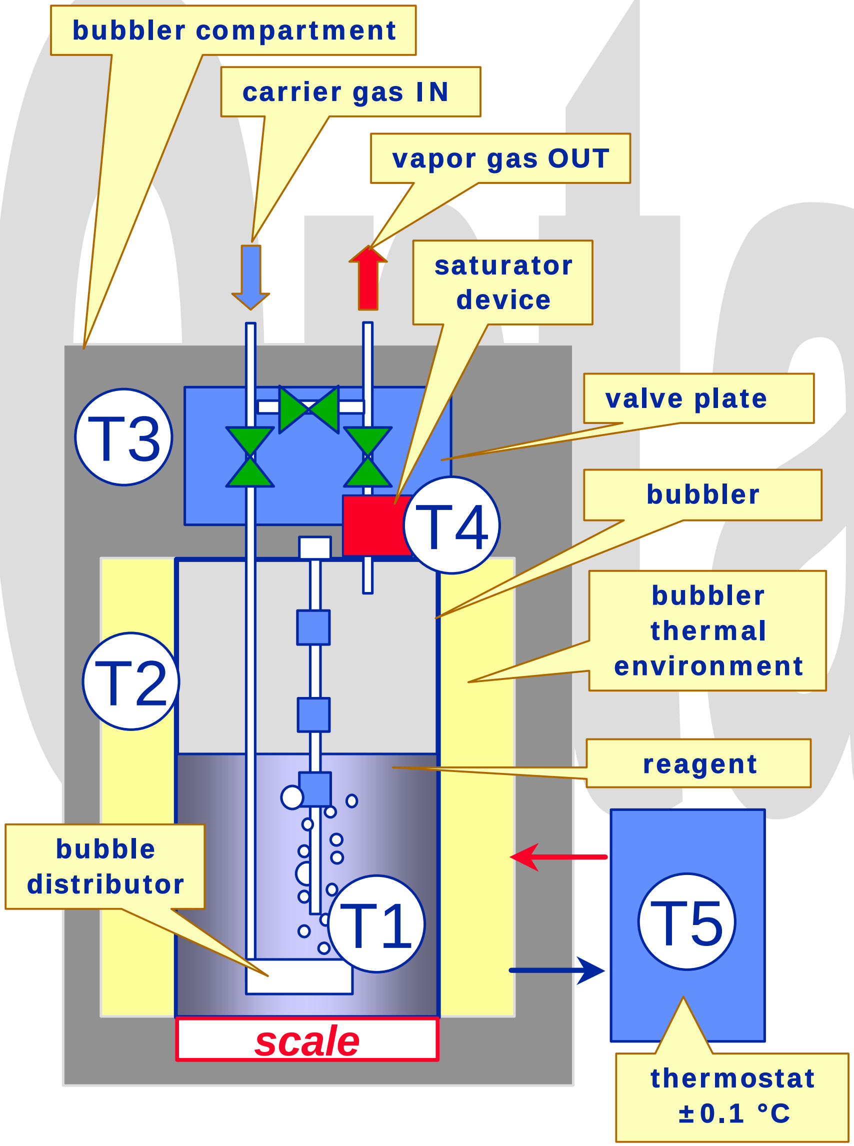
- **chlorides: $SiCl_4$, $GeCl_4$, $POCl_3$ and BBr_3 for specialty fibers (so called high vapor pressure precursors)**
  - their vapor is generated by bubbling carrier gas through liquid in bubblers
- **some precursors are available in the form of gases**
  - fluorine (as C_2F_6, SiF_4 or SF_6, BCl_3,...)
- **rare earth metals and aluminum (used in fabrication of active fibers) are not available in gaseous or liquid form, other methods are used:**
  - solution doping
    - by soaking (most widely used method for **rare earth** doped preforms)
    - by aerosol
  - direct evaporation from solids at high temperature
    - for **rare earth** doping from **chelate**
    - for **aluminum** from $AlCl_3$ or from metal

In large-scale fabrication of single mode fiber preforms, where yield and cost are most important, precision and repeatability of reagent delivery depends mostly on bubblers:

- **bubbler performance (vaporization stability and repeatability)**
- **mass flow controllers for carrier and other reagent gas flows**
- **construction of MCVD gas cabinet, bubbler compartments and control of downstream pressure**

MCVD Bubbler Limitations (3)

Schematic view of a bubbler:



Vaporization from bubblers is a very sensitive process, depending on a number of parameters:

- **most important parameters:**
  - carrier gas flow
  - temperature of the bubbler itself, the liquid inside and the saturator (if used)
  - temperature of the piping and components after the vapor exit from bubbler
  - downstream pressure
  - bubble size and number distribution
- **second order influences:**
  - bubbler design and construction
  - liquid level in the bubbler
  - production environment
- **bubblers are far from ideal vapor generators:**
  - for repeatable and precise operation they need stable and repeatable carrier flow
  - in most constructions, heat flow from thermal environment cannot compensate quickly enough for temperature drop due to evaporation of chlorides, resulting in reduced vapor flow in function of carrier flow
  - evaporation efficiency depends on carrier flow
  - with time bubble size and count changes
  - as vapor mixtures from up to 3 bubblers are used, variations of liquid level can affect refractive index significantly more than from single bubbler evaporation rate variation

Improving Reagent Delivery (4)

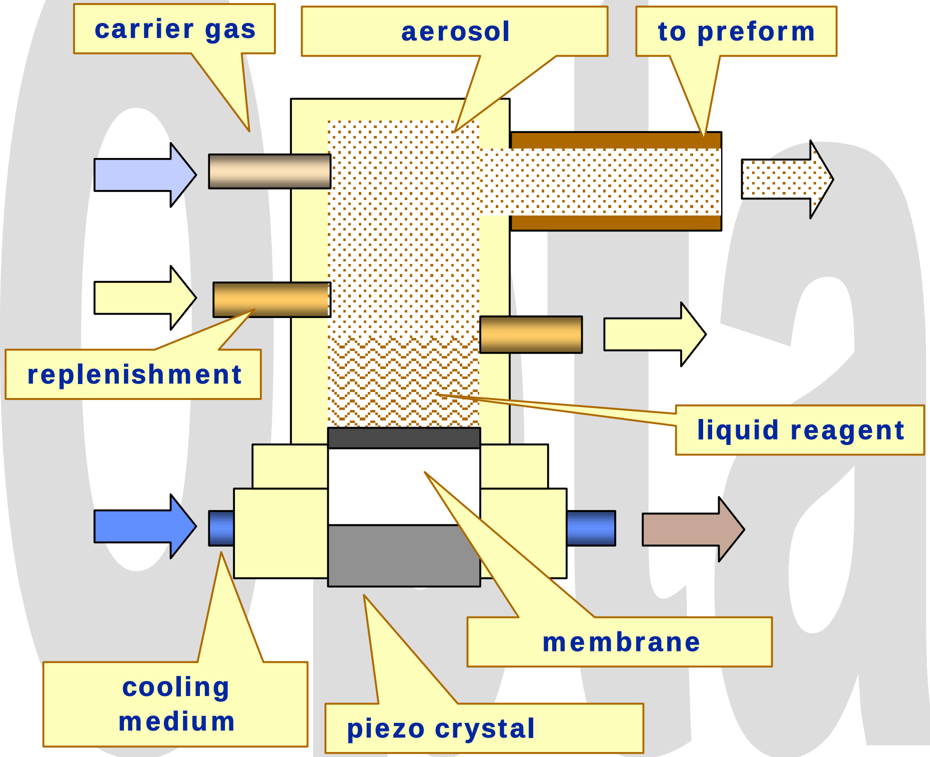
Optacore is working actively on improvement of reagent delivery systems in MCVD by improving on bubbler limitations:

- **study and evaluation of other vapor generation methods for liquid precursor materials:**
  - direct evaporation
  - liquid delivery and vaporization sources
- **with the goal to reduce vapor flow dependence on:**
  - filling level
  - thermal stabilization of the source and carrier flow
  - long- and short - term flow variations due to design and downstream pressure variations

Optacore is also developing methods for delivery of specialty fiber reagents from low vapor pressure precursors or solutions by use of:

- **high temperature evaporation**
- **aerosol doping techniques**

Aerosol doping in MCVD (5)

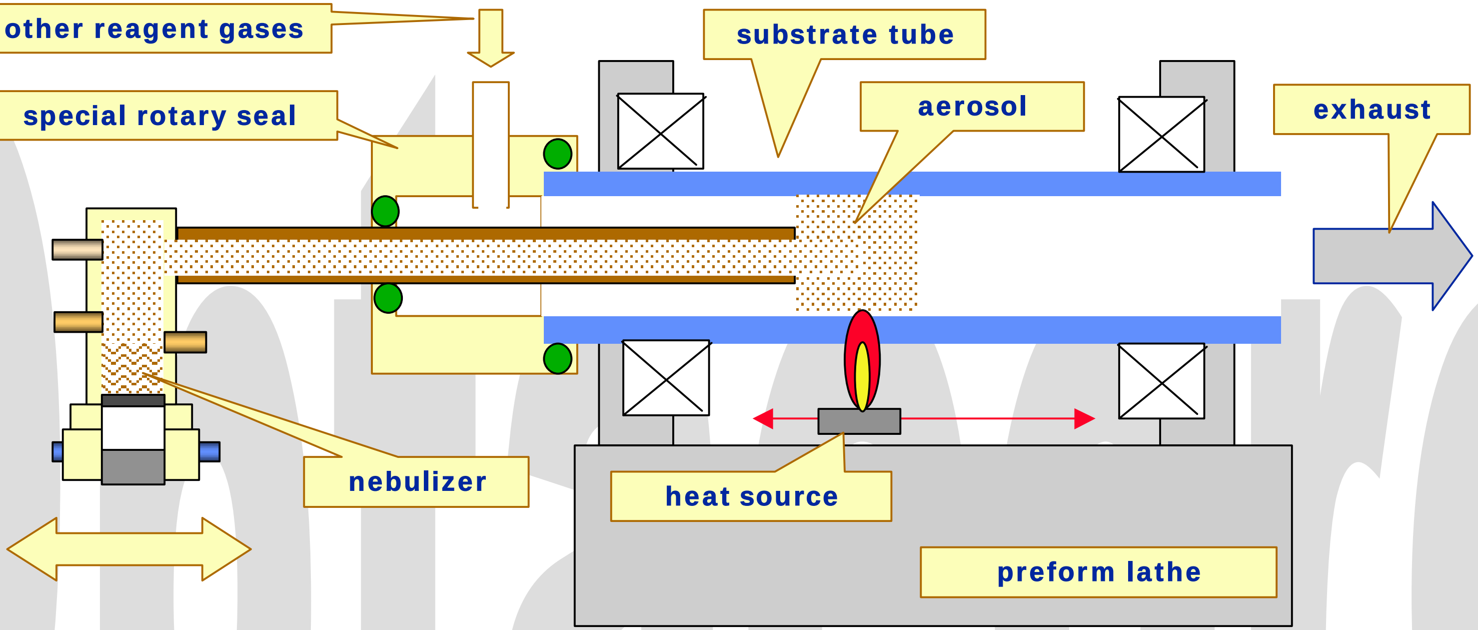


Principle of operation:

aerosol generator with ultrasonic nebulizer (T.F. Morse et al.) :

- ultrasonic nebulizer uses ultrasound beam, directed towards air interface, to atomize liquids. Under proper conditions, very fine, dense fog (aerosol) of particles is produced. Particle size depends on the beam power and frequency and average particle sizes well below 1 micron can be produced
- using nebulizer, practically any solution of reagents in suitable solvent can be atomized and led to CVD reaction by carrier gas flow
- small particle size ("nanoparticles") ensures that the fog does not condense back to liquid too quickly and can penetrate porous glass layers suitably
- this method permits use of special reagents in CVD process

Aerosol doping in MCVD (6)



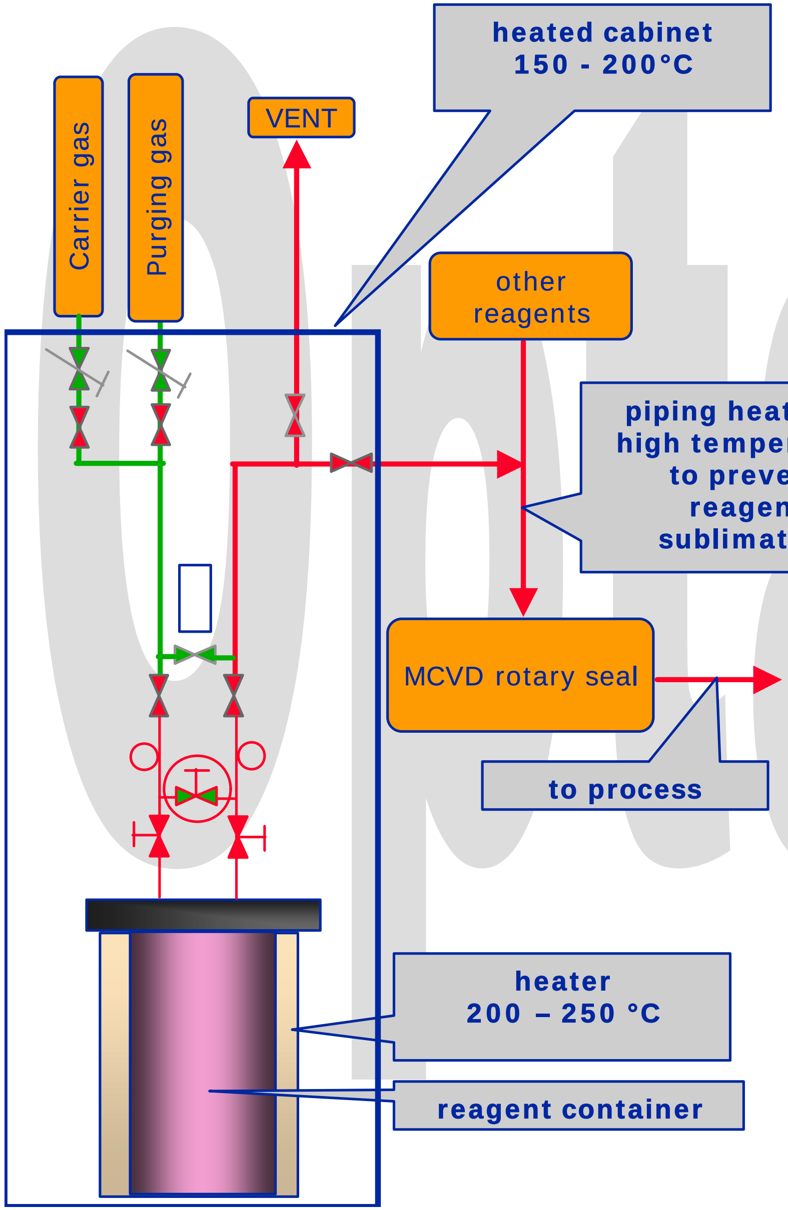
One possible use of aerosol generator in MCVD process (T.F. Morse et al.)

Aerosol process allows use of a wide choice of precursor and reagent materials in combination with MCVD process or in a CVD process based only on aerosol reagents:

- metal and transition elements
- rare earth elements
- organometallic materials

Optacore can deliver accessories and subsystems for aerosol doping, including special designs of rotary seals (see "Accessories" page) with sliding delivery tube

Direct evaporation of solids in MCVD *(7)*



Direct evaporation of solids:

- **suitable for reagents:**
  - which do not exist in liquid or gaseous phase
  - with low vapor pressure at room temperature
- **advantages:**
  - limited choice of reagents but a few most important available
  - important as Al ion doping method
- **disadvantages:**
  - purity of reagents
  - high temperature processing (200 – 250 °C or more)
  - specialized maintenance of equipment and parts
  - expensive components
  - possibility of clogging in lines due to sublimation

Typical applications:

- **evaporation of chelate:**
  - for example: La(thd)$_3$ or 2,2,6,6-tethrametyl- 3,5-heptadione
  - see next page for vapor pressure of most important chelate materials
- **evaporation of aluminum:**
  - from $AlCl_3$ x 6 H_2O
  - from metal Al

Direct evaporation of solids in MCVD (8)