# PVD Resists: Environmentally friendly resists using physical vapor deposition

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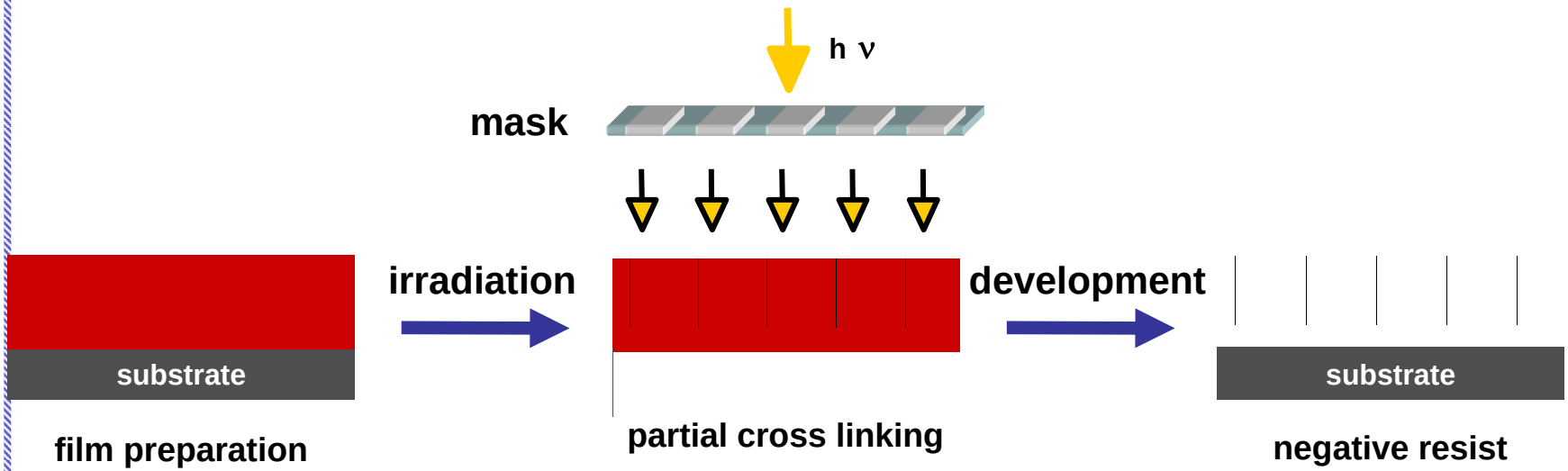
Cornell University

UNIVERSITÄT BAYREUTH

# Outline

- Physical Vapor Deposition (PVD)
  - Process
  - Benefits
  - Materials Requirements
- Novelty of PVD Process
  - Combinatorial Processing
  - Composition Gradients
- All-Dry Lithography
  - Processes
  - Results

# Solvent Free Photopatterning




## Film preparation

| | |
|---|---|
| **solution** | *state of the art* |
| **dry** | ***on going research*** |

## Development

| | |
|---|---|
| **solution** | *state of the art* |
| **solution** | *state of the art* |

# Why Prepare a film via PVD?

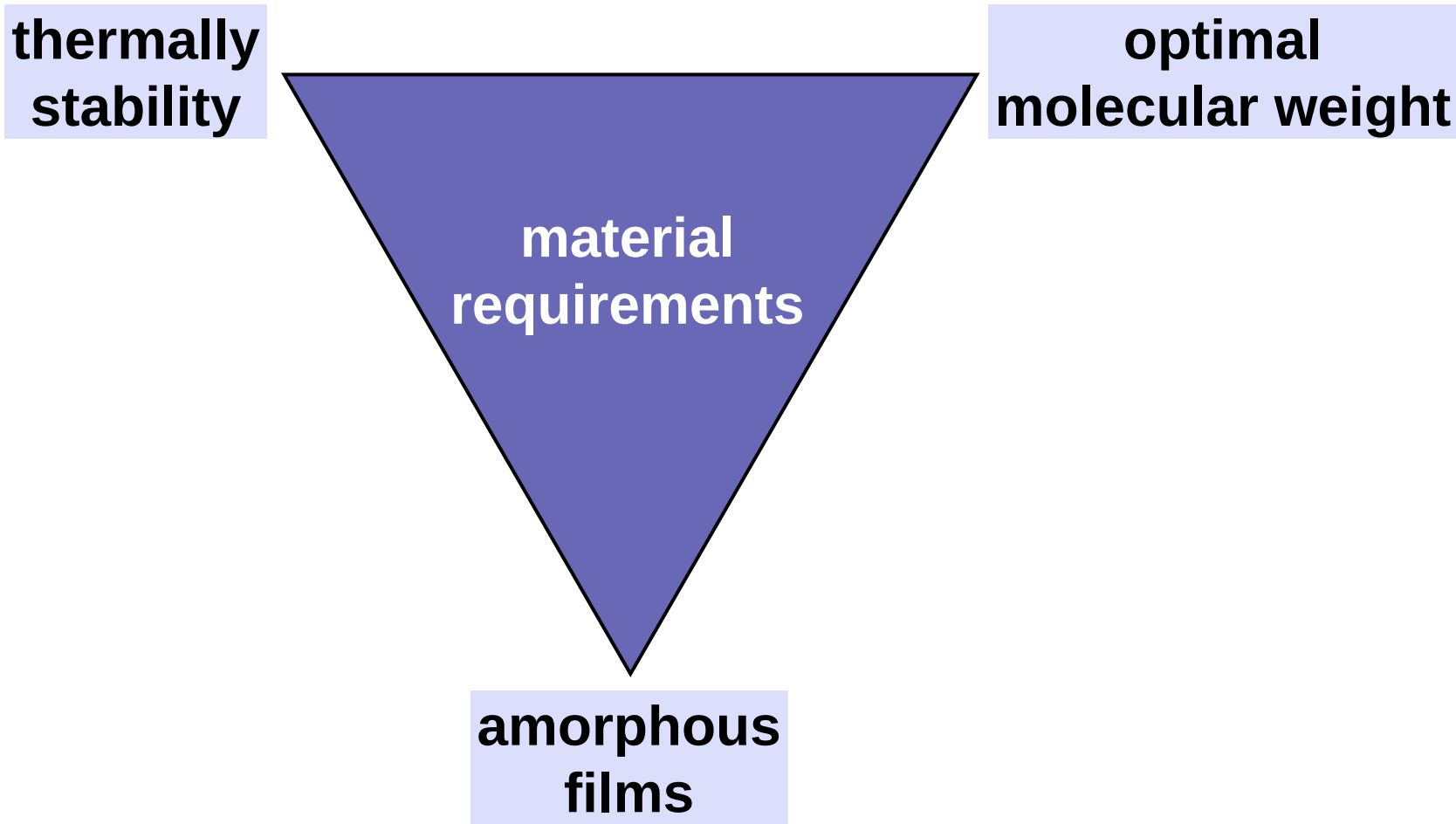
## Solution-based processes:

- **solvents has to be dust-free, no impurities**
  - ⇨ defects, pinholes
  - ⇨ rougher surface
  - ⇨ wetting, dewetting phenomena
- **wasteful in terms of solvent use**
- **loss of valuable resist materials**

## Physical Vapor Deposition:

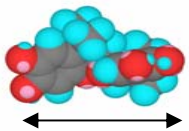
- **precise layer thickness control in the nanometer range**
- **resulting films are very uniform**
- **usability of insoluble materials**
- **applicability of a combinatorial PVD approach*)**

# Physical Vapor Deposition



# Molecular Glasses

**Low molecular weight amorphous materials**

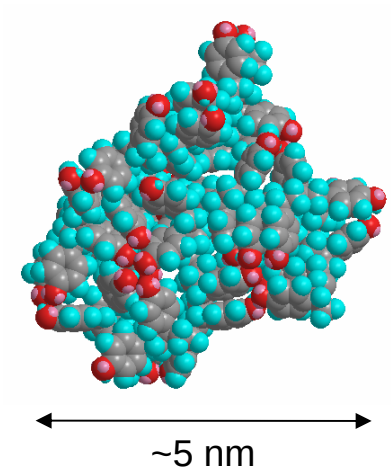


~1-2 nm

- **Defined by their bulky, rigid structure**
- **Thermally stable, high glass transition temperature (Tg)**
- **Monodisperse**
- **High purity (purified by common chromatographic techniques)**

**…As opposed to traditional polymeric resists**

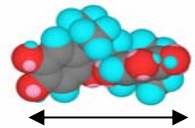
- **MW varies from 5,000 to 25,000 g/mol**
- **polydisperse**



~5 nm

# Molecular Glasses

**Low molecular weight amorphous materials**



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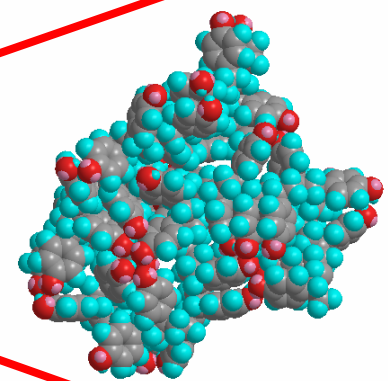


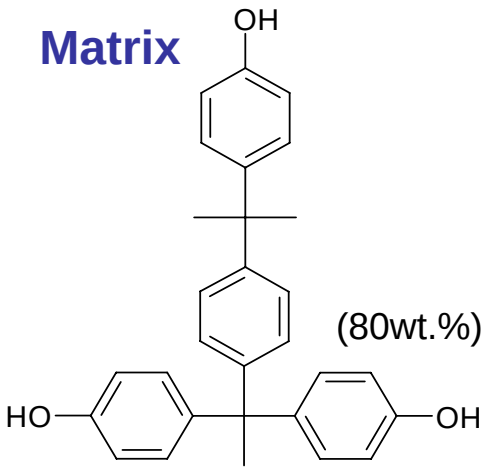
~5 nm

# Molecular Glass Photoresists

***Advantages:***

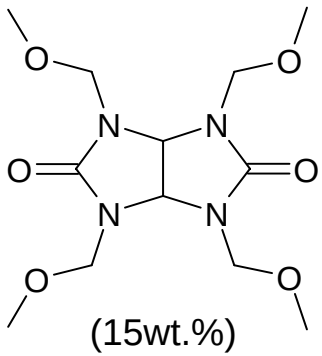
- **exact defined molecular weight**
- **small intrinsic molecular size**

**Matrix**



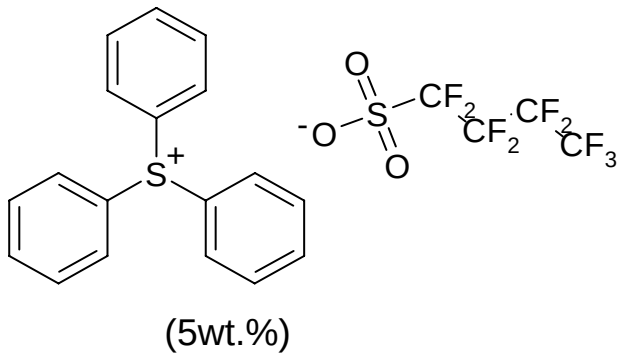

Tris(4−hydroxyphenyl)−1−ethyl−4−isoprobylbenzene

**Cross linker**




Powderlink® 1174

**Photo acid generators**




✓ solvent casting

**vapor depositable ?**

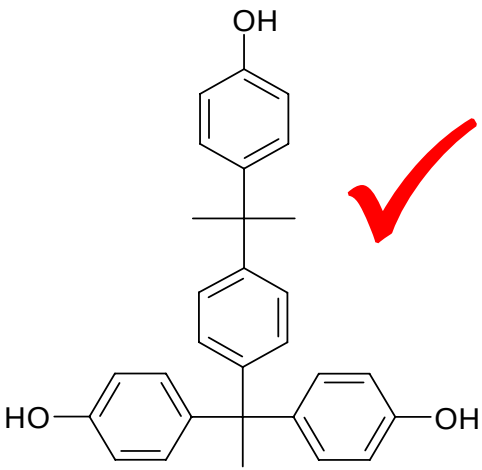
a) D. Yang; S. W. Chang, C. K. Ober, *J. Mater. Chem.* **16**, 1693 (2006); b) J. Dai; S. W. Chang; A. Hamad; D. Yang; N. Felix, C. K. Ober, *Chem. Mater.* **18**, 3404 (2006); c) S. W. Chang; R. Ayothi; D. Bratton; D. Yang; N. Felix; H. B. Cao; H. Deng, C. K. Ober, *J. Mater. Chem.* **16**, 1470 (2006); d) R. Ayothi; S. W. Chang; N. Felix; H. B. Cao; H. Deng; Y. Wang, C. K. Ober, *J. Photopolym. Sci. Technol.* **19**, 515 (2006).

# Molecular Glass Photoresists

***Vapor deposition materials demand*** :

thermally stable, sufficient high molecular weight, but not too high,
no crystallization in thin layers, …

**Matrix**




**Cross linker**

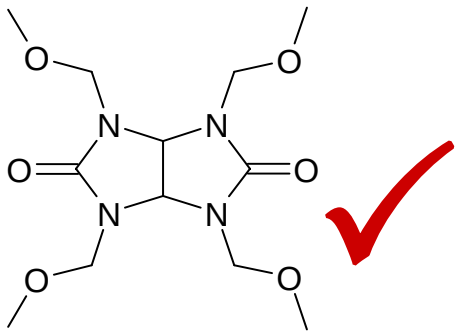
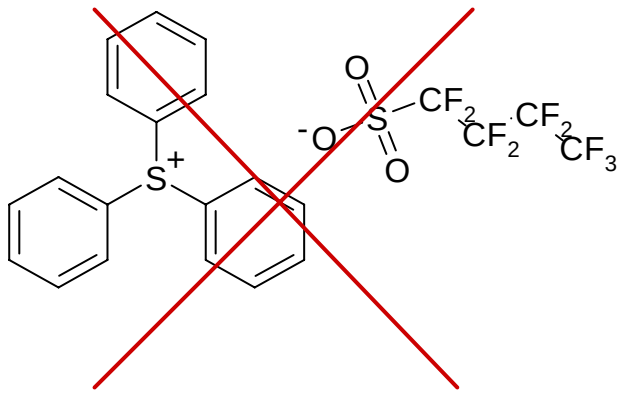


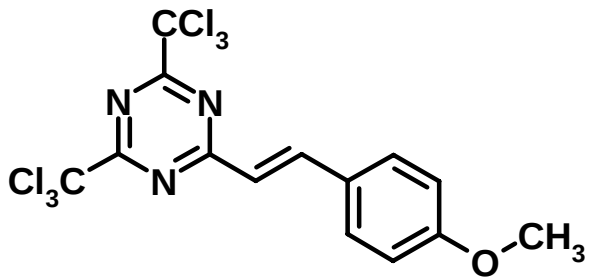

**Photo acid generators**




Suitable non-ionic PAGs needed

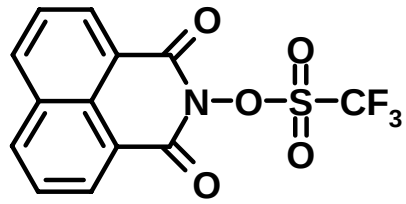
# Vapor Depositable Photoacid Generators

**Triazine derivative**

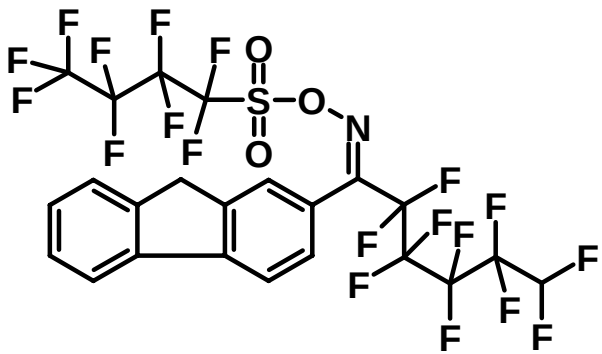



vapor deposition ✓

**Triflate**



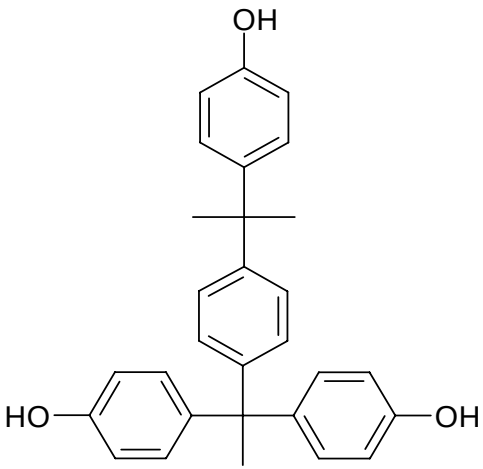

vapor deposition ✓




vapor deposition ✓

# Vapor Depositable Molecular Glass Photoresists

**Matrix**




**Cross linker**

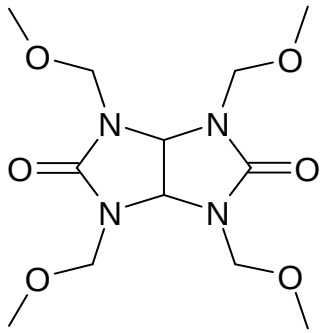
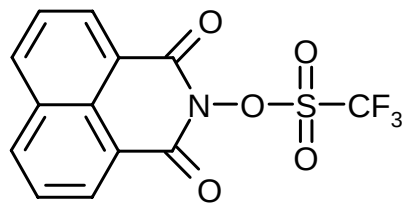
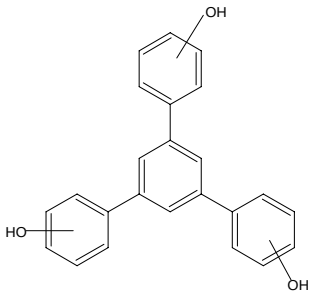
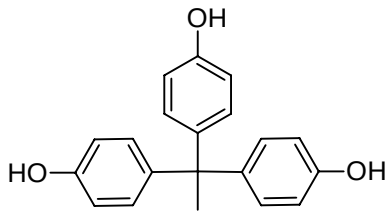


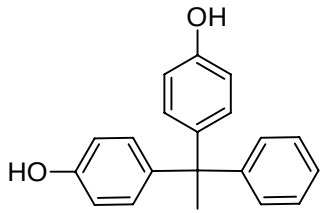

**Photo acid generators**

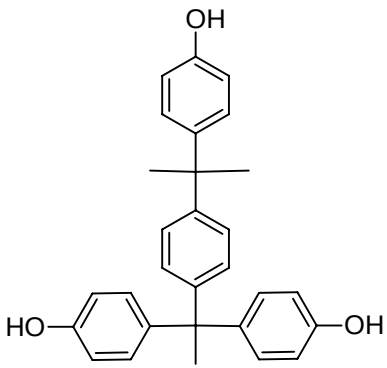


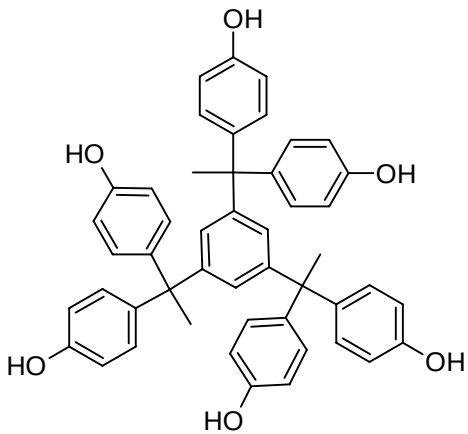
# Vapor Deposited Molecular Glasses

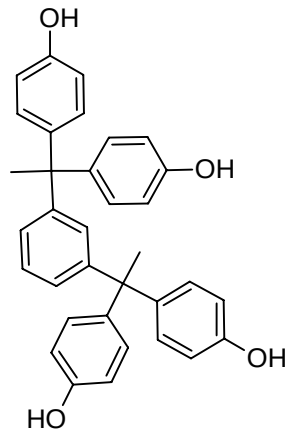


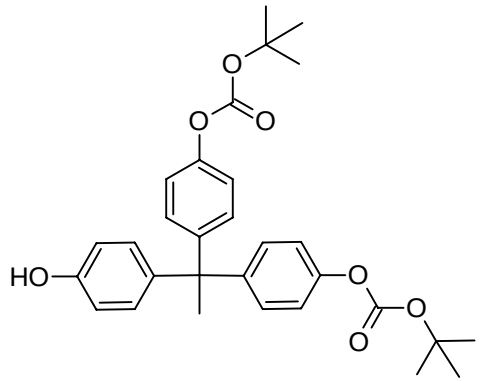



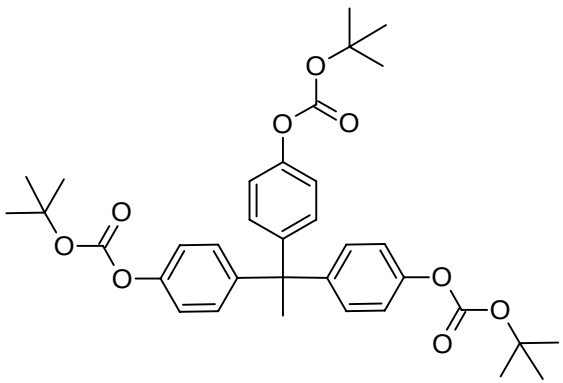



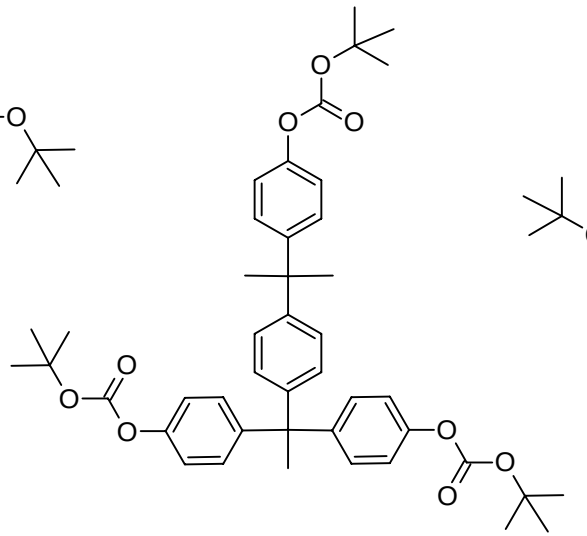

Short list of a complete library of resists

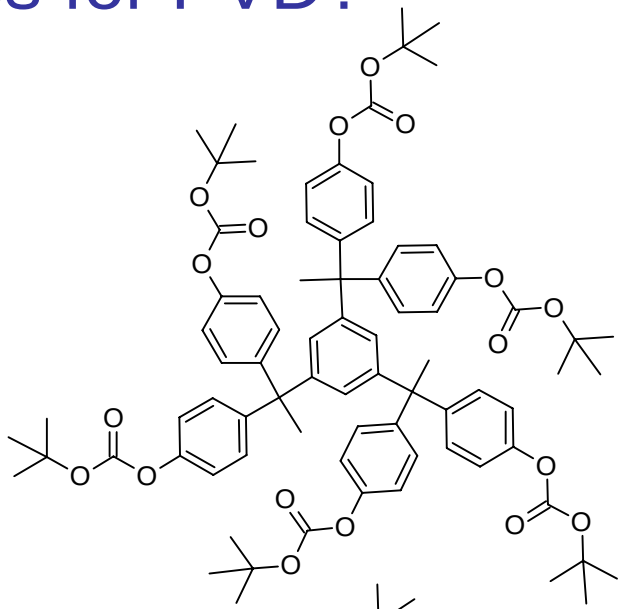
All molecules were used as negative tone resists with vapor deposited crosslinker and non-ionic PAG

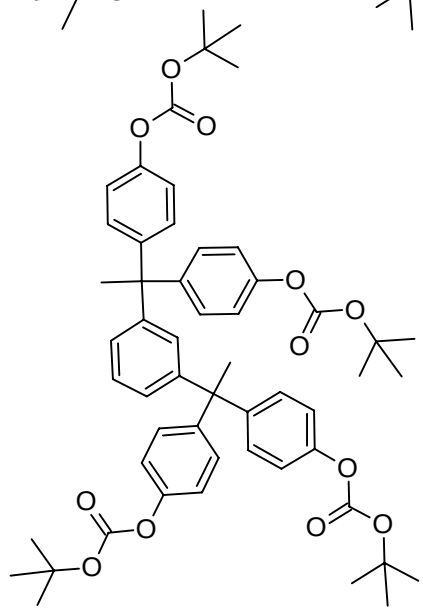
# Positive Tone Molecular Glasses for PVD?







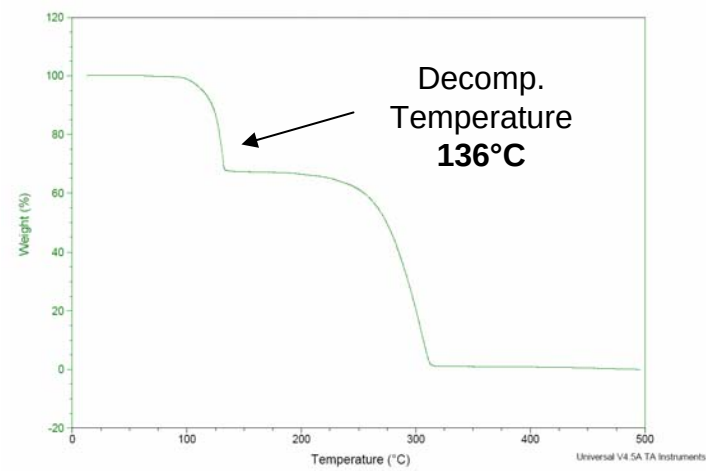


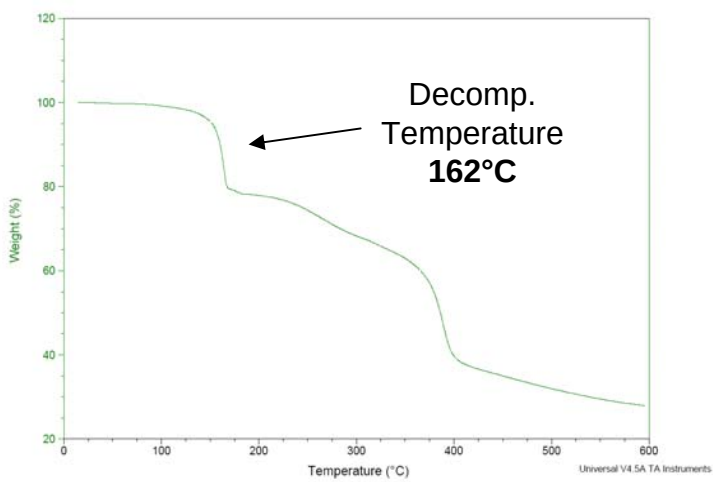


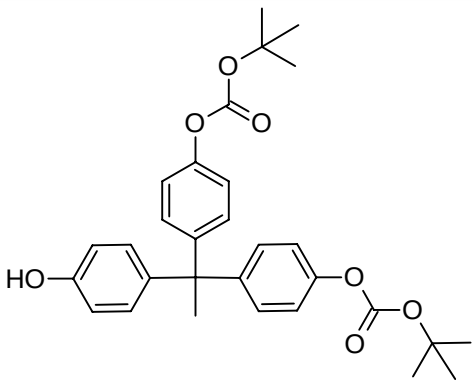
All t-BOC protected molecules showed decomposition during PVD

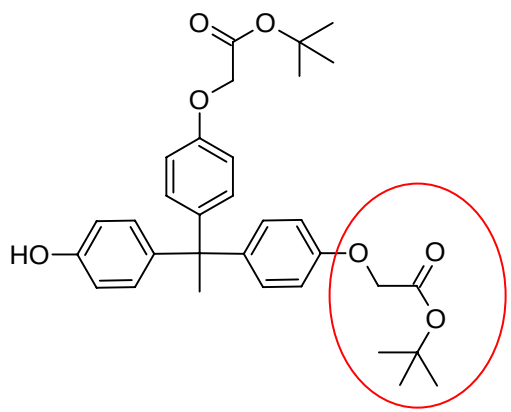
# PVD Protecting Group

TGA curves



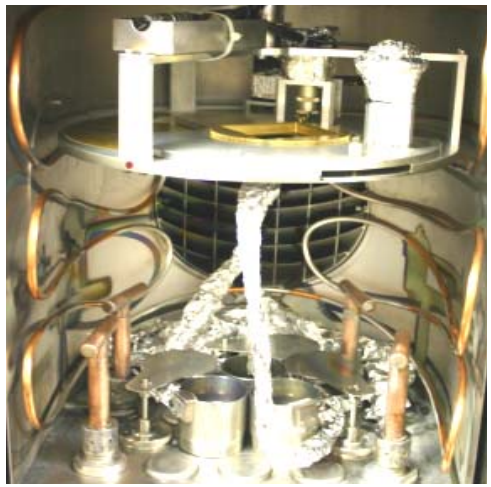

Ester protecting group provides better thermal stability

# Outline

- Physical Vapor Deposition (PVD)
  - Process
  - Benefits
  - Materials Requirements
- **Novelty of PVD Process**
  - **Combinatorial Processing**
  - Composition Gradients
- All-Dry Lithography
  - Processes
  - Results

# Materials Screening and Combinatorial Development of Thin Film Multilayer Electro-Optical Devices

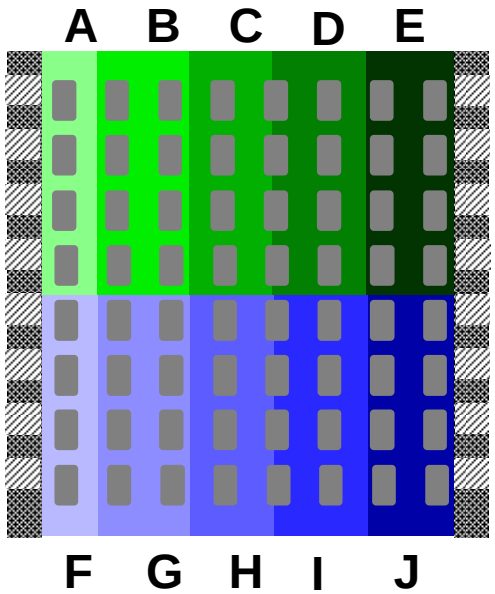
## *Equipment*



Thelakkat, et al.
*Macromol. Rapid Commun.*
**25**, 204 (2004).

Neuber, et al.
*Rev. Sci. Instrum.*
***78,*** *072216/1 (2007).*

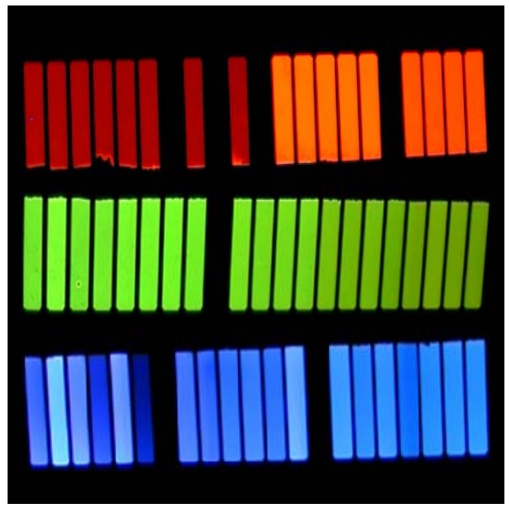
## *Combinatorial Library*




*76 x 76 mm*

Neuber, et al.
*Journal of Materials Chemistry* **16**, 3466 (2006).

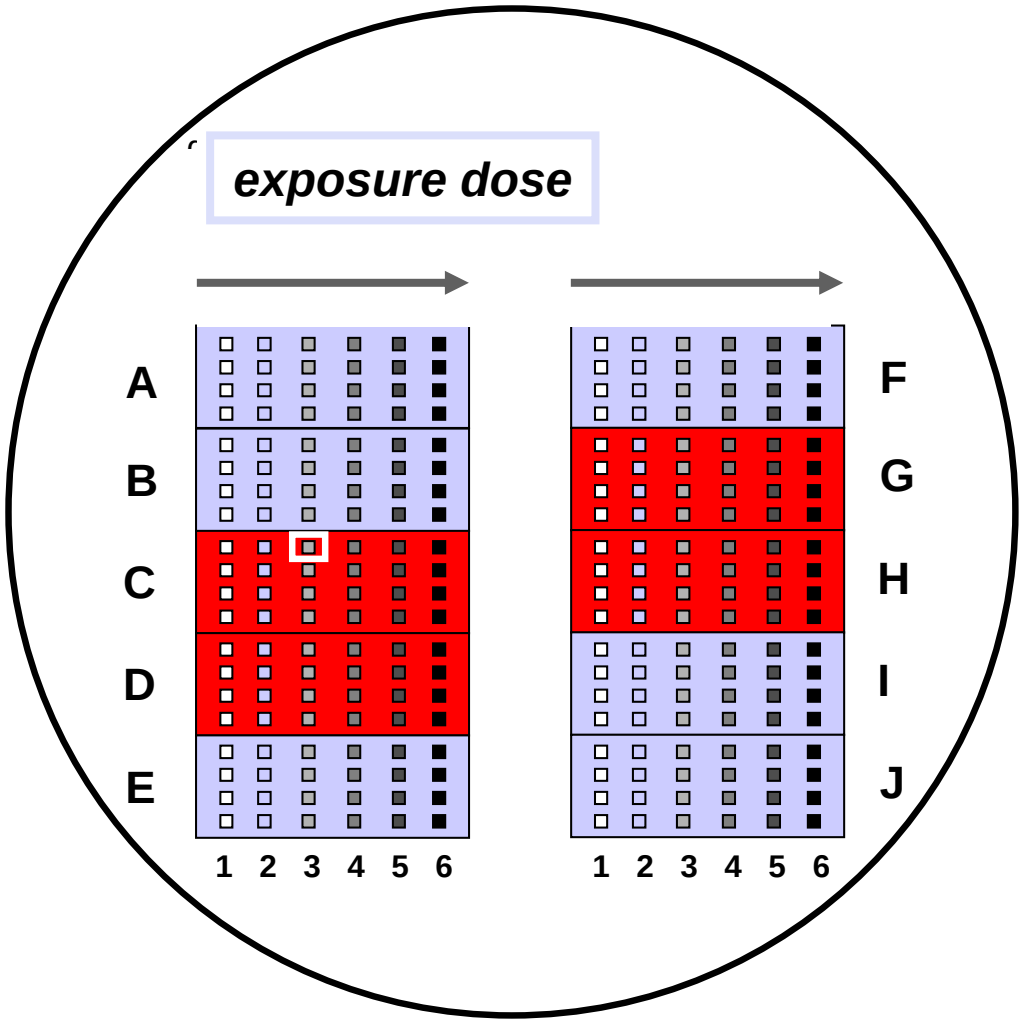
## *Organic Light Emitting Devices*



*76 x 76 mm*

Kreger et al.
*Advanced Functional Materials,*
**17**, 3456 (2007).

# Combinatorial Vapor Deposition of Molecular Glass Photoresists



# Instrumentation

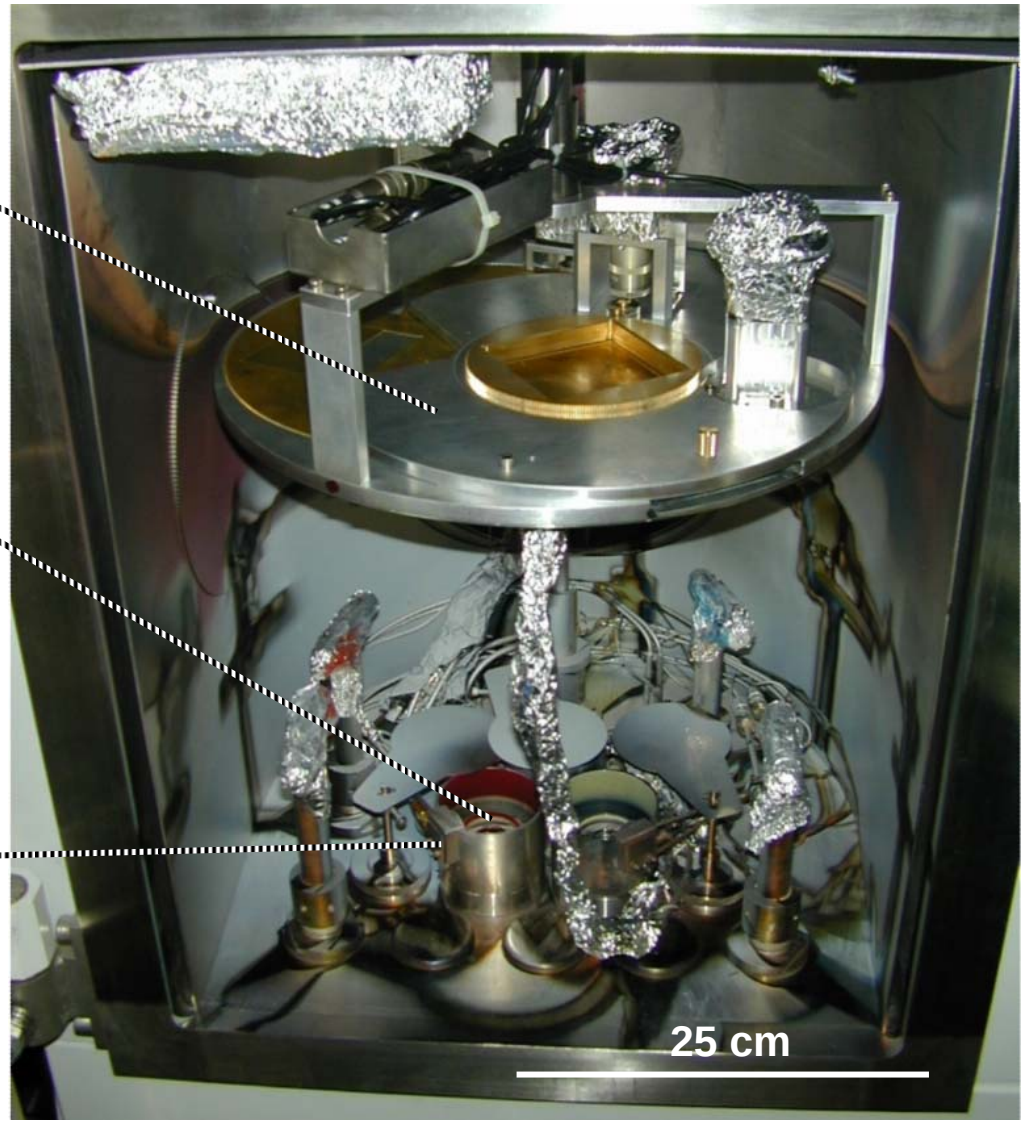
## Rotating combinatorial set-up

## Sources

- 3 effusion cells (organics)
- 2 sources, controlled by electrical resistance (metals)

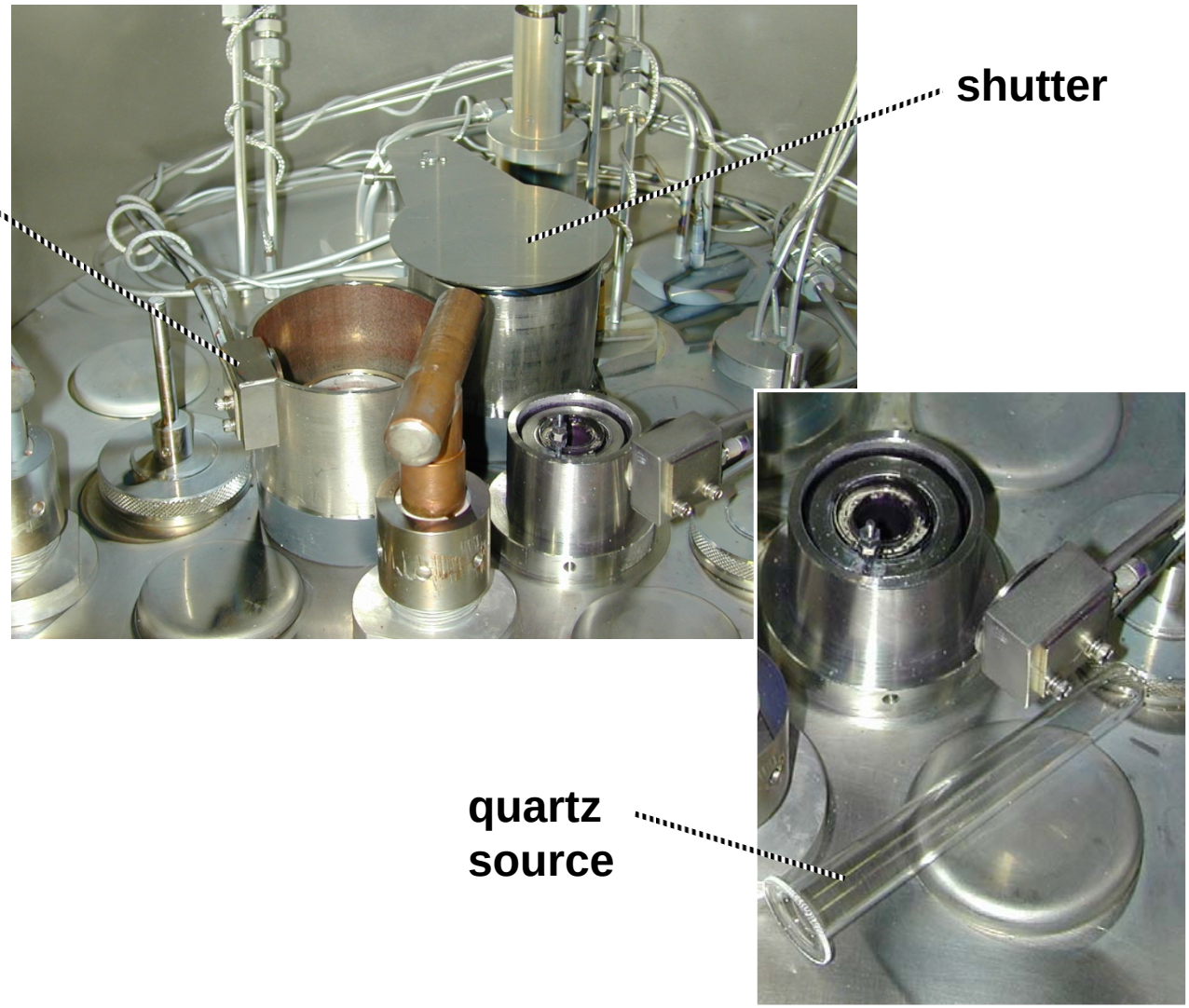
## Monitoring

- Evaporation rates of each effusion cell controlled by a quartz crystal
- each effusion cell closed by a shutter

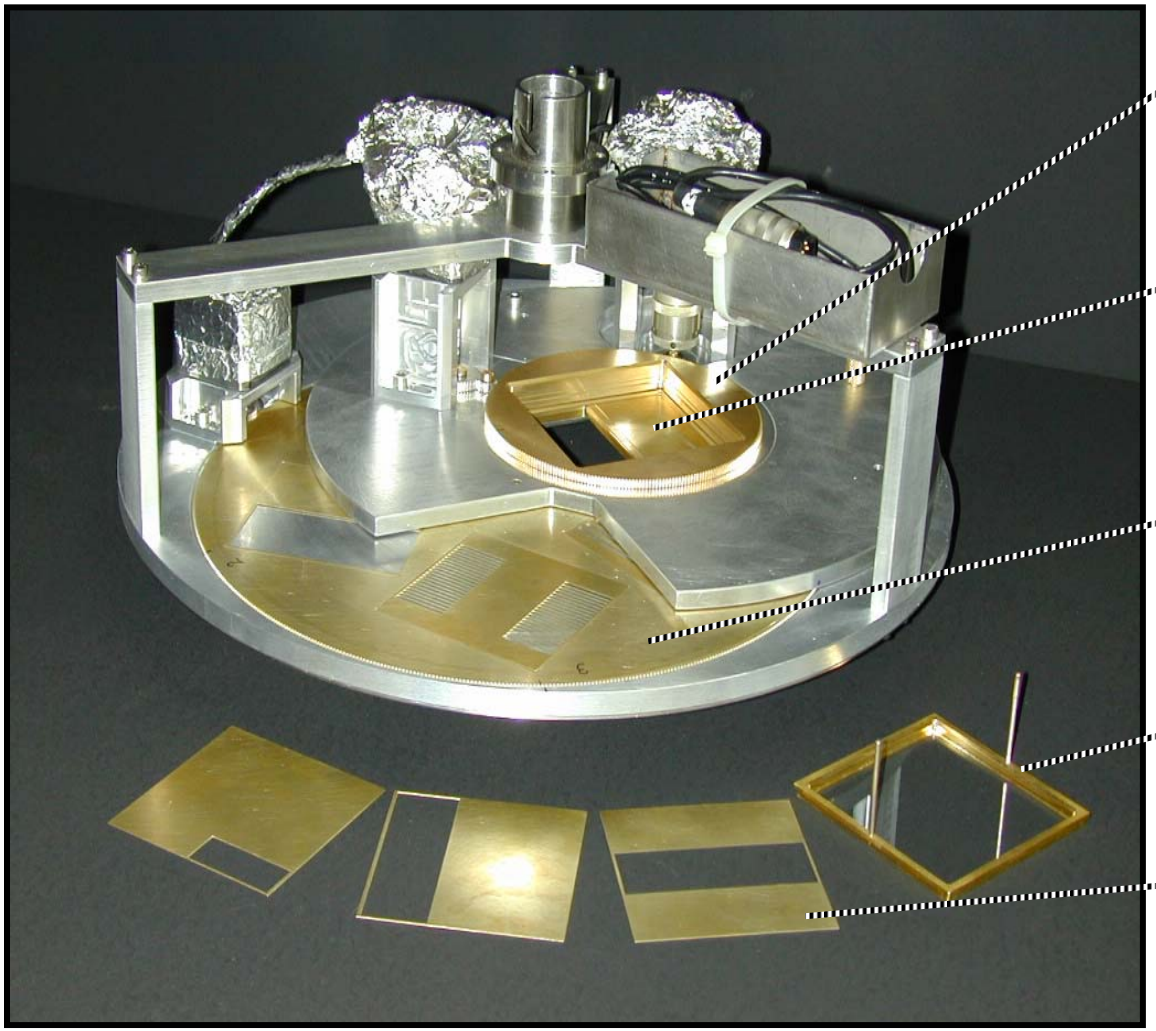



Vapor Deposition Chamber: Balzers PLS 500

# Instrumentation



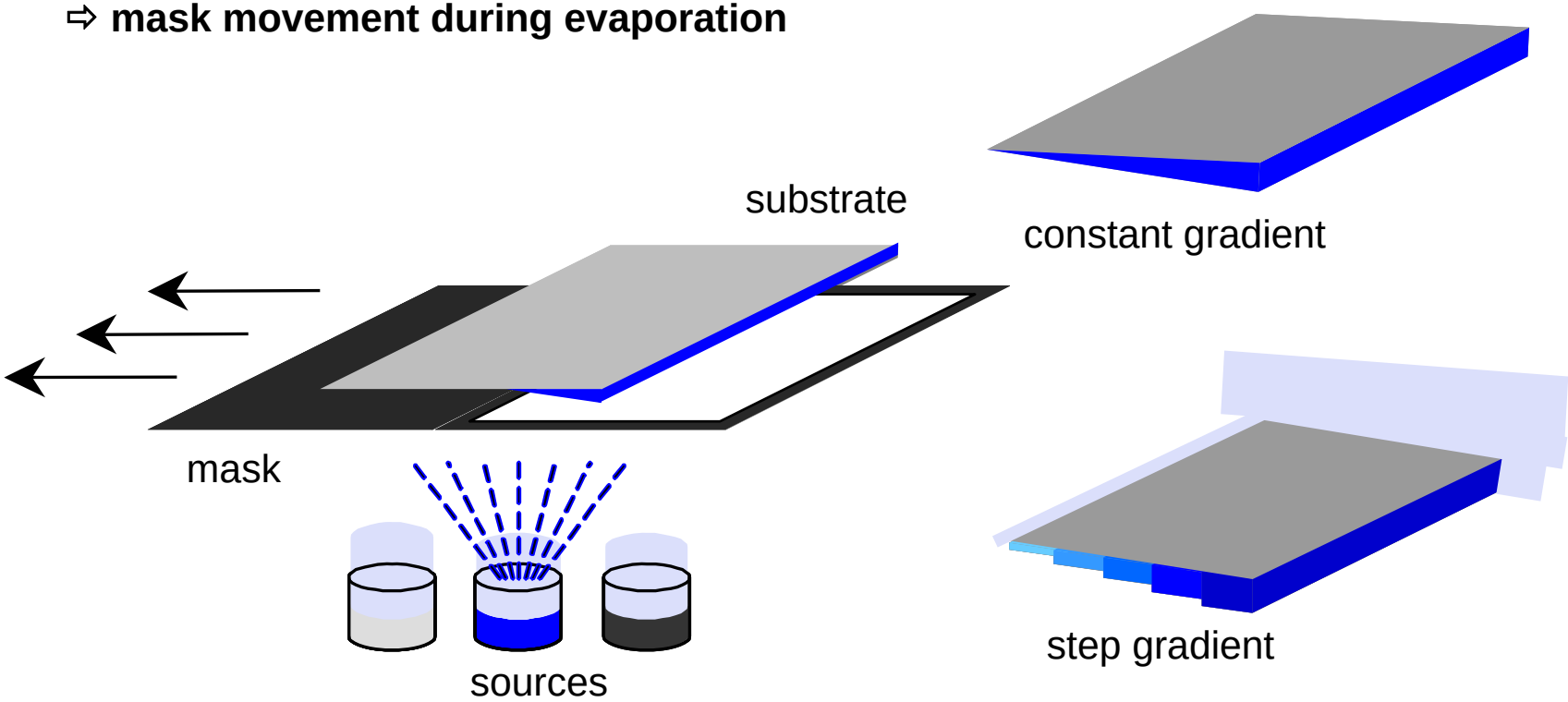
# Instrumentation



# Combinatorial Vapor Deposition

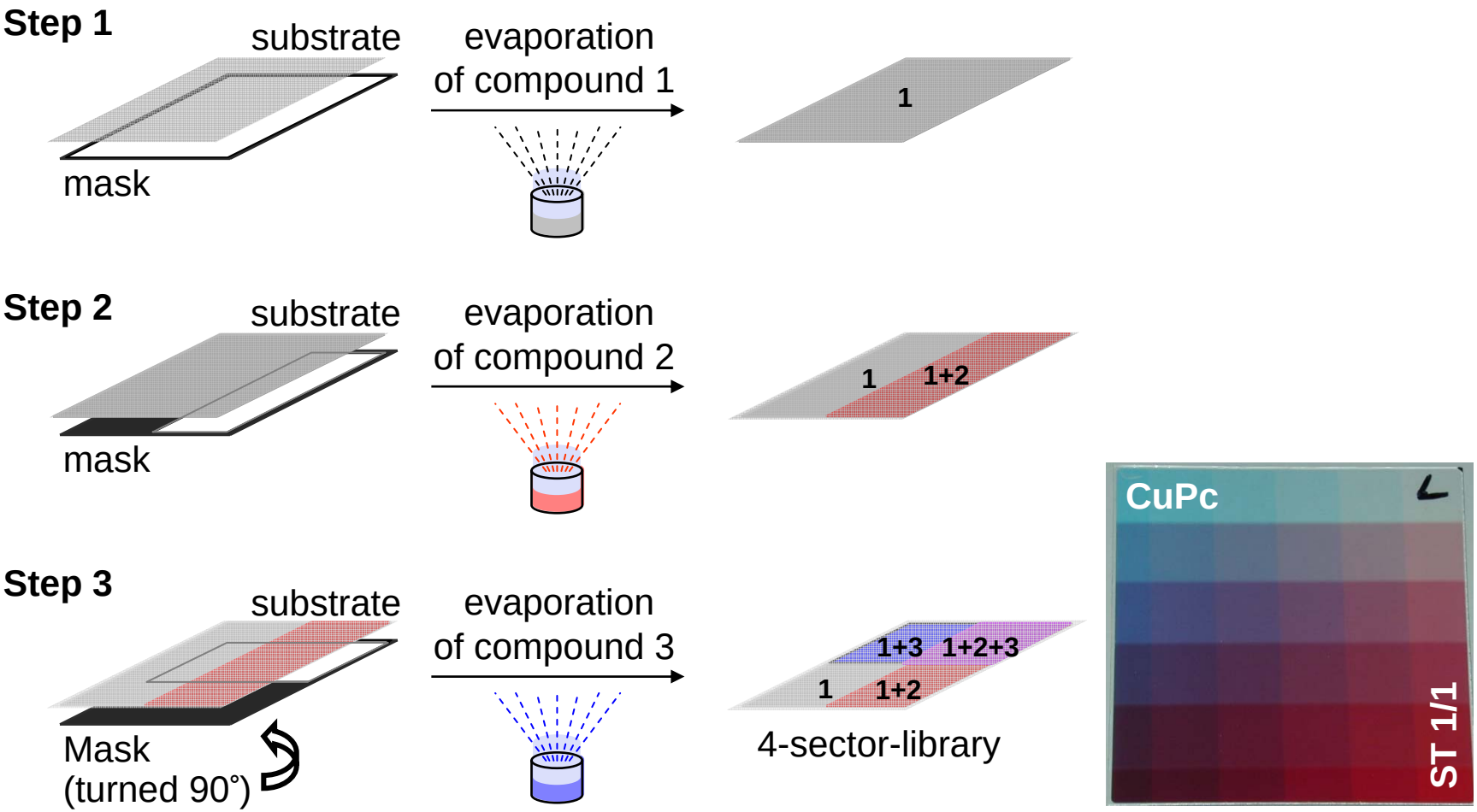
## Preparation of thickness gradients

⇨ **mask movement during evaporation**



# Combinatorial Vapor Deposition

## Preparation of sectors

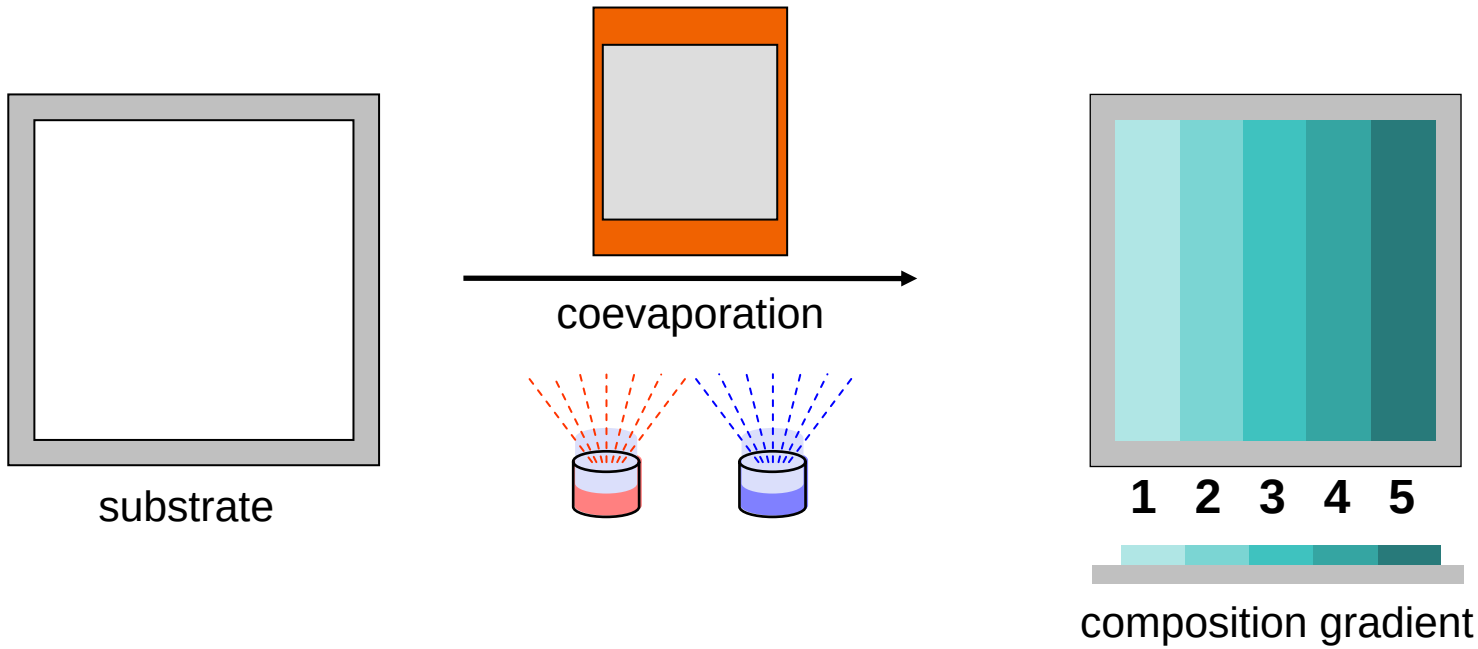



*(M. Bäte)*

# Combinatorial Vapor Deposition

## Preparation of compositions

⇨ **Simultaneous evaporation of two or more compounds with different deposition rates**

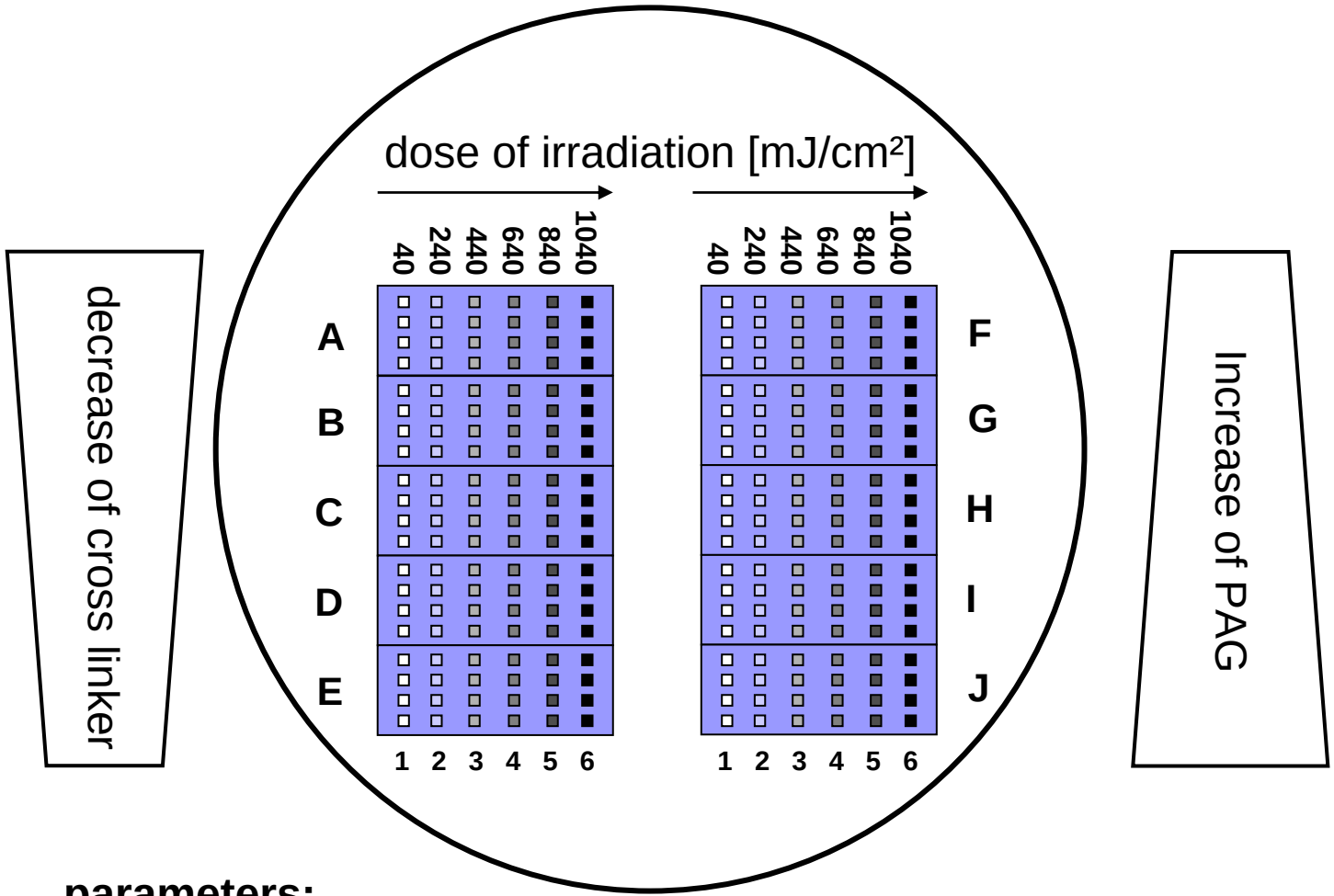


# Combinatorial Vapor Deposition

## Advantages of a combinatorial approach

- much faster than conventional methods
- defined **layer thickness control** in the nanometer range
- efficient screening of **material combinations**
  (completely insoluble materials are applicable, e.g. adamantane derivatives or fluoro compounds for 193 lithography)
- defined preparation of **material composition**
  (internal gradients within one layer or well-defined layer sequences)
- simultaneous optimization of parameters in **one experiment under identical conditions**
- in-situ preparation of **reference devices**

# Combinatorial Library

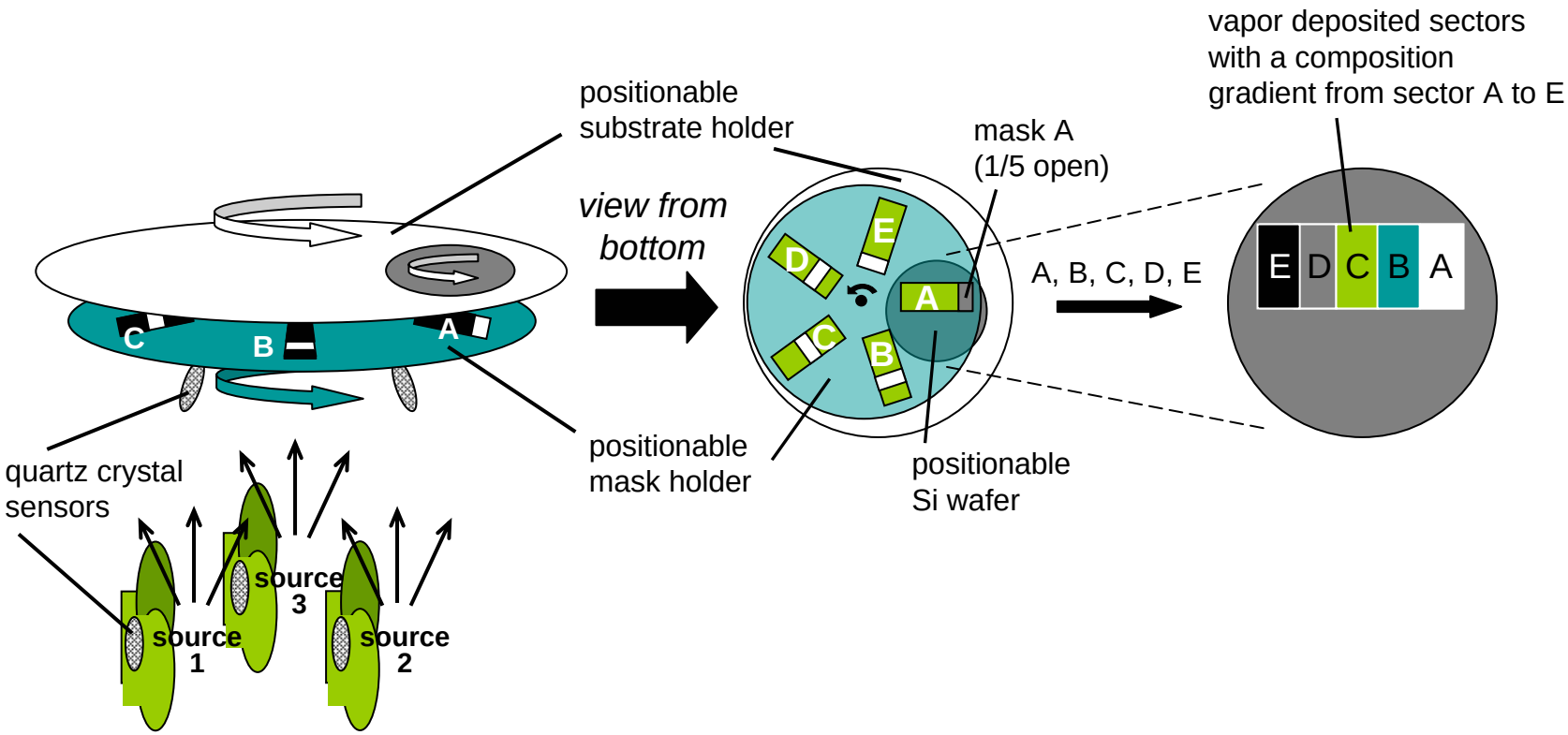



**parameters:**

exposure dose increases from 40 to 1040 mJ/cm² at 365 nm.
PEB 90 °C for 30 s

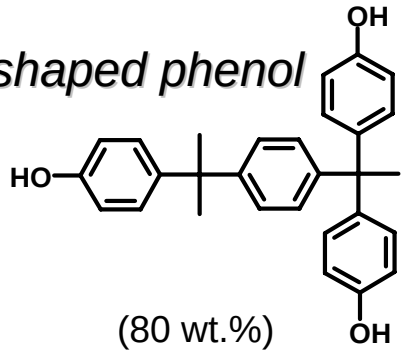
Development: varying TMAH concentration and development times

# Combinatorial Vapor Deposition of Molecular Glass Photoresists



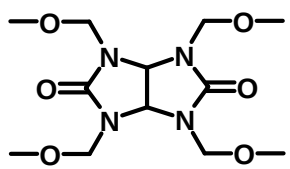
# Combinatorial Vapor Deposition of Molecular Glass Photoresists

*T-shaped phenol*



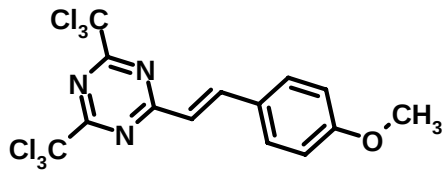

(80 wt.%)

*Cross linker*



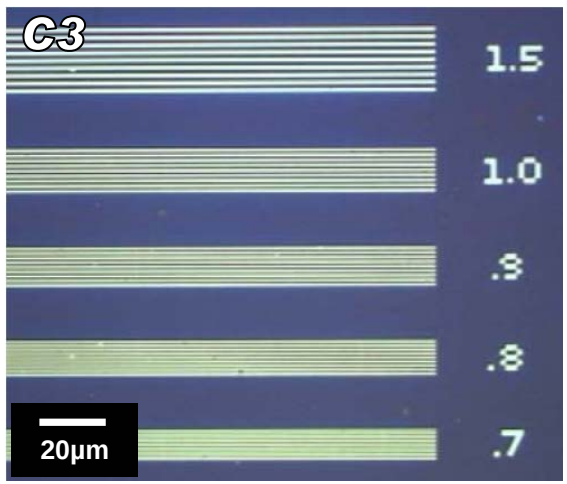
(15 wt.%)

*Photo acid generator*

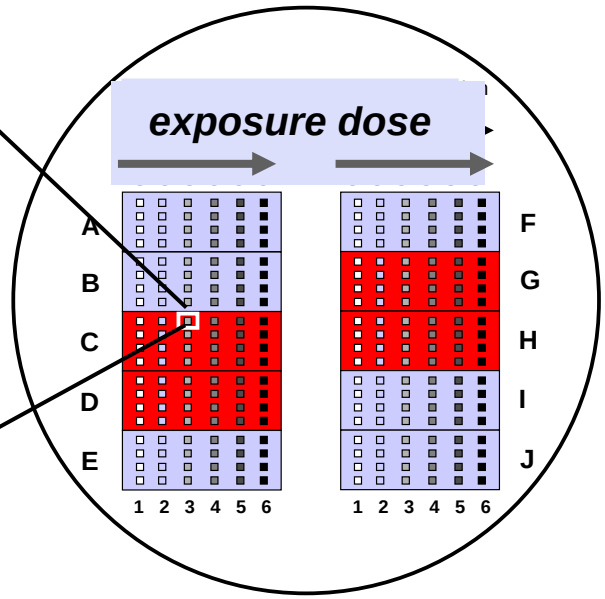



(5 wt.%)

## Photopatterning of evaporated libraries

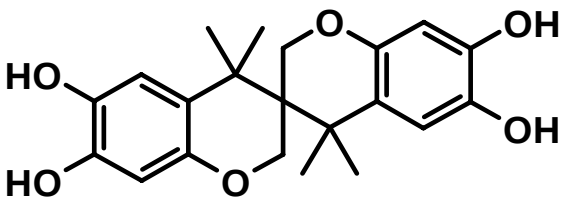



*aqueous base development*

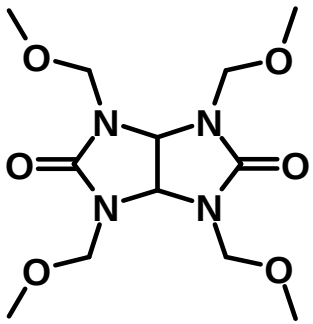



F. Pfeiffer, N.M. Felix, C. Neuber, C. K. Ober, H.-W. Schmidt, *Adv. Funct. Mater.* **17**, 2336 (2007).

# Environmentally Friendly Molecular Glass Photoresists




*Spirobichroman*




*Cross linker*

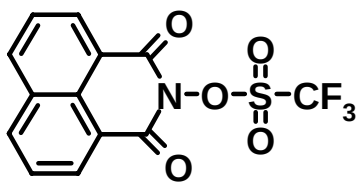
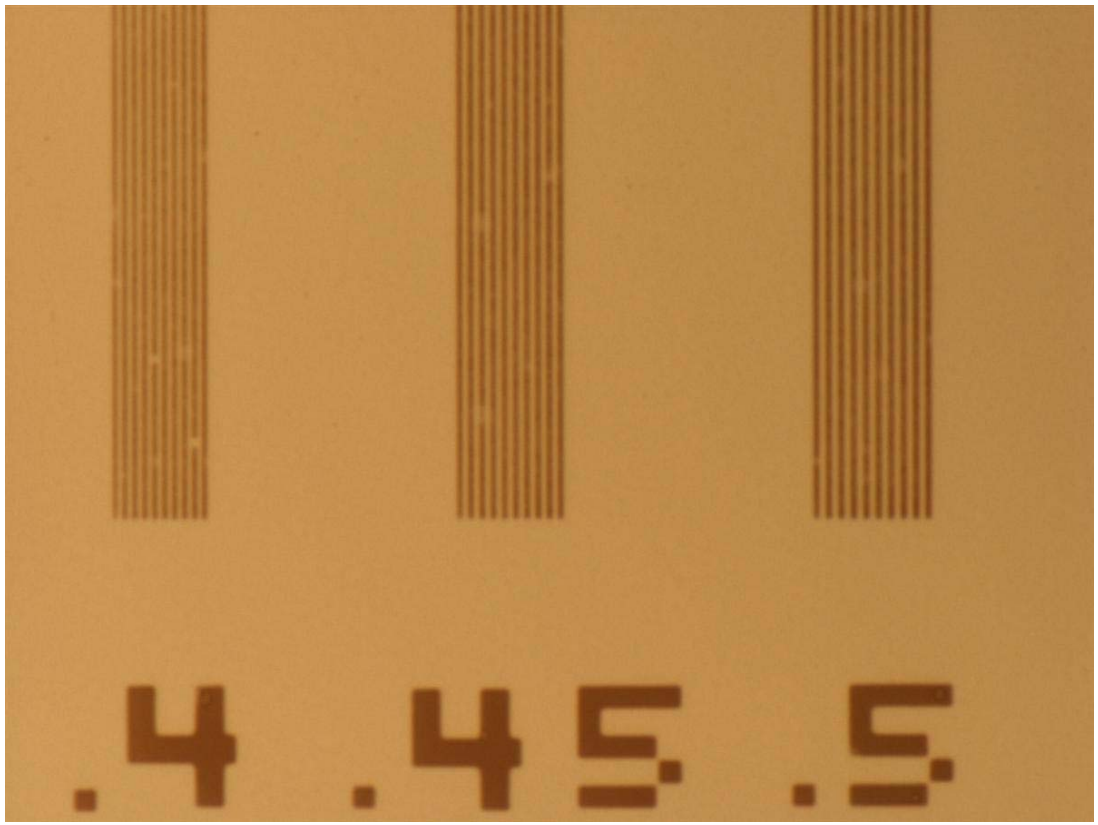



*Photo acid generator*



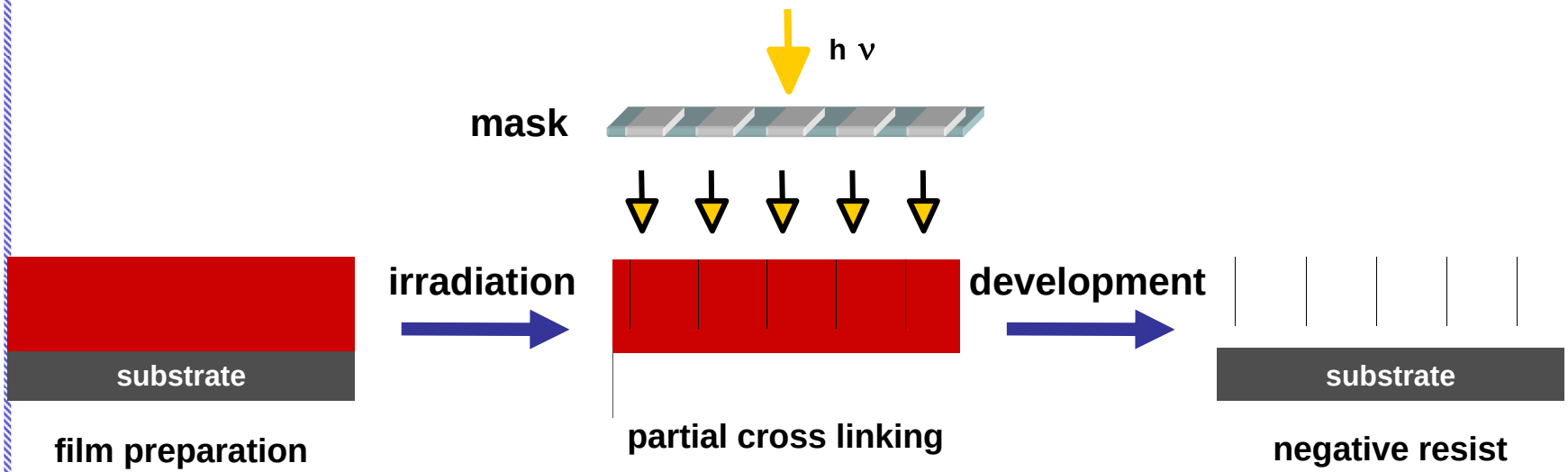

**77.6wt.% spirobichroman, 20.2wt.% cross linker, 2.2wt.% triflate**
**exposure dose 840 mJ/cm$^2$ at 365 nm.**
PEB 90 °C for 30 s, development pure deionized water

F. Pfeiffer, N.M. Felix, C. Neuber, C. K. Ober, H.-W. Schmidt, Phys. Chem. Chem. Phys., 2008, DOI:10.1039/b715819j

# Outline

- Physical Vapor Deposition (PVD)
  - Process
  - Benefits
  - Materials Requirements
- Novelty of PVD Process
  - Combinatorial Processing
  - Composition Gradients
- **All-Dry Lithography**
  - **Processes**
  - **Results**

# On the Way Towards Solvent Free Photopatterning




## Film preparation

**solution** *state of the art*

**dry** ***on going research***

**Physical Vapor Deposition**

## Development

**solution** *state of the art*

**dry** ***on going research***

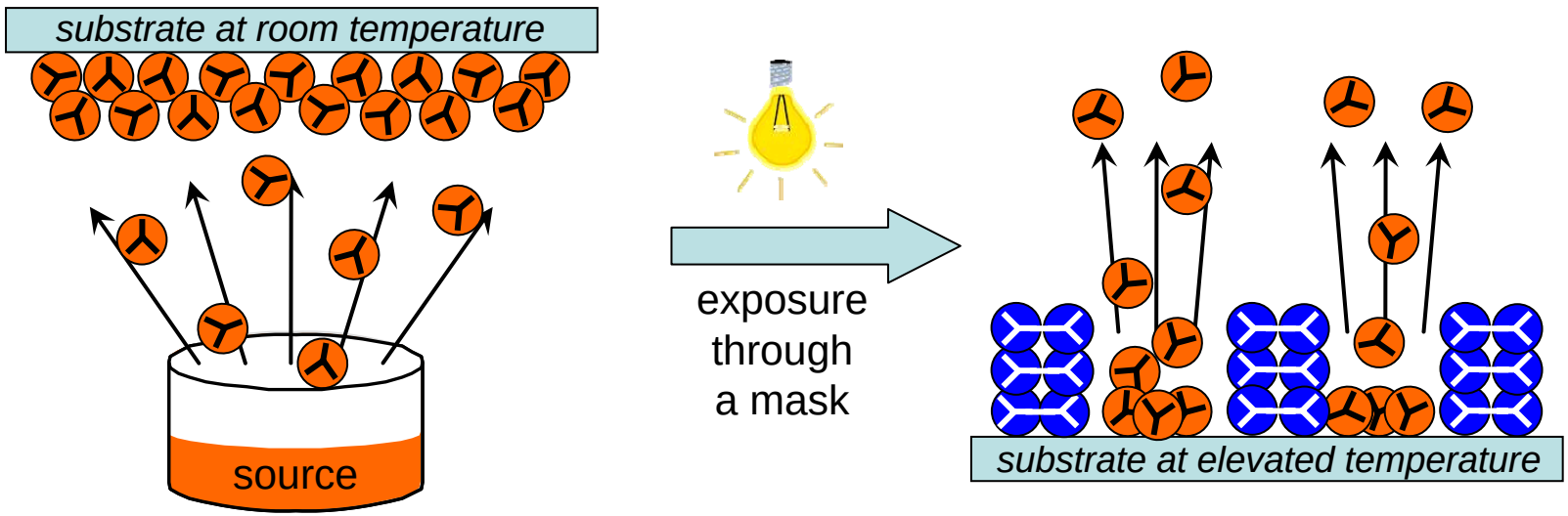
**Vacuum development**

# Solvent-Free Photopatterning

***Contrast is realized by changing molecular weight or intermolecular interactions***

**Film preparation by PVD**

**Vacuum development**

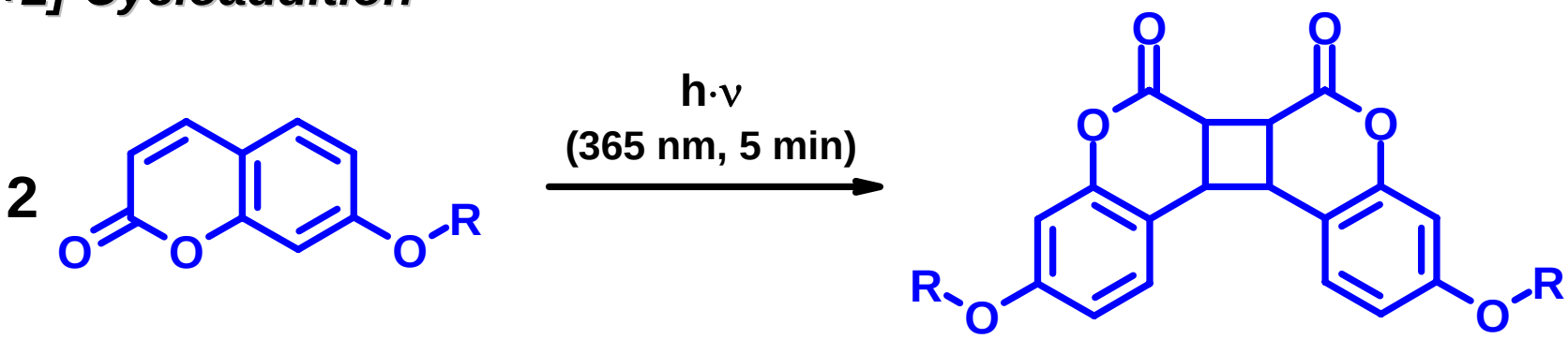



## Important advantages:

- **no PAB and PEB necessary**
- **no solvent residues (plasticizer)**
- **no capillary forces**

# Solvent-Free Photopatterning

***[2+2]-Cycloaddition***



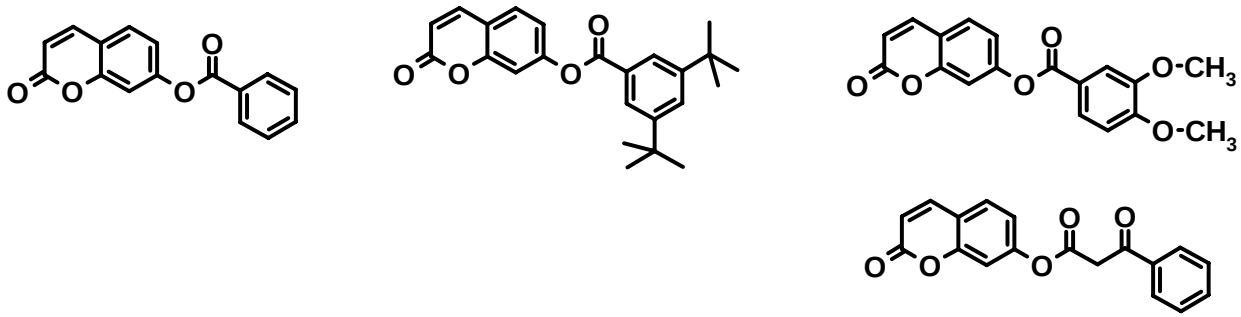

*Coumarine derivative*

*Dimer with an enhanced molecular weight*

# On the Way Towards Solvent-Free Photopatterning

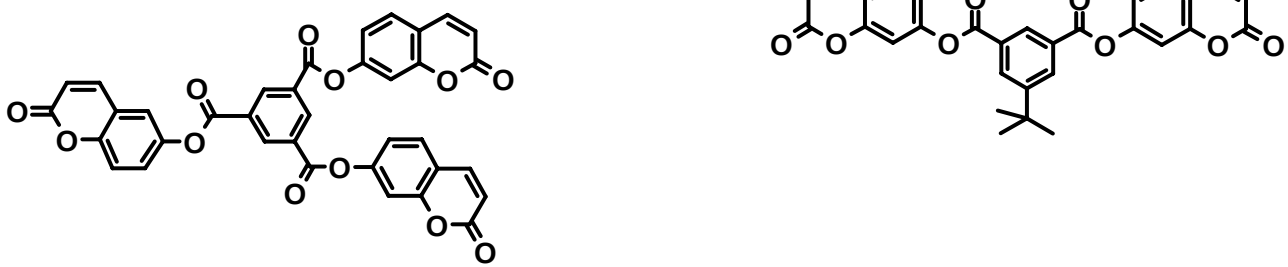
***Synthesized coumarine derivatives:***

**Mono-esters:**




**Bis-esters:**

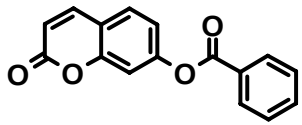
**Tris-ester:**

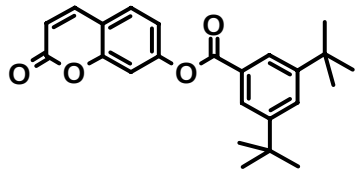


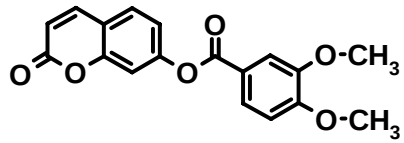
# On the Way Towards Solvent-Free Photopatterning

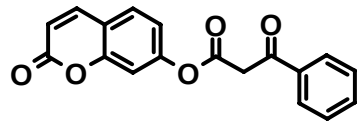
***Synthesized coumarine derivatives:***

**Mono-esters:**

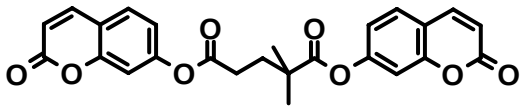


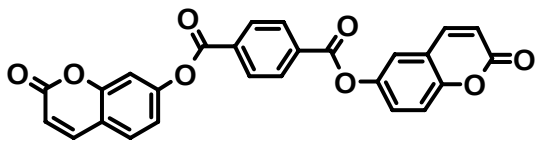


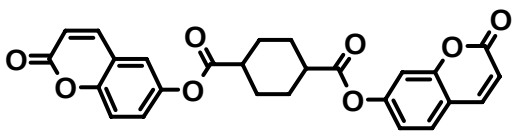


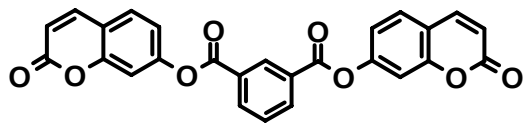



**Bis-esters:**

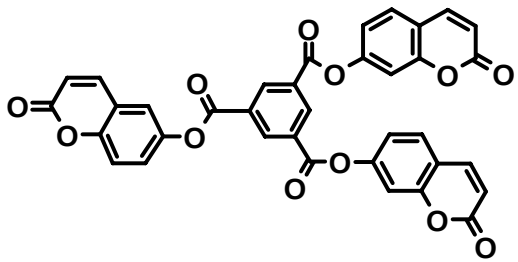


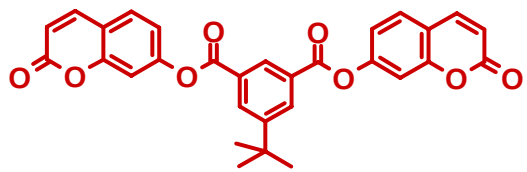






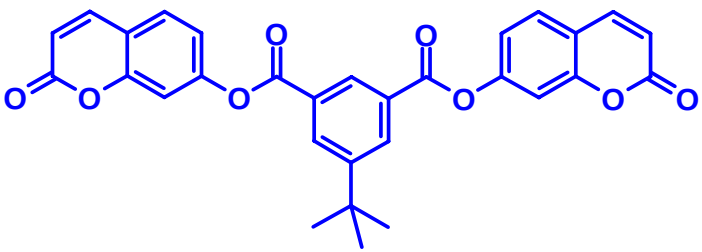
**Tris-ester:**



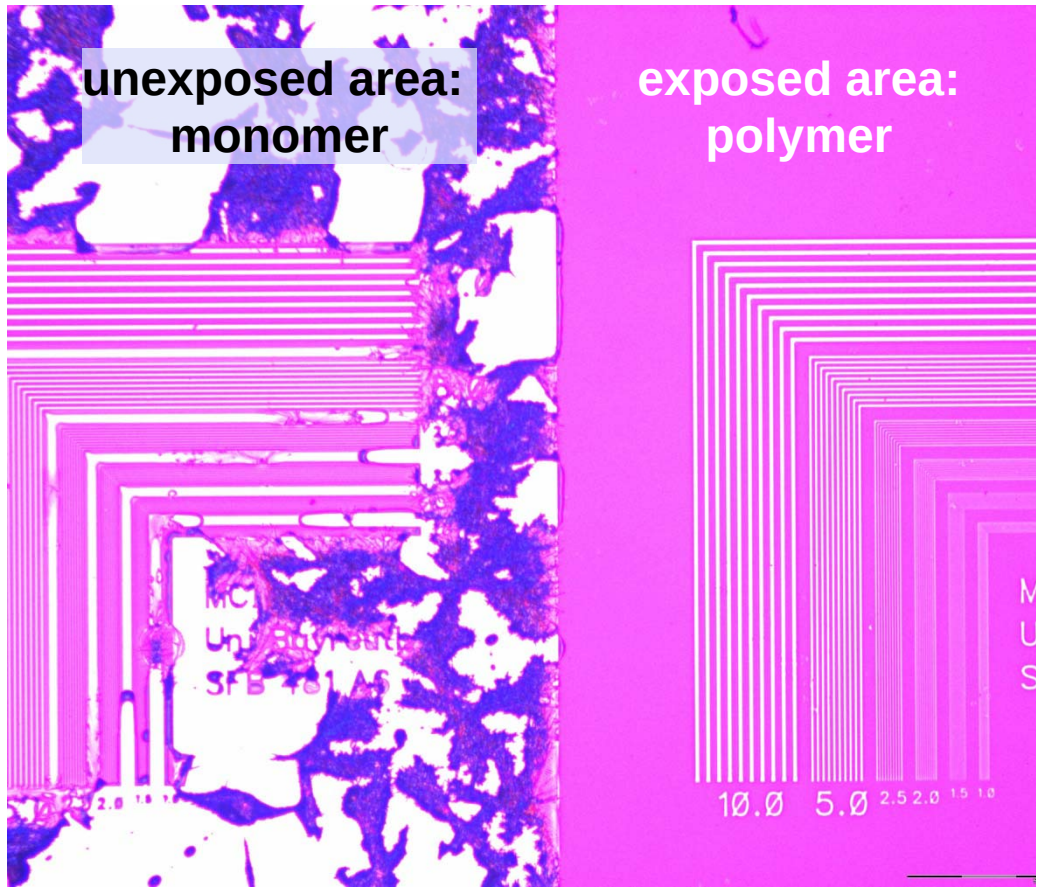


**amorphous glass,**
**but not long-term stable**

# All-Dry Photopatterning



Bis-coumarin ester




**Conditions:**

Evaporation of bis-coumarine ester

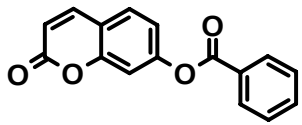
Exposure: *15 min at 365 nm*

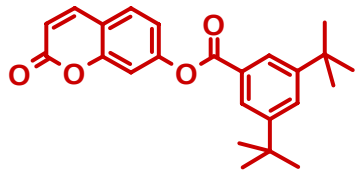
Vacuum development: *15h, 120 ℃, $10^{-5}$ mbar*

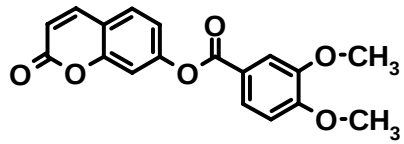
# On the Way Towards Solvent-Free Photopatterning

***Synthesized coumarine derivatives:***

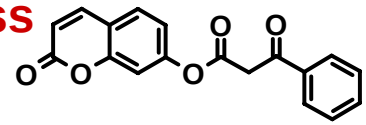
**Mono-esters:**







**amorphous stable glass**

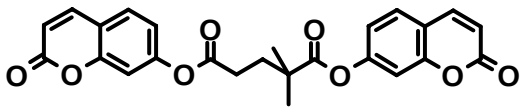


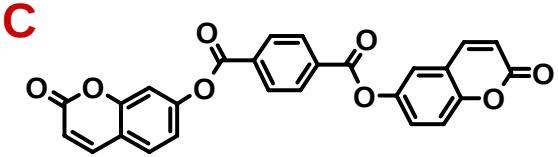
$T_g$: 33 °C

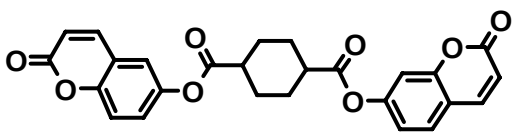
$T_m$: 134 °C

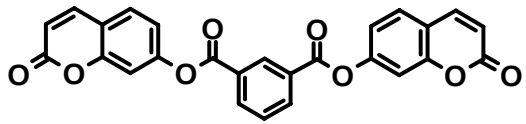
$T_{decomp.}$: 252 °C

**Bis-esters:**

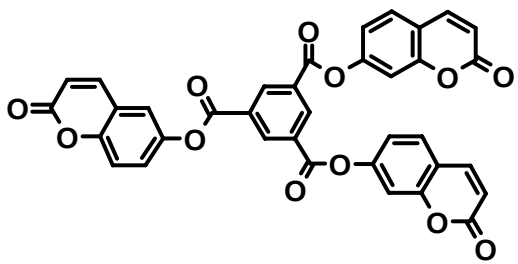


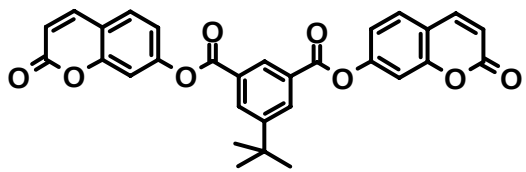






**Tris-ester:**

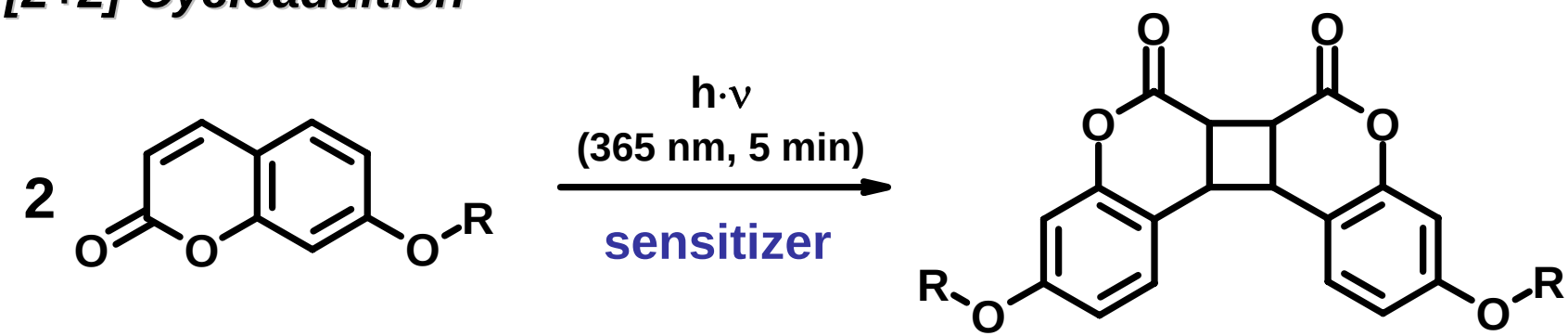




# Solvent-Free Photopatterning

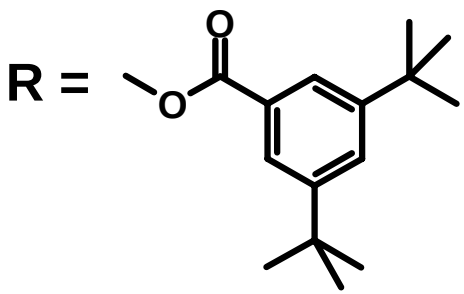
***First system realized by utilizing coumarine derivatives***

***[2+2]-Cycloaddition***

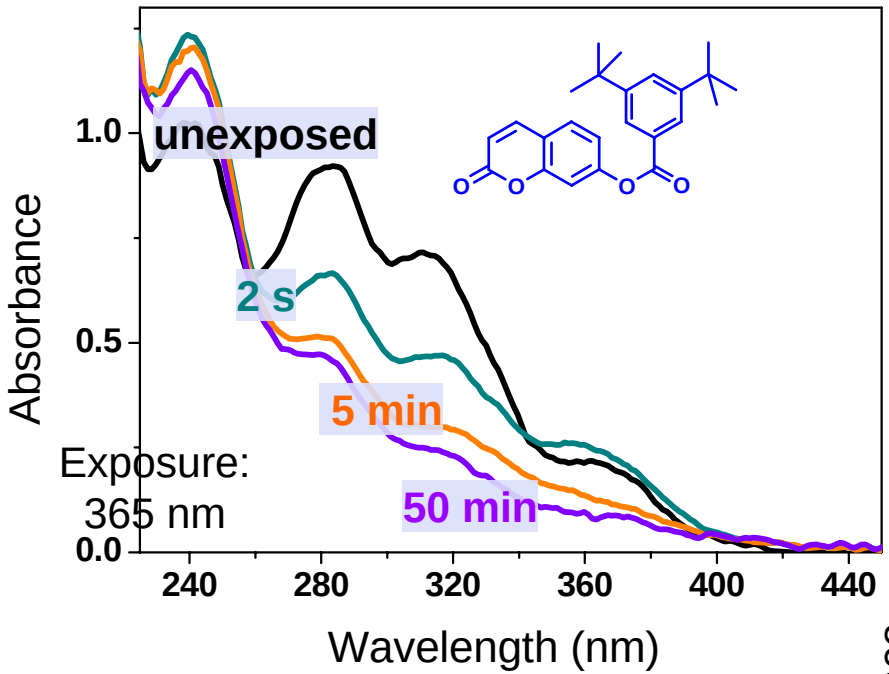



*Coumarine derivative*

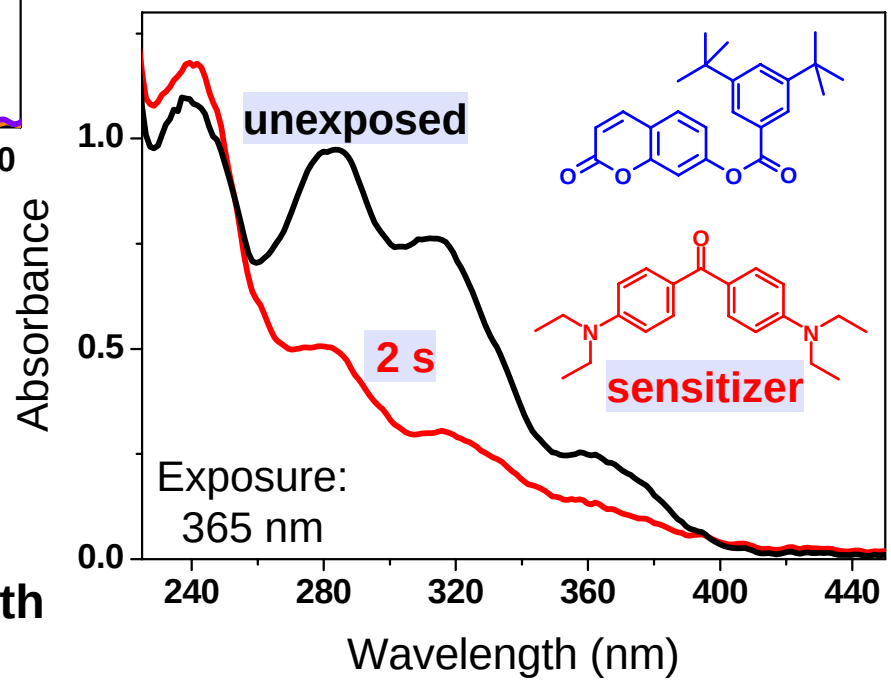
*Dimer with increased molecular weight*



# UV-Vis Characterization of Cycloaddition

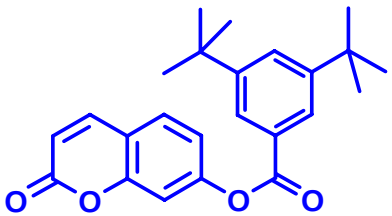



**Coevaporation**

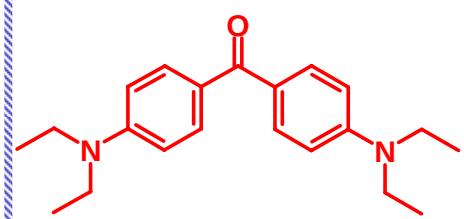



⇨ **Clear increase of sensitivity by the coevaporation of the coumarine with the Michlers ethyl keton**

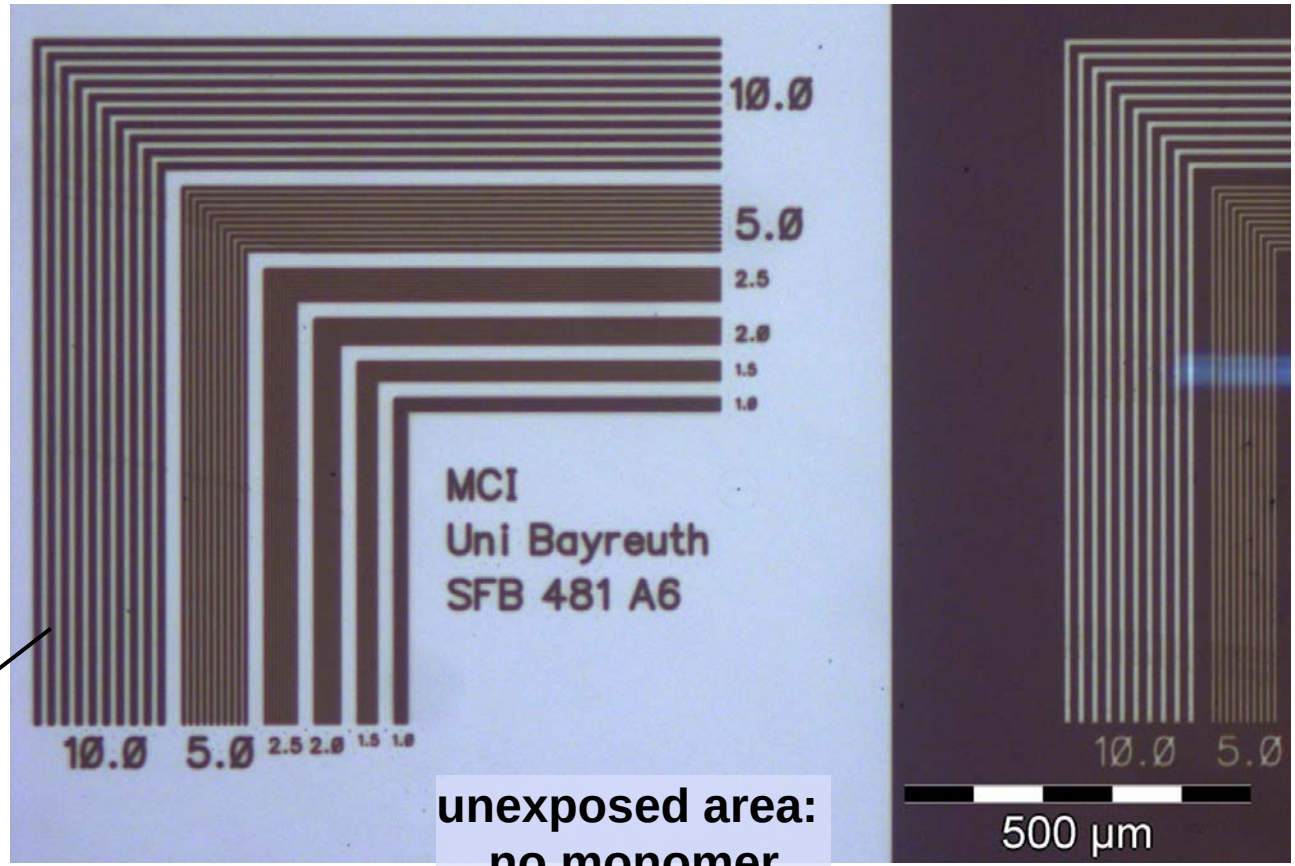
# All-Dry Photopatterning



Mono-coumarin ester



sensitizer




**exposed area: dimer**

**unexposed area: no monomer**

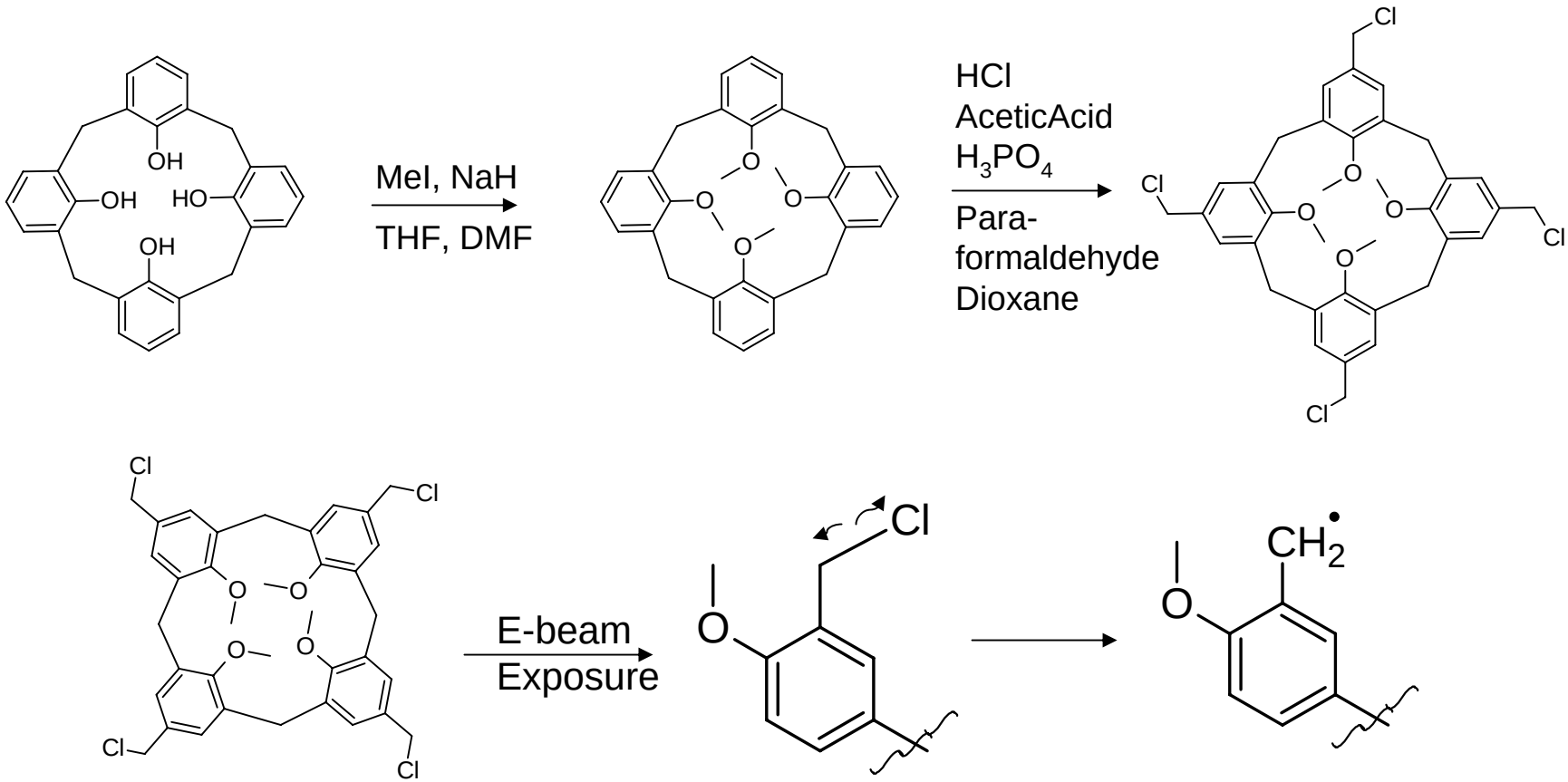
**Conditions:**

Coevaporation of coumarine ester and sensitizer (10wt%)

Exposure: *5 min at 365 nm*

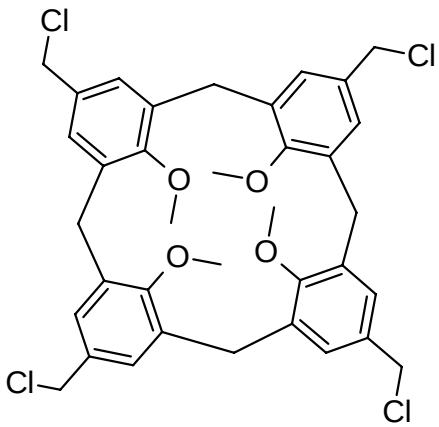
Vacuum development: *15h, 80 ℃, $10^{-5}$ mbar*

# All-Dry Photopatterning



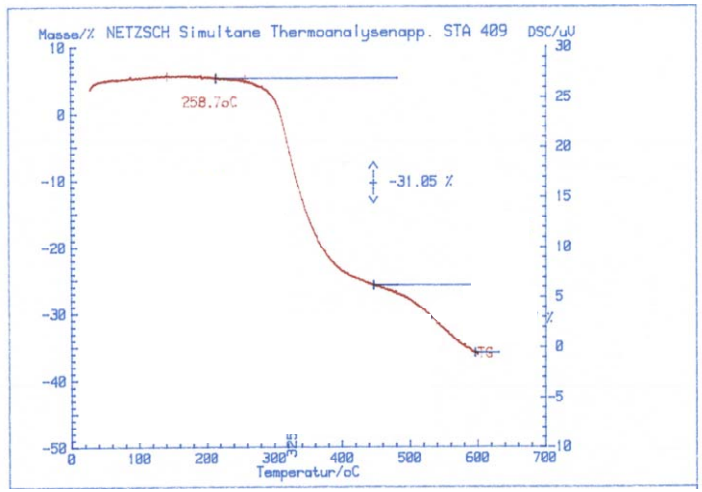

Free radicals generated upon E-beam exposure, radicals will combine to form a dense phenolic network

# All-Dry Photopatterning



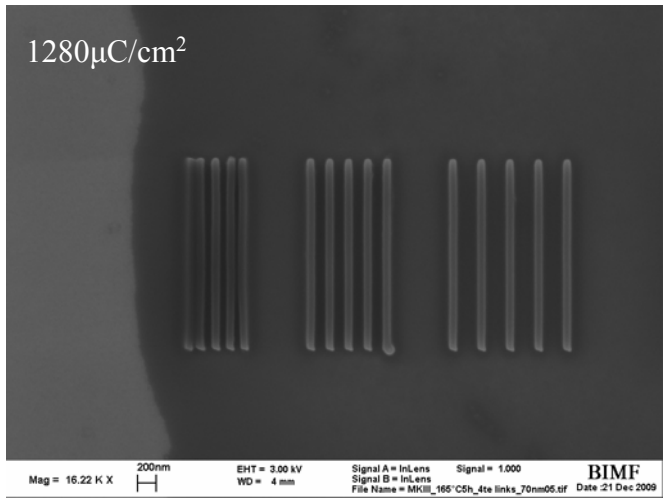

**Successfully vapor deposited on HMDS primed silicon wafer**

**Evaporation temperature: 170ºC**

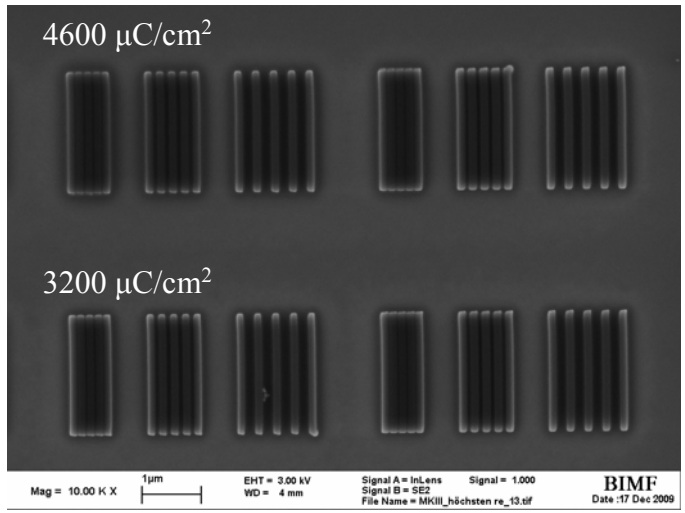



**TGA shows good thermal stability**

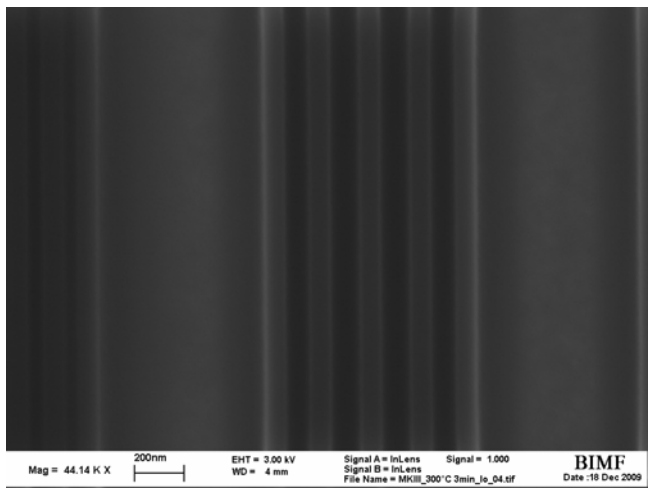
# All-Dry Photopatterning



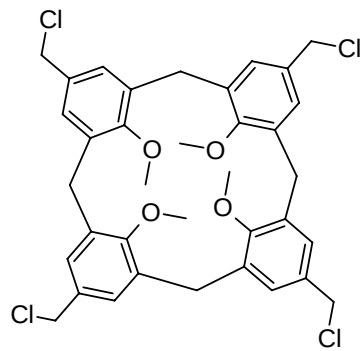

Development: 5h @ 165°C high vacuum




Development: 10min @ 260°C high vacuum




Development: 3 min. @ 300°C high vacuum



# Acknowledgements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