Liquid & Vapor Delivery for ALD/CVD/MOCVD Nanotechnology Development

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Background-Delivery Systems

TriChem
3 Chemical
4-Delivery Points

MOCVD
Bubbler
System

Compact
DLI System

Background-Containers

Application Specific Small Bulk, Ampules, Bubblers & Level Sensing Solutions

Topic Focus-Compact DLI System

- LPCVD Application
- Liquid & DLI System
- Low volume use
- Furnace retrofit
  - Inside furnace enclosure
- Minimal installation cost
- Versatile platform
  - Easily repurposed

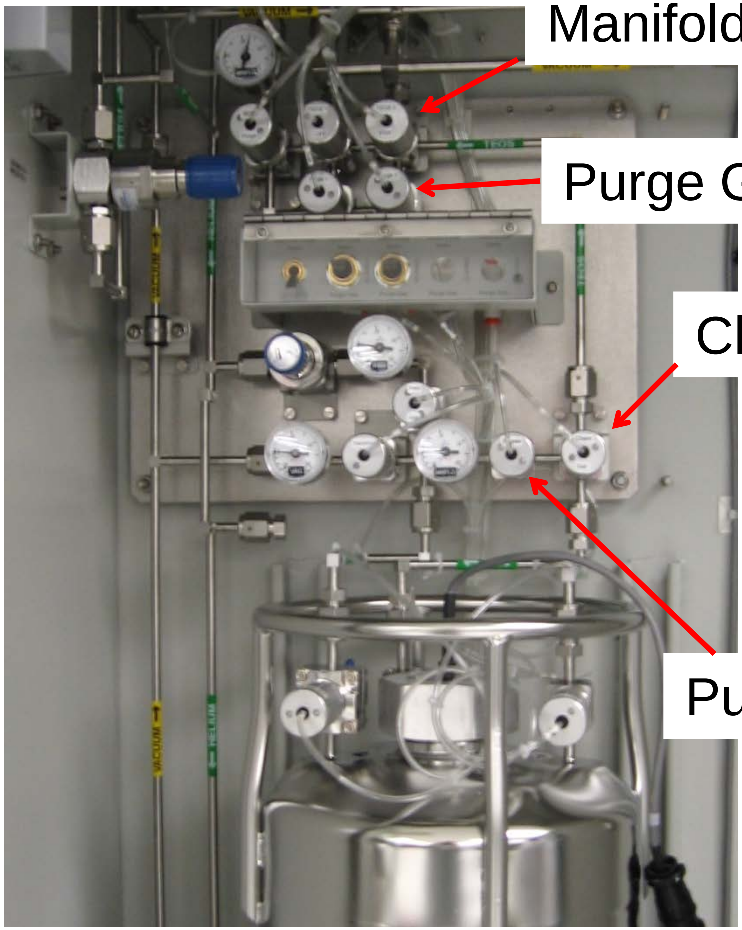
ALD/CVD/MOCVD Applications

- **ALD of high gate oxide for high-performances devices**
- **ALD of top/gate electrode on the gate oxide**
  - Pt, TiN, $SrRuO_3$, WC, Ta_xC_y, $W_wTi_xC_yN_z$ (WTiCN)
- **ALD and MOCVD of catalytic materials**
  - metals, oxides, nitrides,…
- **MOCVD of high k gate oxide for low power devices**
  - HfO_2, $Hf_ySi_yO_z$ (HfSiO), $Hf_wSi_xO_yN_z$ (HfSiON), $Hf_xZr_{1-x}O_2$ ($HfZrO_2$), $Hf_wLa_xO_yN_z$ (HfLaON), $SrTiO_3$, $BaTiO_3$, TiO_2 based materials…
- **MOCVD of III-V and II-VI semiconductor materials**
  - Nitrides, selenides (CISe, CIGSe), sulphides (CIS, ZnS, In_2S_3), SiC…
- **MOCVD of phase change materials for PCRAM applications**
  - Multimetallic alloys, tellurides (GST)
- **MOCVD of high k gate oxide for DRAM applications**
  - $Ba_xSr_{1-x}TiO_3$ (BST)
- **MOCVD of ferroelectric materials for FeRAM applications**
  - SBT, PZT
- **MOCVD of piezoelectric materials for MEMS applications**
  - PZT, PLZT
- **…and more**

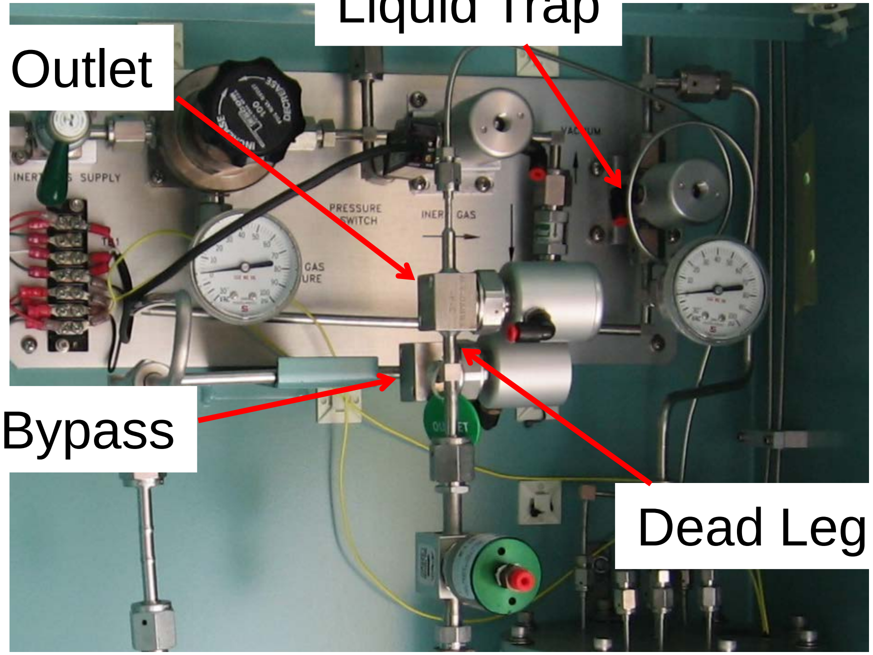
Liquid Delivery & Material Properties

- ALD/CVD/MOCVD precursors are reactive and pose physical and health risks.
- Primary system priority is purgeability to remove trace liquid and vapor residues for:
  - Container replacement
  - Delivery System and process tool service
- Liquids do not behave like gasses
- Liquid physical properties determine purge requirements and system architecture
  - High V.P. liquids require simple purging
  - Low V.P. liquids & solutions require solvent purging that multiplies system complexity
- Delivery piping must be considered

System Design & Purging

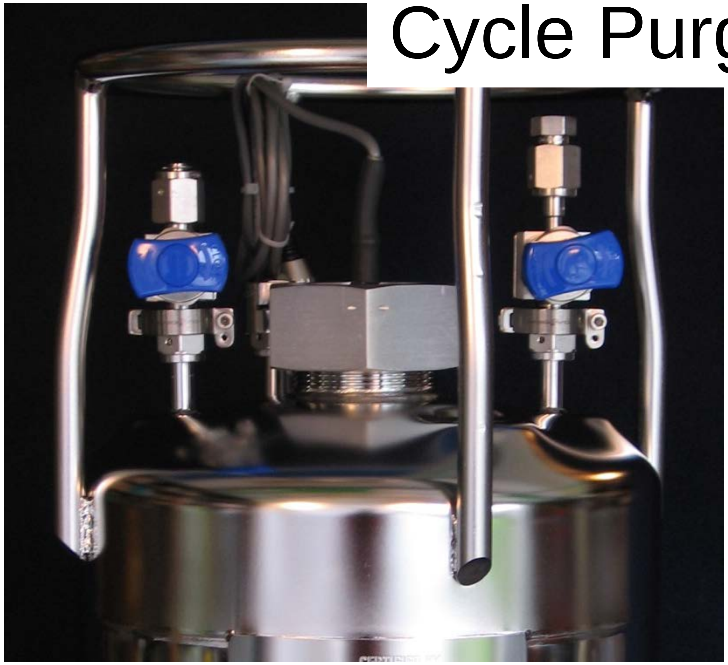


Two systems with the same operation purge differently because of mechanical design.

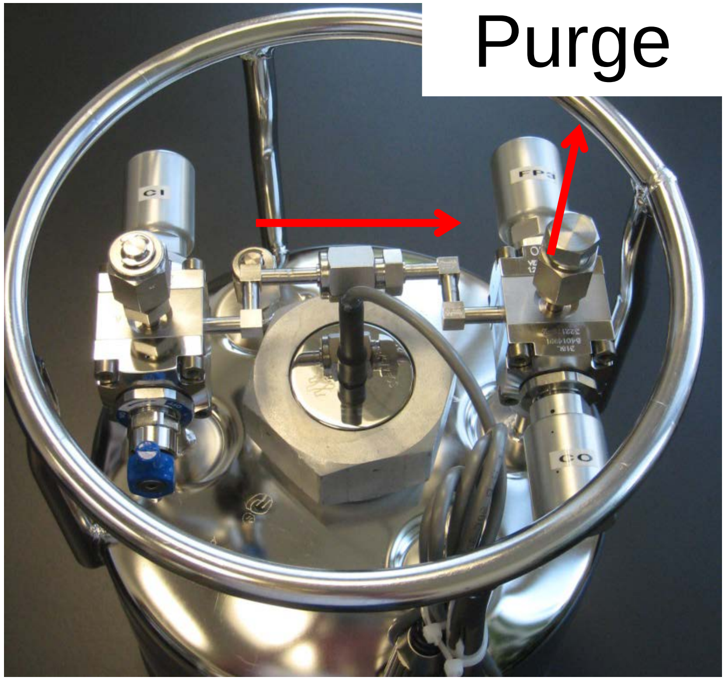


Container Design & Purging

Dead End Cycle Purge



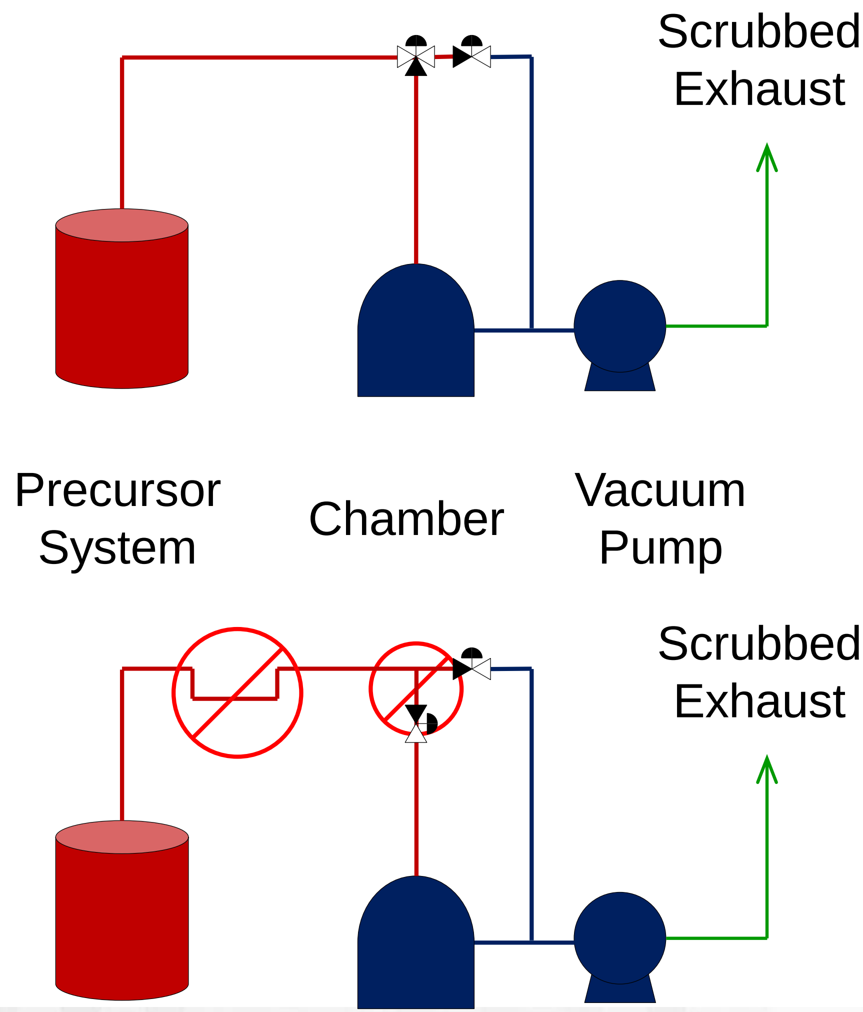
Flowing Purge



Purge Bypass Improves Liquid & Vapor Purging

Delivery line design & purging

- Minimum length
- Minimize diameter
    - Channelling
- High flow outlet to vacuum
- No traps or dead legs



Level Monitoring

- Scales
  - Tare weight vs. contents
- Internal Sensors
  - Float Switch
  - Optical
  - Ultrasonic
    - Point
    - Continuous

5 kg ampule
1.5 kg contents

Vapor Delivery

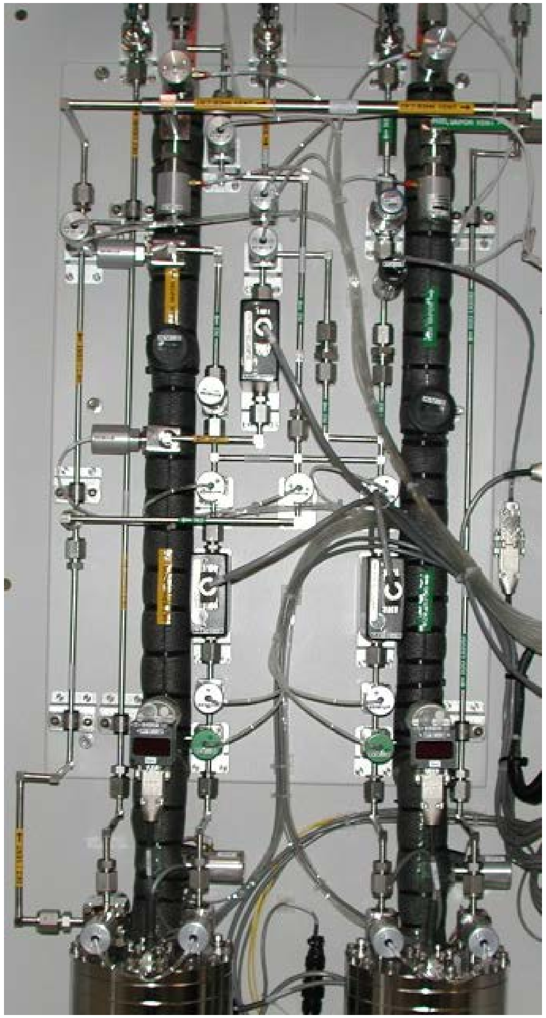
- Solids
  - Sublimation
- Liquids
  - Vapor Draw
    - High V.P. Only
  - Carrier Gas (Bubblers)
    - Pure compounds only
  - Direct Liquid Injection
    - Different methods

Carrier Gas Delivery

- Bubbler held at constant temperature
  - Keeps vapor pressure constant
- Carrier gas saturation variables
  - Physical properties
    - Heat of vaporization
  - Temperature
  - Bubble size
  - Bubble residence time
    - Decreases as level decreases

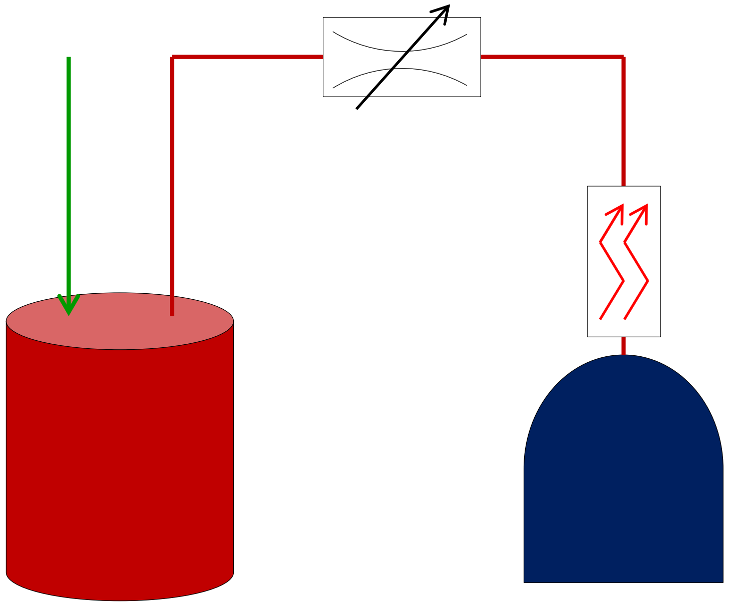
Carrier gas delivery

- Bubblers temp control
  - Bath
  - Recirculaters
  - Peltier Temp Controllers
- Carrier Gas MFC
- Process line pressure monitoring
- Downstream flow control
- Heated process line



Typical direct liquid injection

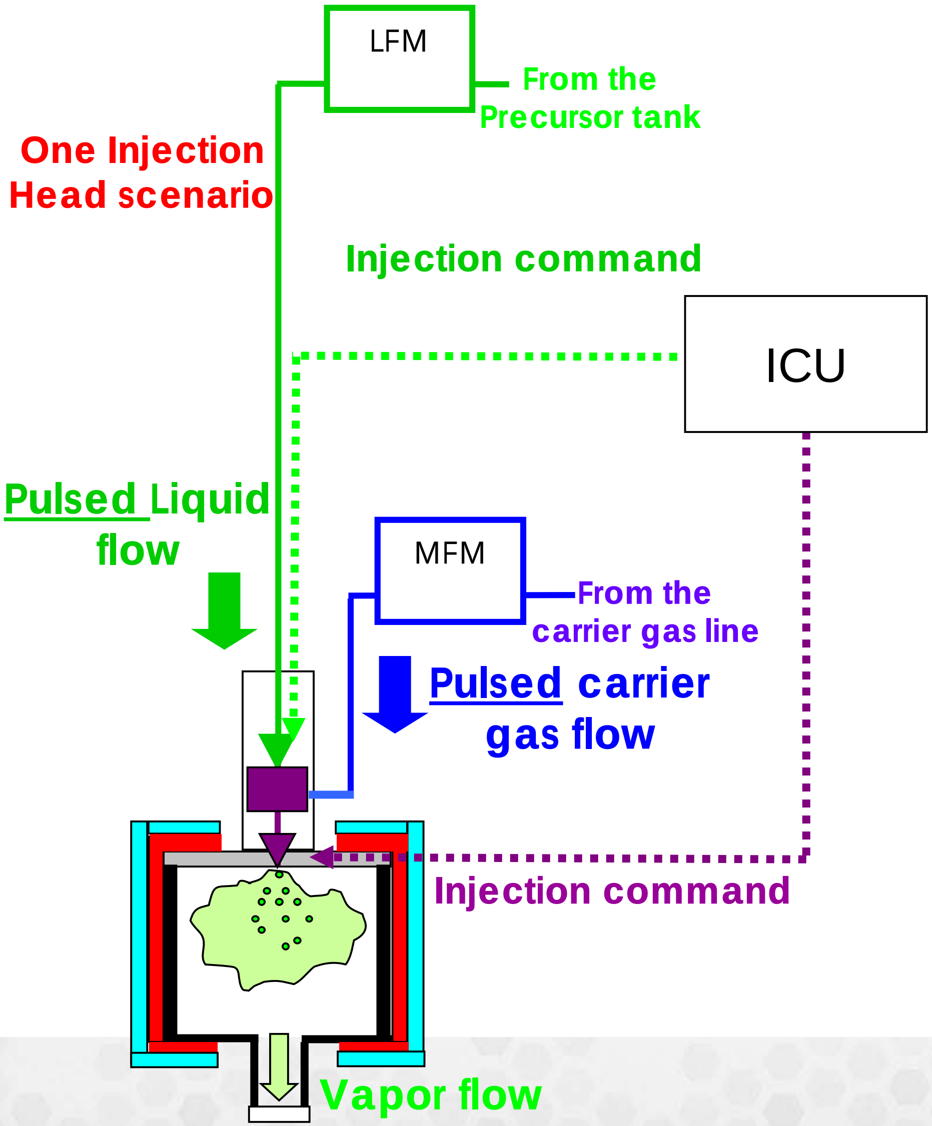
- Ambient temp source
- Regulated push gas
- Liquid mass flow controller
- Vaporization chamber/injector
- Heated line to chamber



Carrier Gas vs. Classical DLI

- Carrier gas
  - Precursor delivery is variable
  - Mixtures cannot be used
  - Solutions cannot be used
  - Inappropriate for temperature sensitive compounds
- Classical DLI
  - Precusor delivery is constant
  - Mixtures can be used
  - Solutions present problems
    - Injectors clog
  - Better for temperature sensitive compounds
  - Atomization is not controlled
  - Precursor build-up in chamber

Pulsed flow direct liquid injection

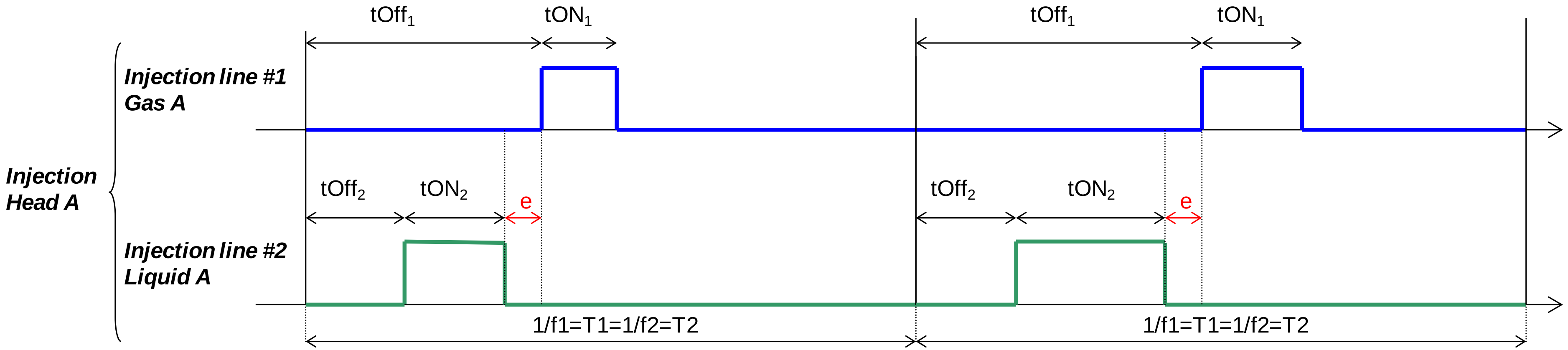


KEMSTREAM
ADVANCED VAPORIZERS

- Regulated precursor push gas
- Regulated inert carrier gas
- Liquid flow monitor
- Mass flow monitor
- Injection control unit
  - Uses LFM and MFM signals to provide independent liquid and gas flow control
  - Controls liquid injector and mixture injector precisely
    - Injectors operate out of phase
- Heated atomizer flash vaporizes precursor into vaporizer
- Vapor flows to chamber

Pulsed injection control

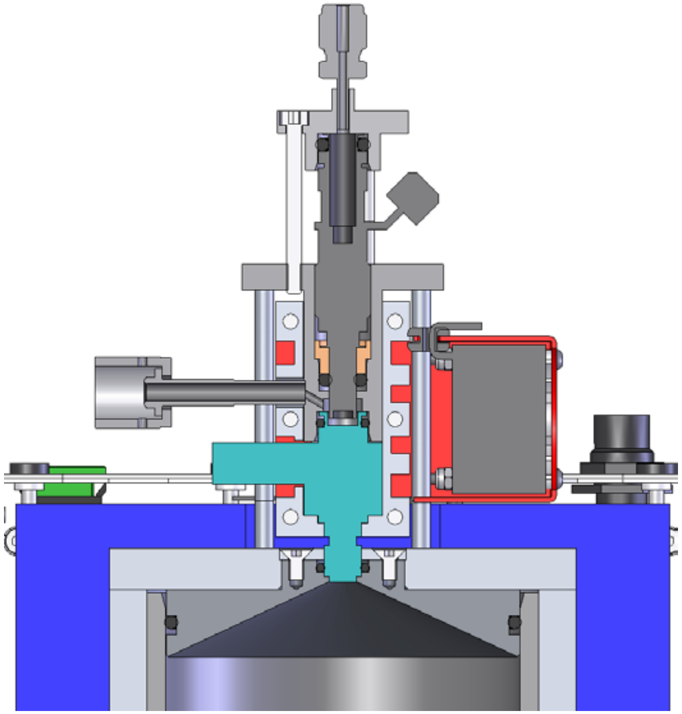
- Gas and liquid injectors operate out of phase
- Pulse width controls mass flow
- Gas pulse blasts liquid through the injector and atomizes the liquid



Injection details

KEMSTREAM
ADVANCED VAPORIZERS

- Pulsed injection of liquid-carrier gas mixture
- Liquid is kept at room temperature thanks to air cooling
  - Minimize risk of thermal decomposition prior to injection
- Strong thermal gradient at mix injector tip
- Thermal protection
  - Thermal switch (NC 70°C)
  - Injection is stopped in case of overheating
- Injector control
  - Working in PWM mode (Pulse Width Modulation) injectors are tuned to contol mass flow
  - Opening time is 1 to 50 msec (typically 1 to 10 msec)
  - Frequency is 0.1 to 50 Hz (typically 1 to 20 Hz)



Pulsed flow vs. classical DLI

KEMSTREAM
ADVANCED VAPORIZERS

- Improved atomization
  - Carrier gas blasting effect leads to smaller droplets
  - Droplet sizes
    - Classical LPI is 100 to 300 µm (LPI = Low Pressure Injection)
    - HPDI is 6 to 60 µm with max population at 22 µm (HPDI = High Pressure Direct Injection)
- New LPI is 5 to 40 µm with max population at 10 µm
- Longer droplet residence time inside the vaporizer
- Delivery method into the vaporizer creates lower velocity droplets and more time to vaporize before reaching the hot walls of the vaporizer
- No injector clogging when solutions are used
    - Mixing of liquid and carrier gas done upstream of valve
    - No dead volume downstream of valve

Additional benefits

KEMSTREAM
ADVANCED VAPORIZERS

- Solutions can be made from higher molecular weight compounds to reduce corrosive problems ($TiCl_4$) to TiIPr
- Pyrophorics can be diluted in solvent to decrease flammability (TMA)

Wide Range of Precurors

- Liquid compounds/precursors
  - Organometallic
    - TEOS, TEOG [Ge(OEt)$_4$], DADBS, BTBAS, n-$C_{18}H_{37}Si(OCH_3)_3$ (n-octadecyl trimethoxysilane), VO(O^{i}Pr)$_3$, silane A-174 (3-Methacryloxypropyltrimethoxysilane), TTIP, TDMAT
  - Organic
    - n-dodecane (n-$C_{12}H_{26}$), n-hexadecane (n-$C_{16}H_{34}$)
    - Monomeres (thermally sensitive, polymerizes easily): glycidyl methacrylate, neopentyl methacrylate, 2-ethylhexyl methacrylate, 2-perfluorohexyl ethyl acrylate (C6)

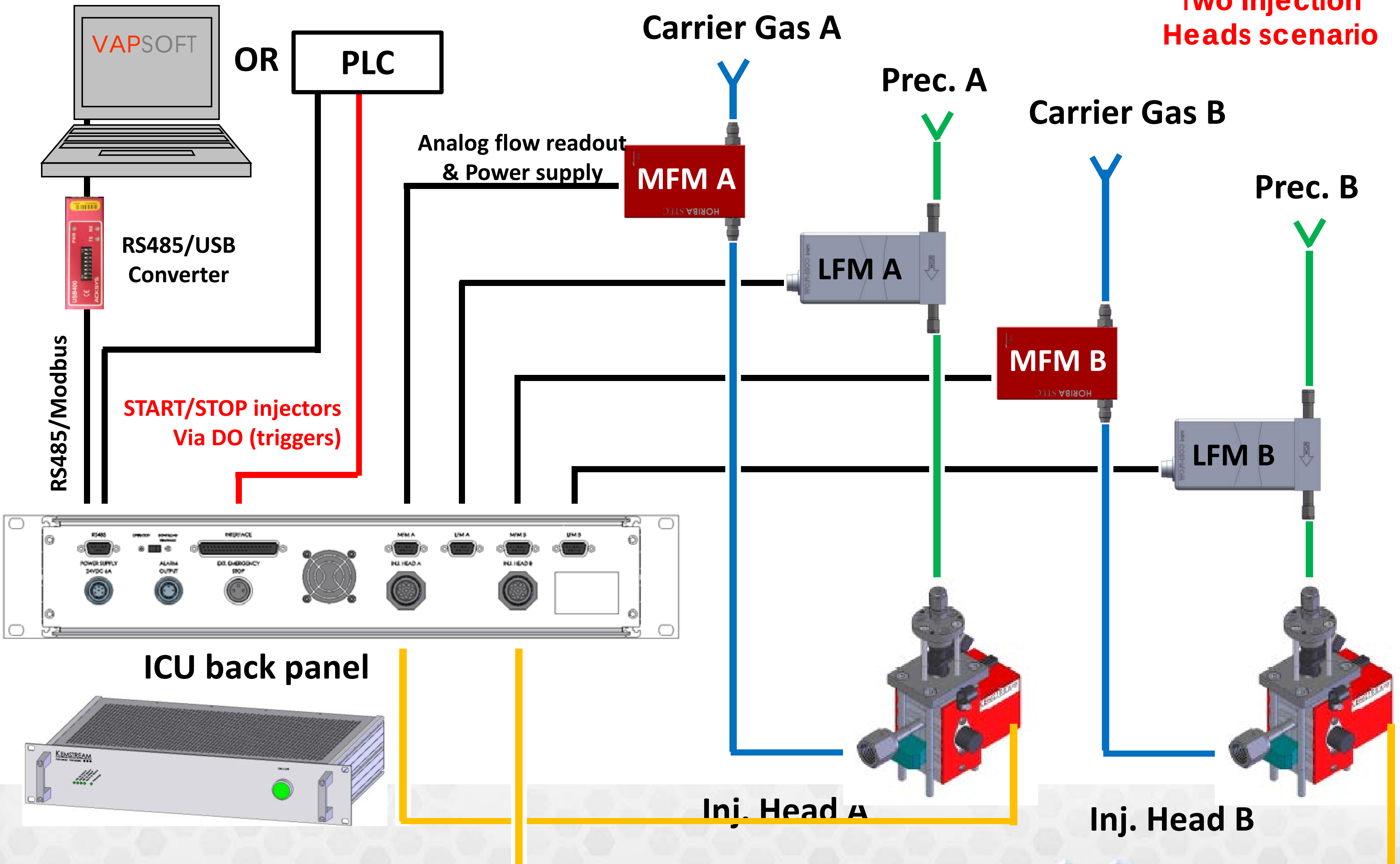
- Solid and liquid organometallic precursors (dissolved in an organic solvent)
  - β-diketonates
    - Al(acac)$_3$, Fe(acac)$_3$, Co(acac)$_3$, Cu(thd)$_2$, Y(thd)$_3$, Zr(thd)$_4$, [Ba(thd)$_2$]$_4$ = "Ba(thd)$_2$", Ba(thd)$_2$(H_2O)$_2$, La(thd)$_3$, Gd(thd)$_3$, Dy(thd)$_3$, Yb(thd)$_3$, Bi(thd)$_3$(LB)
  - Selenium and sulphur containing organometallic compounds (without oxygen)
  - Strontium tridentate β-ketoiminates
  - Carboxylate [M(RCO_2)n]
    - Ag(piv)
  - Alkoxides
    - Hafnium and zirconium amino alkoxides ones
  - Alkyls
    - Pt(Me)$_2$(norbornadiene) and tellurium one
  - Amidos
    - TDMAT, TBTDET, TDEAT and germanium one

Kemstream Vaporizers

- VAPBOX 300 **DLI CVD/ALD vaporizer**
  - Very compact vaporizer with 1 injection head, **220°C** capable, 1 heating zone
  - Pure liquids; solids dissolved in a carrier liquid (solutions)
  - R&D & pilot production
- VAPBOX 500 **DLI CVD/ALD vaporizer**
  - Compact vaporizer with 1 injection head, **250°C** capable, 1 heating zone
  - Pure liquids; solids dissolved in a carrier liquid (solutions)
  - R&D, pilot production and production
  - **High k materials and associated electrodes**: vaporization of transition metals precursors (titanium, zirconium, hafnium, tantalum,...), **Low k materials**: vaporization of polysiloxanes
- VAPBOX 1500 **DLI CVD/ALD vaporizer**
  - Vaporizer with 1 or 2 injection heads, **300°C** capable, 3 independent heating zones
  - **Low vapor pressure liquids**; solids dissolved in a carrier liquid (solutions)
  - R&D, pilot production and production
  - **Very high k materials**: vaporization of "difficult" precursors such as barium, strontium and lanthanides (lanthanum, cerium,...) ones
- VAPBOX 4000 **DLI CVD/ALD vaporizer**
  - Vaporizer with 3 or 4 injection heads, **250°C** capable, 3 or 6 independent heating zones
  - **Low vapor pressure liquids**; solids dissolved in a carrier liquid (solutions)
  - Pilot production and production
  - **PCRAM**: vaporization of germanium, antimony and tellurium precursors, **YBCO, ferroelectric**

Controls

Two Injection Heads scenario



Purdue Birck Technology Center

- LPCVD Project
- Tool retrofit
- Limited process support from tool supplier
- Limited installation space
- Controls integration cost considerations
- Future application opportunity

Installation

CRITICAL SYSTEMS, INC.
Supporting Breakthrough Technologies

Wrap-up

- Implementing CVD liquid and vapor delivery must take into account the nature of the materials
- Evaluating existing equipment capabilities and new requirements allows informed decisions
- Close end-user supplier collaboration creates good outcomes
- Minimizing equipment footprint and installation/implementation costs conserves budget
- Selecting equipment that can be retasked at minimal cost extends value

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