Nanostrukturen-Herstellung

Chemical Vapor deposition (CVD)

PECVD, LPCVD, APCVD, RTP, CCSVT, OVPD, MOCVD,....

- CVD **Principle & Parameter**
- **Deposition of Chalcopyrites**
  - CVD
  - CCSVT
  - MOCVD
- **Organic Solar cells**
  - OVPD

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NANOlino Lab

Classification of deposition techniques

Deposition techniques

Chemical **V**apor **D**eposition (CVD)	**P**hysical **V**apor **D**eposition (PVD)	Other techniques
Epitaxy	- Sputtering - Evaporation - Molecular beam epitaxy	- Electroplating - Electroless - Spin on

General requirements to the processes:

- Low cost of ownership
- high throughput

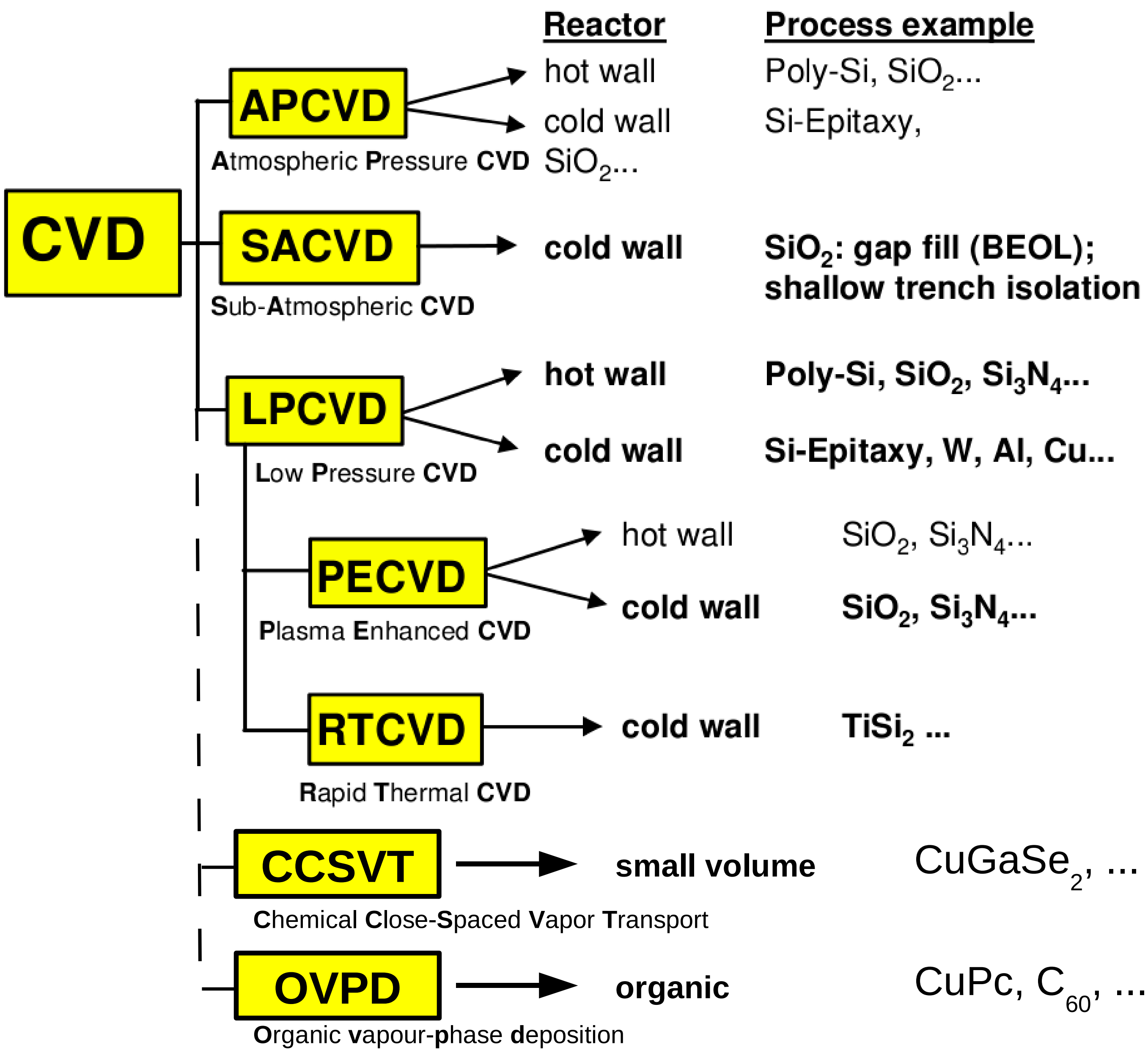
to the films:

- good thickness uniformity
- high purity and density
- controlled composition and stoichiometry
- high degree of structural perfection
- good electrical properties
- excellent adhesion
- good step coverage

Advantages of CVD:

- high purity deposits and very good step coverage can be achieved
- great variety of materials and chemical compositions
- some films cannot be deposited with good properties by other methods
- good economy and process control are possible for many films

Classification and application of CVD techniques

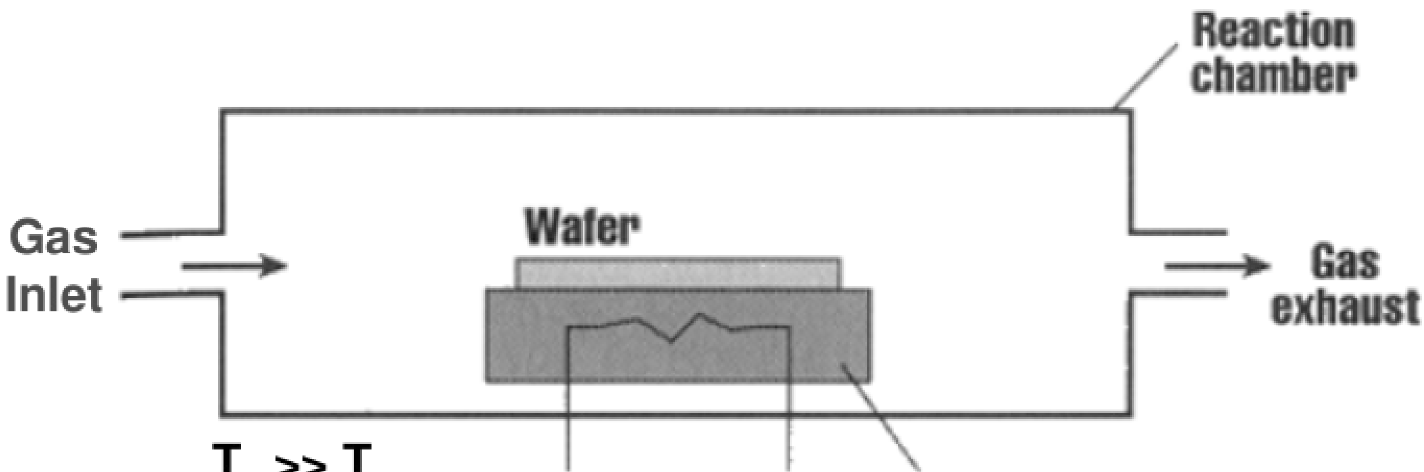


Basics of Chemical Vapor Deposition

- CVD is extremely popular
  - preferred deposition method for wide range of materials
- Simple thermal process
  - modifications also provide alternate energy sources such as plasma or optical excitation to drive chemical reactions even at low temperature
- Allows coverage of high aspect ratio features
  - especially in submicron technologies with very small contacts
- Well suited to deposition of insulating or semiconducting films
  - thin films based on chemical reactions

Simple CVD System for Silicon Deposition

A simple prototype thermal CVD reactor



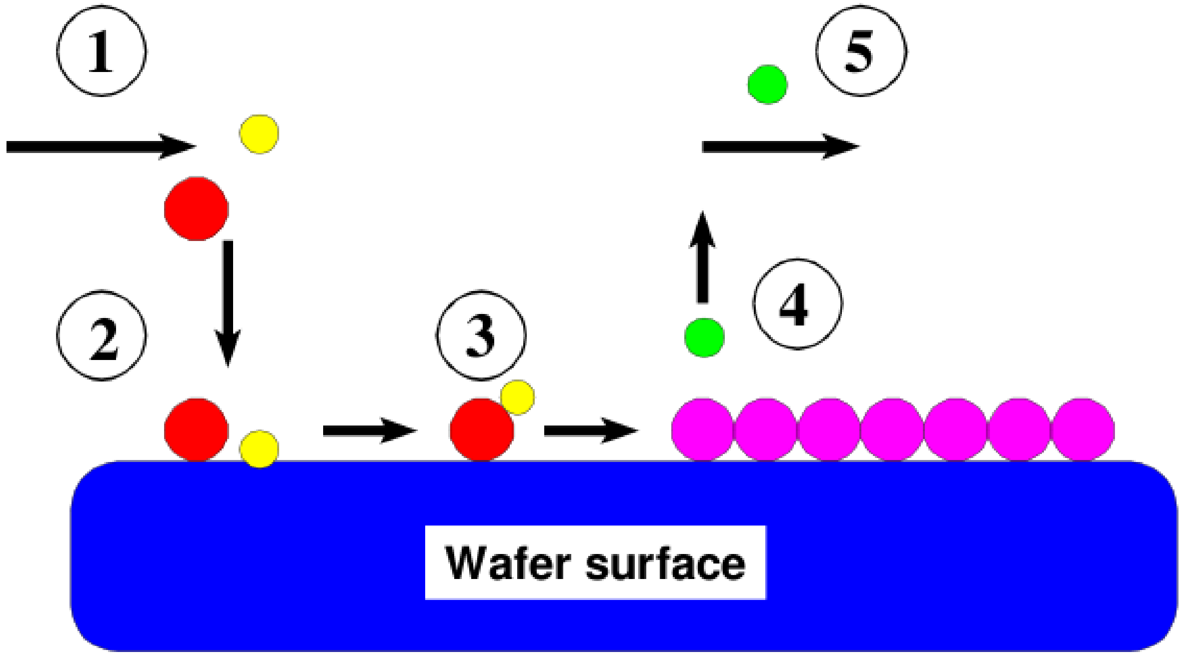
$T_s >> T_w$

to avoid deposition on the walls

$$SiH_4(g) \rightarrow Si(s) + 2H_2(g)$$

- used for the decomposition of silane gas to form polycrystalline silicon
- while the gas flows from left to right the silane starts to decompose when it approaches the hot susceptor
- in order to fight the decreasing silane concentration the gas is diluted in hydrogen
- the flow is slow enough that the pressure in the chamber can be considered uniform

Theoretical background: Elementary processes



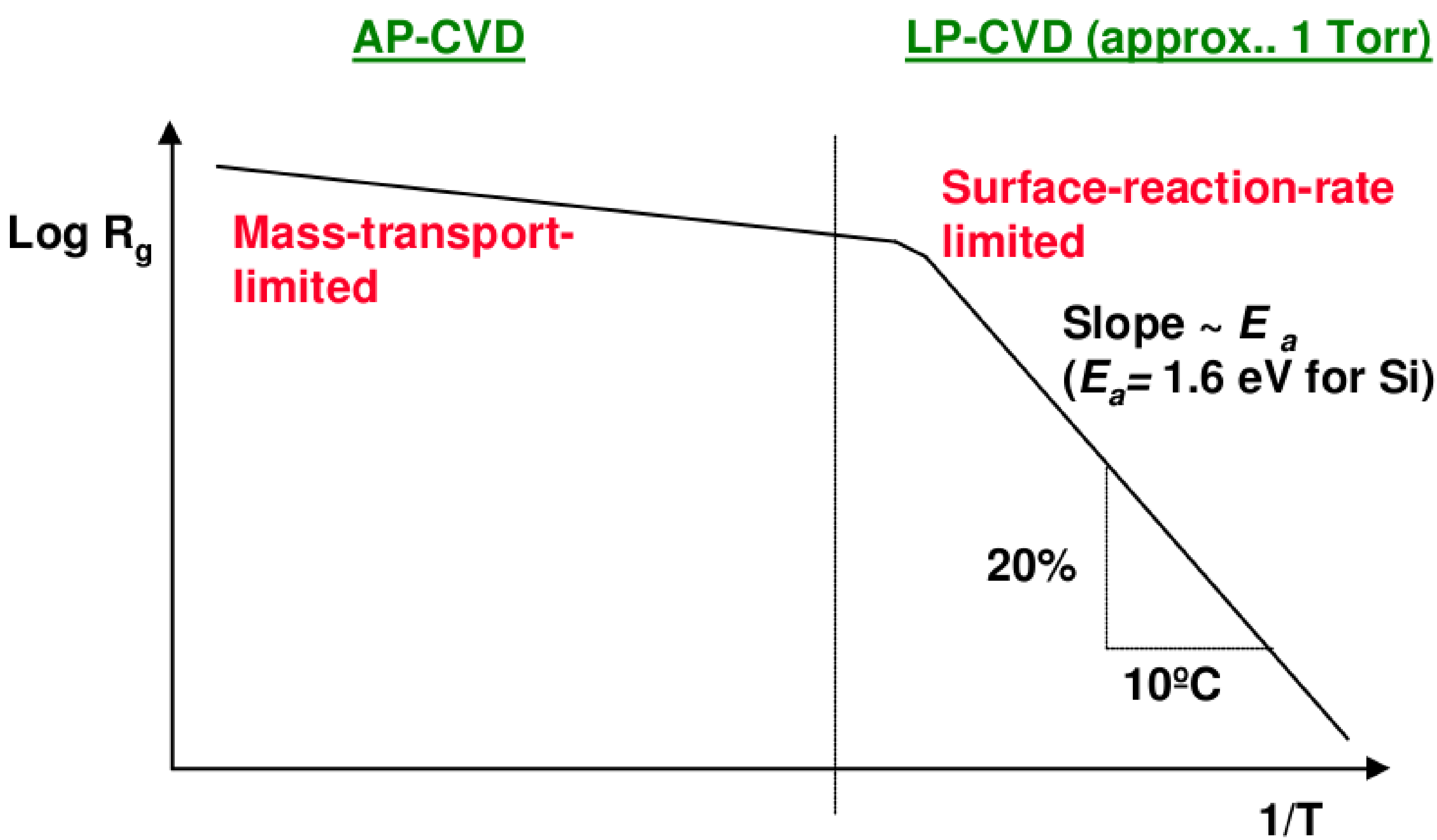
1 Transport of the precursor(s) with the carrier gas to the reaction chamber and to the wafer surface (convection and diffusion)
2 Adsorption or chemisorption of the precursor(s) at the wafer surface
3 Chemical surface reaction (including dissociation and surface diffusion)
4 Film growth, desorption of volatile reaction products, transport of reaction products away from the wafer surface (diffusion)
5 transport of reaction products with the carrier gas out of the reactor

Variables to be Controlled

- Deposition process includes:
  - force convection
  - boundary-layer diffusion
  - surface absorption
  - decomposition
  - surface diffusion
  - incorporation

- **Variables to be controlled for film properties**
  - **Temperature**
  - **Pressure**
  - **Flow Rate**
  - **Position**
  - **Reactant Ratio**

Deposition Rate Limits



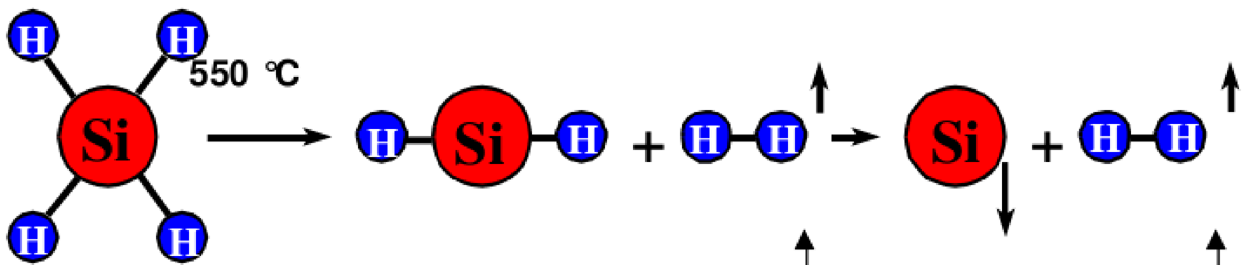
The aforementioned steps are sequential, hence the one that occurs at slowest rate will determine the deposition rate.

These rate-determining steps can be grouped into gas-phase processes and surface processes.

Theoretical background: Reaction types

<u>Pyrolysis:</u> Thermal decomposition of gaseous species (hydrides, carbonyls, organometallic compounds) on hot substrates

→ **Example:** ***LPCVD of polycrystalline or amorphous silicon films***



$$SiH_4 \longrightarrow SiH_2 + H_2\uparrow \longrightarrow Si\downarrow + H_2\uparrow$$

<u>Oxidation:</u> CVD of SiO_2 *and glasses* by reaction of gaseous hydrides or halides of Si *and dopants* with oxygen or oxygen-containing compounds

→ **Example:** ***LPCVD of PSG***

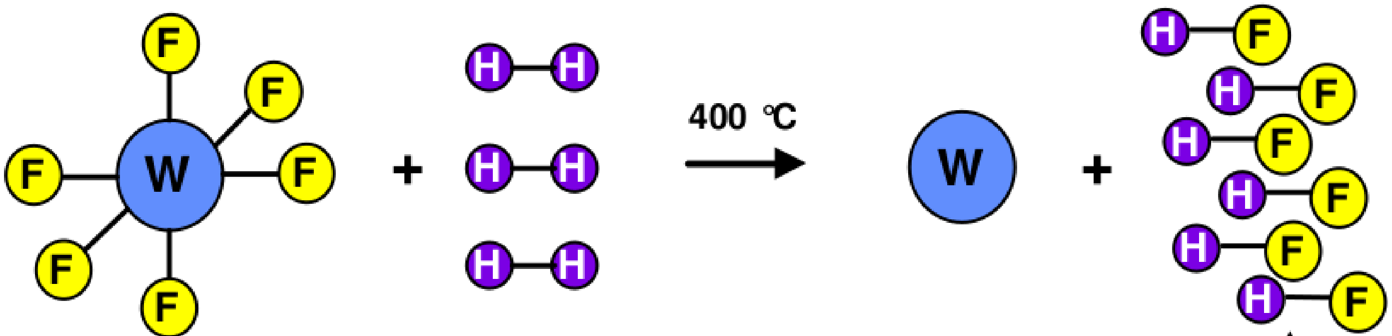
$$SiH_4 + O_2 \xrightarrow{450\ °C} SiO_2\downarrow + 2\ H_2\uparrow$$

$$4\ PH_3 + 5\ O_2 \xrightarrow{450\ °C} 2\ P_2O_5\downarrow + 6\ H_2\uparrow$$

Theoretical background: Reaction types

<u>Reduction:</u> **Reaction of halides or oxygen-containing compounds with hydrogen or hydrogen-containing compounds to generate solid deposits and gaseous byproducts**

→ Examples: *LPCVD of Tungsten, blanket deposition*



$$WF_6 + 3\ H_2 \longrightarrow W\downarrow + 6\ HF\uparrow$$

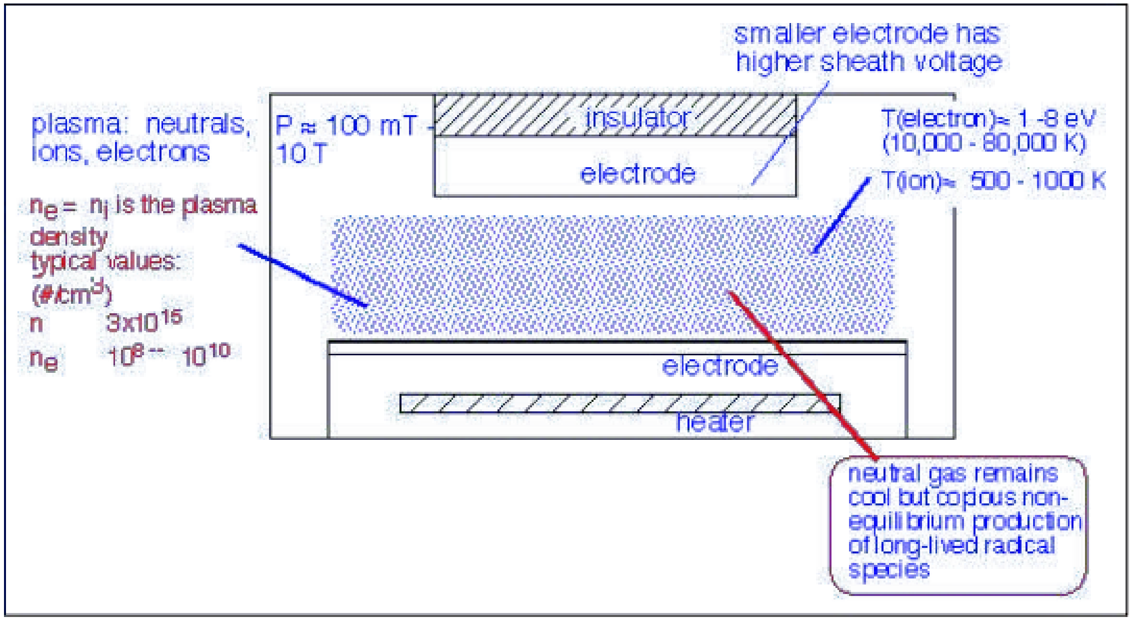
LPCVD of Tungsten, selective deposition

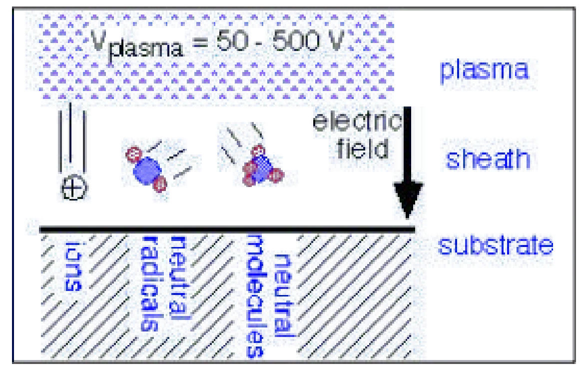
$$2\ WF_6 + 3\ SiH_4 \xrightarrow{250\ ^\circ C} 2\ W\downarrow + 3\ SiF_4\uparrow + 6\ H_2\uparrow$$

$$WF_6 + 2\ SiH_4 \xrightarrow{250\ ^\circ C} W\downarrow + 3\ SiHF_3\uparrow + 3\ H_2\uparrow$$

PECVD (Plasma Enhanced CVD)

PECVD Reactor; parameter





gas flow:	10...10.000 sccm	electrode spacing:	10...100 mm
pressure:	0.5...15 Torr	rf power:	100...1.000 W
temperature:	300...550 ℃	rf frequency:	13.56 MHz, 400 kHz ...

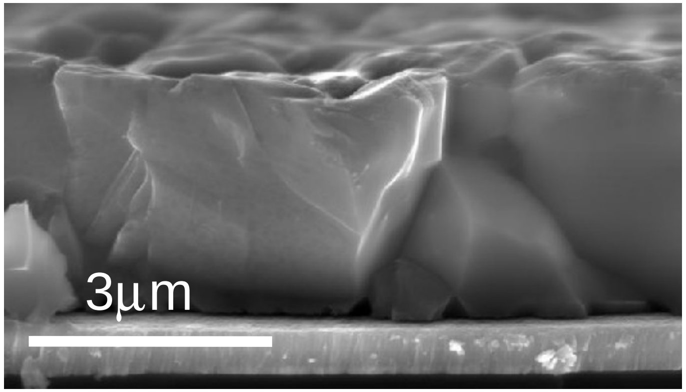
$CuGaSe_2$ in solar cells

- $Cu(In,Ga)Se_2$ (CIGS) in thin film solar cells
- High quality cells (polycrystalline)

→**efficiency >20%**

→Many properties not understood yet

(why is it good, loss mechanisms, defects…)



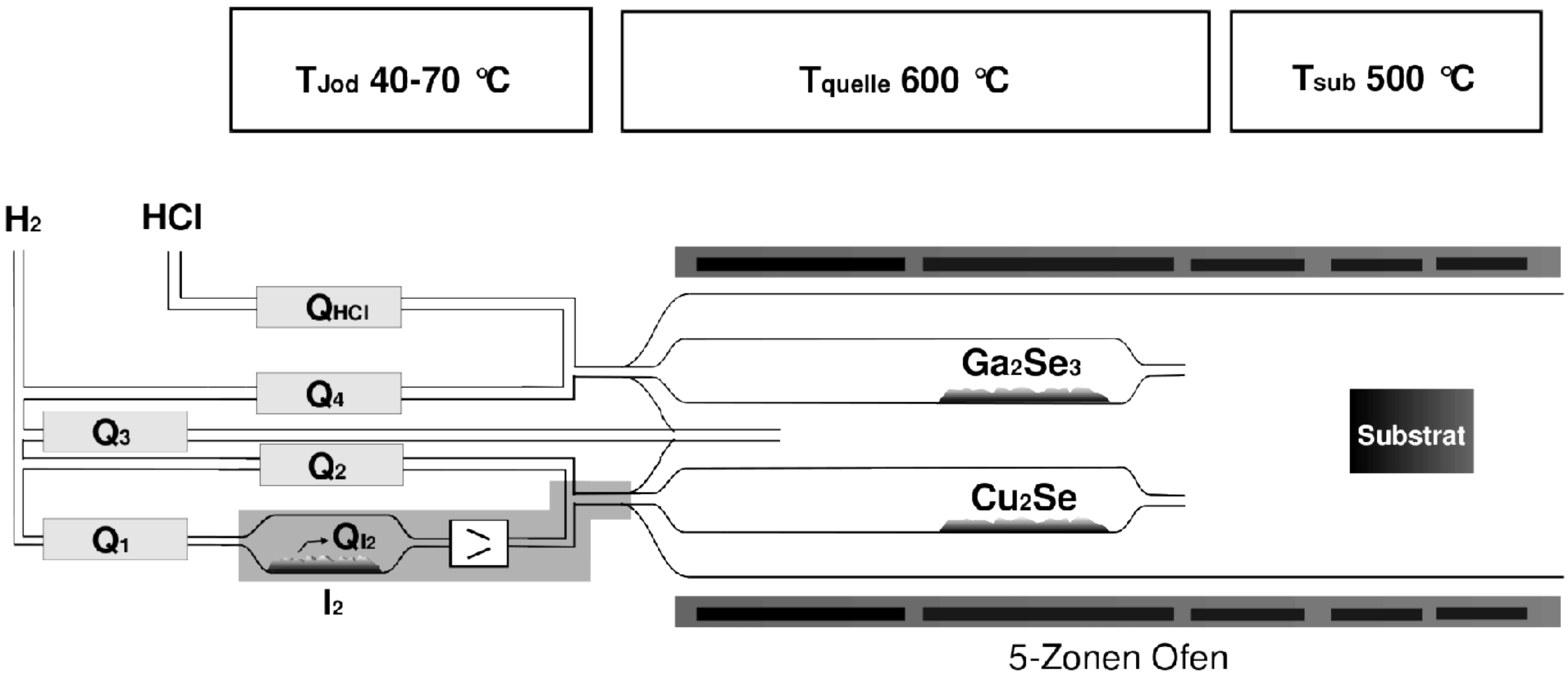
→Analysis is difficult (polycrystalline absorber)

Single crystalline thin films for fundamental analysis needed

→ **epitaxial $CuGaSe_2$ layers**

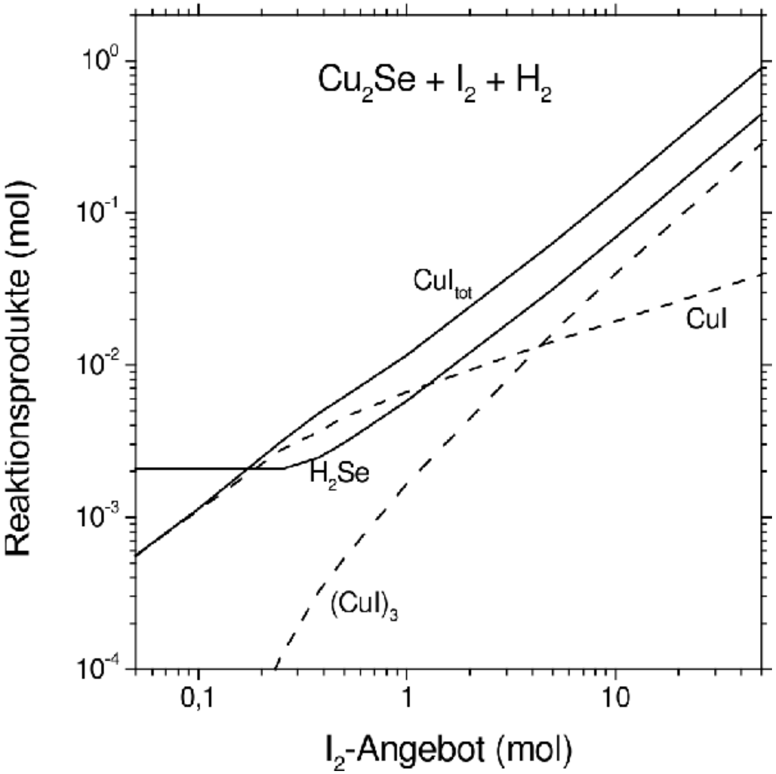
Journal of Crystal Growth 315 (2011) 82–86

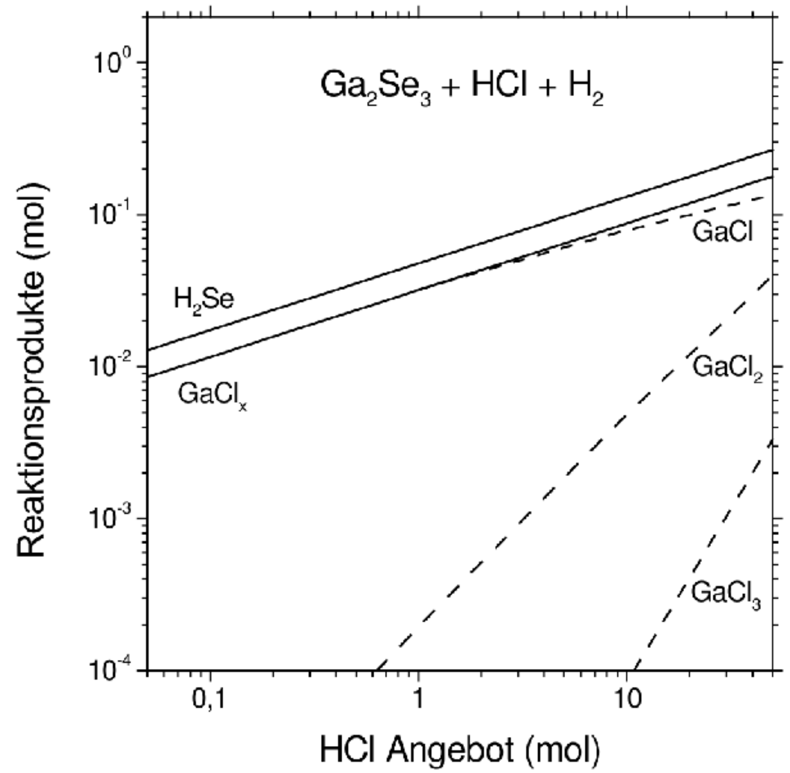
CVD of $CuGaSe_2$



PhD Thesis, D. Fischer 2000, FU-Berlin

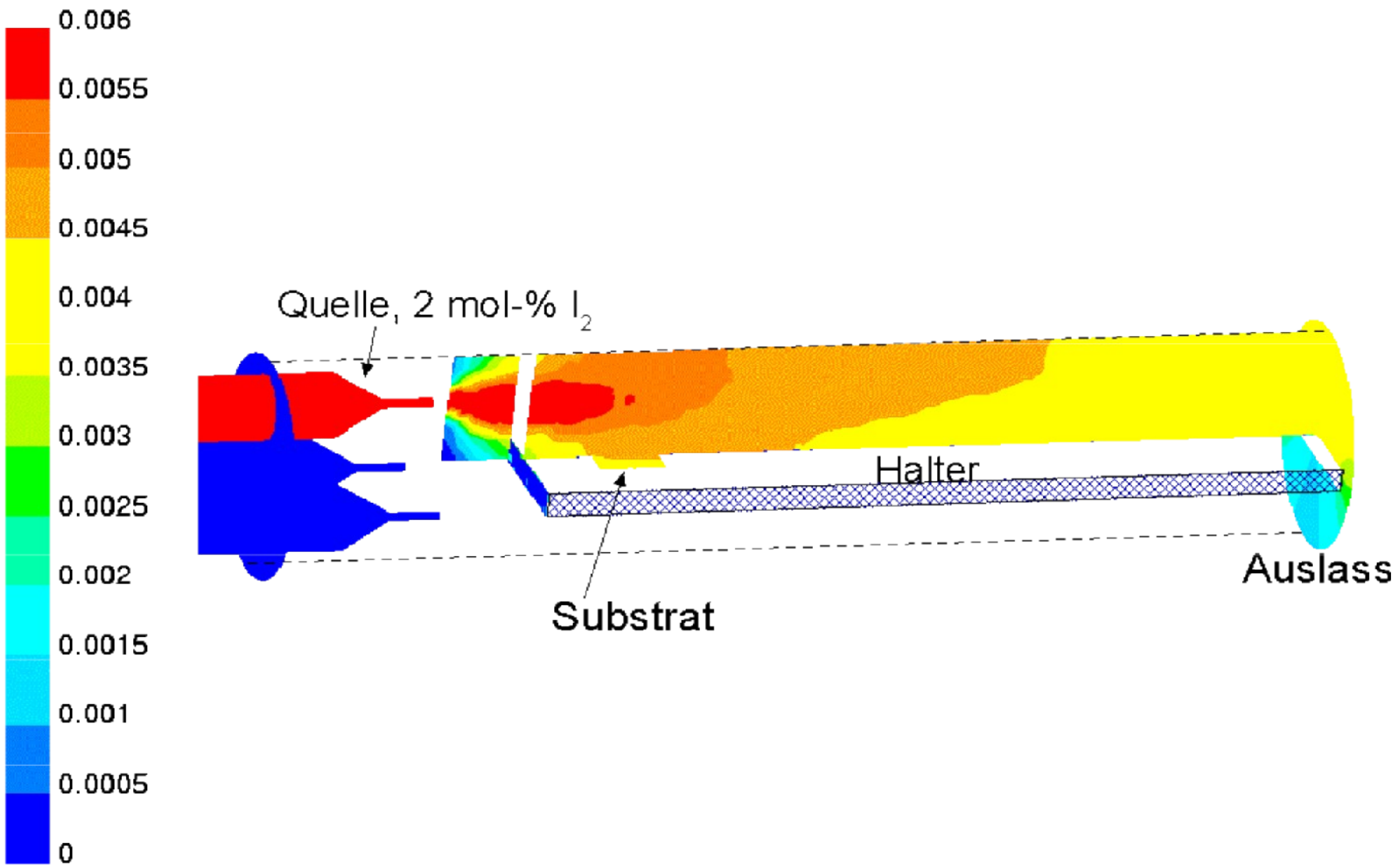
Reaction Products





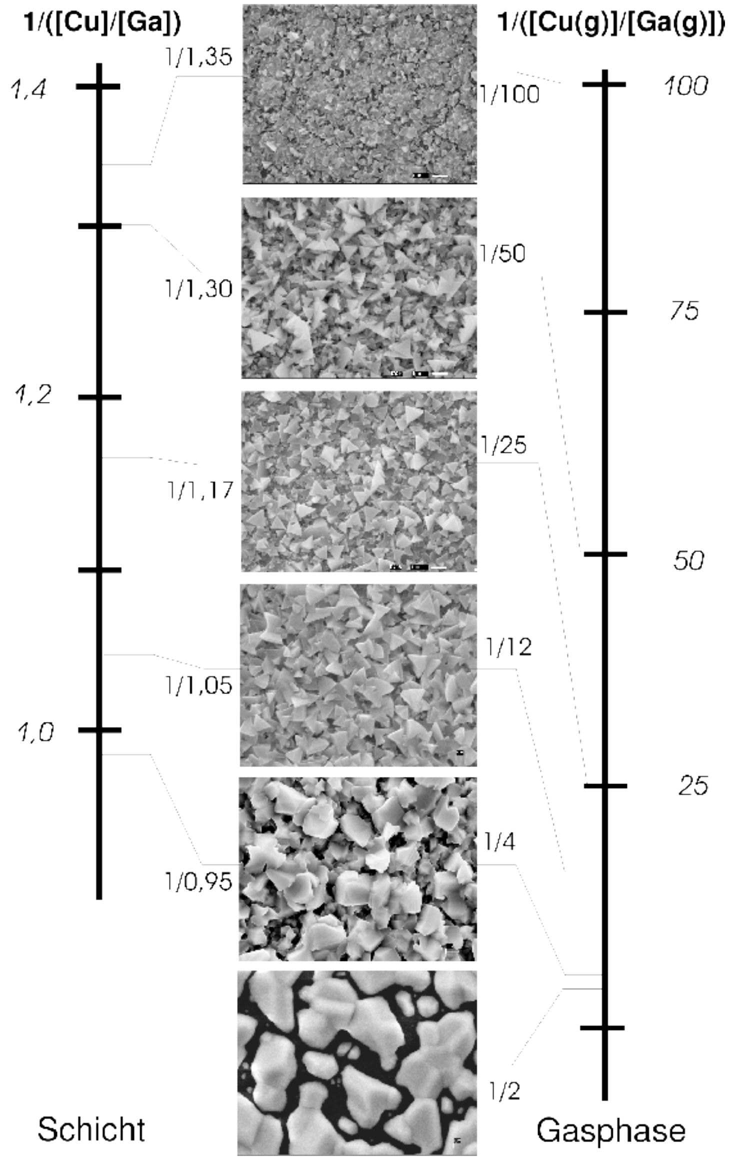
PhD Thesis, D. Fischer 2000, FU-Berlin

CVD gas steam, I_2 concentration



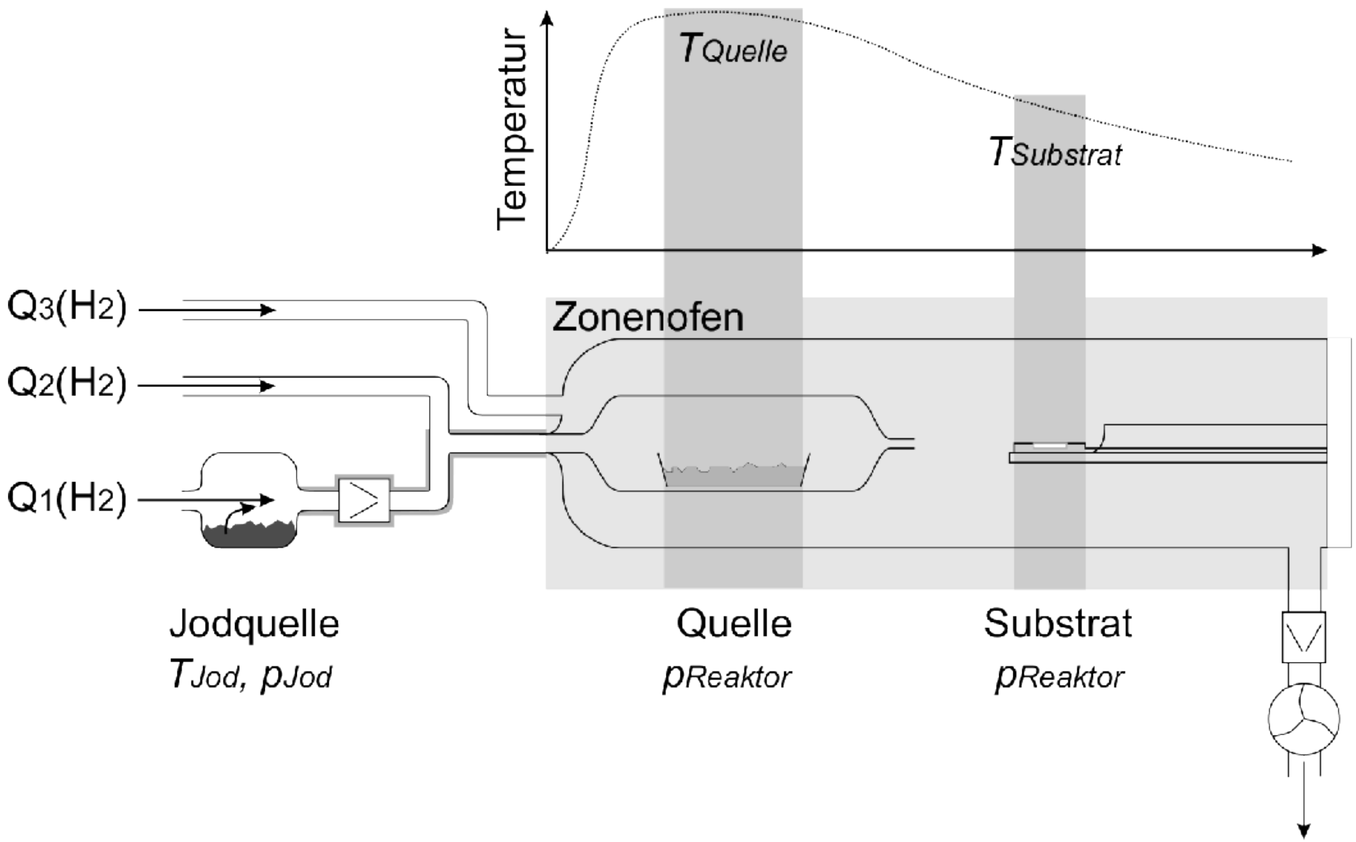
PhD Thesis, D. Fischer 2000, FU-Berlin

Film Composition & Structure



CVD of ZnSe

$$\mathrm{ZnSe(s) + I_2(g) \longrightarrow ZnI_2(g) + Se(g)}$$



PhD Thesis, A. Rumberg 2001, FU-Berlin

ZnSe buffer layer for $CuGaSe_2$ solar cells

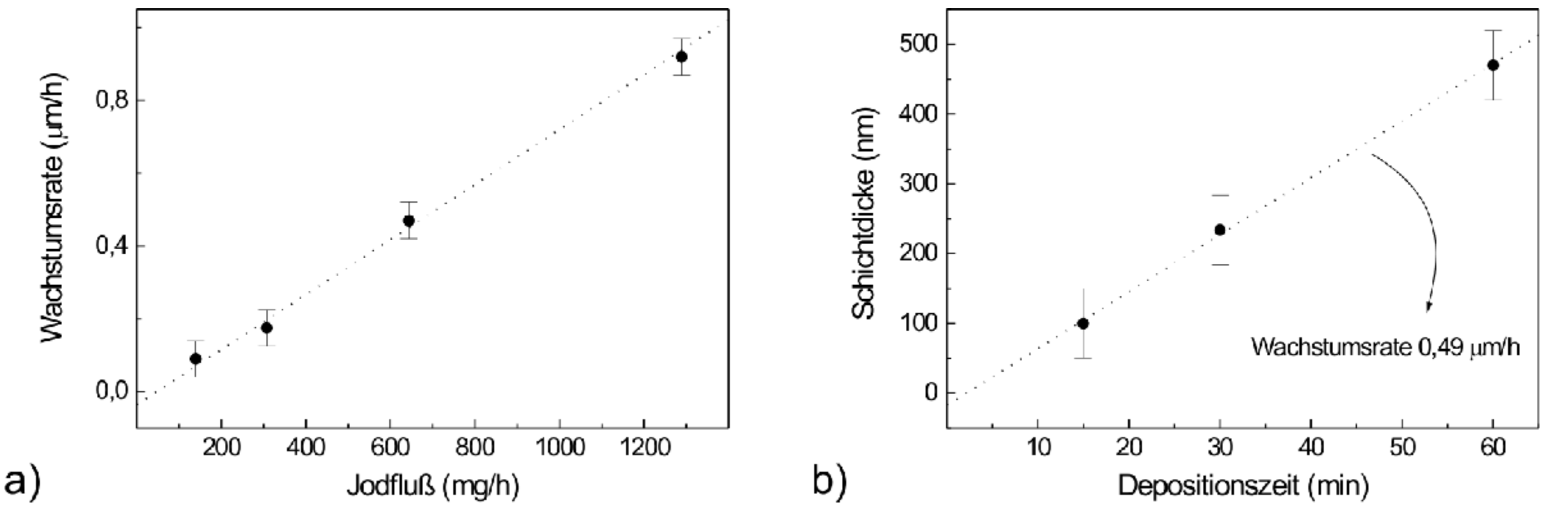


Abbildung 5.1: a) ZnSe–Wachstumsrate als Funktion der Jodtransportrate, b) Schichtdicke über der Depositionszeit, jeweils korrigiert um die Dicke der Keimschicht (100 nm) (Quellen /Substrattemperatur 550/350 °C)

PhD Thesis, A. Rumberg 2001, FU-Berlin

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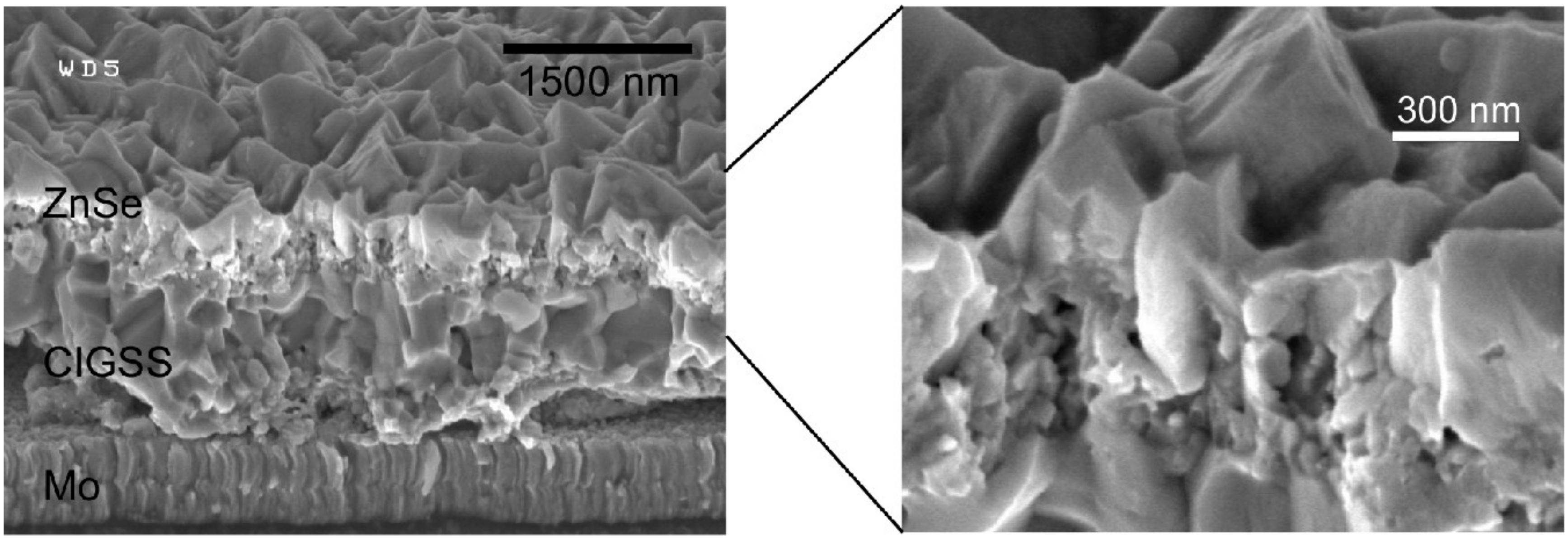


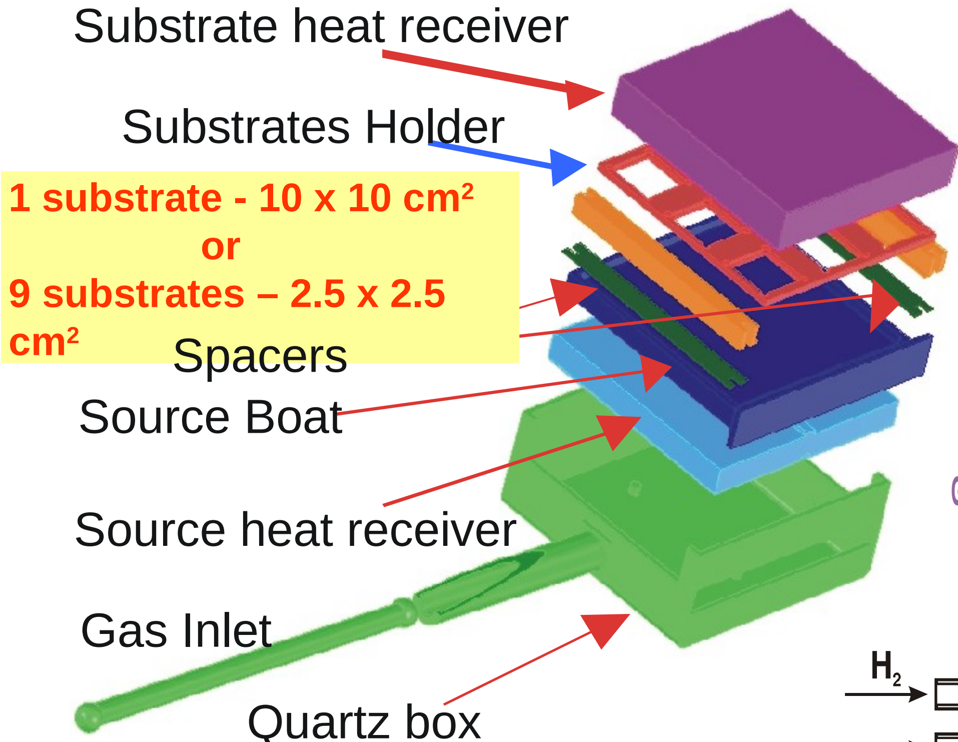
Chemical closed-space vapor transport (CCSVT)

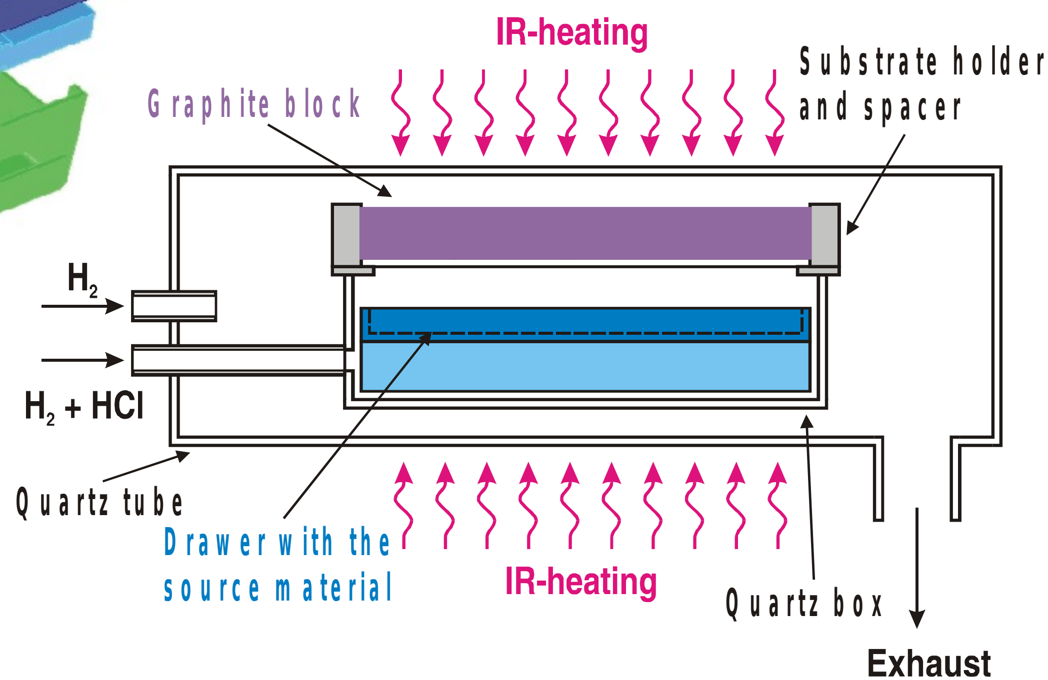
Benefits for $CuGaSe_2$ deposition:

- Taking advantage of the CVT and closed -space vapor transport (CSVT) techniques, namely, fast volatilization of source materials by reaction with halogens such as molecular I_2 , Cl_2 or HCl to gaseous halogenides which occurs at significantly lower temperatures
- Using III-VI compounds exhibiting low sublimation temperatures in combination with copper-selenides and -sulfides
- Employing advantages of the rapid thermal processing (RTP), thermal annealing of the metal precursors deposited on large areas

Thin Solid Films 451 – 452 (2004) 556–561

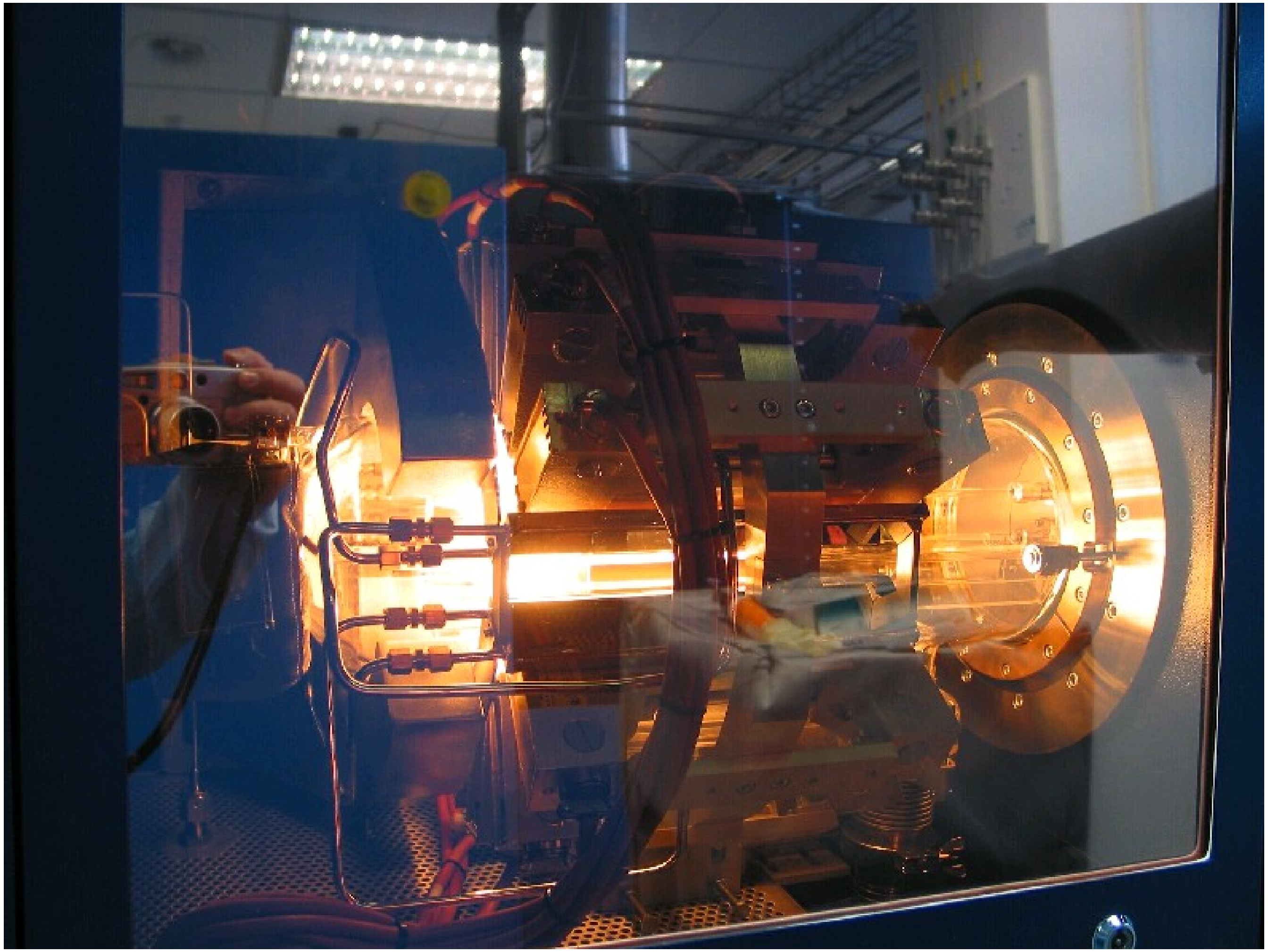
CCSVT Apparatus





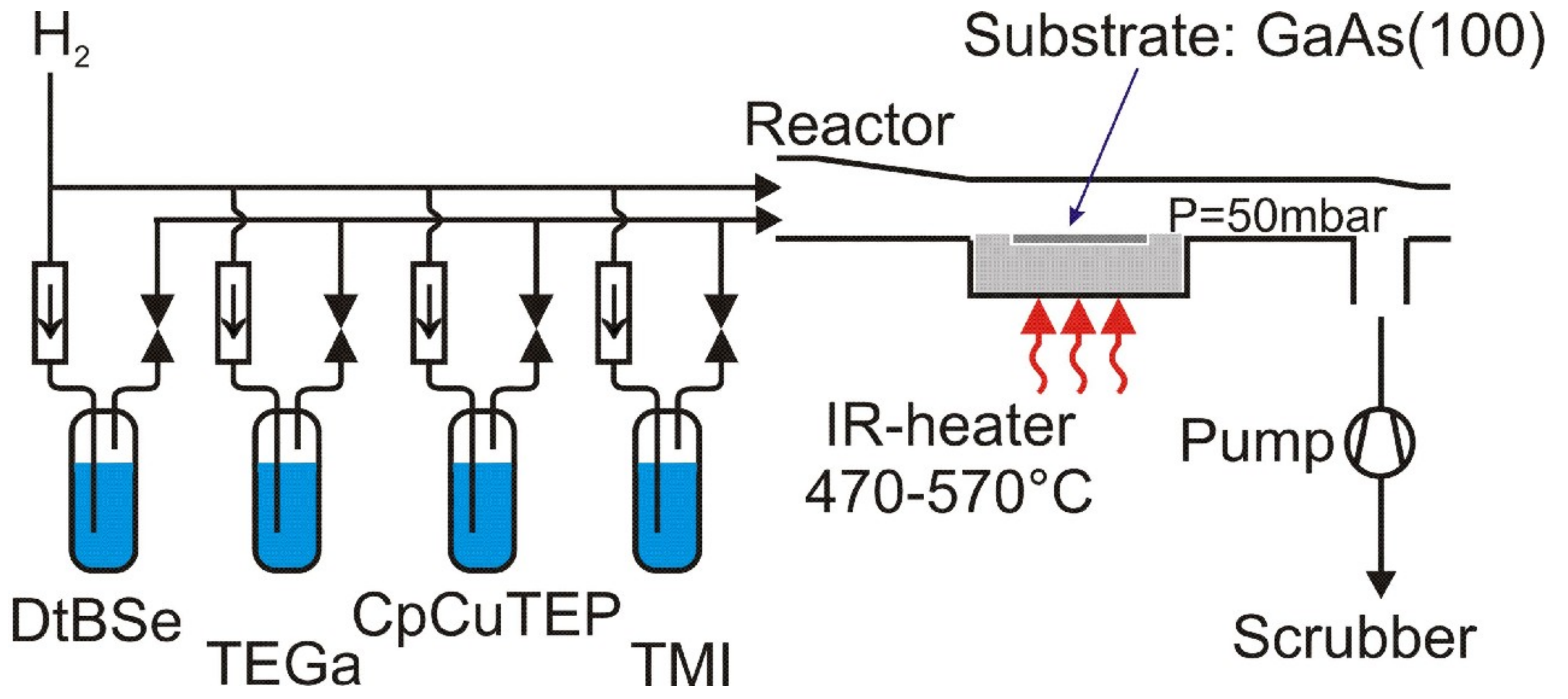
Thin Solid Films 451 – 452 (2004) 556–561

CCSVT Apparatus



MOCVD, Metalorganic Chemical Vapor Deposition

MOVPE (Metalorganic vapor phase epitaxy)



MO precursors for Cu, Ga, Se:

- CpCuTEP Cyclopentadienyl-Copper-Triethylphosphine
- TEGa Triethylgallium
- DtBSe Ditertiarybutylselenide

S. Siebentritt, Laboratory for Photovoltaics, University of Luxembourg, 51 Rue du Brill, L-4422 Belvaux, Luxembourg

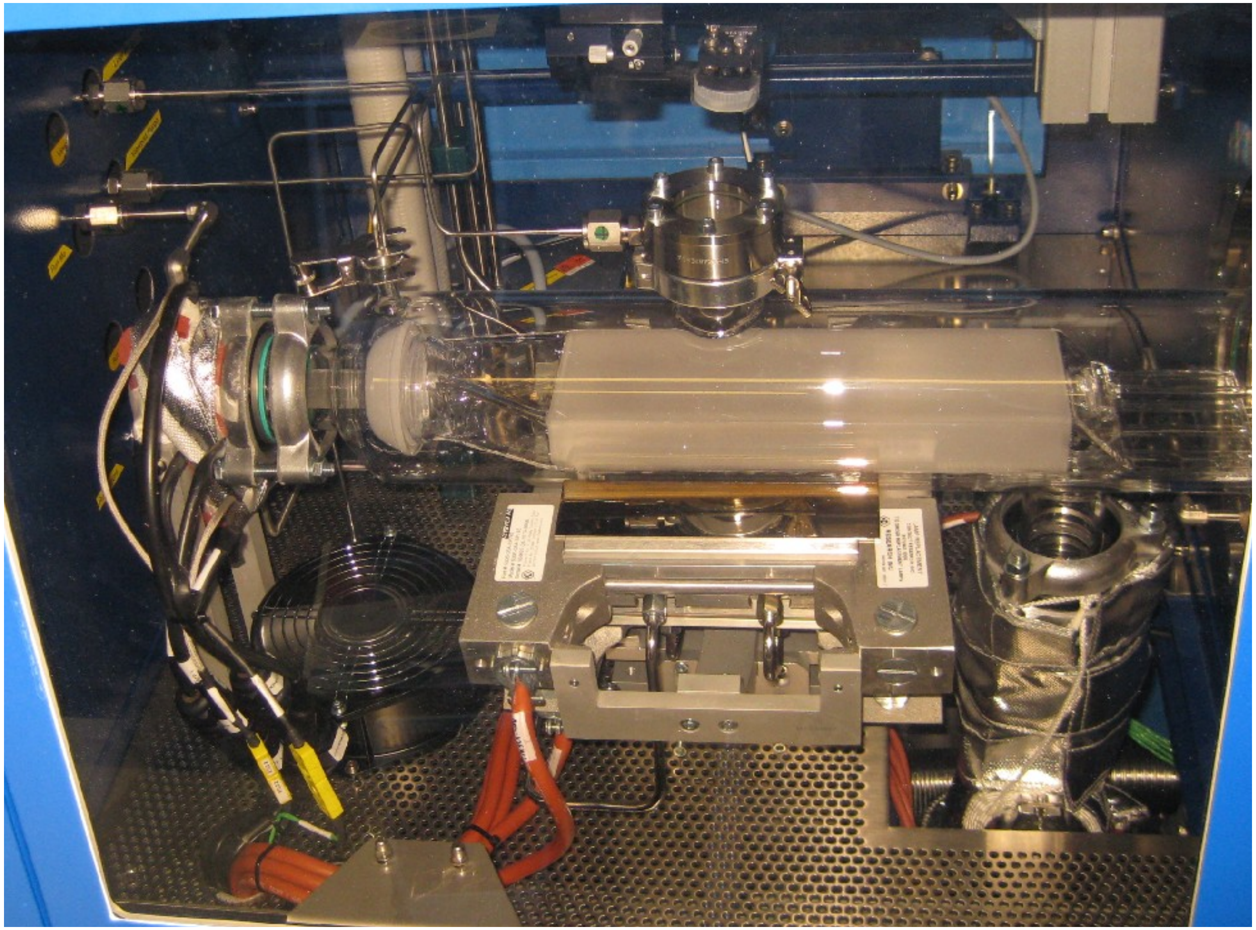
The MOVPE process

System: Aixtron AIX 200 (2'' wafer)

Pressure: 50mbar

Temperature: 570°C

Substrate: GaAs (100)



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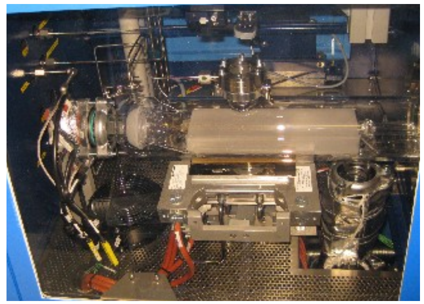

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- CpCuTEP — Cyclopentadienyl-Copper-Triethylphosphine
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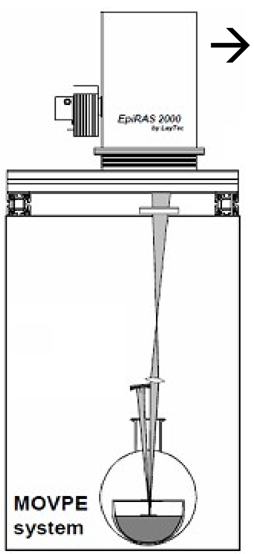
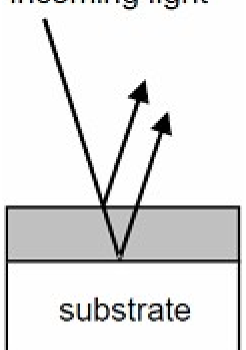
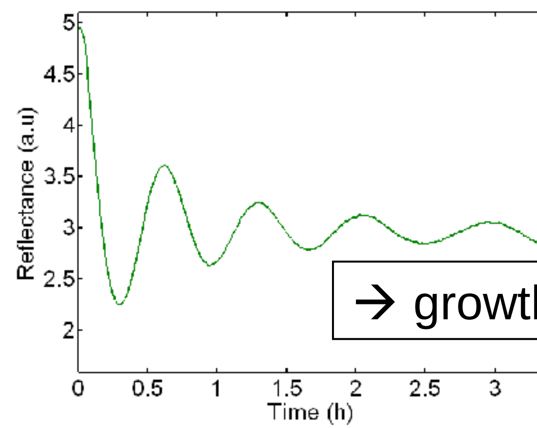
- DtBSe — Ditertiarybutylselenide

In-situ monitoring: EpiRas - Laytec



→ RAS + Reflectance





→ growth rate ≈100nm/h

1. Reflection at surface → roughness
2. Fabry-Perot oscillations → thickness

$CuGaSe_2$ with various compositions

$CuGaSe_2$ still forms under strong deviations from [Cu/Ga]=1

From phase diagram:

Cu-poor [Cu/Ga]=1 Cu-rich

Cu-poor $CuGaSe_2$ ([Cu/Ga] < 1)

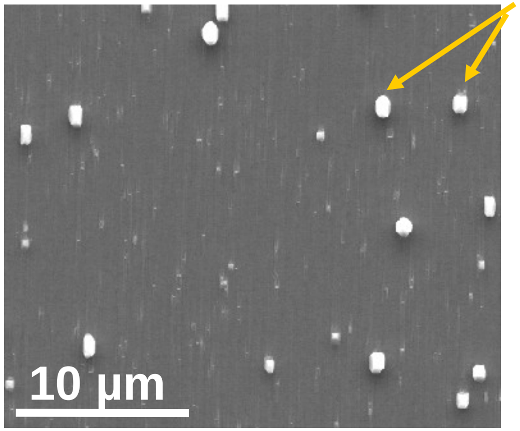
Stoichiometric $CuGaSe_2$ ([Cu/Ga] = 1)

+ secondary phase: Cu_xSe

Co-existing phases, what happens during growth?

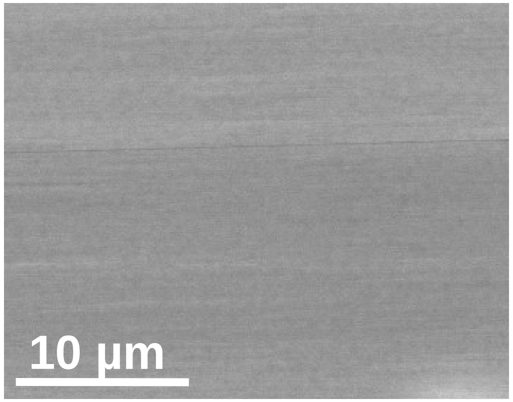
$CuGaSe_2$ grown under various [Cu/Ga] ratios

Cu-rich



Cu_xSe crystals

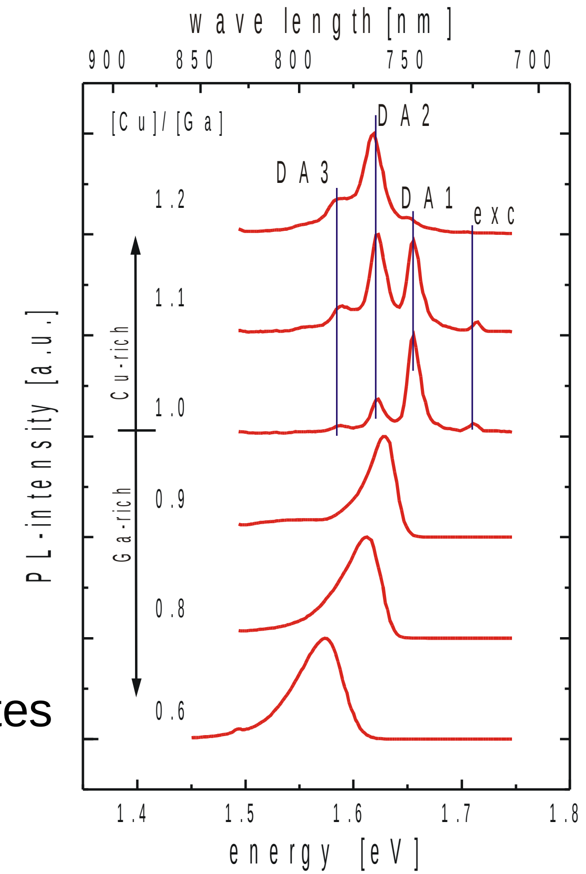
Cu-poor



PL depends on Cu/Ga ratio:

Cu-rich PL shows:
- Donor-Acceptor transitions
- Excitonic transitions

Cu-poor:
- Transitions from defect states

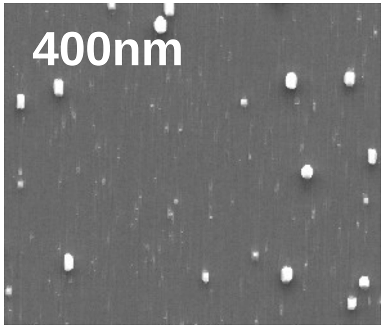


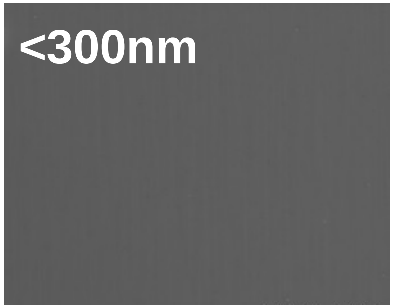
[Bauknecht, A., Siebentritt, S., Albert, J., Lux-Steiner, M. C., J. Appl. Phys., 89 (2001) 4391-4400]

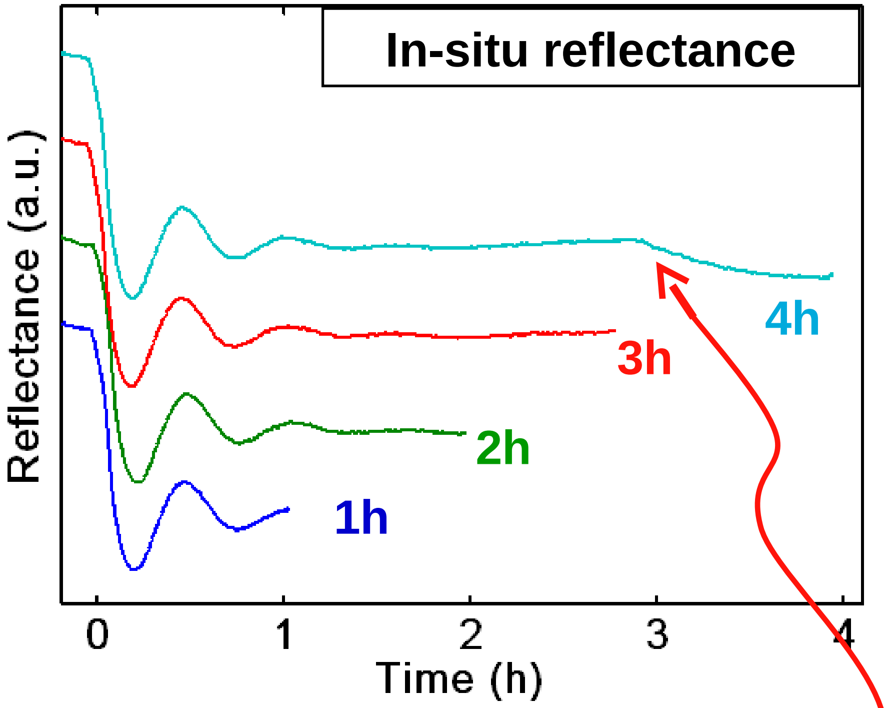
Analyzing time evolution of two phase system

Time evolution of secondary phase Cu_xSe:

Cu-rich standard recipe (4h = 400nm) was stopped at 1h...4h

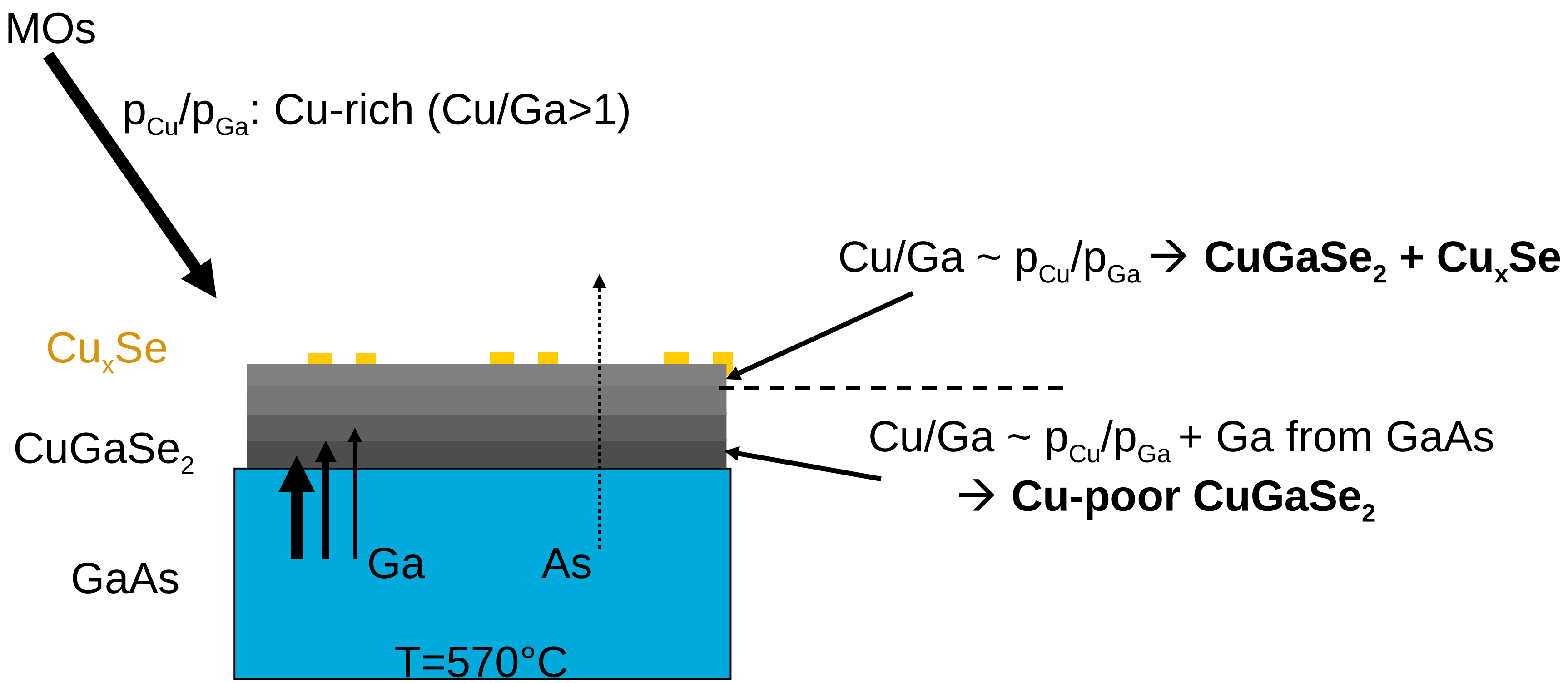






No Cu_xSe on short runs! Appear at 3→4h, **WHY?!**

Proposed growth model

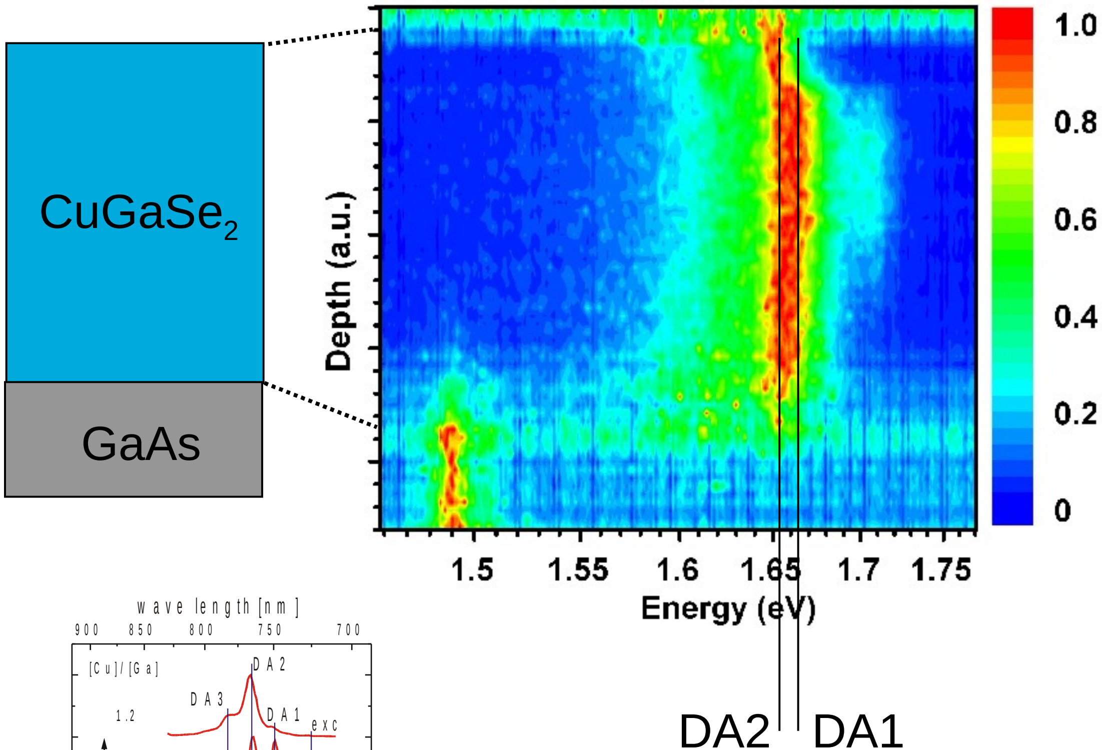


1. **Cu-poor $CuGaSe_2$**
2. **stoichiometric $CuGaSe_2$ + Cu_xSe**

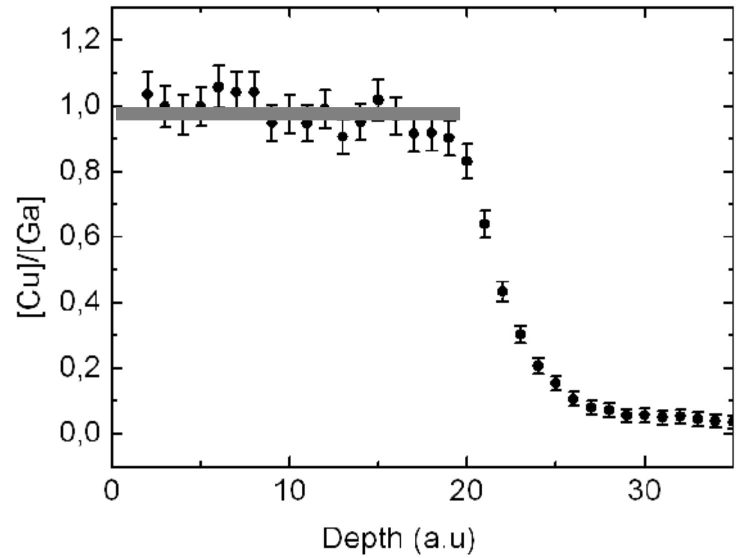
→ Gradient in composition profile?

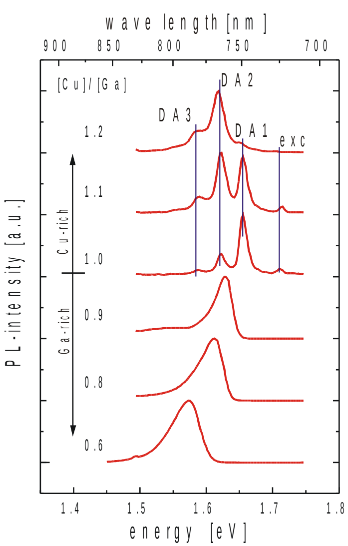
Depth profile of [Cu/Ga]-ratio

Cathodoluminescence



Auger spectroscopy





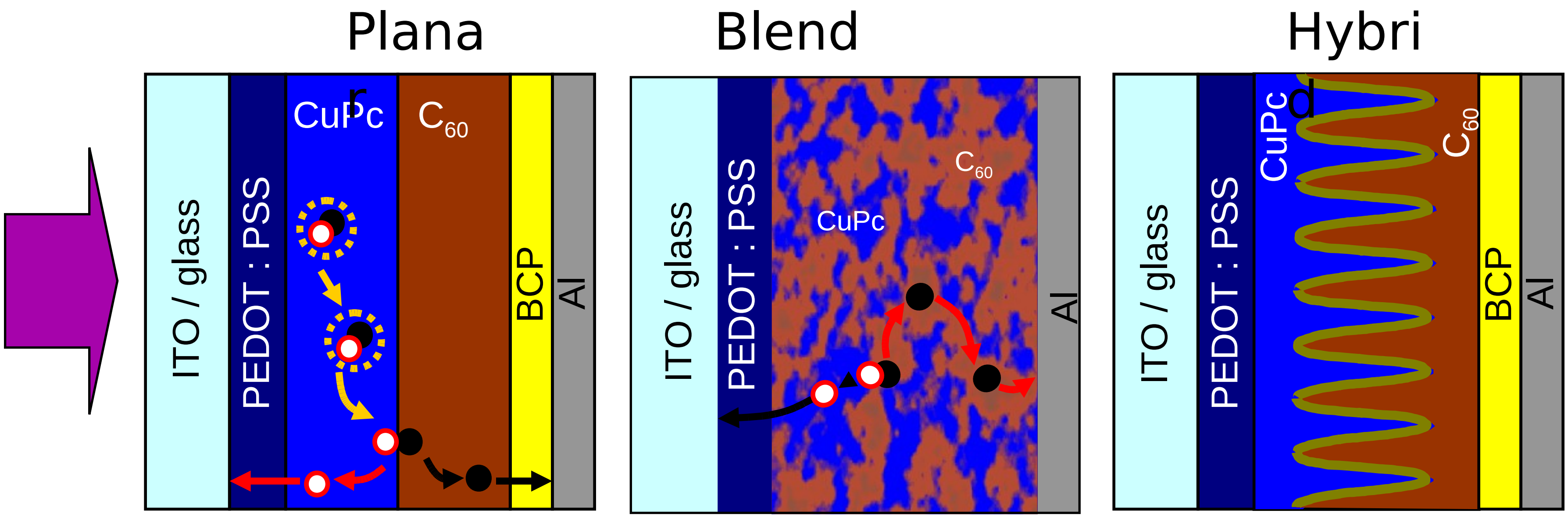
→ Cu-rich fingerprint

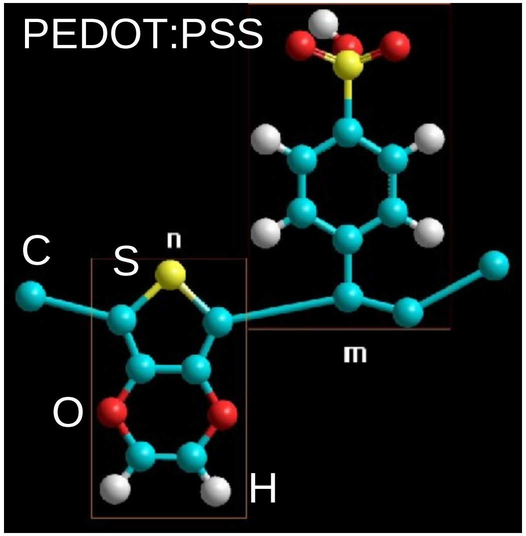
→ [Cu/Ga]=1 for entire layer

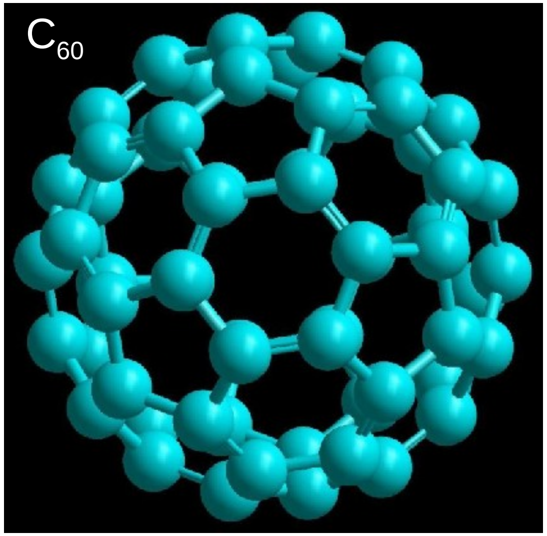
Homogeneous depth profile

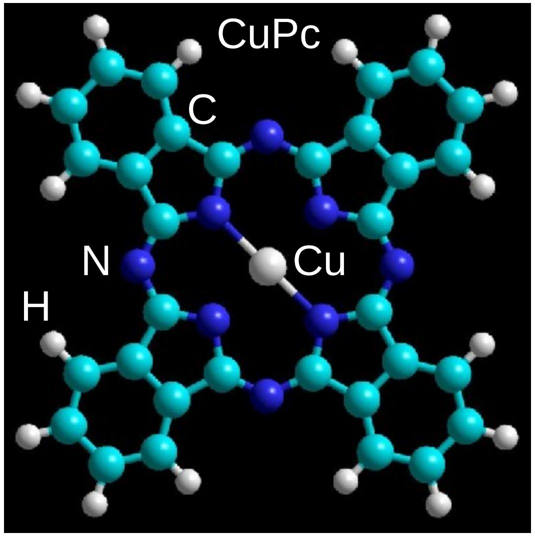
Due to high mobility of Cu:
>100x larger than for Ga and Se

Organic Solar Cells



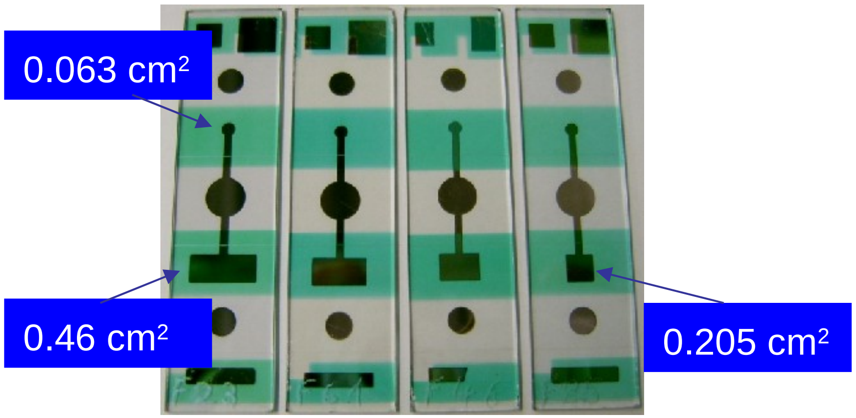


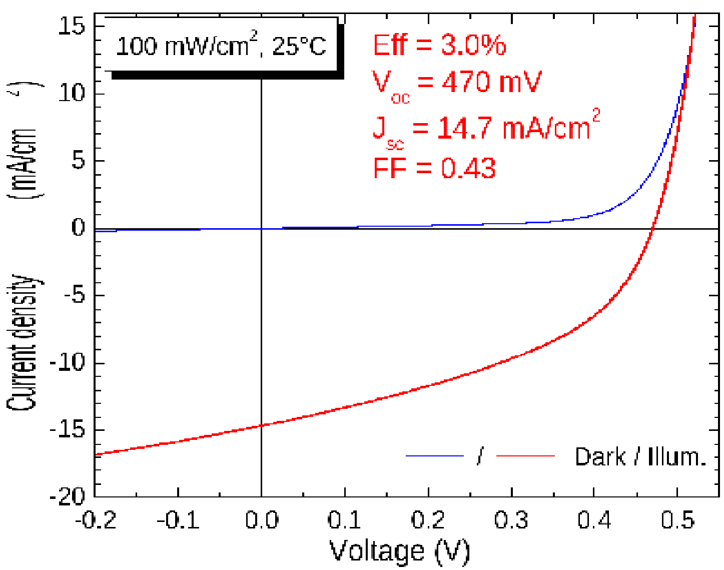




Device concepts & achievements

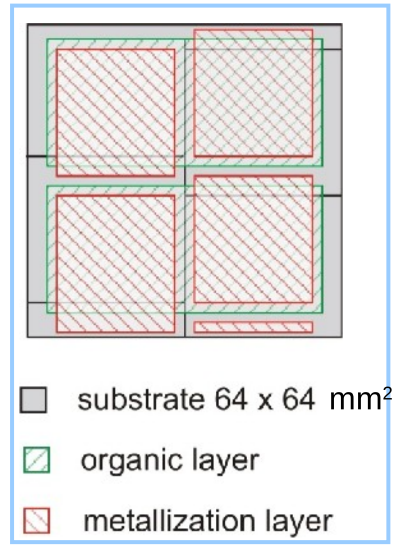
Organic solar cells

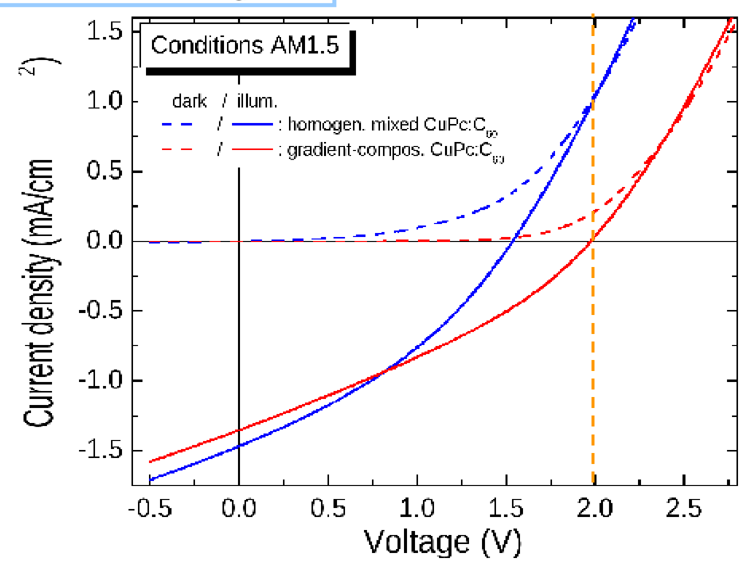




[1]M. Rusu *et al.*, *Thin Solid Films* 516 (2008) 7160.
[2]M. Rusu *et al.*, Springer special issue (2009).

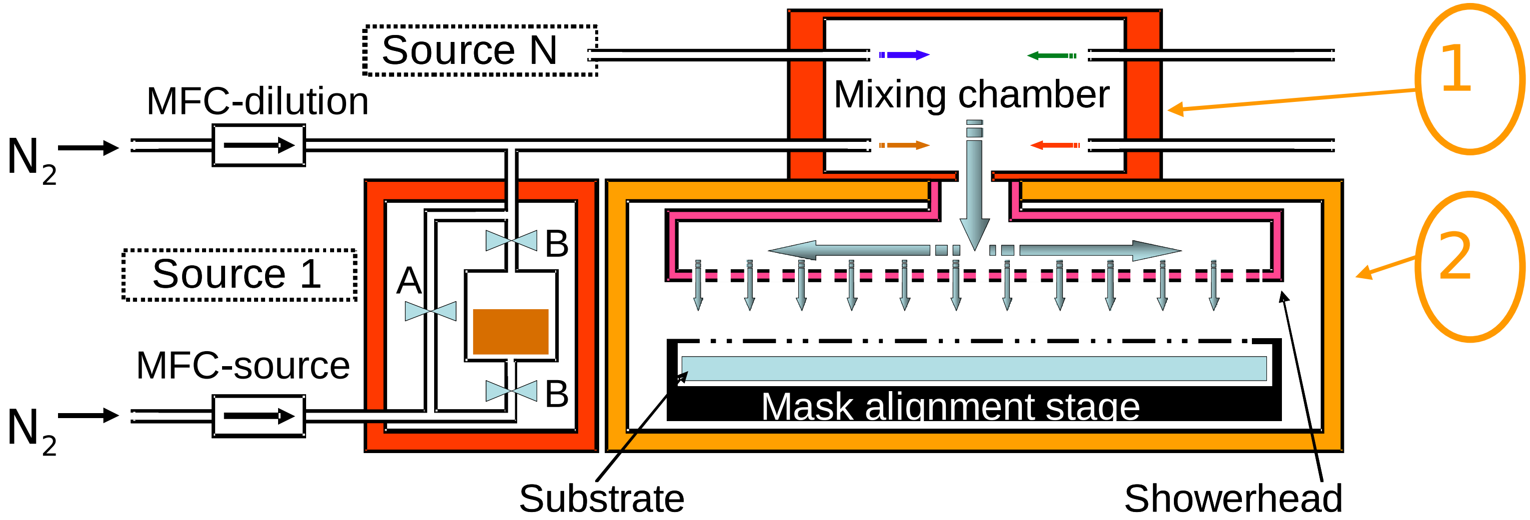
First PV mini-modules



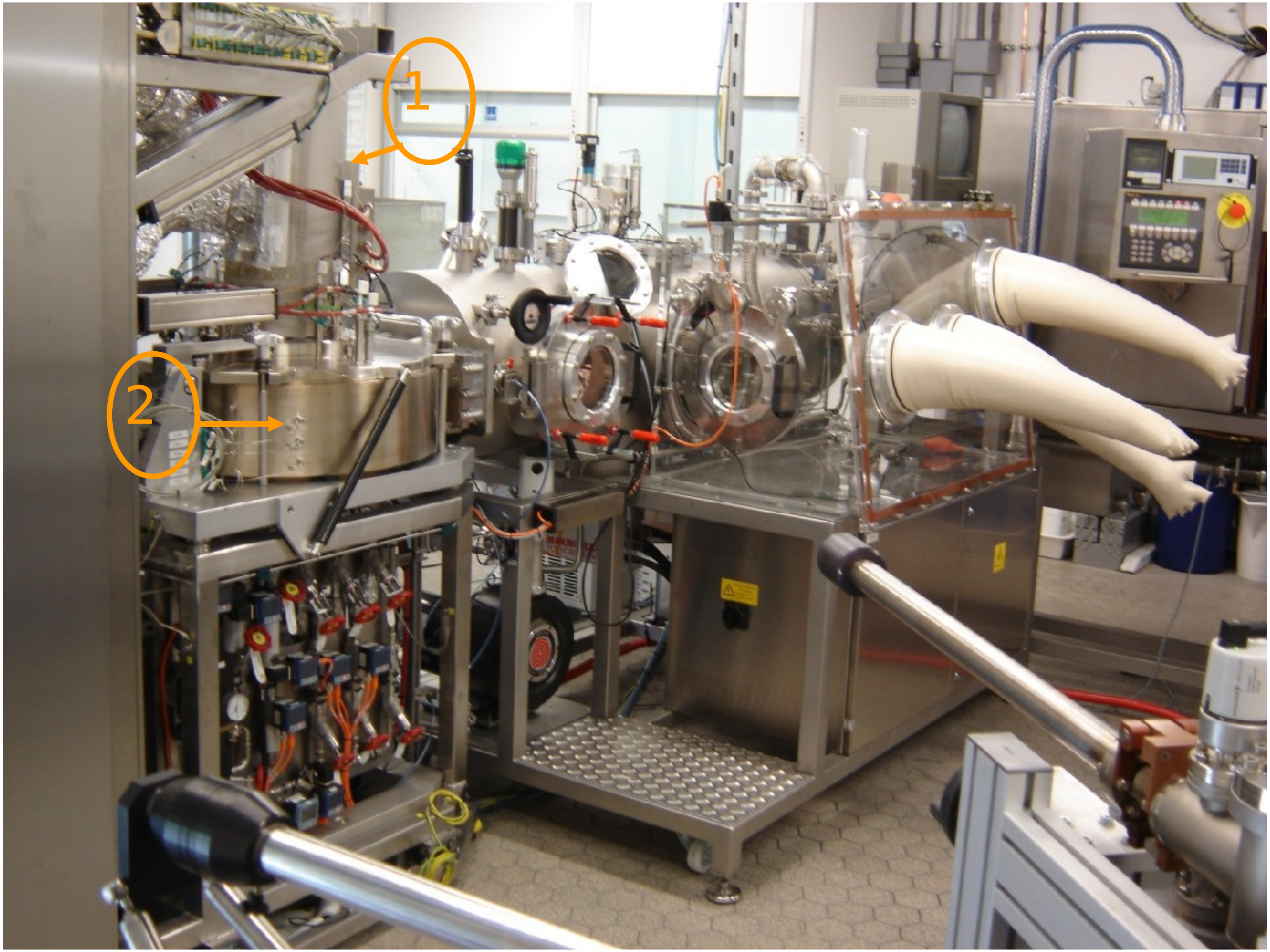


[1]M. Rusu *et al.*, *23rd EUPVSEC,* WIP-Renewable Energies, ISBN: 3-936338-24-8, 2008, p. 679-681.

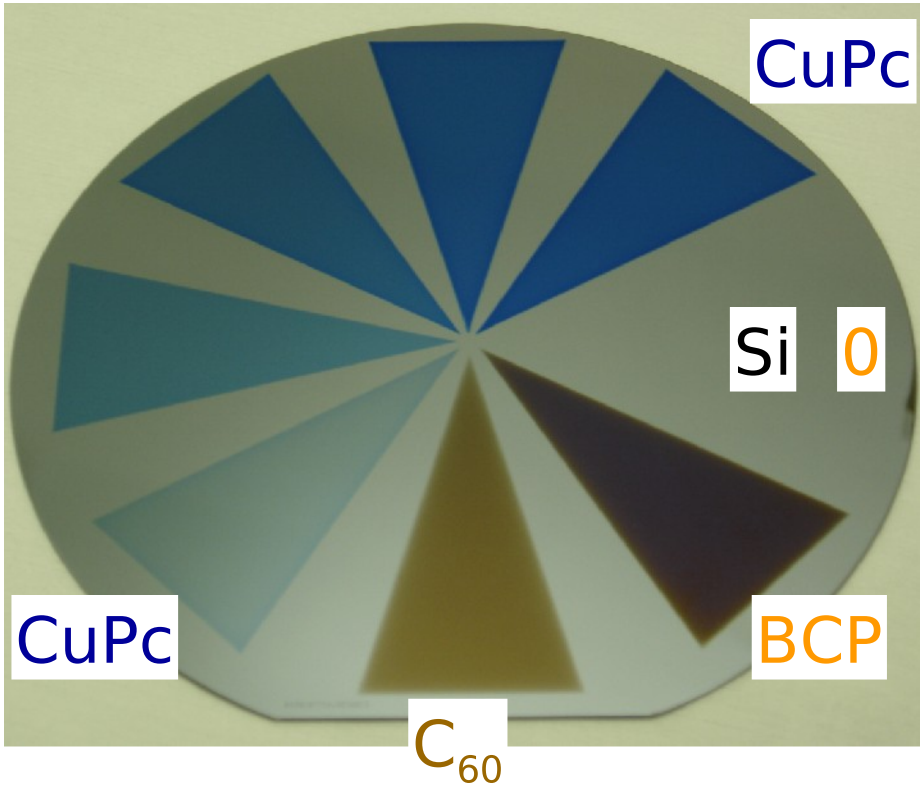
Organic vapor phase deposition - **OVPD**

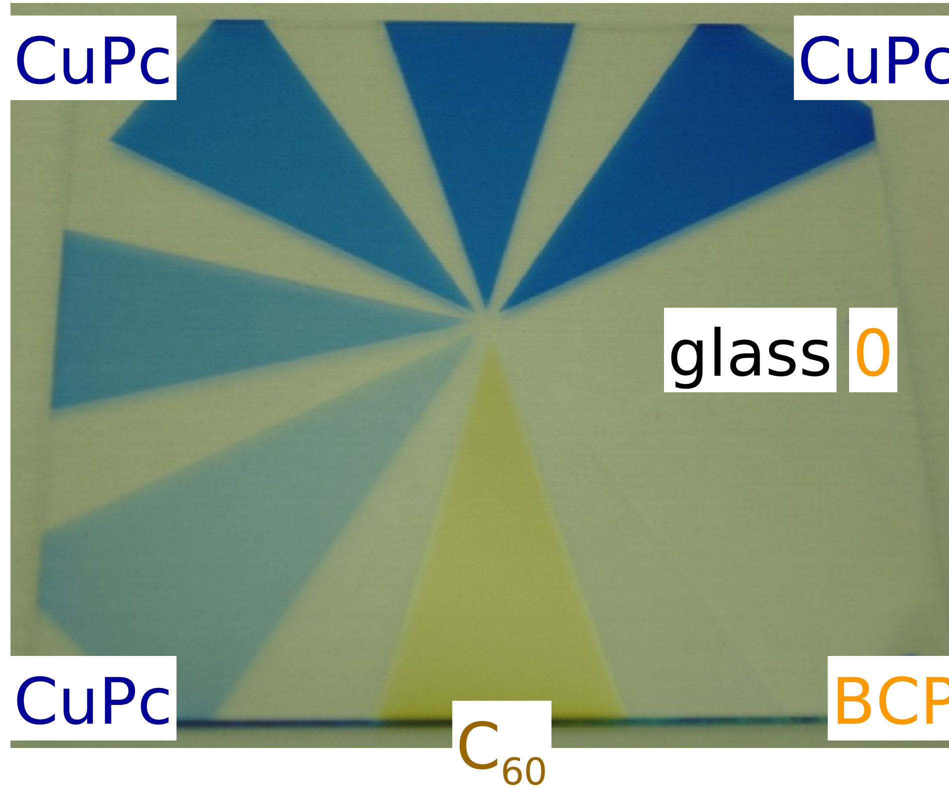


[1]M. Rusu *et al.*, *Renewable Energy* 33 (2008) 254.


1
2

CuPc, C_{60} and BCP by OVPD



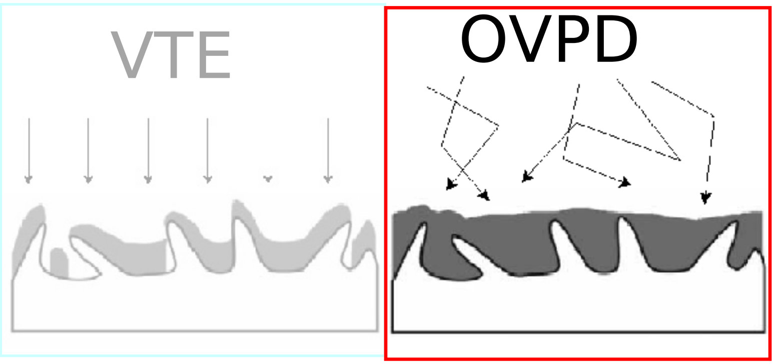


150 mm

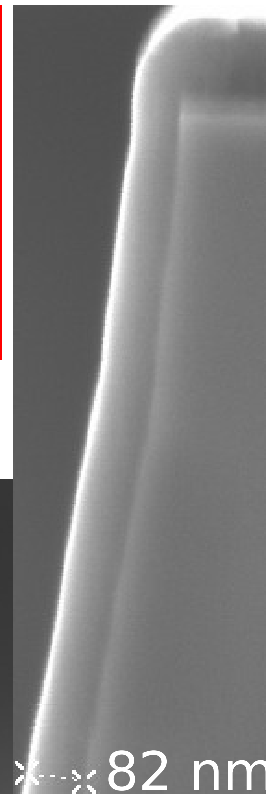
100 cm^2

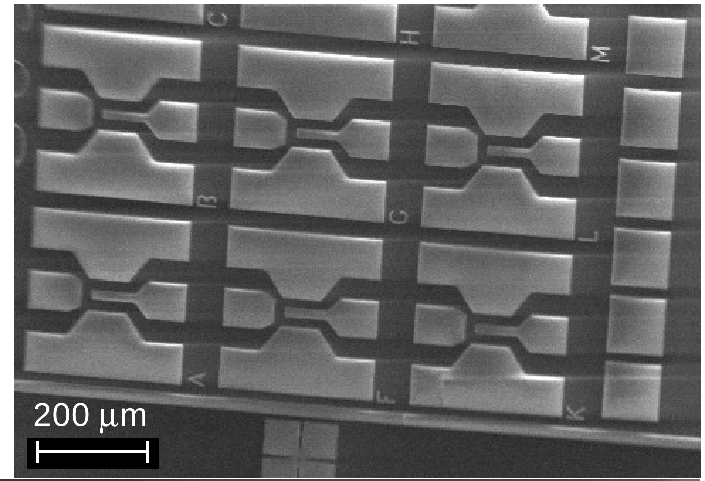
- Homogeneous deposition
  - Deposition areas show sharp edges
    - No ‘memory’ effects are observed
      - Deposition process reproducible

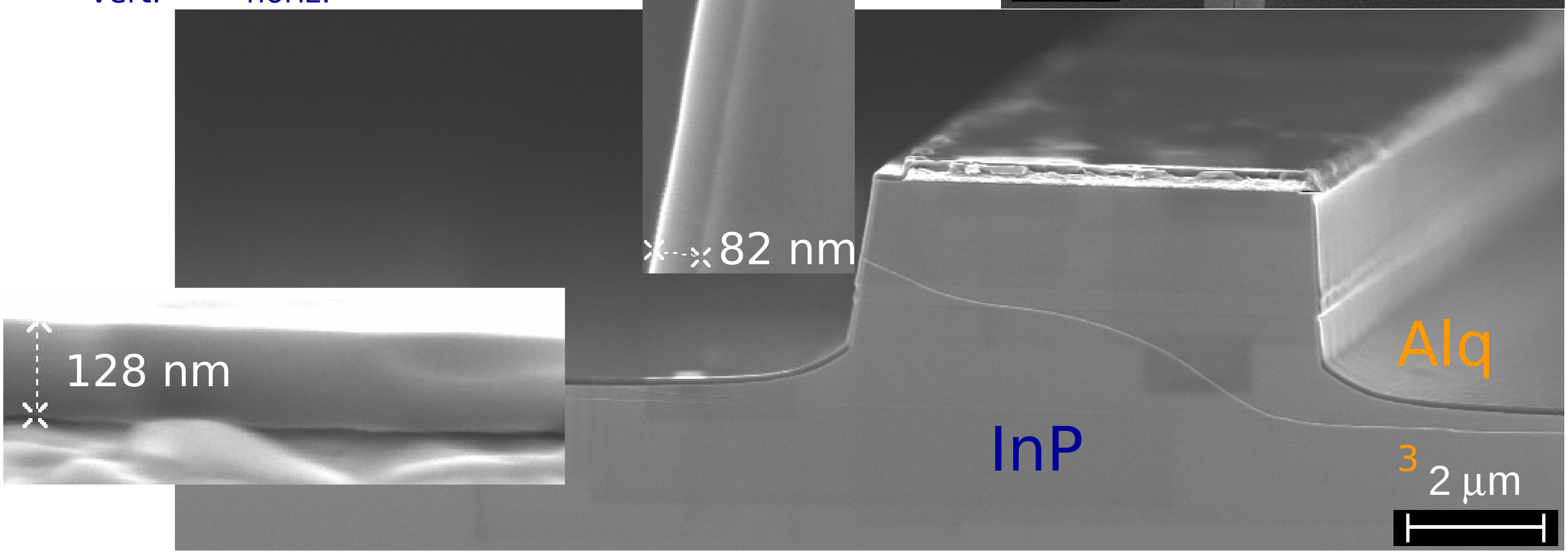
OVPD: Prove of the diffusion-controlled process



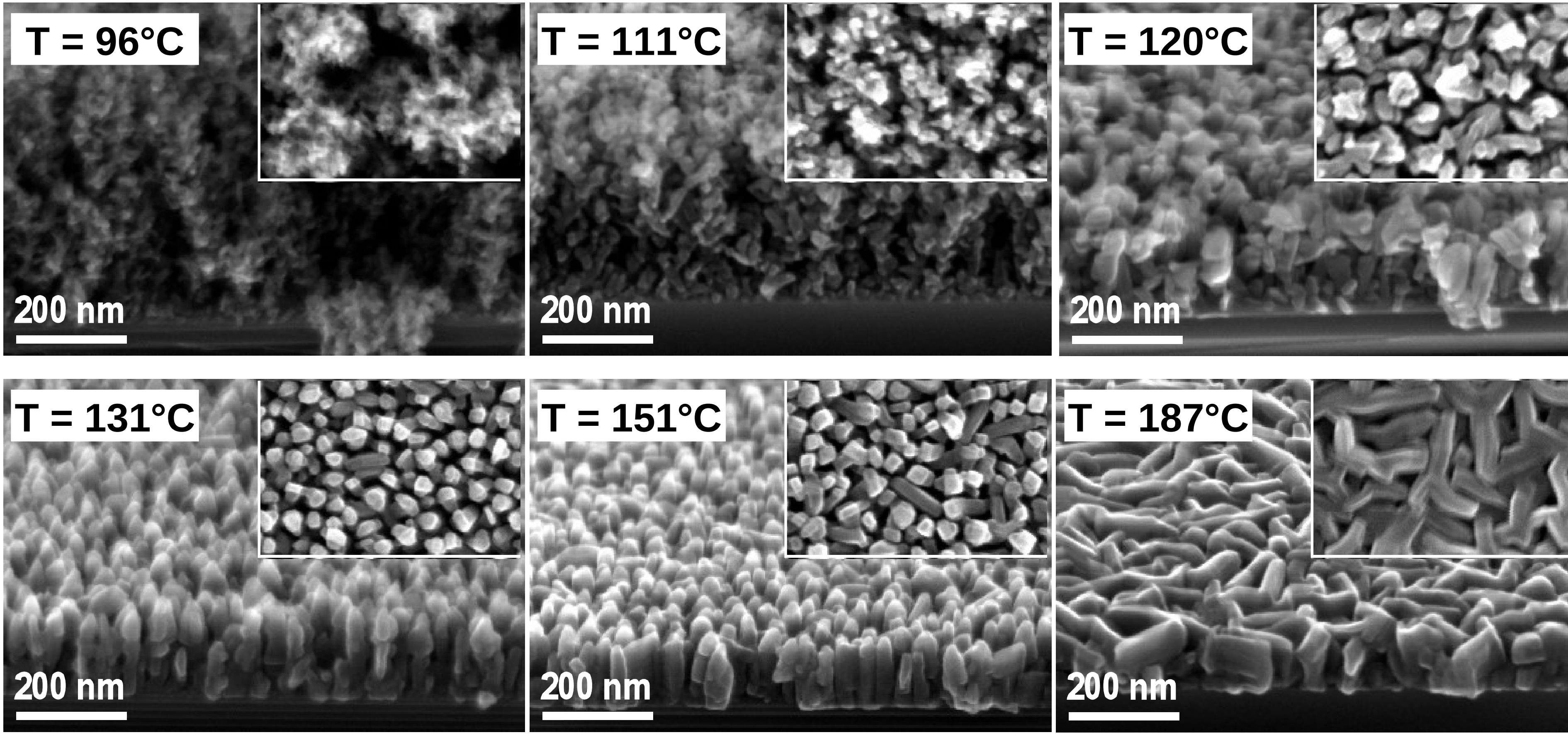
$d_{vert.} / d_{horiz.} = 0.64$







CuPc layers on Si<100>

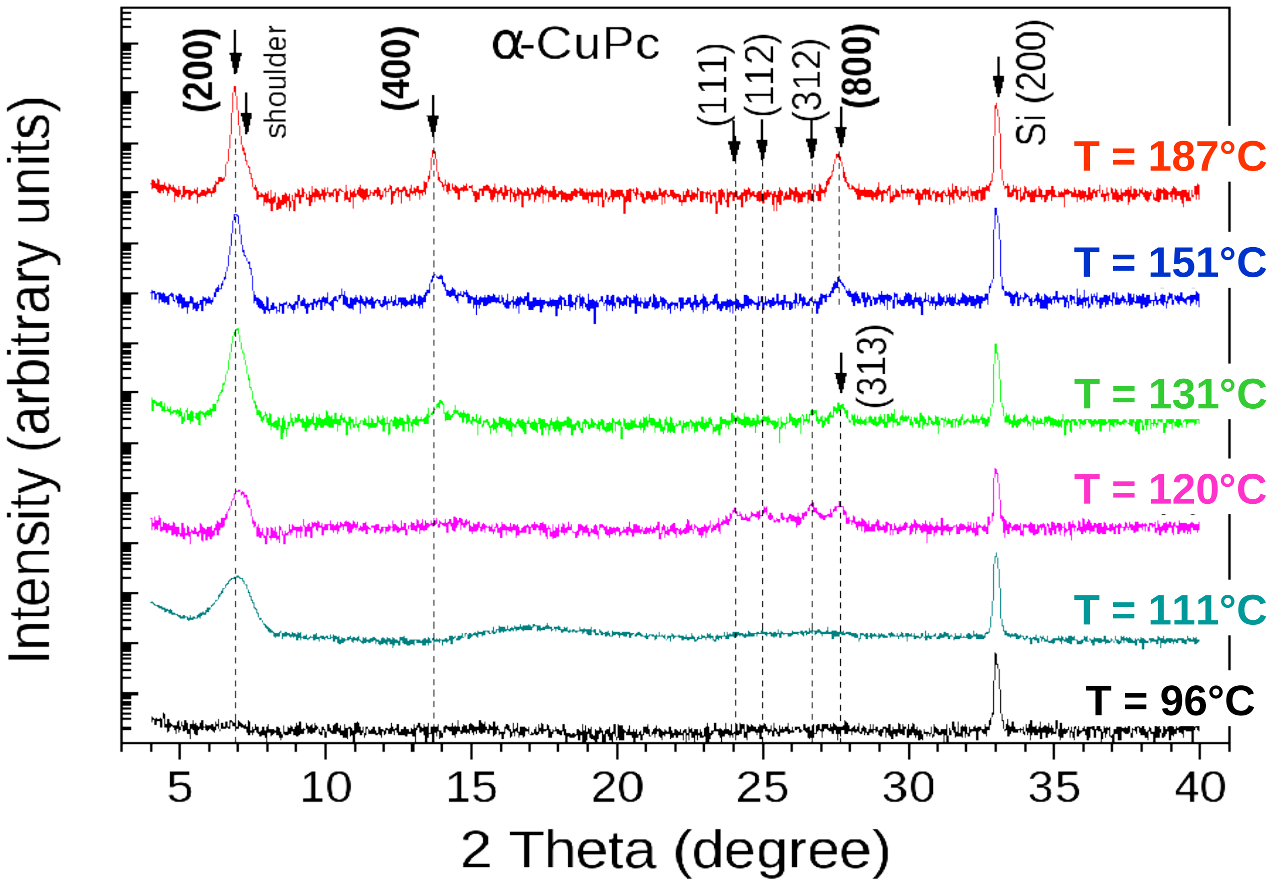


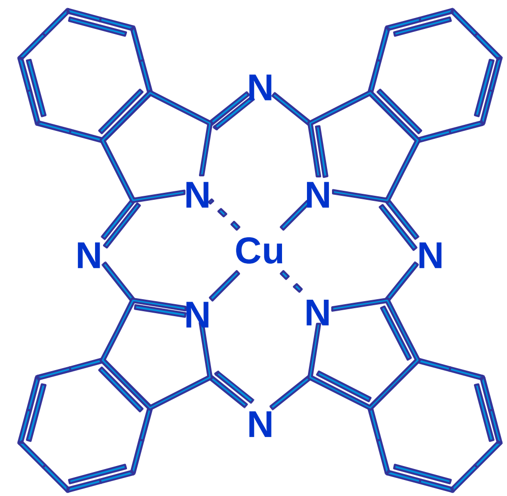
CuPc film structure develops through a coalescence process

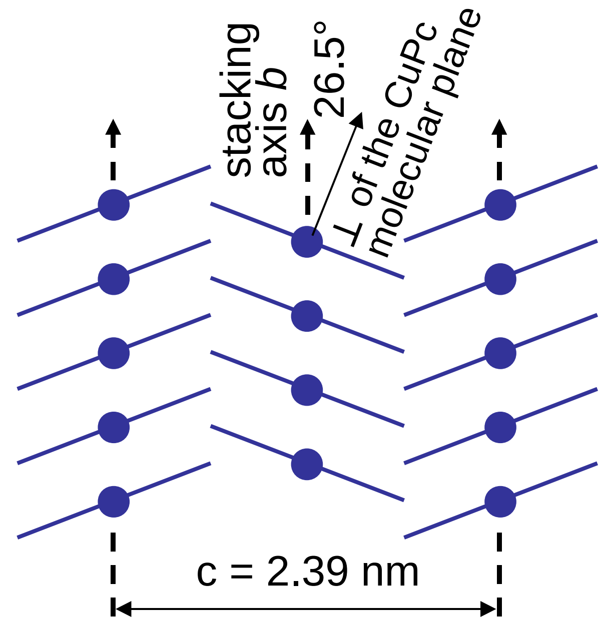
Columnar and elongated rod-like crystallites

Crystallite dimensions and spacing comparable to the excitons diffusion length

M. Rusu et al. , *Thin Solid Films* 516 (2008) 7160., M. Rusu et al., *Proc. 22nd EUPVSEC-2007*.







Elevated substrate temperature enhances the <100> preferential orientation of the monoclinic α-CuPc polymorph