CHEMICAL BEAM EPITAXY LASER-ASSISTED
Sybilla equipment

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SUMMARY

Why we need a New Tool?

CBE-CBVD & Sybilla Equipment

Combinatorial Growth

Additive Growth

Some Functional Materials

Conclusion & Outlook
GLOBAL CONTEXT & 3D-OXIDES
Oxide thin films offer unique opportunities:

- Replace scarce or toxic elements
- Multi-functional materials for new devices (More than Moore)

However, they are far more complex:

- Huge amount of combinations
- Higher temperatures for epitaxy and crystals quality
- Strong material properties variations for non perfect crystals
- Complex Figures of Merit for multi-functional materials
Chemical Beam Epitaxy Laser-Assisted (CBE-LA)

Sybilla Equipment
CBE STRENGTHS & WEAKNESSES

CHEMICAL PRECURSORS IN MOLECULAR VACUUM

CBE VS. PVD TECHNIQUES

- Chemical selectivity (2 different regimes)
- Lower process temperatures
- Less sensitive to gas contamination (reduced getter effects)
- Small gas sources for better control

- Chemistry
- Complex multi-parameter process

CBE VS. CVD TECHNIQUES

MOLECULAR Vacuum

- No gas phase reaction
- No boundary layers with slow diffusive processes
- Line of sight & easy impinging rates modeling
- UHV characterization techniques
- Beam-assisted deposition & use of very reactive species

- Reduced number of available precursors
## Available Chemical Precursors

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<td>Rg</td>
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- Mastered in 3D-oxides
- Under investigation in house
- Reported in literature
- Radioactive, toxic or unstable
- Semiconductors in literature
- Oxygen plasma

**Context & 3D-Oxides**  
**CBE-CBVD & Sybilla Equipment**  
**Combinatorial Growth**  
**Additive growth**  
**Some Applications**
Sybilla for 450 mm substrates set-up

Single wafer Sybilla-450 mm
Merging CVD and MBE assets

Windows for assisted deposition or characterization techniques

Context &3D-Oxides
CBE-CBVD & Sybilla Equipment
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SIDE AND TOP VIEWS OF SYBILLA EQUIPMENT

Radiative substrate heater
Substrate
Stencil Mask
Punctual sources with Knudsen effusion
Pre-chamber quarter
Precursor A
Precursor B
Precursor C
Precursor D
Precursor E

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## SYBILLA (CBE-LA) PERFORMANCES

### Agile and Disruptive R&D, Reliable and Cost Efficient Production

| **Growth rates:** | 5 nm h\(^{-1}\) up to 20 µm h\(^{-1}\) |
| **Layer Quality:** | Epitaxial to highly porous thin films |
| **Substrate size:** | Scalable to any size |
| **Number of elements:** | Actually 1-5, but scalable to 6 or even more |

| **R&D results uptake:** | Very fast as the same equipment is used |
| **Process modification:** | Very fast: process is not geometry dependent |

| **Precursors use:** | From 10% up to as high as 65% |
| **Equipment life-time:** | Extensive (different materials/applications) |
| **Costs of ownership:** | Possibly lower than few € / cm\(^2\) |

**Combinatorial production:** Monolithic integration of ≠ functionalities
COMBINATORIAL
PreCURSOR FLOW GRADIENTS

Wagner et al. (2016) ACS Combinatorial Science, 18(3) 154

1 active quarter - Flow ratio: 6
2 active quarters - Flow ratio: 4.6
3 active quarters - Flow ratio: 3.3
4 active quarters - Flow ratio: 2.2
5 active quarters - Flow ratio: 1.5
6 active quarters - Homogeneous +/-2%

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**Very High Thickness Uniformity 18” Substrates**

**Context & 3D-Oxides**

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**Combinatorial Growth**

**Additive growth**

**Some Applications**

+/- 1.5% uniformity

+/- 0.5% uniformity

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<tr>
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<th>All points</th>
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<td>stdv</td>
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<td>Homogeneity</td>
<td>1.03%</td>
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Wagner et al. (2016) ACS Combinatorial Science, 18(3) 154

**Combining with 3 Elements**

**Simulation vs Experimental Data**

Material Properties vs Composition

Wagner et al. (2016) ACS Combinatorial Science, 18(3) 154

**Combining with 3 Elements**

**Simulation vs Experimental Data**

Context & 3D-Oxides  CBE-CBVD & Sybilla Equipment  Combinatorial Growth  Additive growth  Some Applications
COMBINATORIAL IN-SITU SPECTRAL REFLECTOMETRY

**a)**
- **Flow**
- **Point 1**
- **Point 2**
- **Point 3**
- **Point 4**
- **Point 5**
- **Point 6**
- **Point 7**
- **Point 8**
- **Point 9**
- **Point 10**
- **Point 11**
- **Point 12**
- **Point 13**
- **Point 14**
- **Point 15**
- **Point 16**
- **Point 17**
- **Point 18**
- **Point 19**
- **Point 20**
- **Point 21**

**b)**
- **Deposition**
- **END**

**c)**
- **Experimental thickness**
- **Calculated model**

**Graphs and Data:***
- **Thickness (nm)**
- **Time (s)**

**Text:**
- **Mass Transport Limited Regime conditions**

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**Context:**
- &3D-Oxides
- CBE-CBVD & Sybilla Equipment
- **Combinatorial Growth**

**Additive growth**
- Some Applications
MATERIAL PROPERTIES VS THICKNESS

3D-PYRAMID LIKE STRUCTURE

ROUGHNESS INCREASING WITH THICKNESS FOR COLUMNAR GROWN TiO₂ ANATASE
ADDITIVE GROWTH
PATTERNED SUBSTATES / STENCIL MASKS
Deposition on patterned substrates

- 1st precursor:
  - Deposit
  - Trench profile

- 2nd precursor:
  - Flow
  - Deposit

- Two precursors:
  - Flow
  - Trench profile
  - Mixed deposit

Additive growth
**Chemical Patterning (Separated Elements)**

EDX mapping

Optical microscope picture of the layer 80 nm for TiO$_2$,
40 nm for Nb$_2$O$_5$

Context & 3D-Oxides

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CHEMICAL PATTERNING (SUPERPOSED ELEMENTS)

Source 1  Source 2

Mask

Substrate

Deposit 1  Deposit 2

Deposit sum

Context & 3D-Oxides  CBE-CBVD & Sybilla Equipment  Combinatorial Growth  Additive growth  Some Applications
Variable electrical conductivity. Most functional properties can be modulated and patterned.
ADDITIVE GROWTH
CBE-LASER-ASSISTED

3D-OXIDES
MULTI-FUNCTIONAL THIN FILMS
ENERGY Source | Thin Film Colour | TiO$_2$ layer (thickness nm)
--- | --- | ---
Thermal deposition | Blue | 70.0
Fluence 1 | Yellow | 112.7
Fluence 2 | Blue | 190.3
Fluence 3 | Red | 360.6
Fluence 4 | Blue | 402.1

DEPOSITION / ABLATION / ETCHING IS LIMITED TO THE IRRADIATED AREA

Low Temperature 330°C

Laser gradient added energy

Mass Transport Limited Growth

GR Enhancement x6

Chemical Reaction Limited Growth
Selective modification of TiO$_2$ thin films properties

Refractive index fine tuning

BandGap shifting (Tauc Model)

Film densification
Laser 3D-Patterning (Chemical Composition)

In-situ reflectivity

$\text{Ti}_x\text{Si}_{1-x}\text{O}_2$

330°C

1 Hz

370°C

2 Hz

400°C

5 Hz

450°C

10 Hz

$0.2 \, \mu\text{m}$

330°C

1 Hz

370°C

2 Hz

400°C

5 Hz

450°C

10 Hz

$\text{THERMAL GROWTH}$

$\text{THERMAL GROWTH + LASER}$

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COMBINATORIAL & ADDITIVE GROWTH

Combinatorial structures obtained via a stencil mask

Top-down patterning

Bottom-up patterning

Some Applications

Additive growth
FUNCTIONAL MATERIALS
LiNbO$_3$

Combinatorial Chemical Beam Epitaxy of Lithium Niobate Thin Films on Sapphire
DOI:10.1149/1.3519843

Single orientation 006/0012
Rocking curves: FWHM 0,03°
Roughness RMS 1,39 nm
Raman: ok
Refractive index: 2,26 < n < 2,31
EPITAXIAL BaTiO$_3$ ON Si (EPFL AND IBM)

Reference: Low Temperature Epitaxial Barium Titanate Thin Film Growth in High Vacuum CVD; M. Reinke et als; Adv. Mater. Interfaces 2017, 1700116 DOI: 10.1002/admi.201700116
CONCLUSION & OUTLOOK
Top level properties on many different materials:
LiNbO$_3$, BaTiO$_3$, SrTiO$_3$, TiO$_2$, Hf$_{(1-x-y)}$Ti$_x$Zr$_y$O$_2$, Nb$_2$O$_5$, Ta$_2$O$_5$, Al$_2$O$_3$, ZnO, Vo$_x$, etc...

Upscalable to production
1. Very high control accuracy on process
2. Lower thermal budget (CMOS compatible)
3. Large substrates (mass production)
4. More elaborated architectures for better devices
A DISRUPTIVE TOOL FOR NEW OXIDE THIN FILMS DEVICES

FAST COMBINATORIAL

PROCESS CONDITIONS

CHEMICAL COMPOSITION

3D-GEOMETRY

INTERFACES

NEW MATERIALS

NEW ARCHITECTURES

SINGLE-STEP PATTERNING

SELF-ASSEMBLY

PATTERNED SUBSTRATES

Stencil Masks

Beam-Assisted

DISRUPTIVE DEVICES

FAST TECHNOLOGICAL APPROACH ADDRESSING SIMULTANEOUSLY SEVERAL MARKETS
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