UV Polymers for Nanoimprint Lithography

Holger Schmitt, Christoph Lehrer

University of Erlangen-Nuremberg
Chair of Electron Devices

Fraunhofer Institute of Integrated Systems and Device Technology
(IISB) in Erlangen

2nd FORNEL Workshop on Nanoelectronics, March 15, 2006

Outline

- Introduction
- Chemical Composition of UV Polymers
- UV curing at 375 nm
- Adhesion Mold / UV Polymer / Substrate
- Residual layer thickness
- Summary and Outlook

Introduction

- Transfer of structures with sizes below 100 nm very important
  - Electronics, Information Technology → data storage, integrated circuits
  - Medicine, Biology, Chemistry → biosensors
  - Optics → lenses

- Key technology: High Resolution Lithography
  - DUV Stepper: state of the art
  - Extreme Ultraviolet (EUV): high costs
  - Electron beam writer, Ion beam writer: low throughput
  - Nanoimprint Lithography (NIL)

Introduction

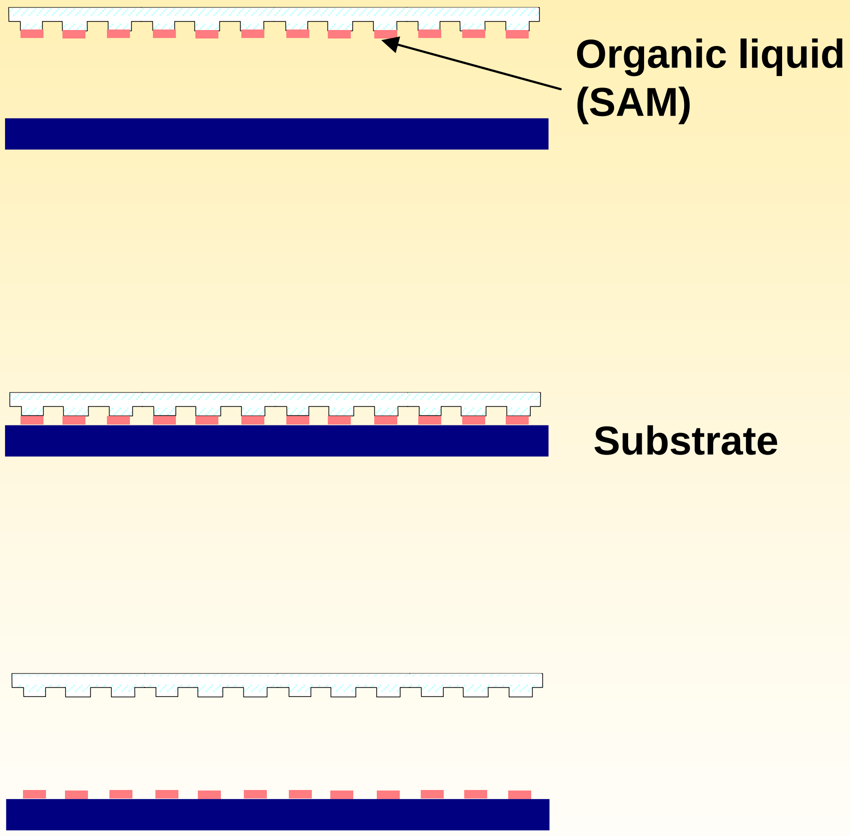
Nanoimprint Lithography

- **Micro Contact Printing (μ-CP) (Soft Lithography)**
- **Hot Embossing**
- **UV Nanoimprint Lithography (UV-NIL)**

Introduction

Nanoimprint Lithography

- **Micro Contact Printing (µ-CP) (Soft Lithography)**
- Hot Embossing
- UV Nanoimprint Lithography (UV-NIL)



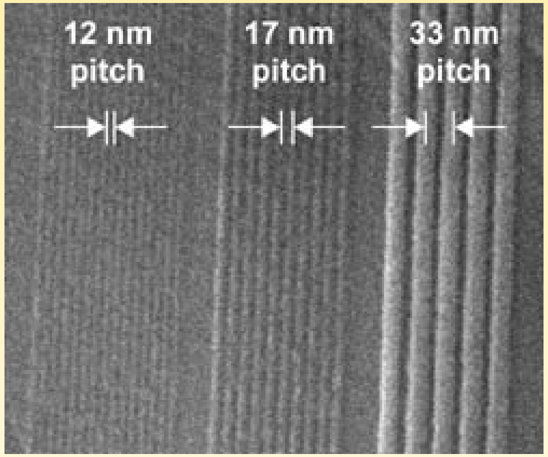
Introduction

Nanoimprint Lithography

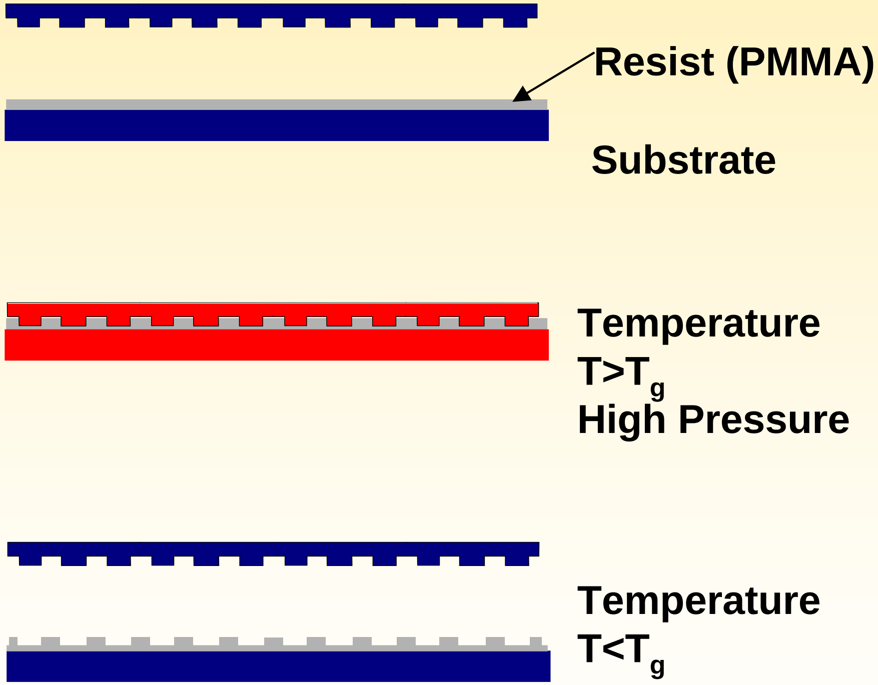
Micro Contact Printing (µ-CP) (Soft Lithography)

Hot Embossing

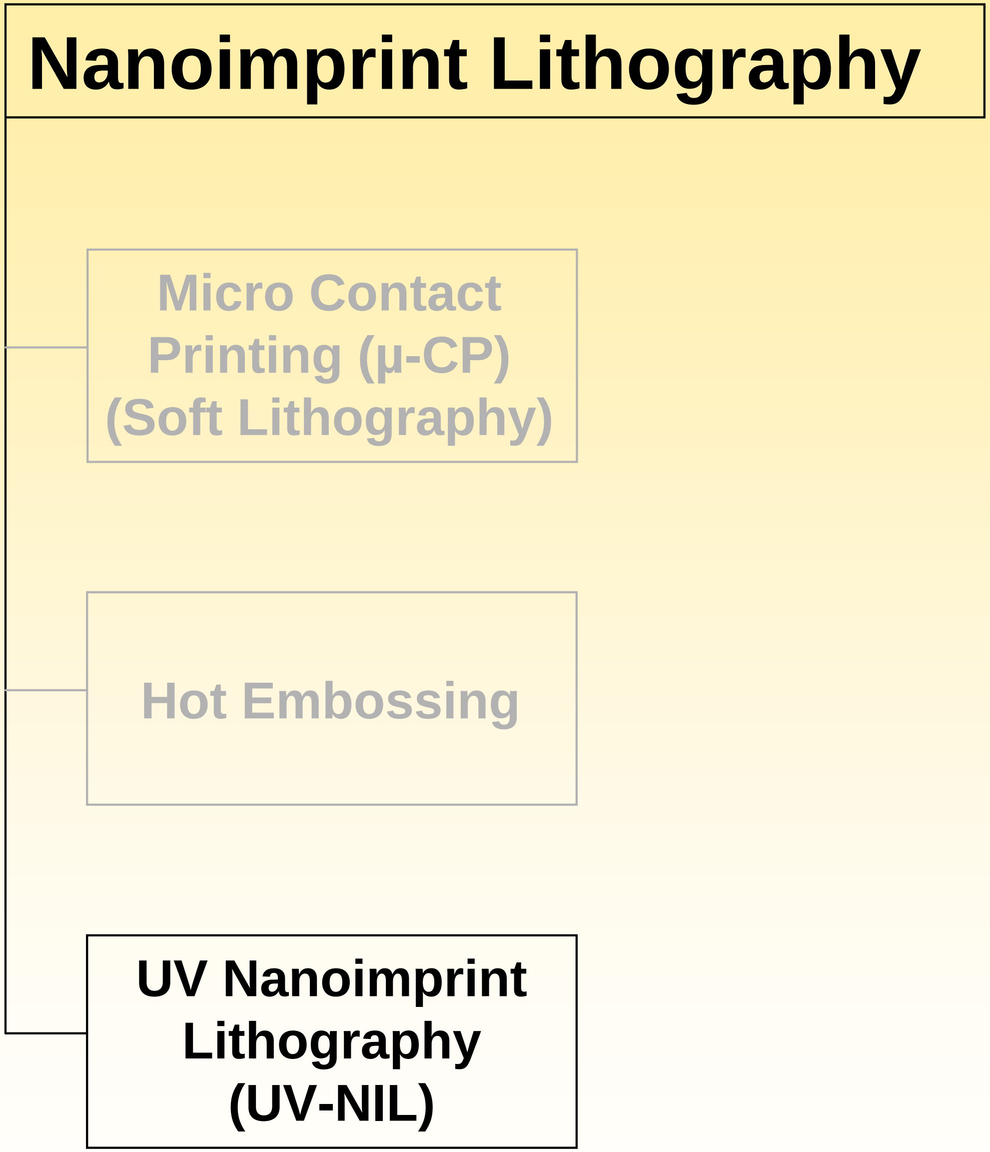
UV Nanoimprint Lithography (UV-NIL)



Source: Nanonex



Introduction



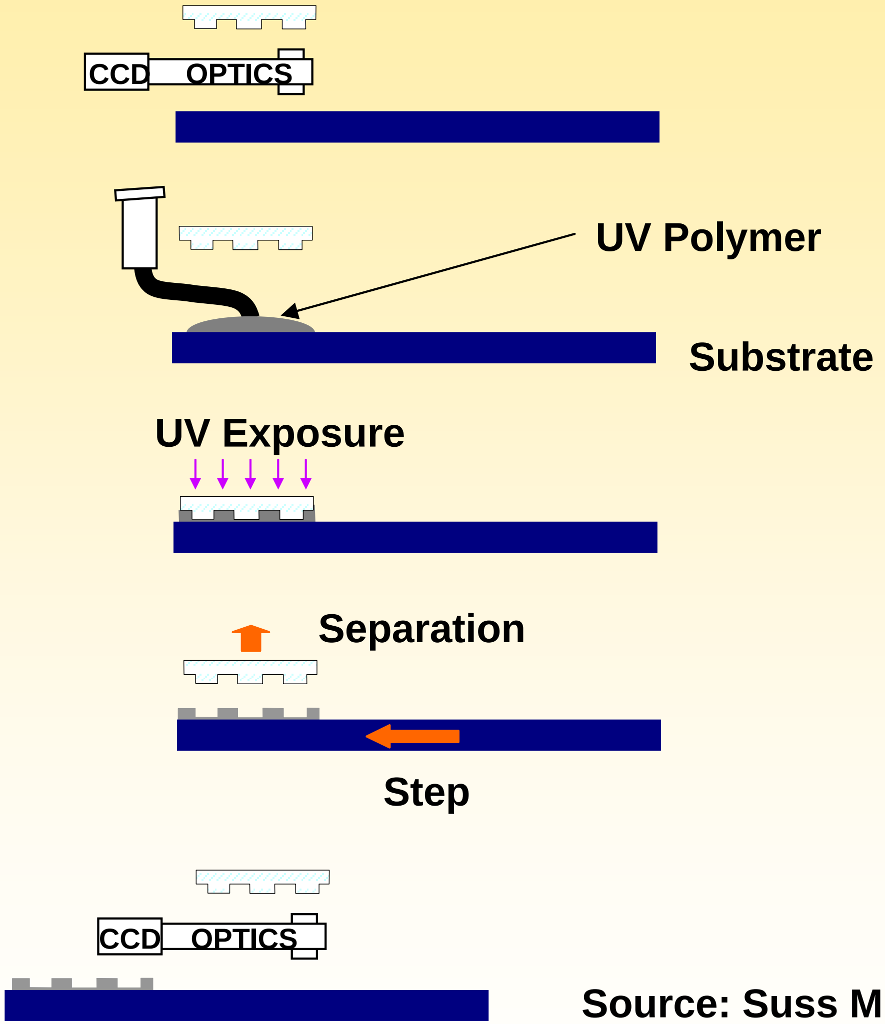
Nanoimprint Lithography

Micro Contact Printing (μ-CP) (Soft Lithography)

Hot Embossing

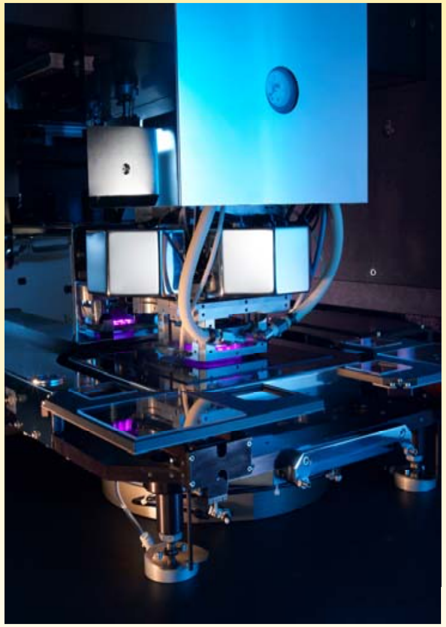
UV Nanoimprint Lithography (UV-NIL)

UV NIL: S-FIL (Step and Flash)



Source: Suss MicroTec

Introduction



Source: Suss MicroTec

Mold

- ✓ Own
- ✓ Quantiscript, Photronics

Imprint System

- ✓ NPS 300 Suss MicroTec

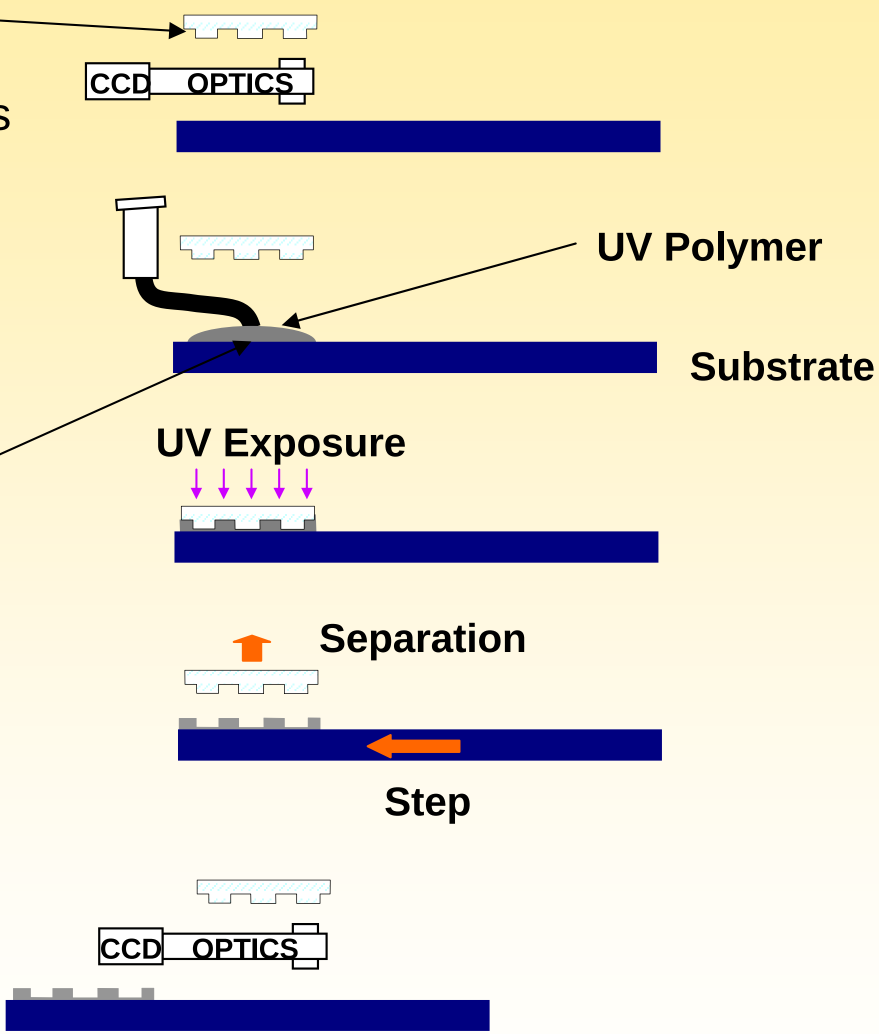
UV Polymer

- fast curing
- adhesion properties
- residual layer thickness
- etch resistance

Process technology

- structure transfer in the substrate
- overlay

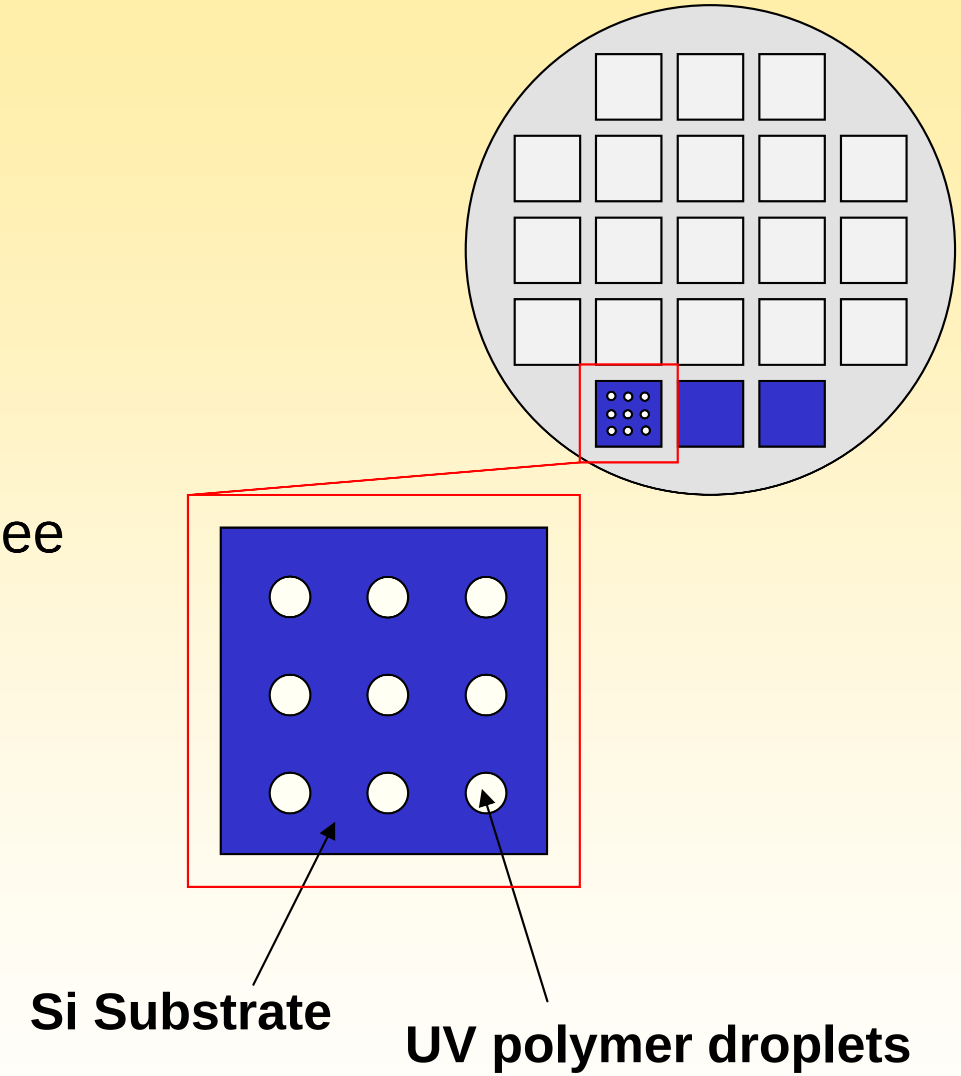
UV NIL: S-FIL (Step and Flash)



Introduction

UV Polymers

- Special properties
- Availability
- Evaluation of UV Polymers: solvent-free
  - UV glue for optical components
  - Dental UV sealant
  - UV NIL Polymers



Outline

- Introduction
- Chemical Composition of UV Polymers
- UV curing at 375 nm
- Adhesion Mold / UV Polymer / Substrate
- Residual layer thickness
- Summary and Outlook

Chemical Composition

S-FIL UV Polymers

- ➢ Organic acrylates provide low viscosity; vinyl ethers
- ➢ Organic Crosslinker
- ➢ Additives
  - Silicon-containing acrylate monomer
  - Flourinated compounds
- ➢ Photoinitiator
  - Cationic photoinitiator
  - Free radical photoinitiator

Outline

- Introduction
- Chemical Composition
- UV curing at 375 nm
- Adhesion Mold / UV Polymer / Substrate
- Residual layer thickness
- Summary and Outlook

UV curing at 375 nm

- Requirement of fast curing times

- Cationic Photoinitiator
  - Insensitve to oxygen
  - Low curing rates
  - Acids, heavy metals are harmful to semiconductors

- Free radical Photoinitiator
  - Great variety
  - High curing rates
  - Sensitive to oxygen → particle, process gas

UV curing at 375 nm

Results	Time (s) at 120 mW/cm^2	Remarks
➢ Sealant: Helioseal	25	
	Time (s) at 30 mW/cm^2	
➢ UV glue: NOA 61	20	
➢ UV NIL Polymers		
- Inoflex RP+	< 5	sensitive to oxygen
- PAK 01	< 5	sensitive to oxygen
- NIF 2	10	sensitive to oxygen
- NIF 1	10	sensitive to oxygen
- Z Resit	< 5	sensitive to oxygen

Increase in Power up to 120 mW/cm^2 possible → embrittlement

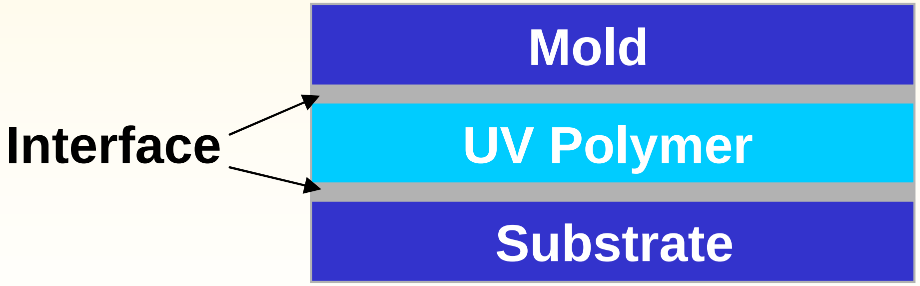
Outline

- Introduction
- Chemical Composition
- UV curing at 375 nm
- Adhesion Mold / UV Polymer / Substrate
- Residual layer thickness
- Summary and Outlook

Adhesion Mold / UV Polymer / Substrate

- Adhesion properties
  - Mold / UV Polymer → no adhesion
  - Substrate / UV Polymer → good adhesion

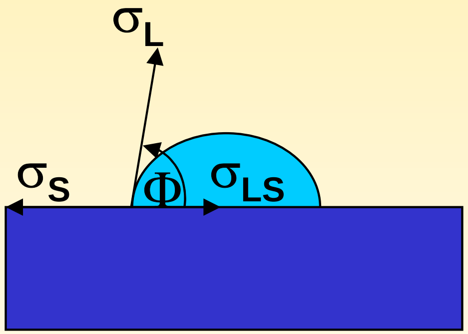
- Interface reaction: various influences
  - Mechanical adhesion
  - Wetting
  - Specific adhesion mainly caused by intermolecular bindings



Adhesion Mold / UV Polymer / Substrate

Wetting:

Contact angle measurments



***ARC: Anti Reflective Coating**

****Mold: Quartz treated with FTCS**

	Contact angle (°)			
	Si	Si / HMDS	Si / ARC*	Mold**
NOA 61	23,7	41,8		68,3
Helioseal	15	26,7		66,2
Inoflex RP+	14,9	31,9	✓8	67,9
PAK 01	✓9,4	20,3	✓8,7	66,5
NIF 2	16,3	12,3	✓6,1	33,7
NIF 1	15,8	11,4	✓5,9	34,2
Z Resist	✓6,3	25,8	10,6	65,4

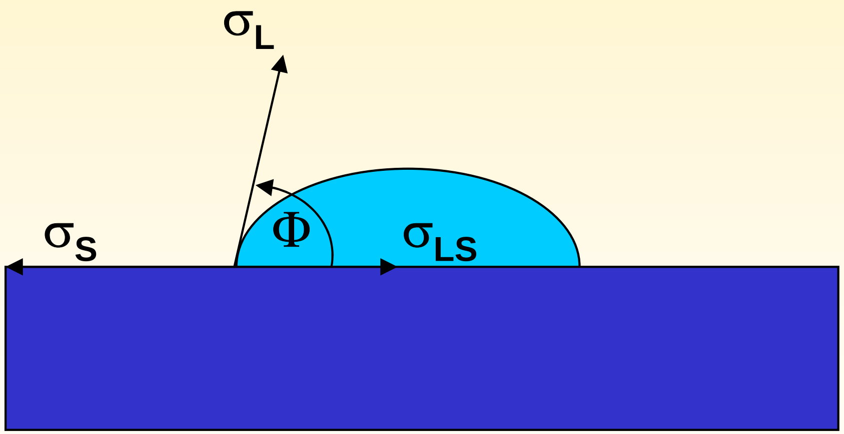
Adhesion Mold / UV Polymer / Substrate

Surface tension σ

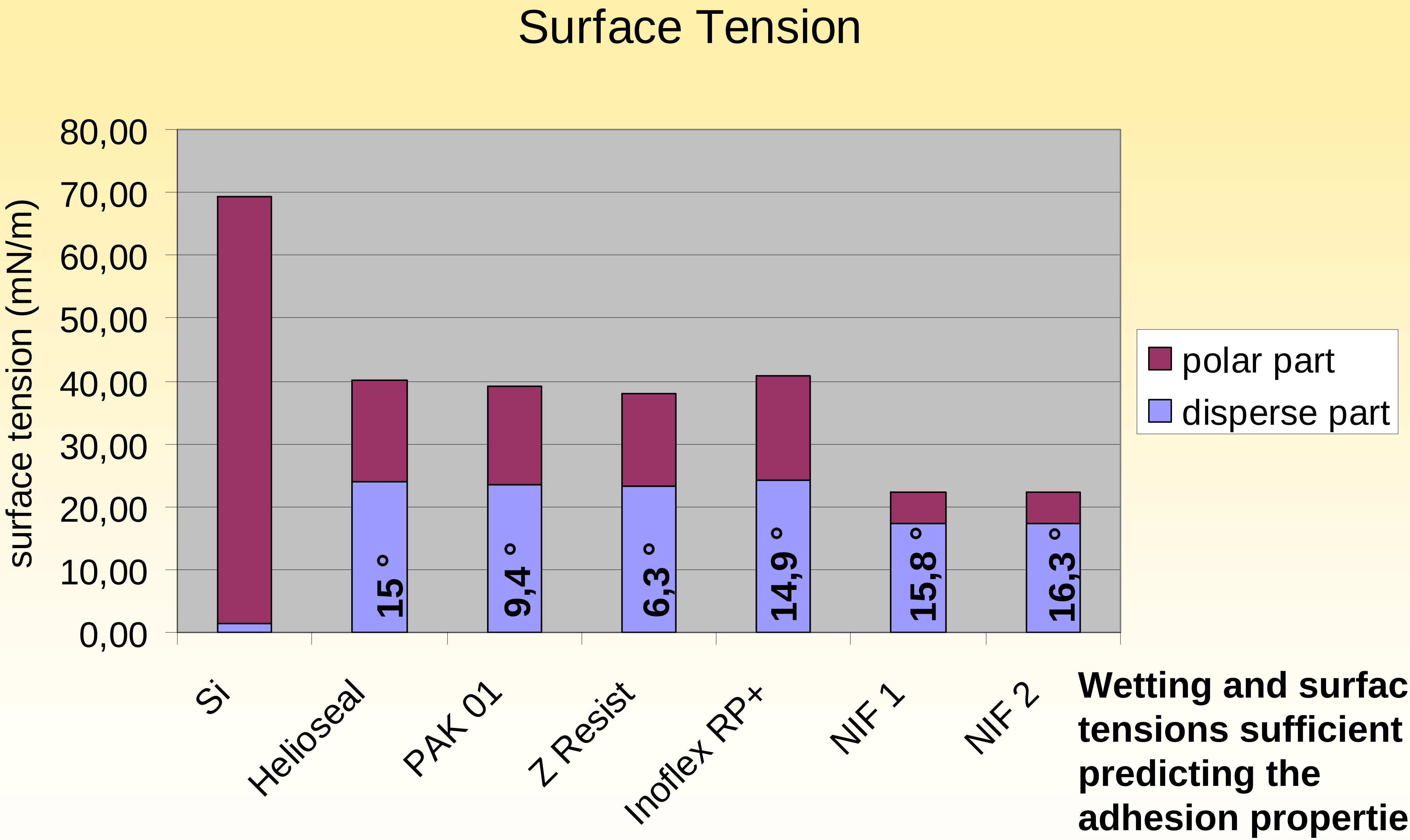
- Method by Owen, Wendt combined with Young equatation
  → polar and disperse part of the surface tension σ
- Possible to predict adhesion properties?

Young equatation:

$$\sigma_S = \sigma_{LS} + \sigma_L * \cos \Phi$$



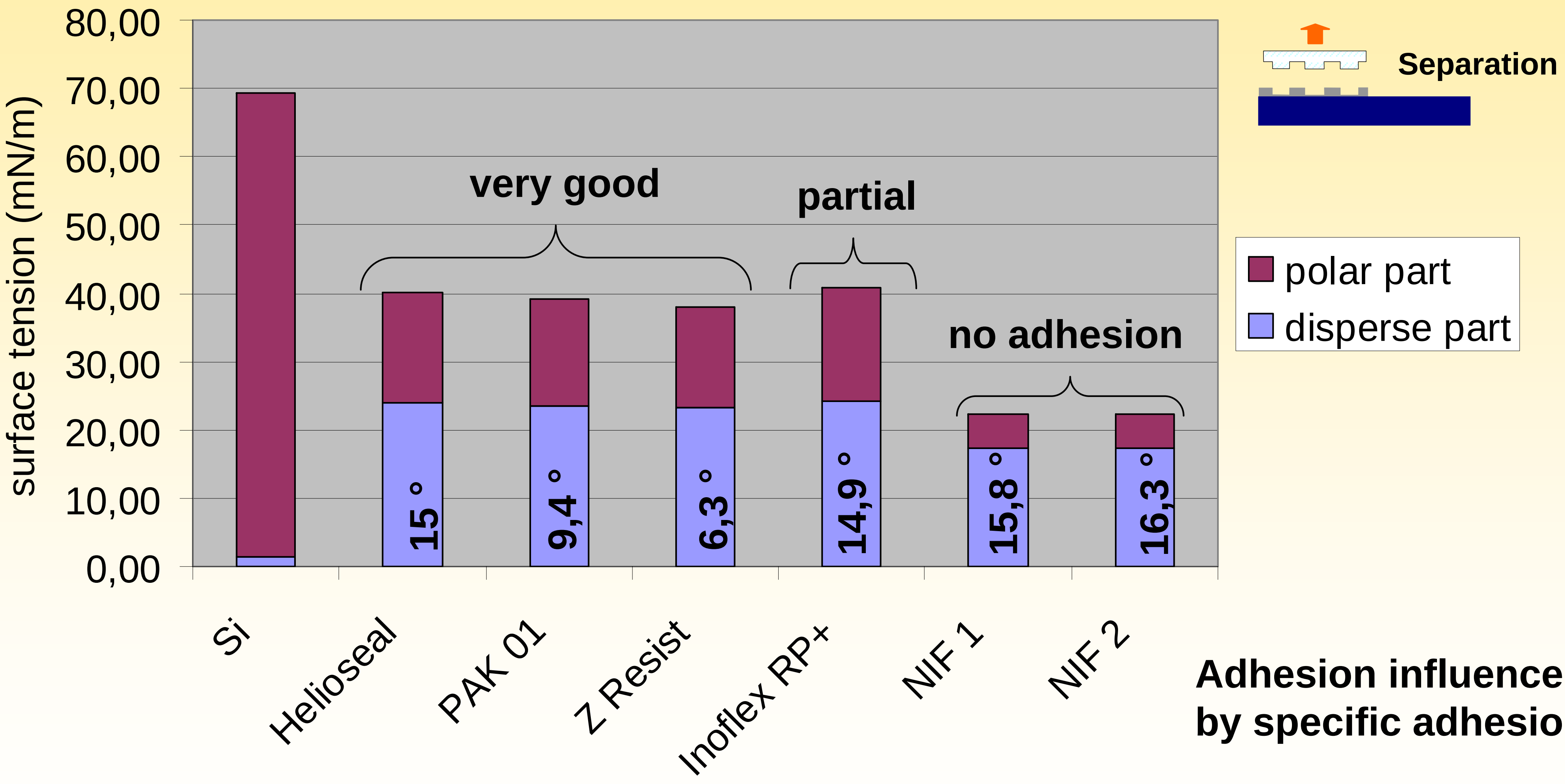
Adhesion Mold / UV Polymer / Substrate



Wetting and surface tensions sufficient for predicting the adhesion properties?

Adhesion Mold / UV Polymer / Substrate

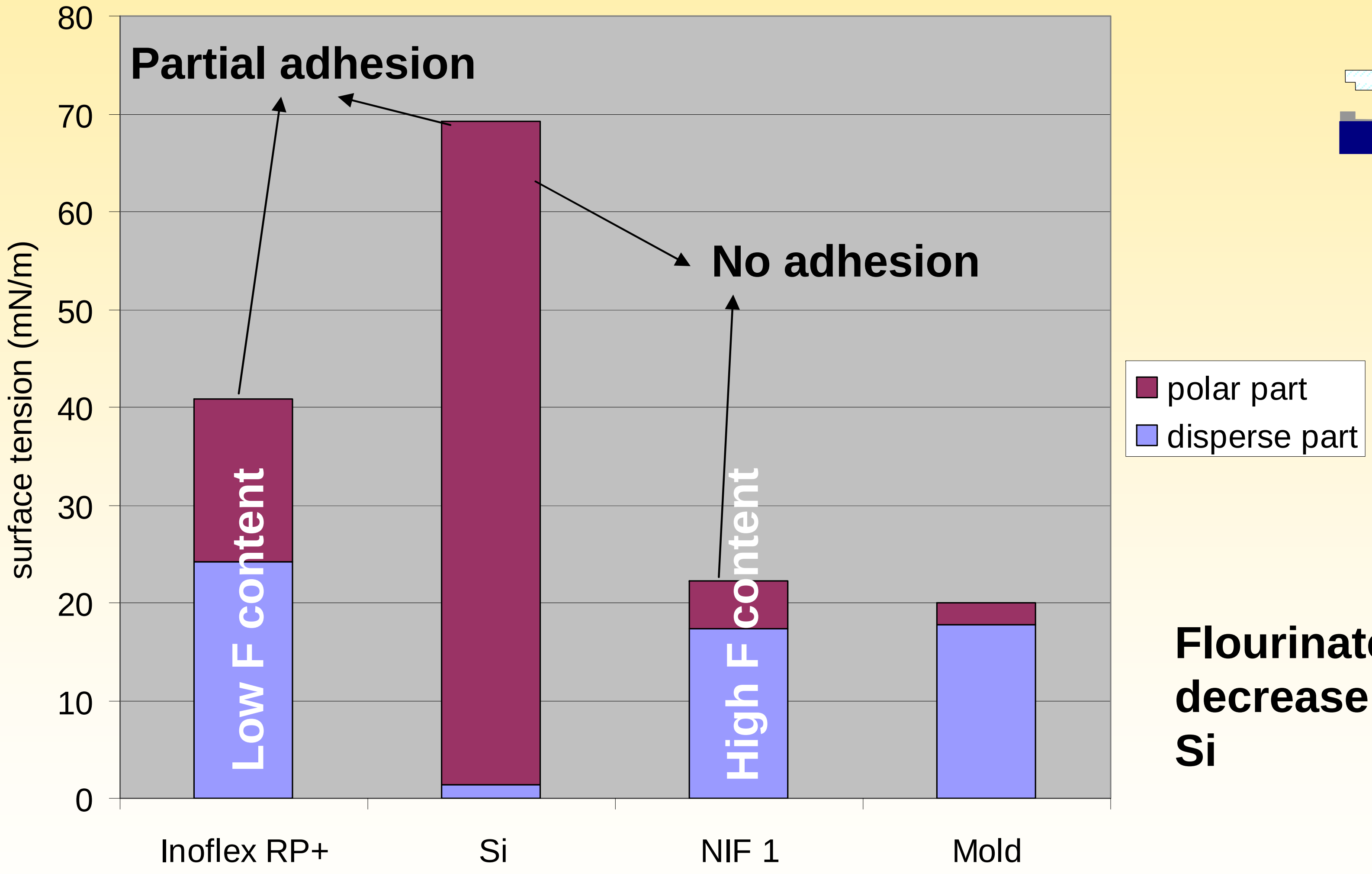
Adhesion of UV Polymers to Si substrate

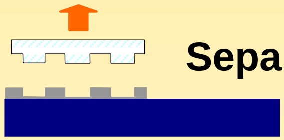


Adhesion influenced by specific adhesion

Adhesion Mold / UV Polymer / Substrate

Adhesion of fluorinated UV Polymers to Si substrate

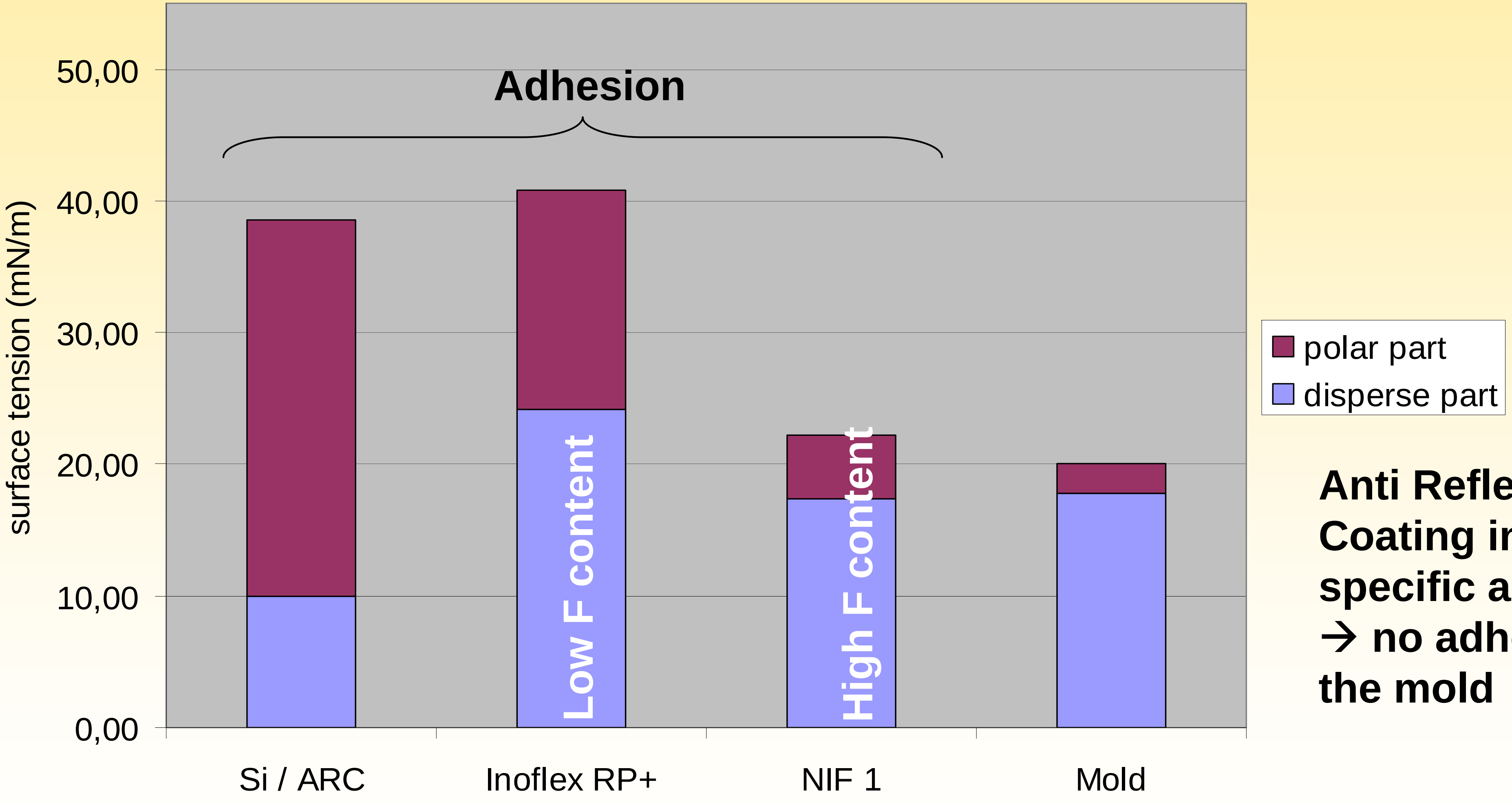




Flourinated compounds decrease the sticking to Si

Adhesion Mold / UV Polymer / Substrate

Adhesion of fluorinated UV Polymers to ARC coated substrate



Anti Reflective Coating increases specific adhesion → no adhesion to the mold

Adhesion Mold / UV Polymer / Substrate

Adhesion behaviour

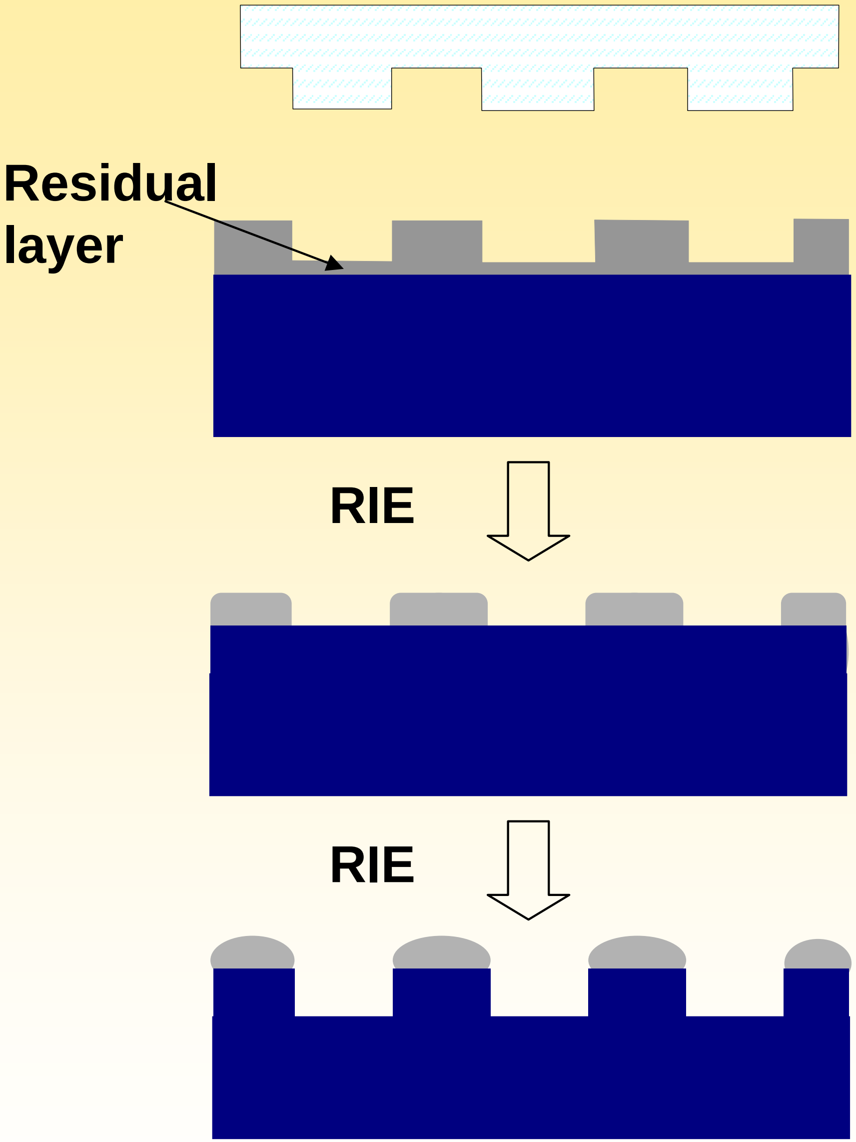
	Si	Mold	Si / HMDS	Mold	Si / ARC	Mold
NOA 61						
Helioseal	++	--				
Inoflex RP+	+	-	0	0	++	--
PAK 01	++	--	++	--	++	--
NIF 2	--	++	0	0	++	--
NIF 1	--	++	0	0	++	--
Z Resist	++	--	-	+	--	++

Outline

- Introduction
- Chemical Composition
- UV curing at 375 nm
- Adhesion Mold / UV Polymer / Substrate
- Residual layer thickness
- Summary and Outlook

Residual layer thickness

- ➢ Structure transfer into substrate
- ➢ Loss of dimensional accuracy



Important for structure transfer into substrate:
structure hight > residual layer

→ Residual layer < 100 nm

Residual layer thickness

- Structure transfer into substrate
- Loss of dimensional accuracy
- Viscosity, initial volume

$$if \quad h_f \ll h_0$$

$$h_f = \sqrt{\frac{s^2 \cdot t_f}{2p}} \cdot \sqrt{\eta}$$

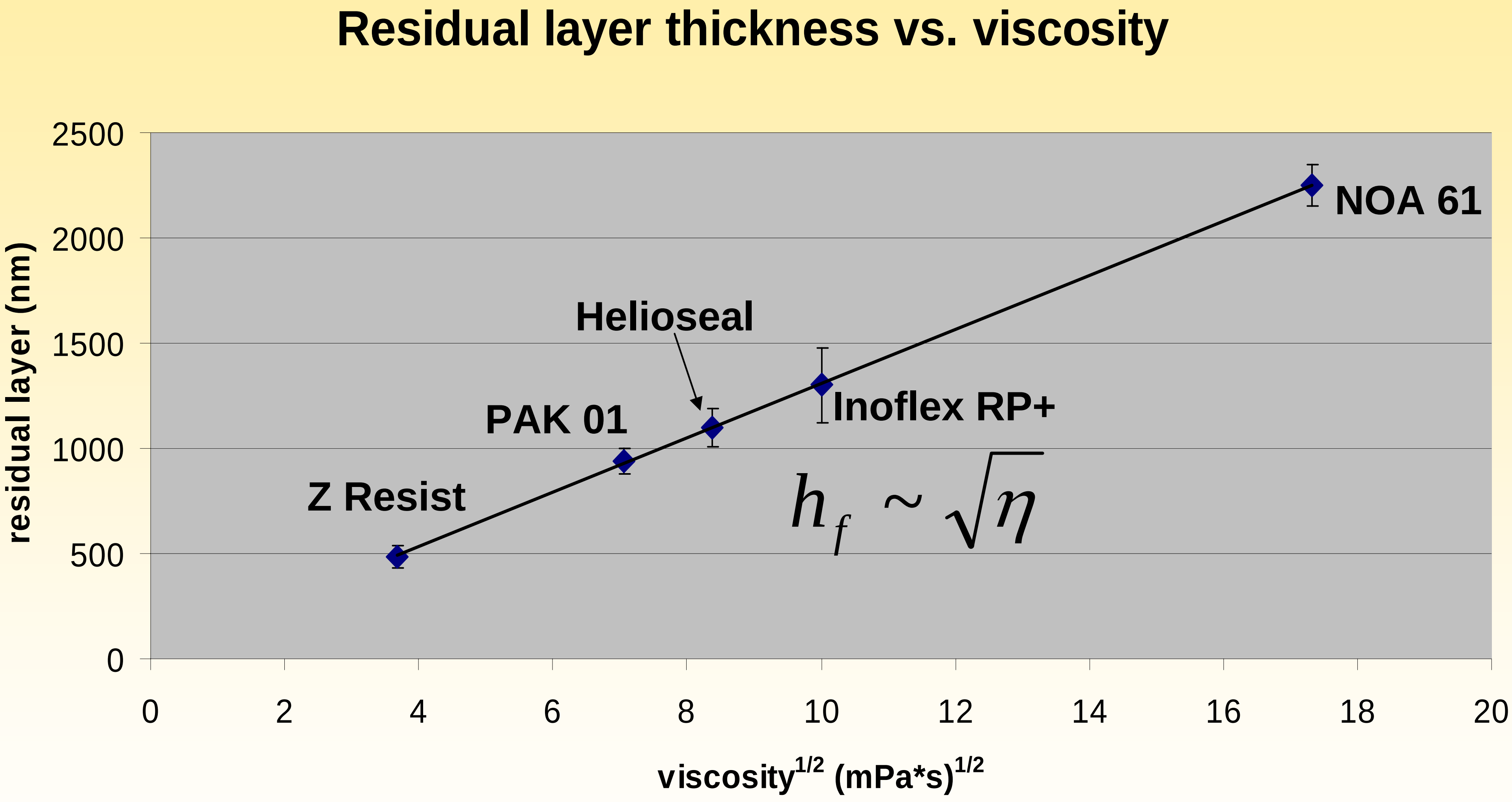
$$\Rightarrow h_f \sim \sqrt{\eta}$$

h_f: final thickness
h_o: initial thickness
s: distance
t_f: imprint time
p: pressure
η: viscosity

Residual layer thickness

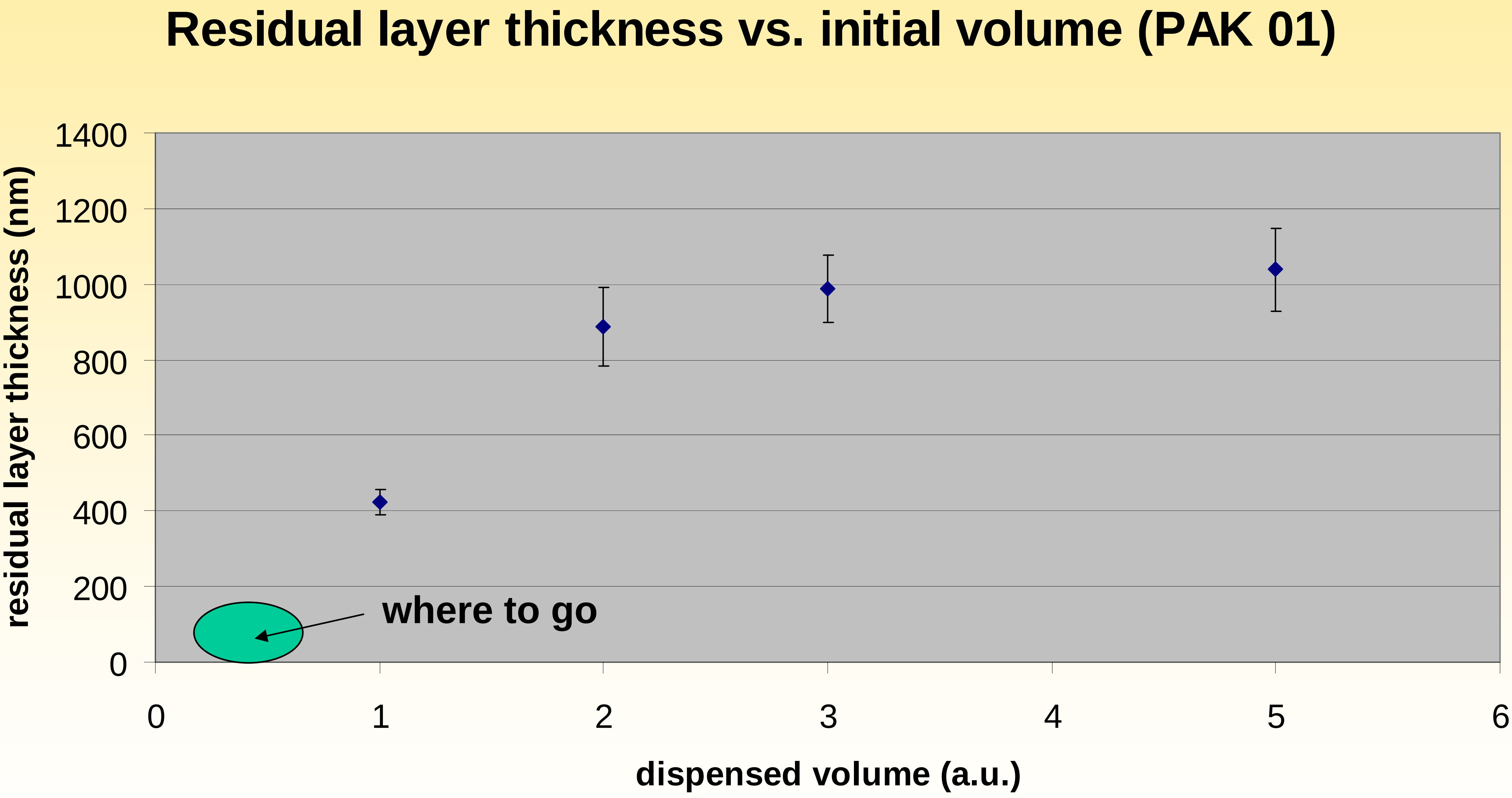
UV Polymers	Viscosity (mPa*s)	Remarks
➢ UV glue: NOA 61	300	to high, Mercaptoester
➢ Sealant:		
- Helioseal	70 – 75	
- Fissurit	?	to high
- Clinpro Sealant	?	to high
➢ UV NIL Polymers		
- Inoflex RP+	100	
- PAK 01	50	
- NIF 2	24,5	
- NIF 1	14,5	
- Z Resist	12 – 14	

Residual layer thickness



$$h_f \sim \sqrt{\eta}$$

Residual layer thickness

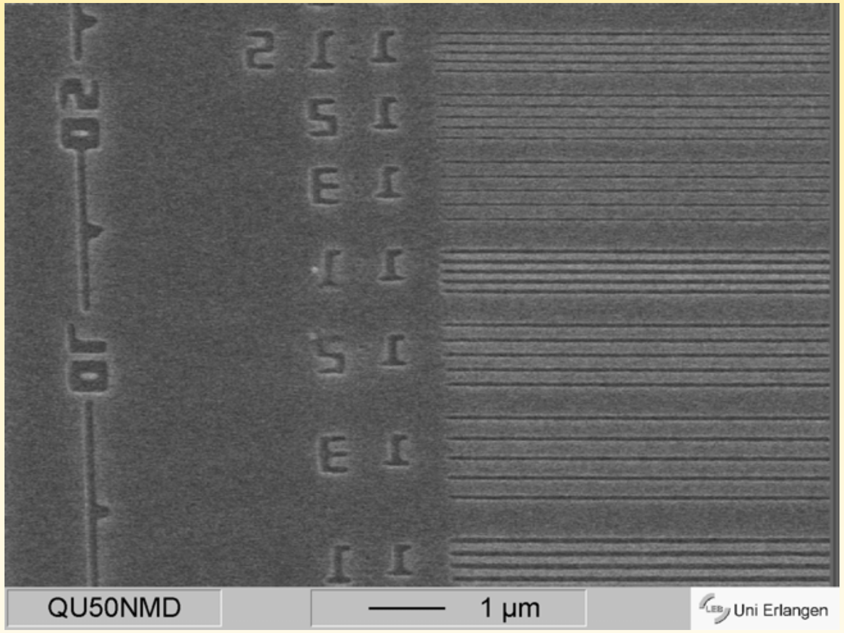


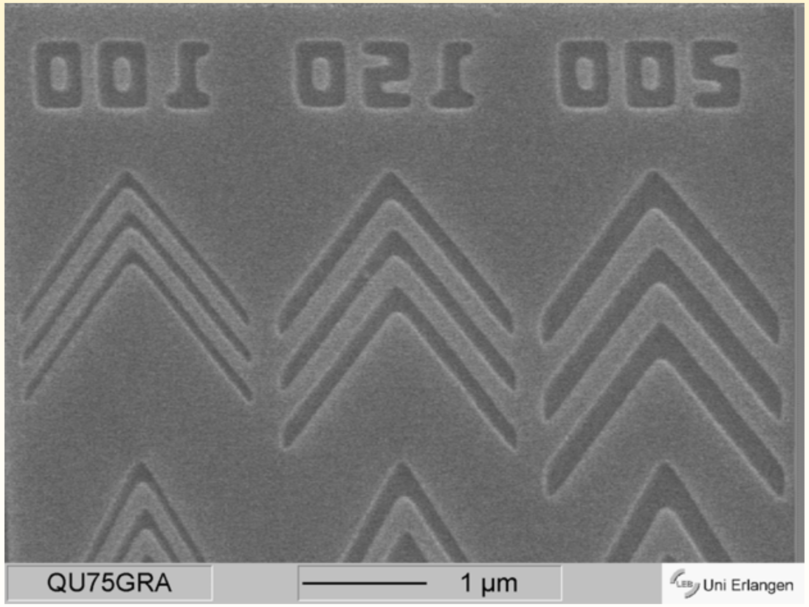
Summary and Outlook

- Chemical composition of UV Polymers
- Properties of UV Polymers
- UV sealant, UV glues not appropriate
- UV NIL polymers: NIF 1 and Z Resist
- Ink Jet system combined with low viscosity resist

Summary and Outlook

Nanoimprints with NPS 300 in PAK 01





Adhesion Mold / UV Polymer / Substrate