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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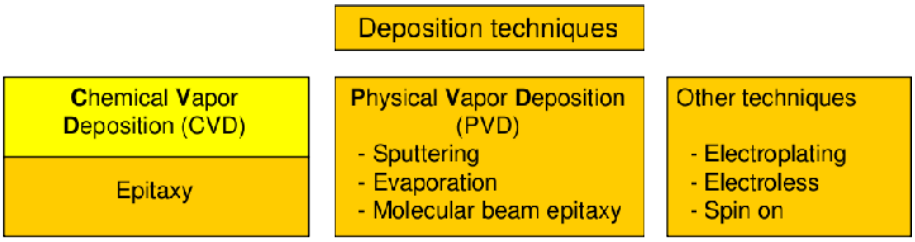
Classification of deposition techniques



Deposition techniques

Chemical Vapor Deposition (CVD)

Epitaxy

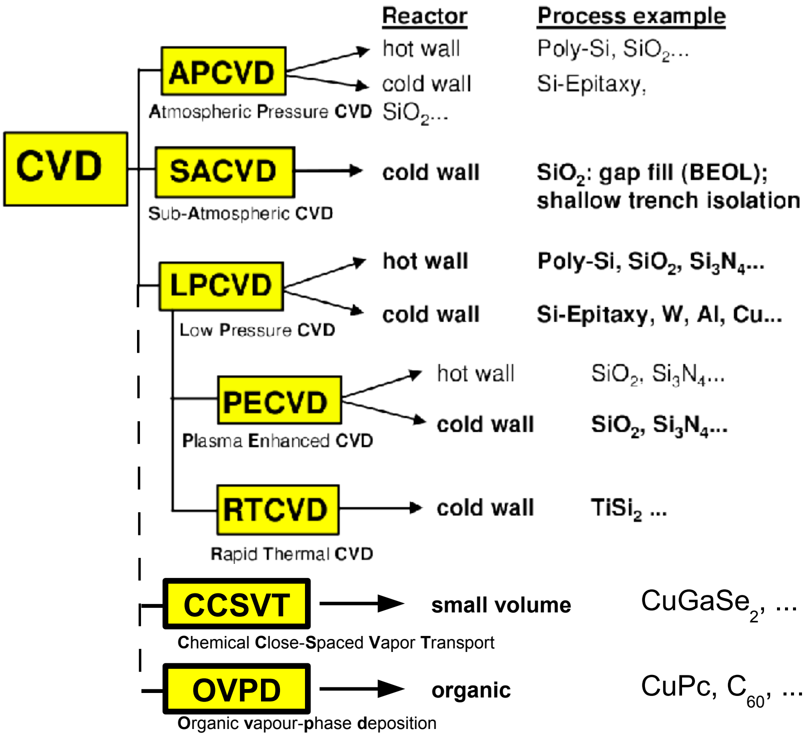
Physical Vapor Deposition (PVD)
- Sputtering
- Evaporation
- Molecular beam epitaxy

Other techniques
- 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



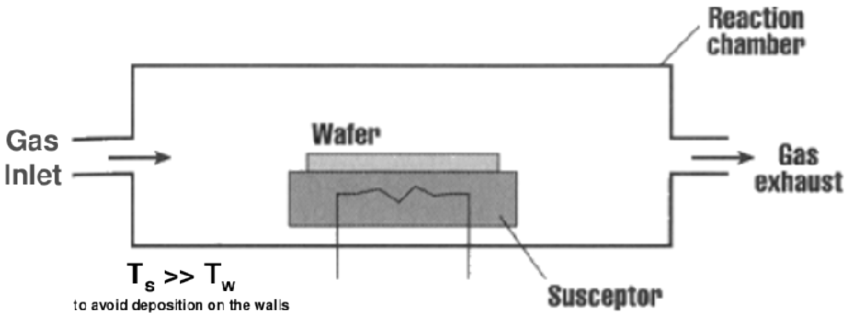
		Reactor	Process example
CVD	APCVD Atmospheric Pressure CVD	hot wall	Poly-Si, SiO_2...
		cold wall	Si-Epitaxy, SiO_2...
	SACVD Sub-Atmospheric CVD	cold wall	SiO_2: gap fill (BEOL); shallow trench isolation
	LPCVD Low Pressure CVD	hot wall	Poly-Si, SiO_2, Si_3N_4...
		cold wall	Si-Epitaxy, W, Al, Cu...
	PECVD Plasma Enhanced CVD	hot wall	SiO_2, Si_3N_4...
		cold wall	SiO_2, Si_3N_4...
	RTCVD Rapid Thermal CVD	cold wall	$TiSi_2$ ...
	CCSVT Chemical Close-Spaced Vapor Transport	small volume	$CuGaSe_2$, ...
	OVPD Organic vapour-phase deposition	organic	CuPc, C_{60}, ...

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



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

- 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

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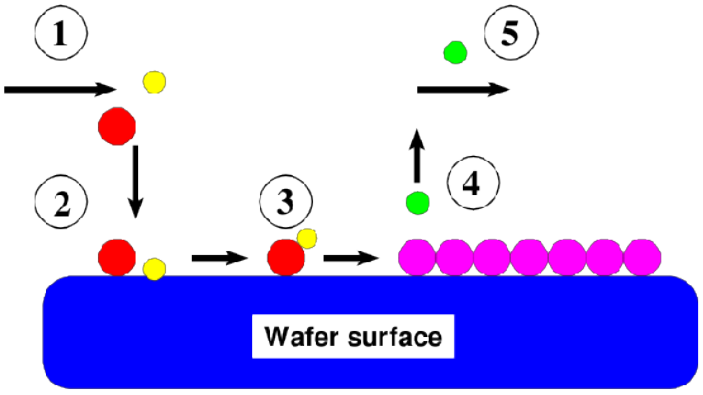
Theoretical background: Elementary processes



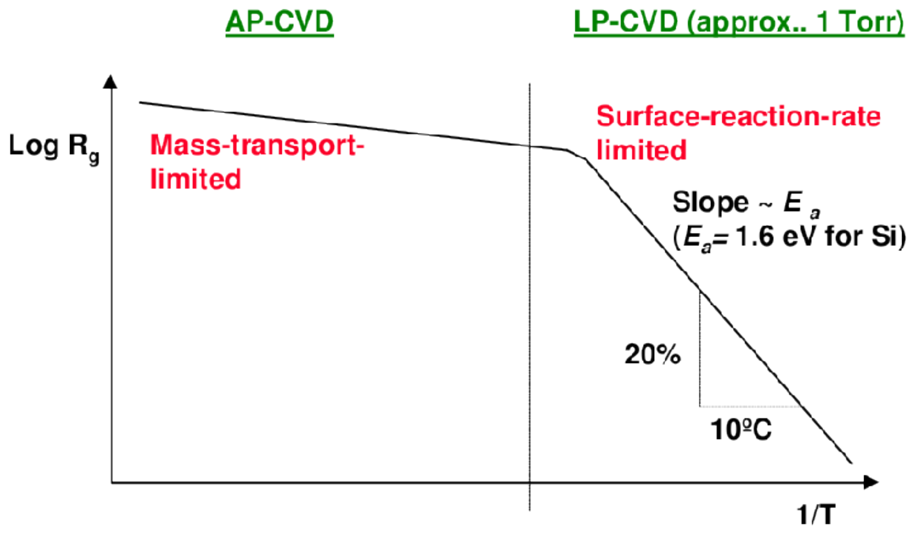
1 Transport of the precursor(s) with the carrier gas to the reaction chamber and to the wafer surface (convection and diffusion)
2 Adsorption or chemisorption of the precursor(s) at the wafer surface
3 Chemical surface reaction (including dissociation and surface diffusion)
4 Film growth, desorption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

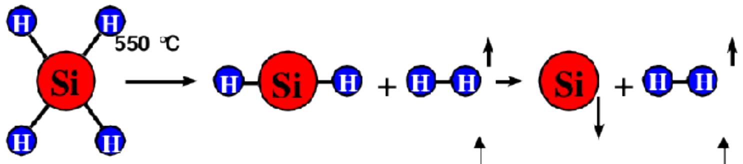


The aforementioned steps are sequential, hence the one that occurs at slowest rate will determine the deposition rate.
These rate-determining steps can be grouped into gas-phase processes and surface processes.

Theoretical background: Reaction types

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

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



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

Oxidation: 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*

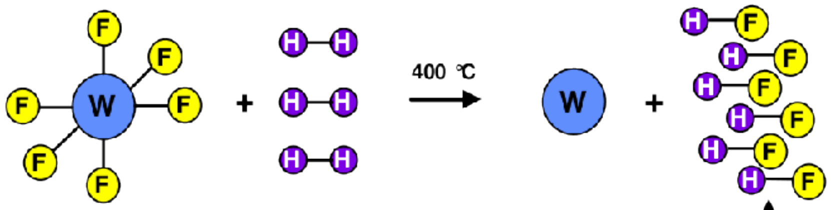
$$SiH_4 + O_2 \xrightarrow{450\ ^\circ C} SiO_2\downarrow + 2\ H_2\uparrow$$

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

Theoretical background: Reaction types

Reduction: 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*



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

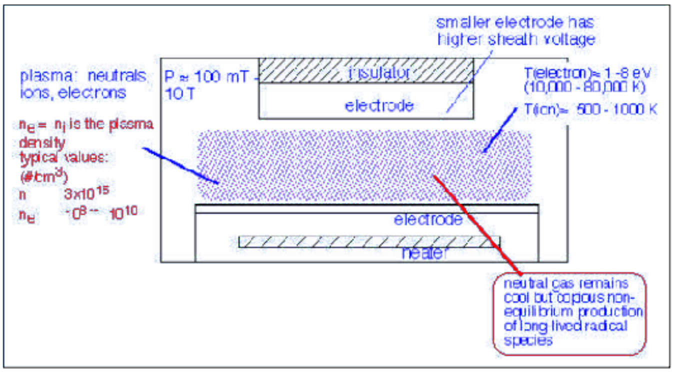
LPCVD of Tungsten, selective deposition

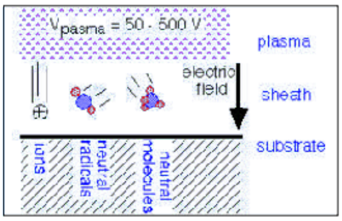
$$2\ WF_6 + 3\ SiH_4 \xrightarrow{250\ ^\circ C} 2\ W\downarrow + 3\ SiF_4\uparrow + 6\ \uparrow$$
H_2

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

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 °C	rf frequency:	13.56 MHz, 400 kHz ...

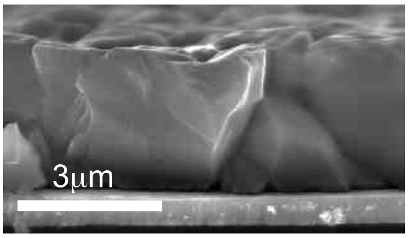
CuGaSe$_2$ in solar cells

- 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…)



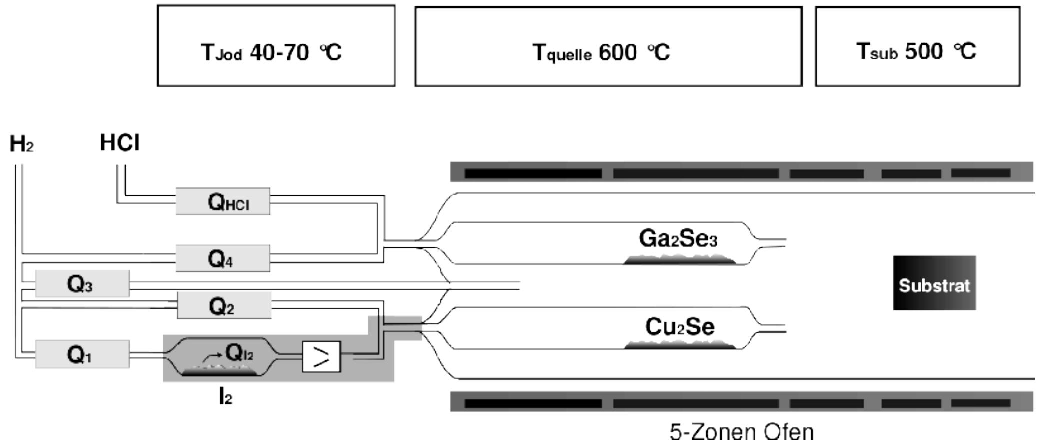
→Analysis is difficult (polycrystalline absorber)

Single crystalline thin films for fundamental analysis needed

→ **epitaxial CuGaSe$_2$ layers**

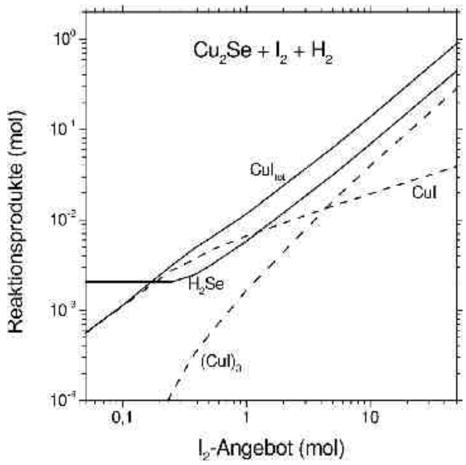
Journal of Crystal Growth 315 (2011) 82–86

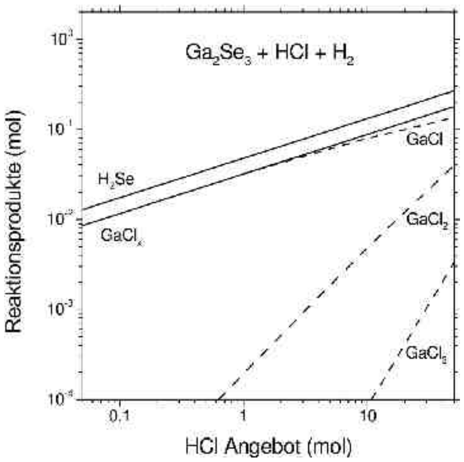
CVD of $CuGaSe_2$



PhD Thesis, D. Fischer 2000, FU-Berlin

Reaction Products





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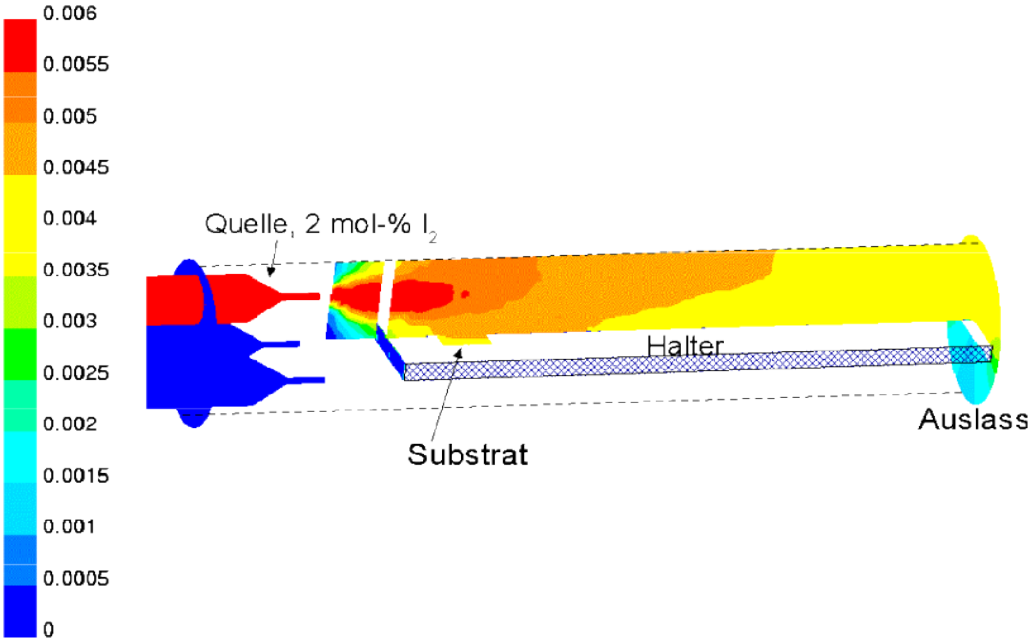
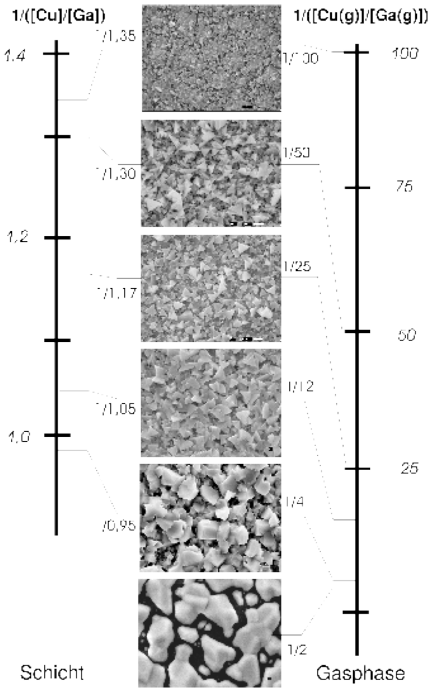
CVD gas steam, I_2 concentration



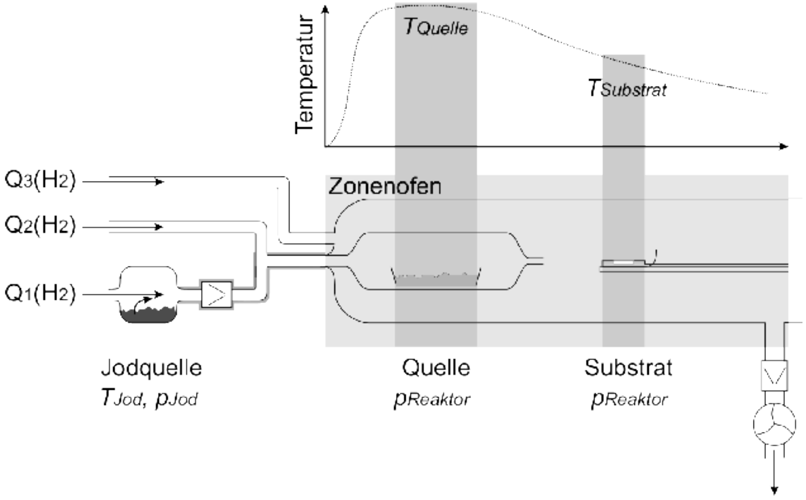
PhD Thesis, D. Fischer 2000, FU-Berlin

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

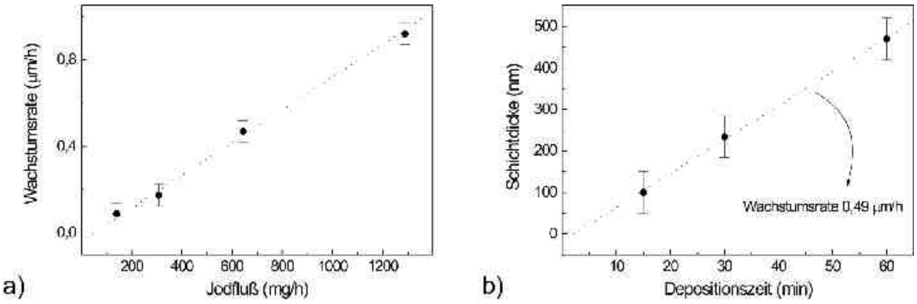
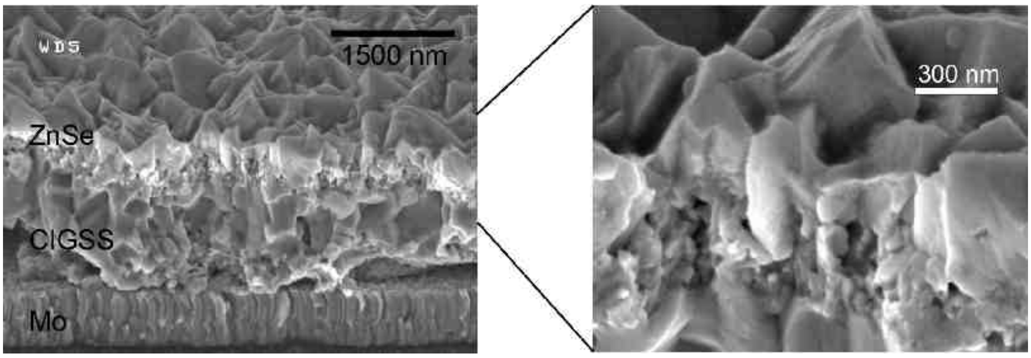


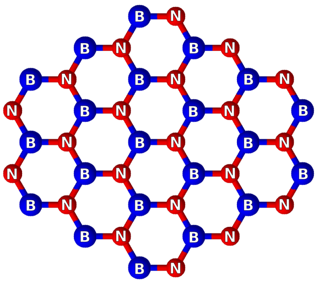
Abbildung 5.1: a) ZnSe Wachstumsrate als Funktion der Jodtransportrate, b) Schichtdicke über der Depositionszeit, jeweils korrigiert um die Dicke der Keimschicht (100 nm) (Quellen /Substrattemperatur 550/350 °C)

PhD Thesis, A. Rumberg 2001, FU-Berlin

ZnSe buffer layer for $CuGaSe_2$ solar cells



Hexagonal Boron Nitride on Rh(111)

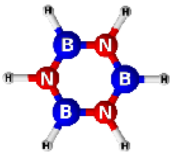


- 3 different height areas are formed
- Meshperiodicity: ~ 3.2 nm
- Holesize: ~ 2 nm
- Binding Energy
  - poreside: 0.49eV
  - wireside : -0.04eV

Exposure of Borazine ($H_6B_3N_3$) vapour to the rhodium (111) surface

<u>Parameters:</u>

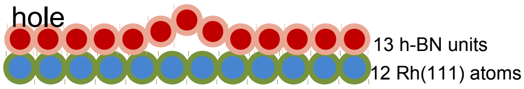
T_{sample} = 520°C
$p_{borazine}$ = 3×10^{-8} mbar
$t_{borazine}$ = 3 min



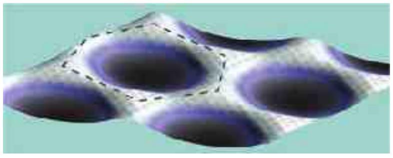
[1] M. Corso et al., Science 303, 217 (2004)
[2] Laskowski et al., Phys. Rev. Lett. 98, 106802 (2007)
[3] Laskowski et al., J. Phys.: Cond. Mat., 20, 064207 (2008)

Sample Preparation

h-BN on Rh(111)

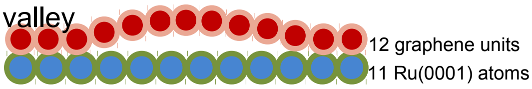


Exposure of borazine on a
Rhodium (111) surface @ 520°C

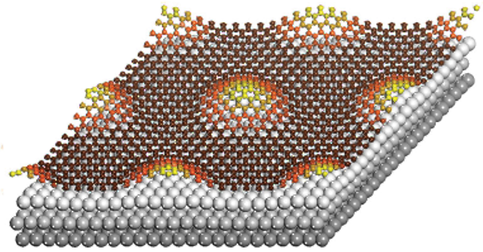


M. Corso et al., Science 303, 217 (2004)
Laskowski et al., Phys. Rev. Lett. 98, 106802 (2007)
Laskowski et al., J. Phys.: Cond. Mat., 20, 064207 (2008)
H. Dil et al., Science 319, 1824-1826, (2008)

Graphene on Ru(0001)



Exposure of ethylene on a Ru(0001)
surface @ 1000°C for 10min



S. Marchini et al. Phys. Rev. B 76, 075429, (2007)
D. Martoccia et al. Phys. Rev. Lett. 101, 126102, (2008)
W. Moritz et al., Phys. Rev. Lett. 104, 136102, (2010)
A. L. Vazquez de Parga et al., Phys. Rev. Lett. 100, 056807, (2008).

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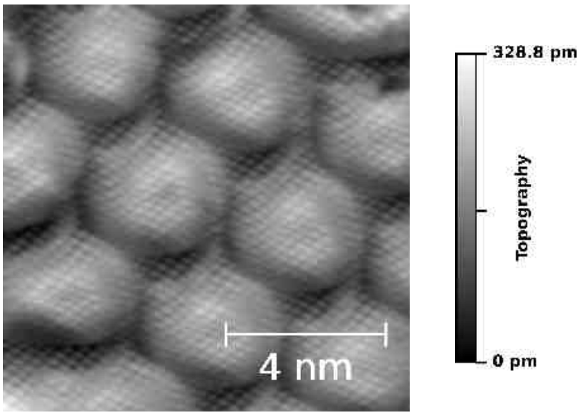
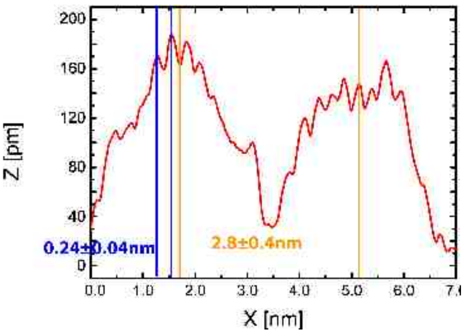
h-BN High Resolution

nc-AFM at RT





- hole – wire distance ~2.8nm
- BN unit cell distance ~240pm
- high resolution only with inverted contrast!?

Δf_{1st} = -180Hz, A_{1st} = 6nm, V_{AC} = 500mV

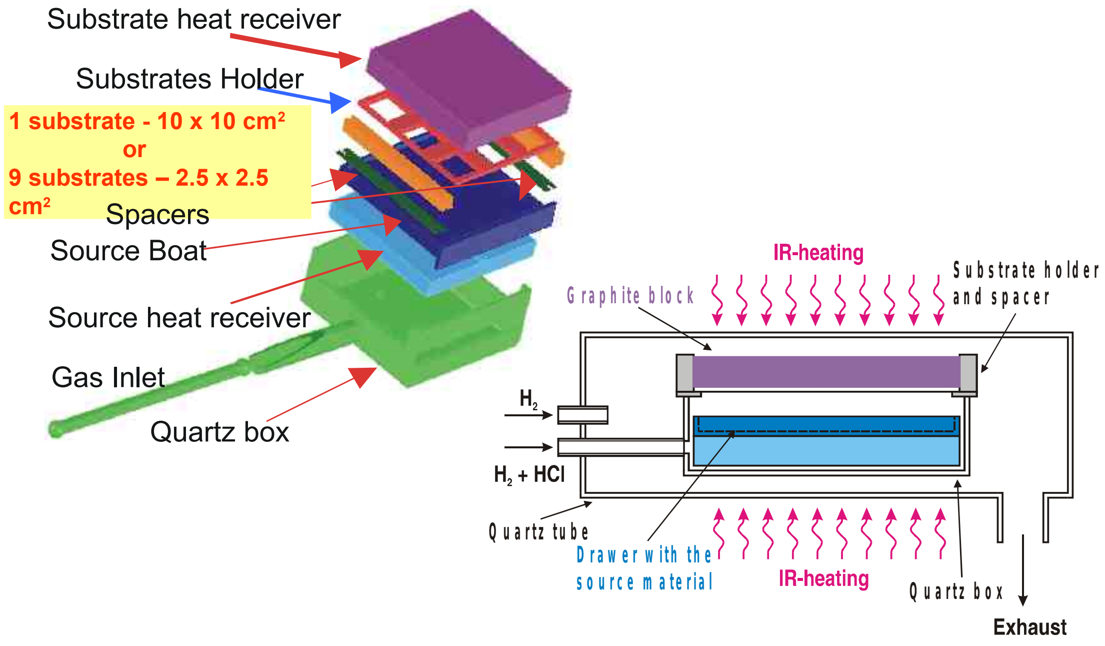
Chemical closed-space vapor transport (CCSVT)

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



Substrate heat receiver

Substrates Holder

1 substrate - 10 x 10 cm^2
or
9 substrates – 2.5 x 2.5 cm^2

Spacers

Source Boat

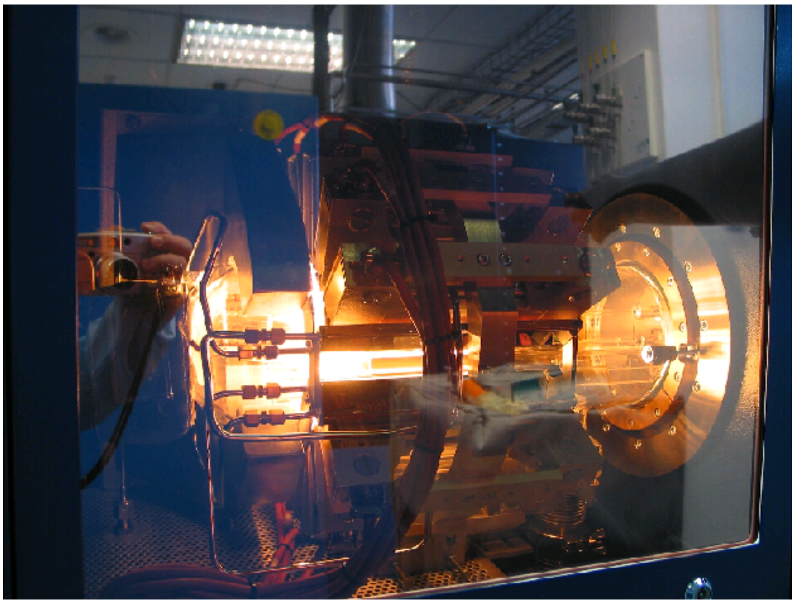
Source heat receiver

Gas Inlet

Quartz box

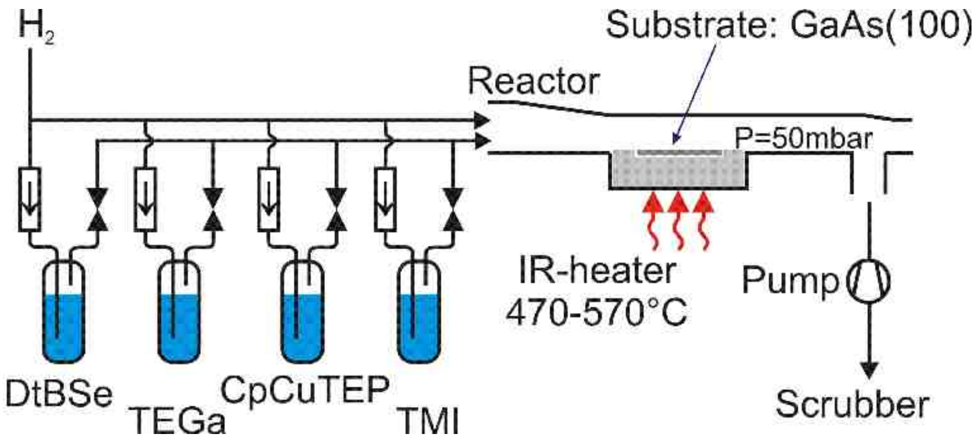
Thin Solid Films 451 – 452 (2004) 556–561

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

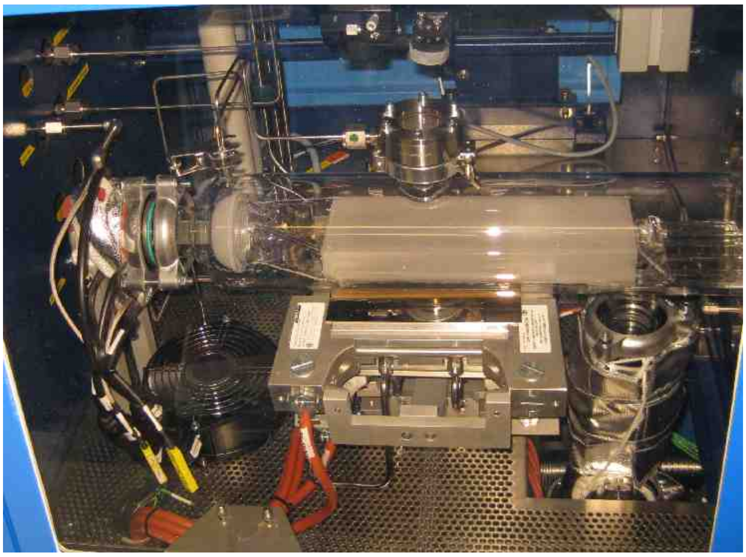
The MOVPE process

System: Aixtron AIX 200 (2'' wafer)

Pressure: 50mbar

Temperature: 570°C

Substrate: GaAs (100)



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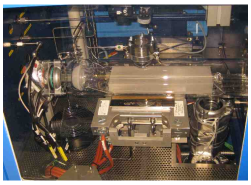

MO precursors for Cu, Ga, Se:

CpCuTEP	Cyclopentadienyl-Copper-Triethylphosphine
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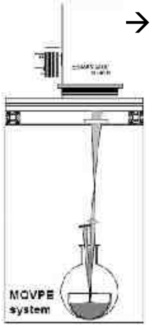
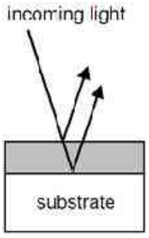
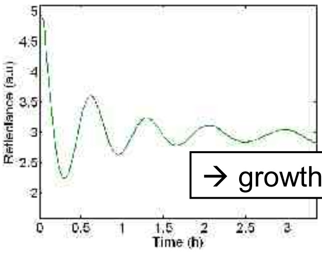
In-situ monitoring: EpiRas - Laytec



→ 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

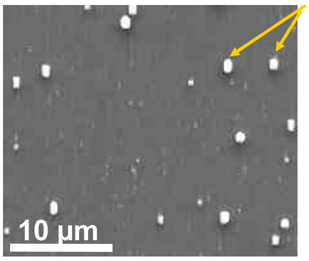
Cu-poor CuGaSe$_2$ ([Cu/Ga] < 1)

Stoichiometric CuGaSe$_2$ ([Cu/Ga] = 1)
+ secondary phase: Cu$_x$Se

Co-existing phases, what happens during growth?

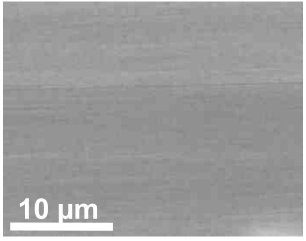
CuGaSe$_2$ grown under various [Cu/Ga] ratios

Cu-rich



Cu$_x$Se crystals

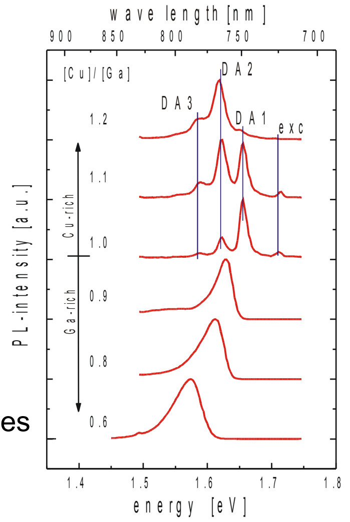
Cu-poor



PL depends on Cu/Ga ratio:

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

Cu-poor:
- Transitions from defect states

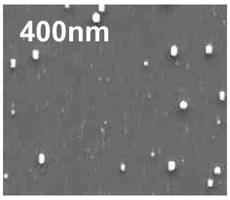


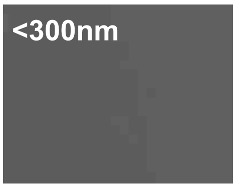
[Bauknecht, A., Siebentritt, S., Albert, J., Lux-Steiner, M. C., J. Appl. Phys., 89 (2001) 4391-4400]

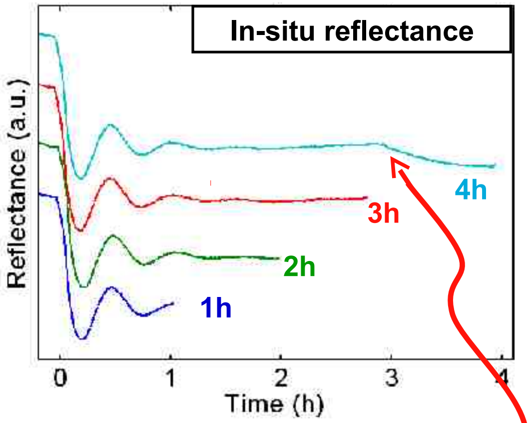
Analyzing time evolution of two phase system

Time evolution of secondary phase Cu_xSe:

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

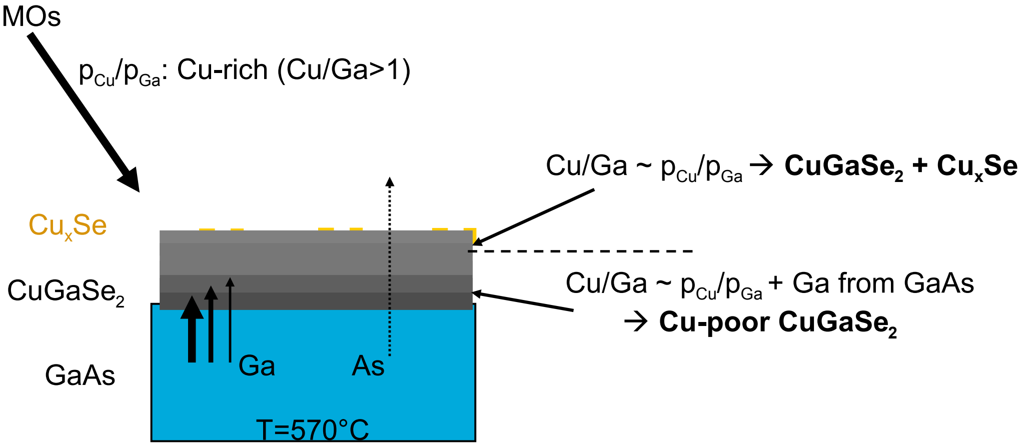






No Cu_xSe on short runs! Appear at 3→4h, **WHY?!**

Proposed growth model



MOs

p_{Cu}/p_{Ga}: Cu-rich (Cu/Ga>1)

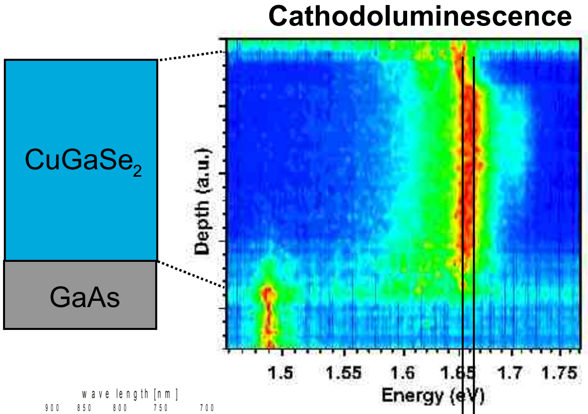
Cu/Ga ~ p_{Cu}/p_{Ga} → **$CuGaSe_2$ + Cu_xSe**

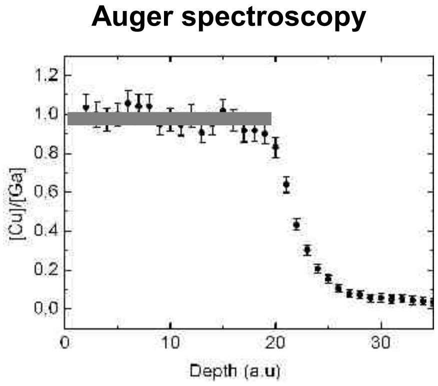
Cu/Ga ~ p_{Cu}/p_{Ga} + Ga from GaAs
→ **Cu-poor $CuGaSe_2$**

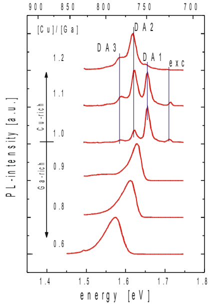
1. **Cu-poor $CuGaSe_2$**
2. **stoichiometric $CuGaSe_2$ + Cu_xSe**

→ **Gradient in composition profile?**

Depth profile of [Cu/Ga]-ratio







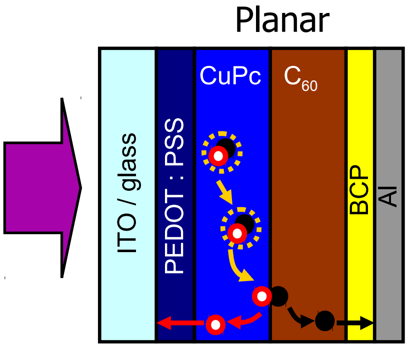
→ Cu-rich fingerprint

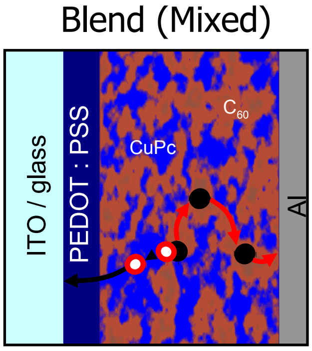
→ [Cu/Ga]=1 for entire layer

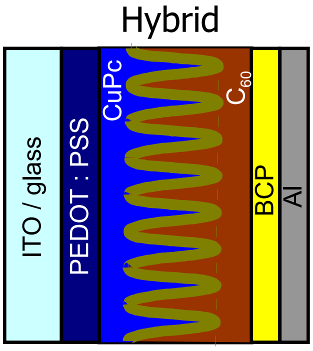
Homogeneous depth profile

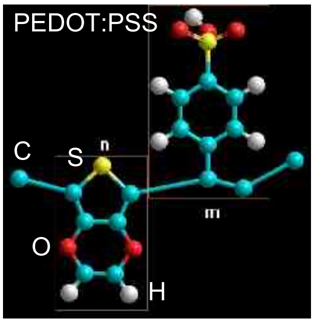
Due to high mobility of Cu:
>100x larger than for Ga and Se

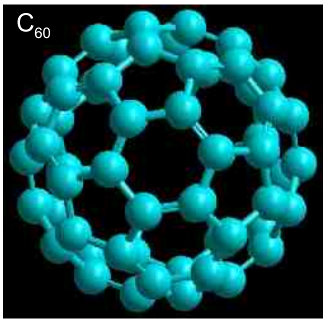
Organic Solar Cells

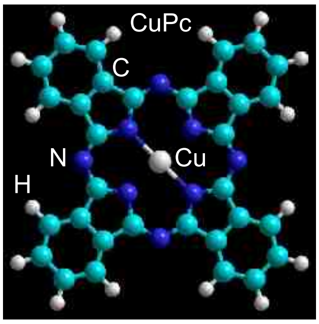






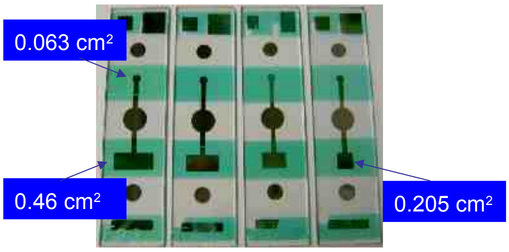


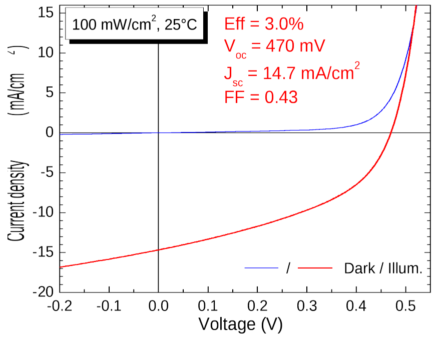




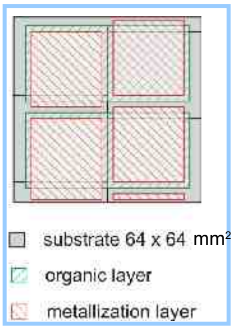
Device concepts & achievements

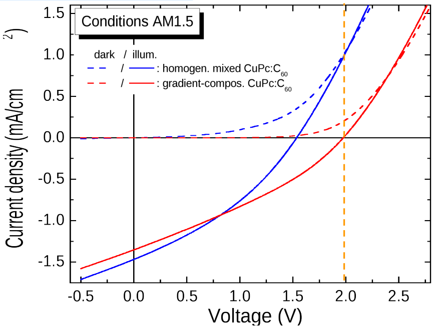
Organic solar cells





First PV mini-modules

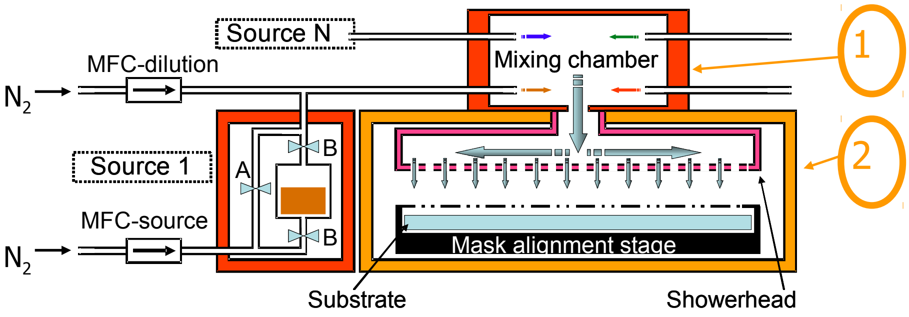




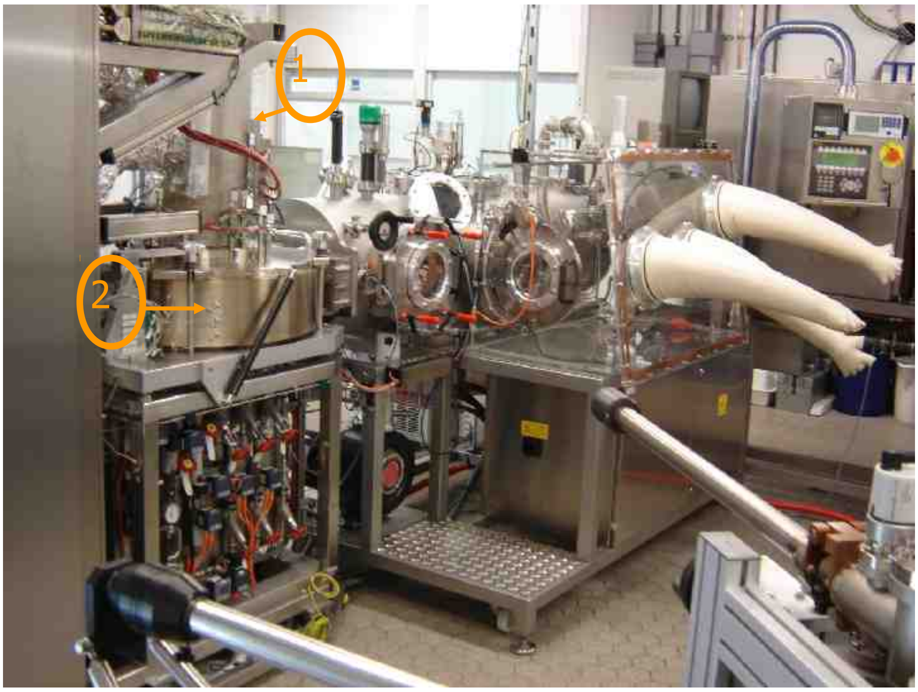
[1]M. Rusu *et al.*, *Thin Solid Films* 516 (2008) 7160.
[2]M. Rusu *et al.*, Springer special issue (2009).

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

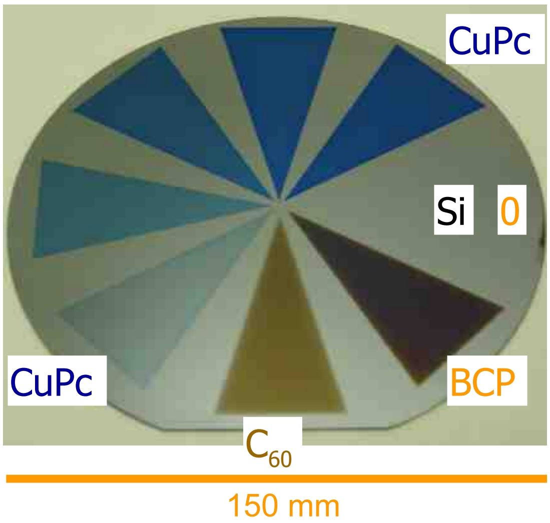
Organic vapor phase deposition - **OVPD**

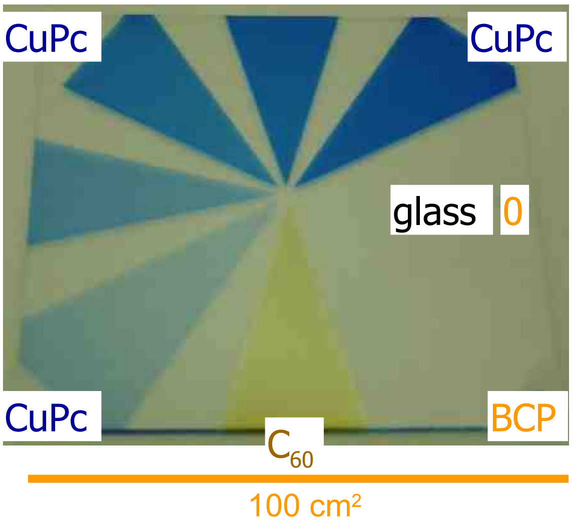


[1]M. Rusu *et al.*, *Renewable Energy* 33 (2008) 254.



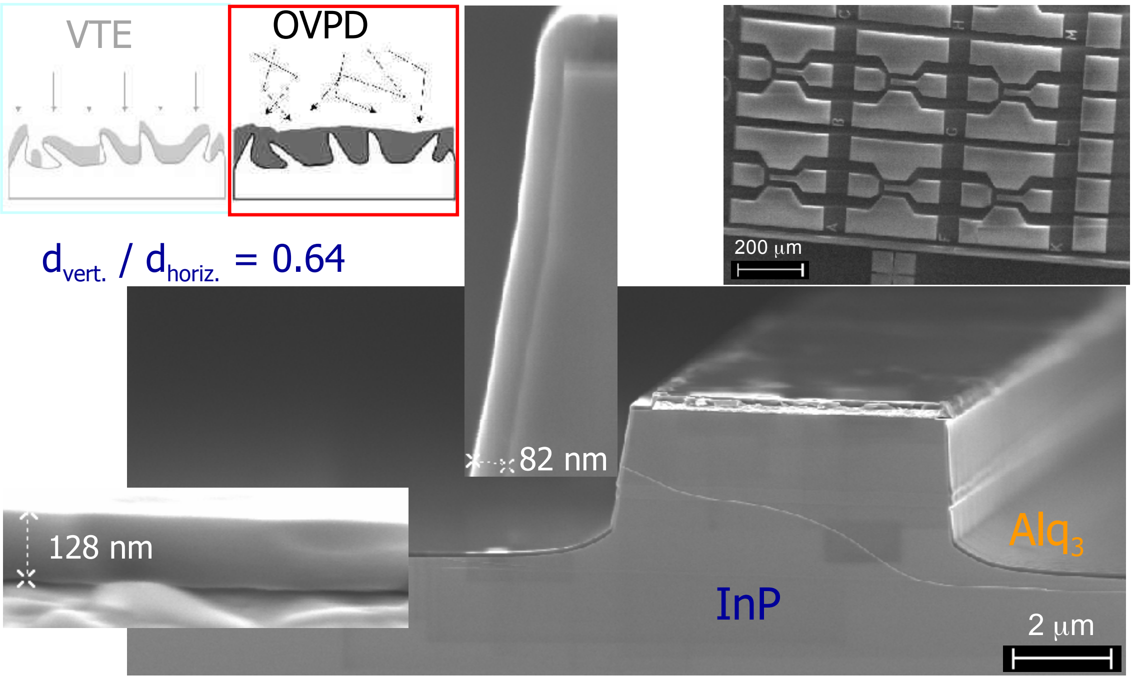
CuPc, C_{60} and BCP by OVPD





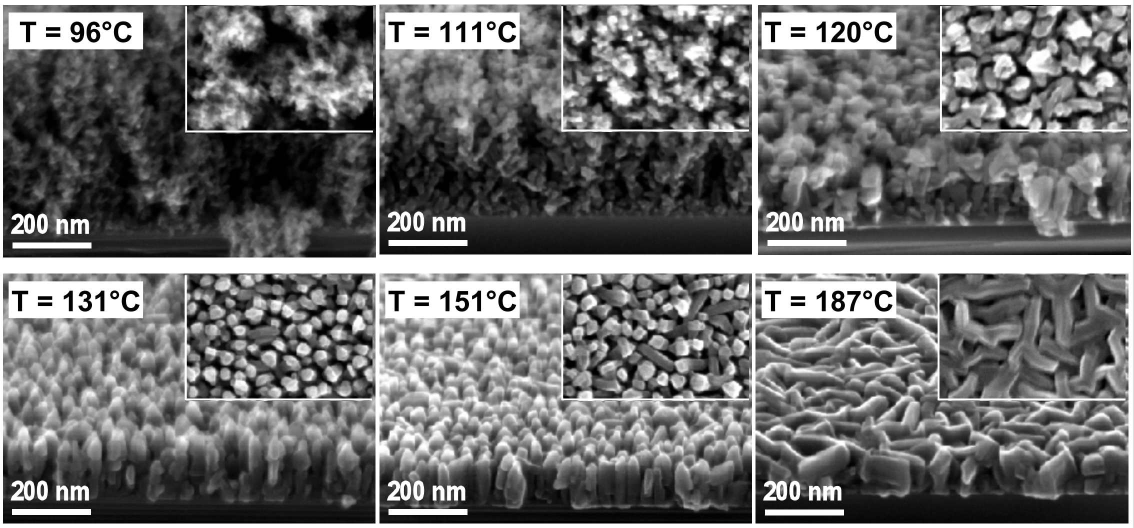
- Homogeneous deposition
    - Deposition areas show sharp edges
        - No ‘memory’ effects are observed
            - Deposition process reproducible

OVPD: Prove of the diffusion-controlled process



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

CuPc layers on Si<100>

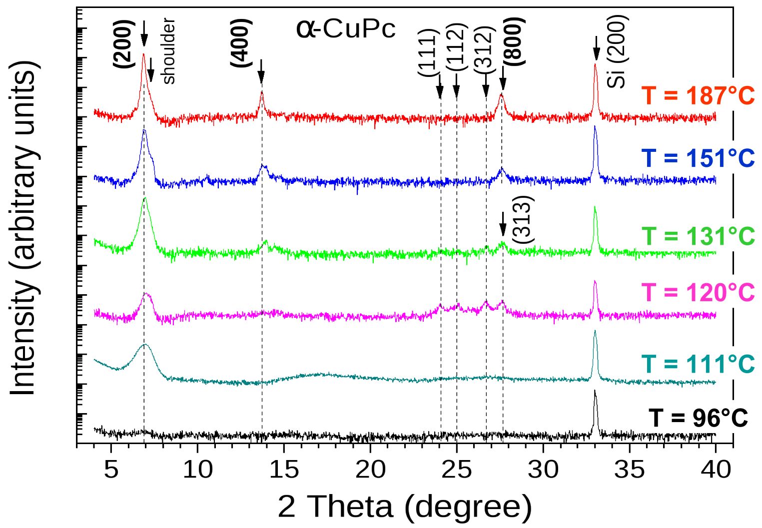


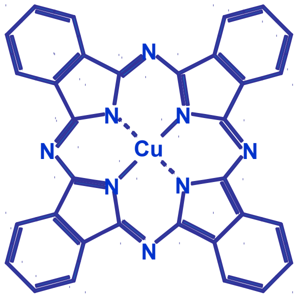
CuPc film structure develops through a coalescence process

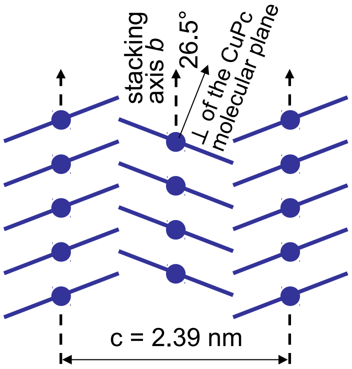
Columnar and elongated rod-like crystallites

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