PC 3242 Part II

Topic	Text Book (Zhen Cui '05)	Lectures
Optical lithography	Chapter 2	1, 2 & 3
Electron Beam Lithography	Chapter 3	4 & 5
Focused Ion Beam Technology	Chapter 4	
Low Energetic Ions (keV)		6, 7 & 8
SIMS	Extra material provided	
FIB in Lithography	Chapter 4	
High Energetic Ions (MeV)	Extra material provided	8
RBS	Extra material provided	9
Light ions in lithography	Extra material provided	10
Etching	Chapter 7	10, 11
Nano Imprint Lithography	Chapter 6	12
3DP Three Dimensional Printing	Extra material provided	13

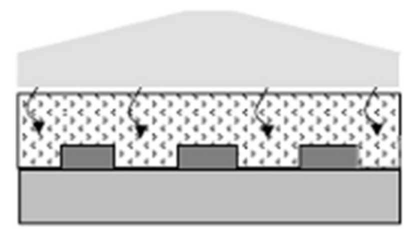
JA van Kan 2024

There are different forms of Nano imprint lithography (NIL)

I Soft Lithography
or
μ-contact printing

Inking and Au coating

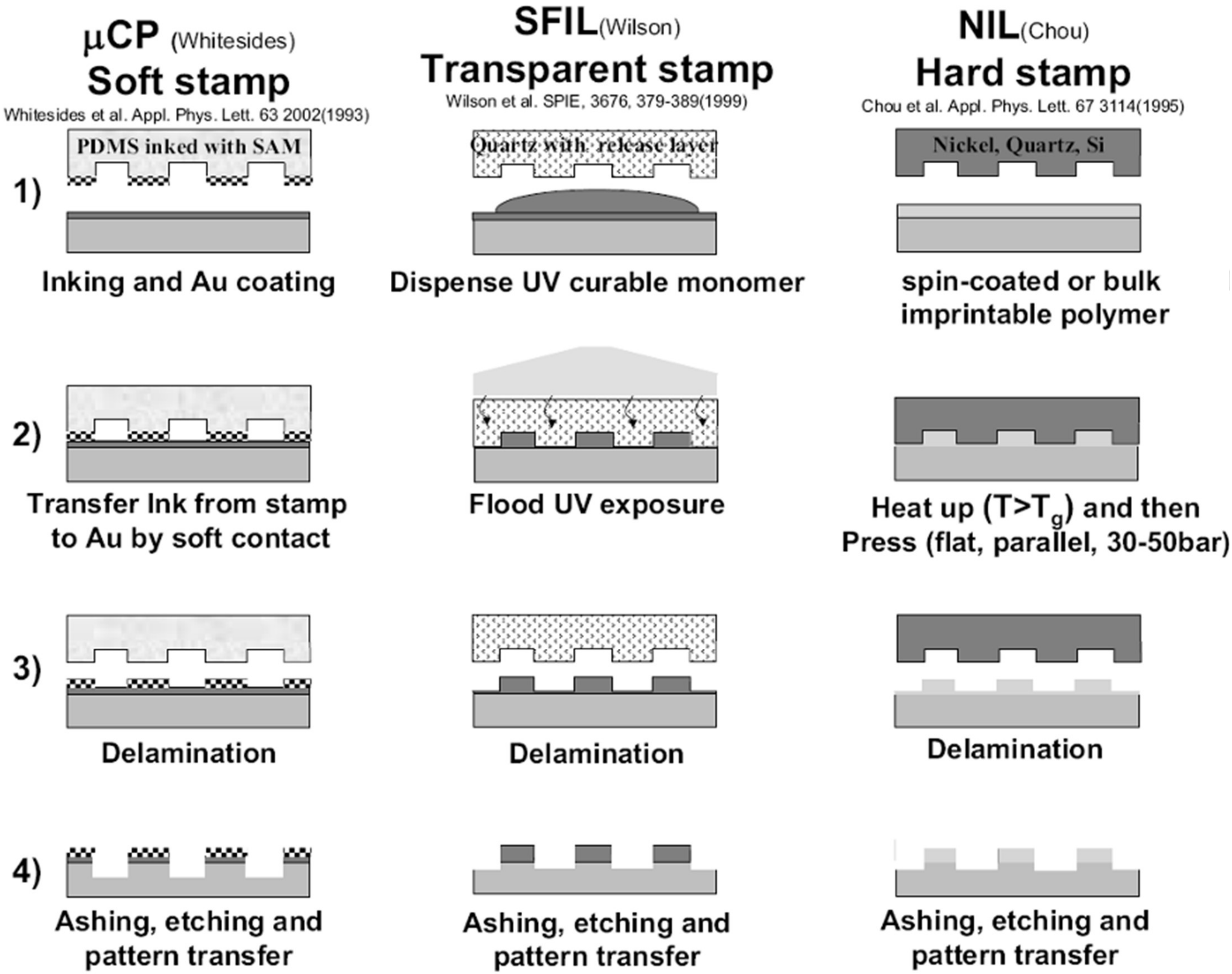
II SFIL Step and Flash nanoimprint lithography



Flood UV exposure

III NIL (some people call this Hot embossing)

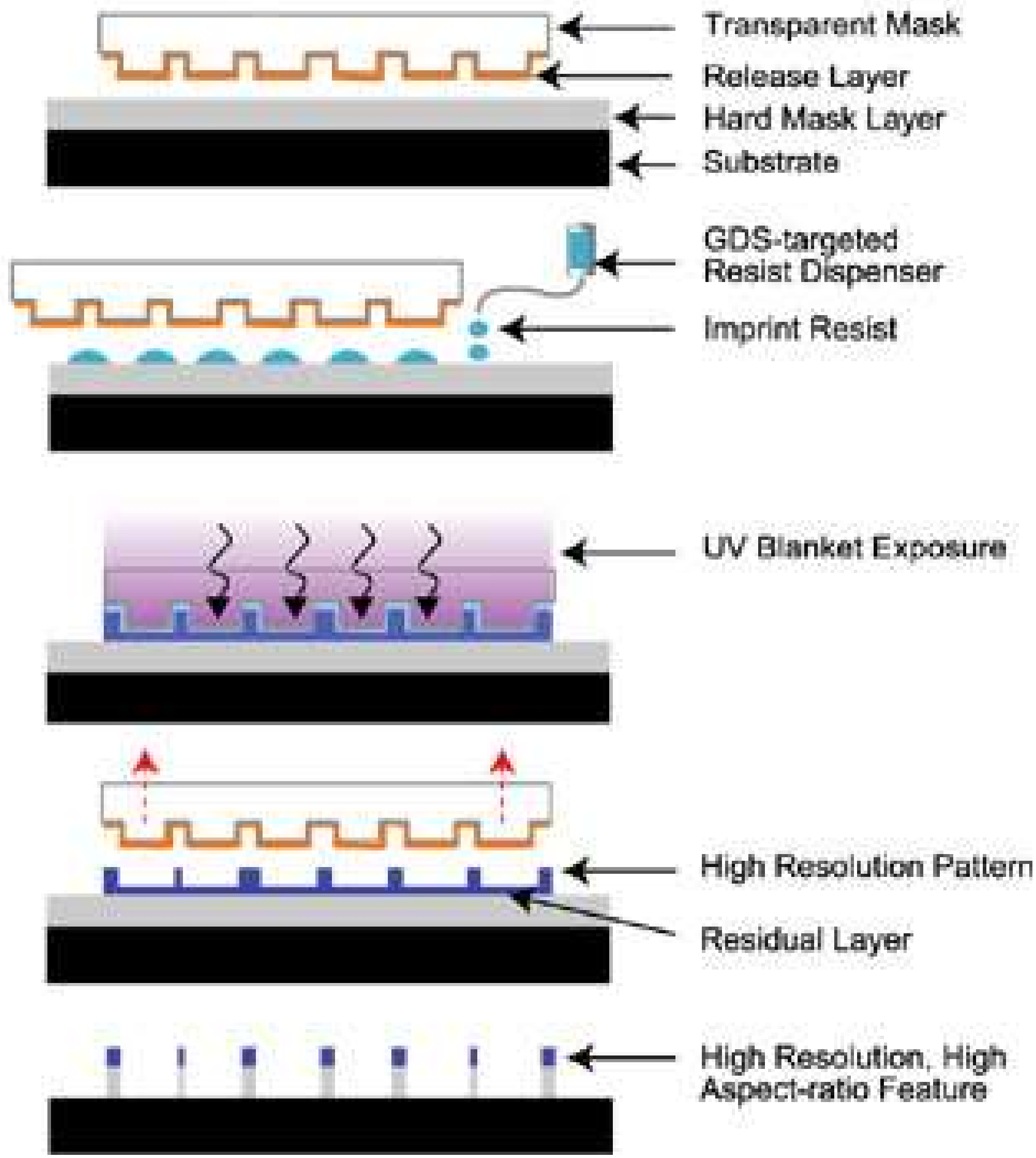
Heat up ($T>T_g$) and then Press (flat, parallel, 30-50bar)


μCP (Whitesides)
Soft stamp
Whitesides et al. Appl. Phys. Lett. 63 2002(1993)
PDMS inked with SAM
1)
Inking and Au coating
2)
Transfer Ink from stamp to Au by soft contact
3)
Delamination
4)
Ashing, etching and pattern transfer
SFIL(Wilson)
Transparent stamp
Wilson et al. SPIE, 3676, 379-389(1999)
Quartz with release layer
Dispense UV curable monomer
Flood UV exposure
Delamination
Ashing, etching and pattern transfer
NIL(Chou)
Hard stamp
Chou et al. Appl. Phys. Lett. 67 3114(1995)
Nickel, Quartz, Si
spin-coated or bulk imprintable polymer
Heat up (T>Tg) and then Press (flat, parallel, 30-50bar)
Delamination
Ashing, etching and pattern transfer

II SFIL Step and Flash nanoimprint lithography

Process Steps

1. **Orient substrate and imprint mask**
2. **Drop-on-Demand™ dispense of UV curable resist**
3. **Close gap and illuminate with UV** (Room Temperature, Low Pressure)
4. **Separate the mask from the substrate**
5. **Descum followed by hard mask etch**



II SFIL Step and Flash nanoimprint lithography

Process Steps

The fused silica surface, coated with a release layer, is gently pressed into a thin layer of low viscosity, silicon-containing monomer.

When illuminated by a UV lamp, the surface is polymerized into a solid layer.

Upon separation of the fused silica template (Mask), the circuit pattern is left on the wafer surface.

A residual layer of polymer between features is eliminated by an etch process, and a perfect replica of the pattern is ready to be used in semiconductor processing for etch or deposition.

III NIL (some people call this Hot embossing)

NIL

Stephen Y. Chou,
Professor of Engineering and the head of the NanoStructure Laboratory at Princeton University.

He pioneered his best-known work, nanoimprint lithography (NIL).

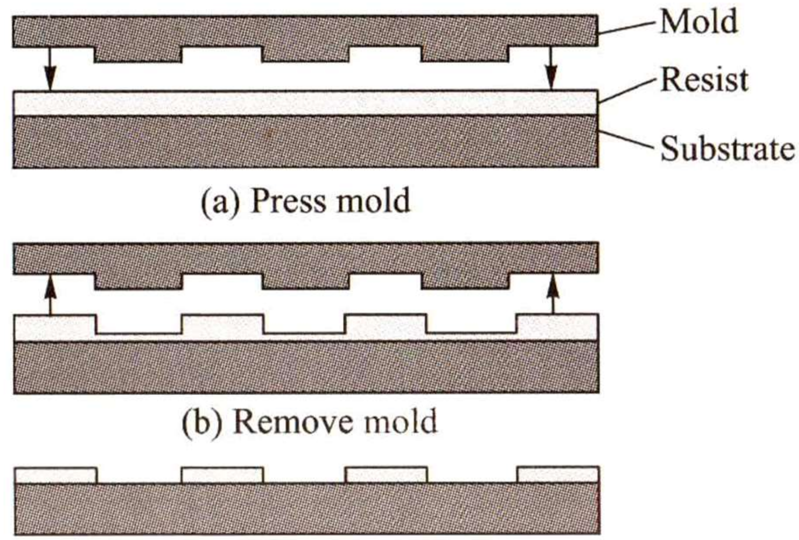
NIL is a revolutionary nanoscale patterning method that allows sub-10 nm patterning over large areas with high throughput and low cost in thermoplastic polymers.

III NIL

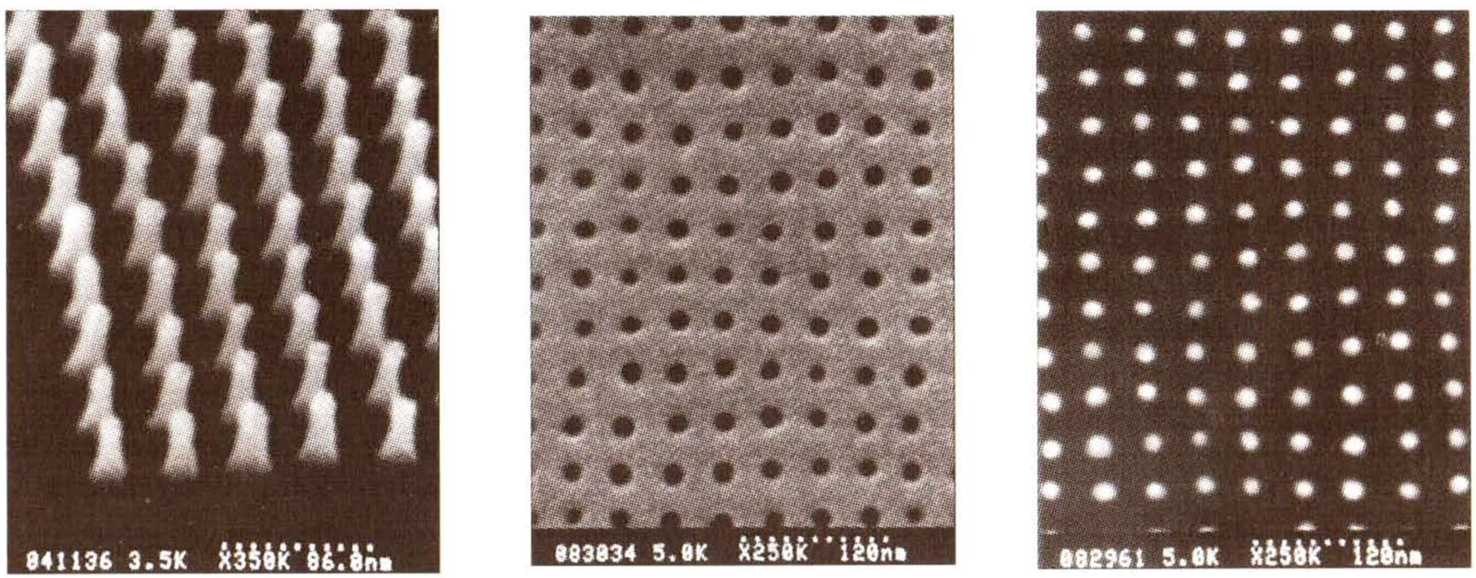
Process Steps

PMMA has typical Molecular mass from 5k to 1M
Glass transition temperature ~ 105C

Imprint conditions:
140-190C
600-1900 psi
41 – 131 bar



(c) RIE


(a) Nanoimprinting master stamp

(b) Nanodots array in PMMA by imprinting

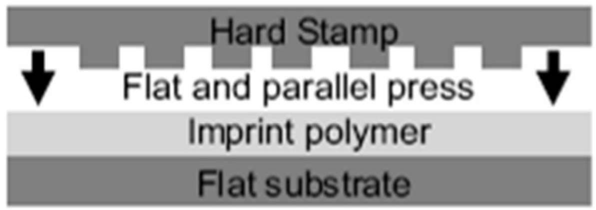
(c) Metal dots obtained by lift-off from the hole array in PMMA

III NIL

Process Steps

Alignment is an issue!

- **Contact**



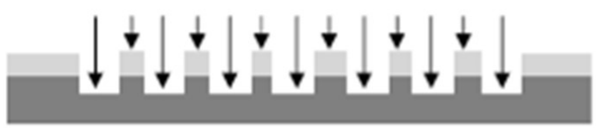
- **Press**

Temperature, and then Press

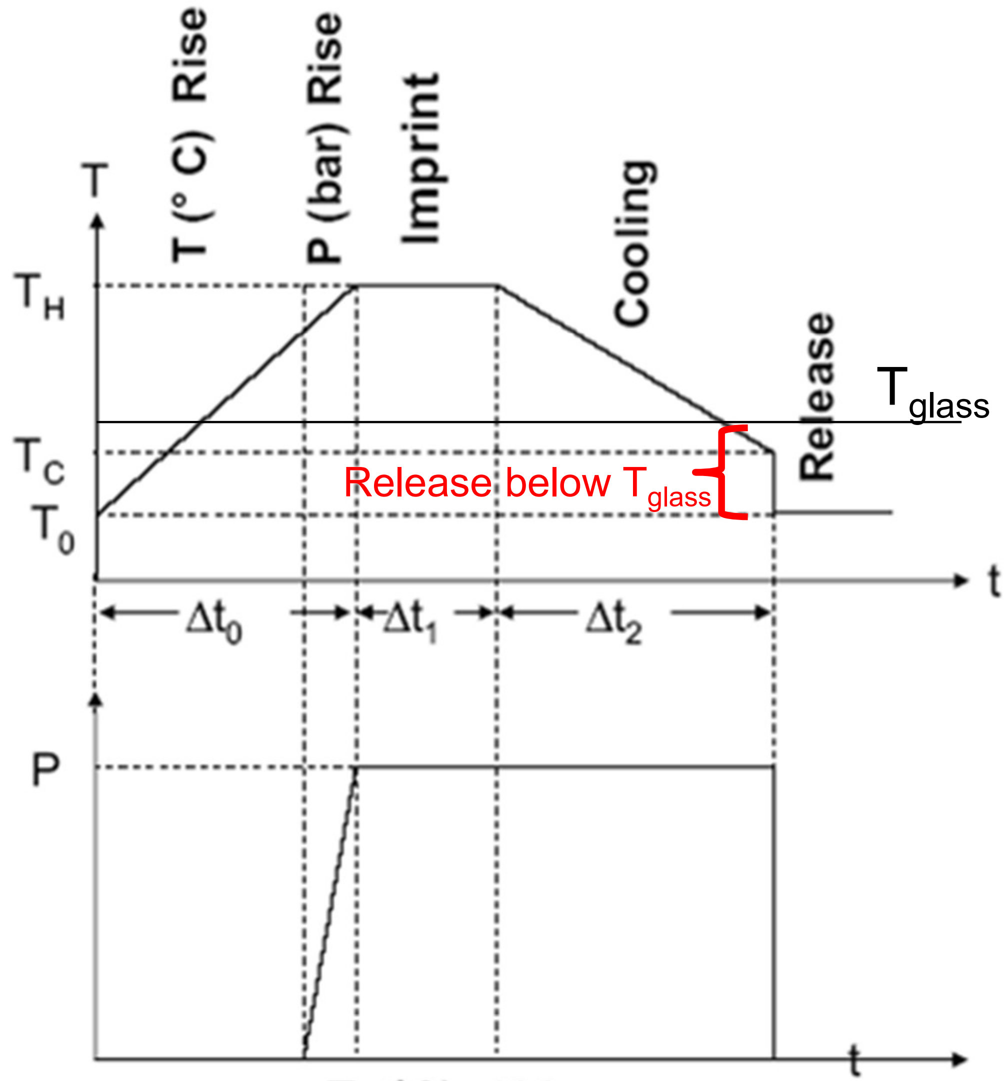
- **Delaminate**

Cooling+Release+delamination

- **Pattern transfer**



Ashing, etching and pattern transfer



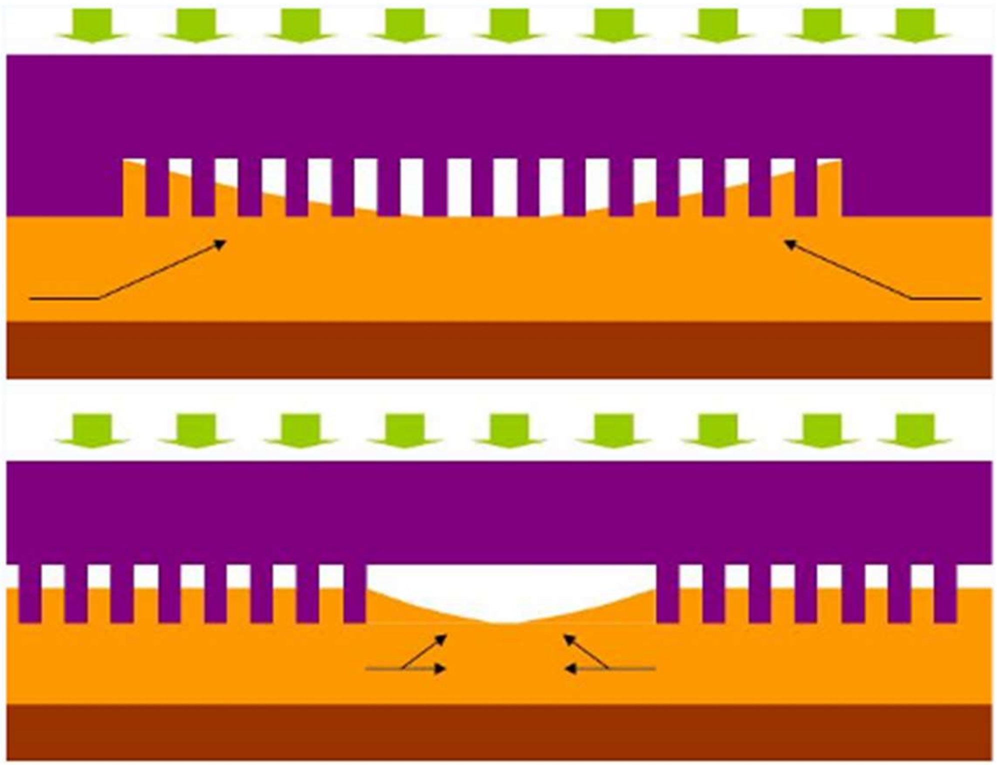
T_H(°C)=190
T_C(°C)=100
P(bar)=40
Δt_1(s)=300
Δt_2(s)=300

III NIL

Process Considerations

Nanoimprint lithography relies on displacing polymer. This could lead to systematic effects over long distances. For example, a large, dense array of protrusions will displace significantly more polymer than an isolated protrusion. Depending on the distance of this isolated protrusion from the array, the isolated feature may not imprint correctly due to polymer displacement and thickening.

Resist holes can form in between groups of protrusions.
Likewise, wider depressions in the template do not fill up with as much polymer as narrower depressions, resulting in misshaped wide lines.
In addition, a depression at the edge of a large array fills up much earlier than one located in the center of the array, resulting in within-array uniformity issues.

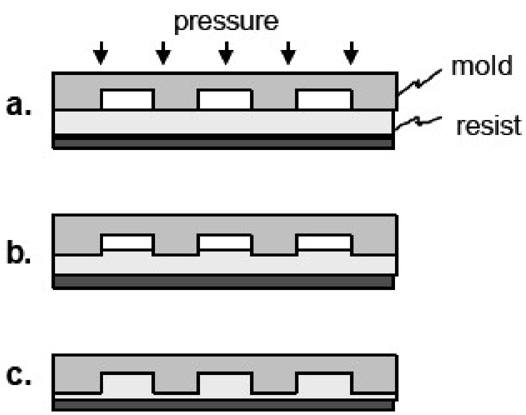


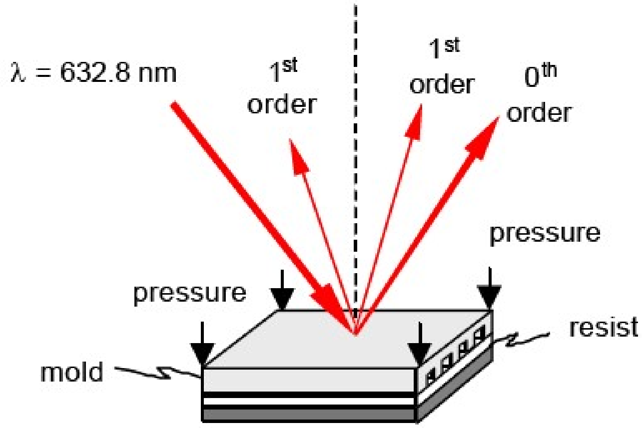
III NIL

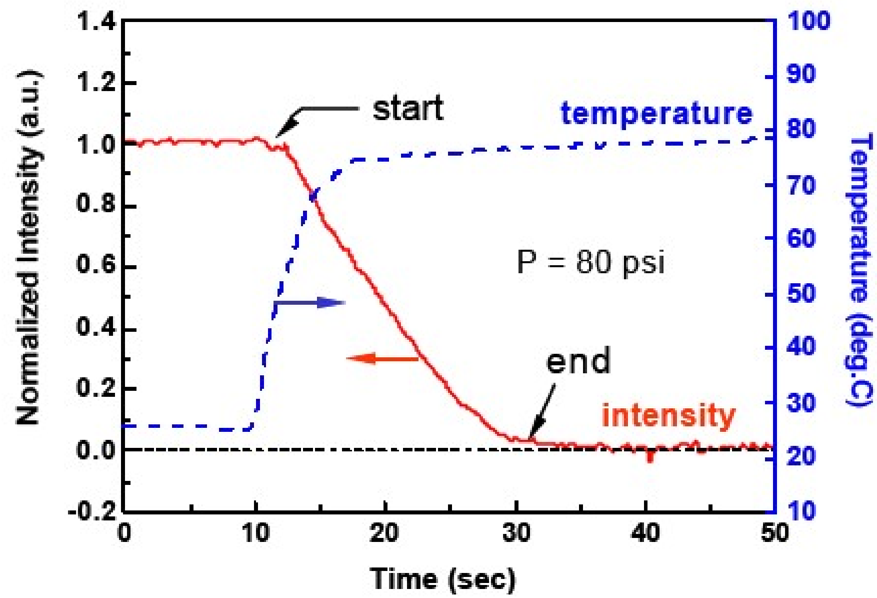
New Developments in Real-time Imprint Monitoring by Scattering-of-light (RIMS)

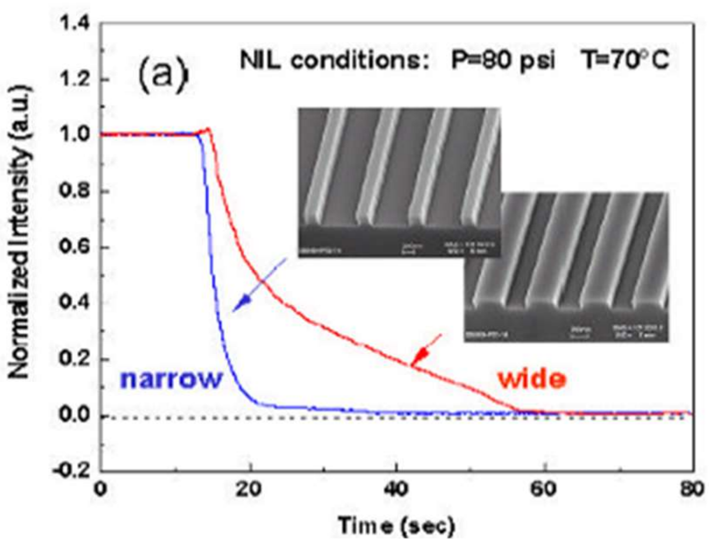
Zhaoning Yu, He Gao, and Stephen Y. Chou
Nanostructure Laboratory, Department of Electrical Engineering
Princeton University, Princeton, NJ 08544

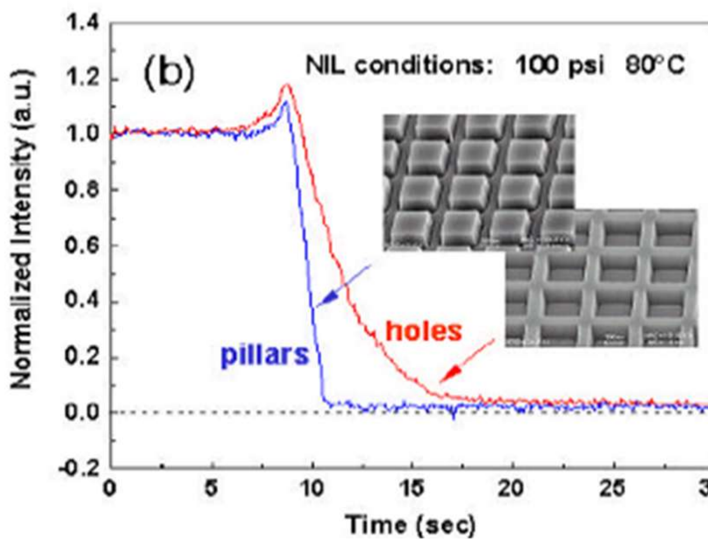
IOP 2007











Size dependent imprinting time!

III NIL

Smallest NIL I have seen!

Polymer Imprint Lithography with Molecular-Scale Resolution

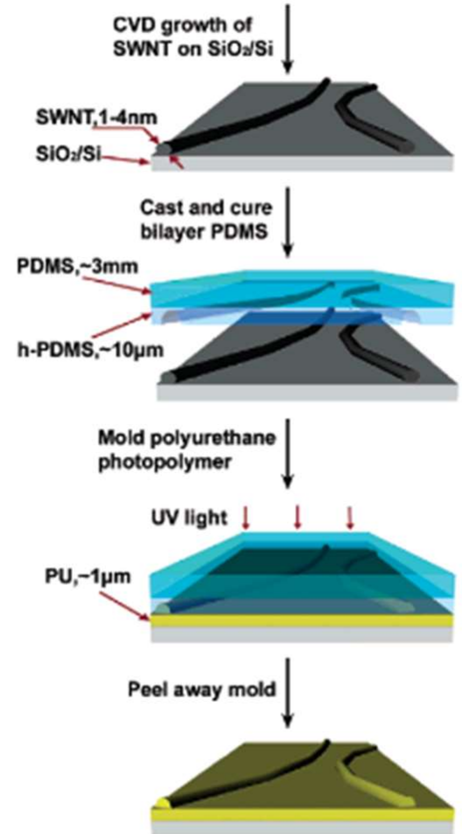
Feng Hua, Yugang Sun, Anshu Gaur, Matthew A. Meitl, Lise Bilhaut, Lolita Rotkina, Jingfeng Wang, Phil Geil, Moonsub Shim, and John A. Rogers*

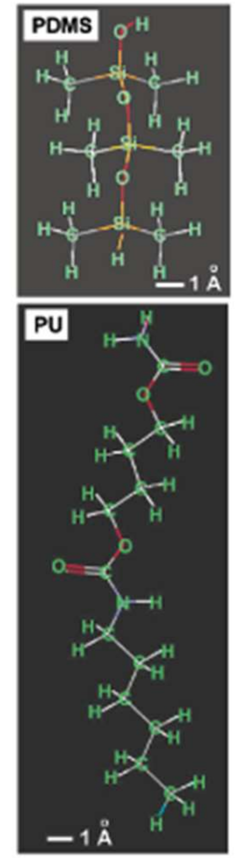
Department of Materials Science and Engineering, Department of Chemistry, Beckman Institute and Seitz Materials Research Laboratory, University of Illinois at Urbana/Champaign, Urbana, Illinois 61801

Anne Shim*

Dow Corning Corporation, Midland, Michigan 48686

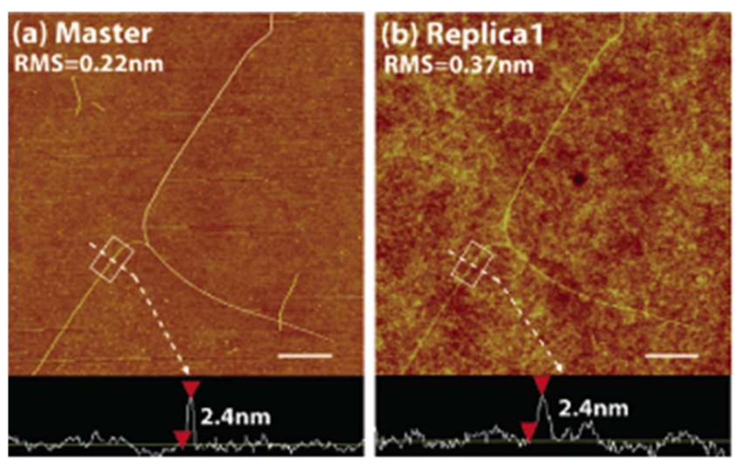
Received October 5, 2004; Revised Manuscript Received October 21, 2004





ABSTRACT

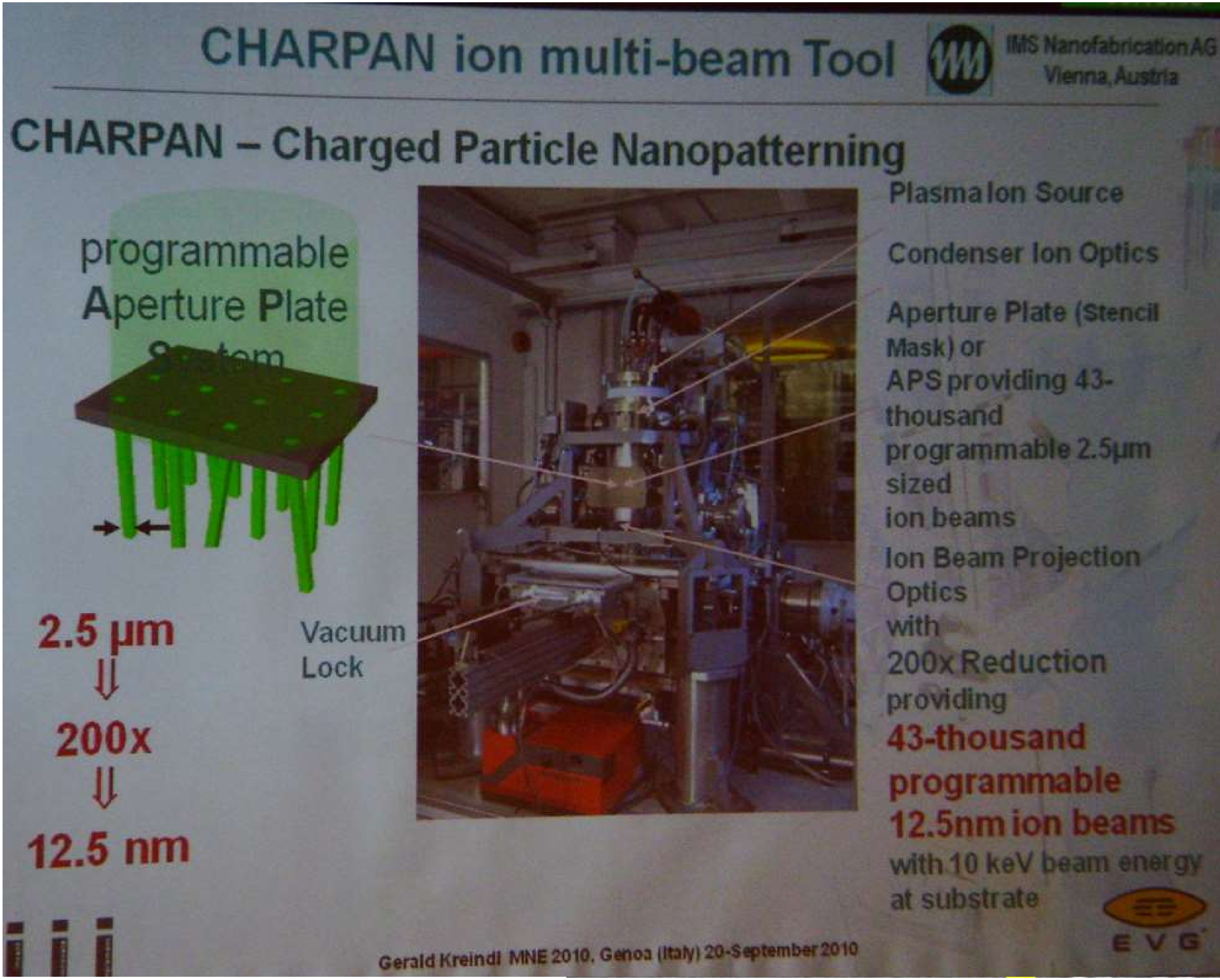
We show that small diameter, single-walled carbon nanotubes can serve as templates for performing polymer imprint lithography with feature sizes as small as 2 nm – comparable to the size of an individual molecule. The angstrom level uniformity in the critical dimensions of the features provided by this unusual type of template provides a unique ability to investigate systematically the resolution of imprint lithography at this molecular scale. Collective results of experiments with several polymer formulations for the molds and the molded materials suggest that the density of cross-links is an important molecular parameter that influences the ultimate resolution in this process. Optimized materials enable reliable, repetitive patterning in this single nanometer range.



In 2016 MRS Fall meeting I saw 0.3 nm step height reproduction in PMMA NIL!

NANO LETTERS

2004
Vol. 4, No. 12
2467–2471


CHARPAN ion multi-beam Tool
IMS Nanofabrication AG
Vienna, Austria
CHARPAN – Charged Particle Nanopatterning
programmable
Aperture Plate
System
2.5 µm
⇓
200x
⇓
12.5 nm
Vacuum
Lock
Plasma Ion Source
Condenser Ion Optics
Aperture Plate (Stencil Mask) or APS providing 43-thousand programmable 2.5µm sized ion beams
Ion Beam Projection Optics with 200x Reduction providing
43-thousand programmable 12.5nm ion beams
with 10 keV beam energy at substrate
EVG
Gerald Kreindl MNE 2010, Genoa (Italy) 20-September 2010

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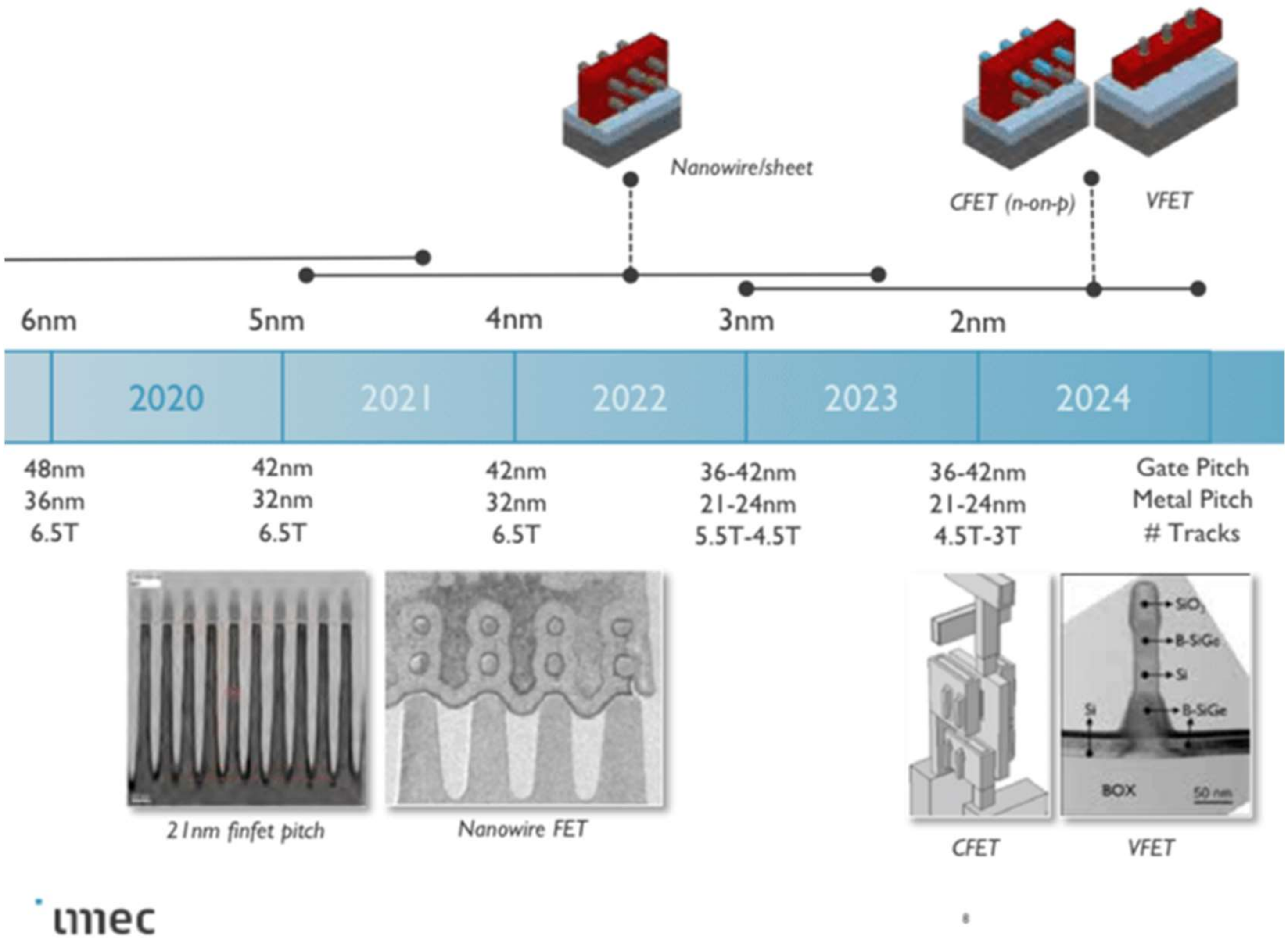
Im

Issues in implementing NIL on large scale

<u>Alignment of multiple imprints</u> 1-2 nm alignment is needed in IC chip fabrication

<u>This is a very big challenge in NIL!</u>

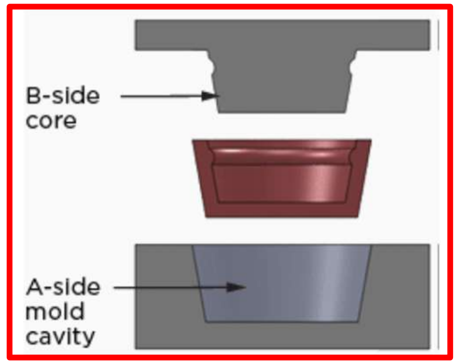


3D Printing
At Nanoscale

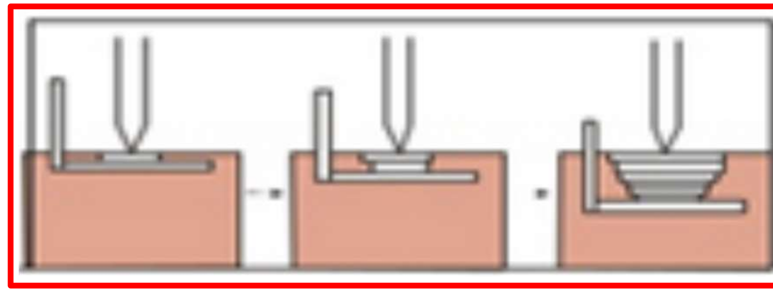
What are (fundamental) methods to structure material?

Four Manufacturing Principles

- **Subtractive**–Material is successively removed from a solid block until the desired shape is reached, such as turning, drilling, grinding and milling
  FIB sputtering can be subtractive

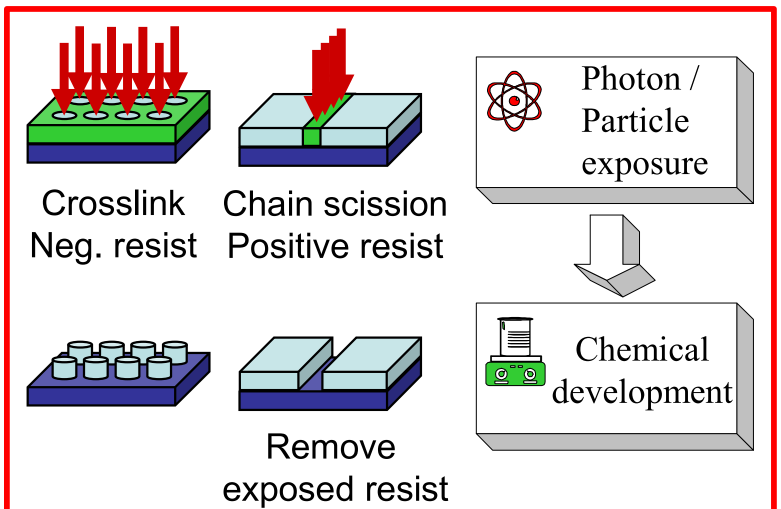


- **Formative**–Mechanical forces/heat are applied to material to form it into the desired shape, such as bending, casting, molding and forming



- **Additive**–Successive layers of material are laid down until the desired shape is created, such as SLA, FDM and SLS
  Charges particle beam assisted deposition

- **Lithography**–Change material
  Development
  Etching

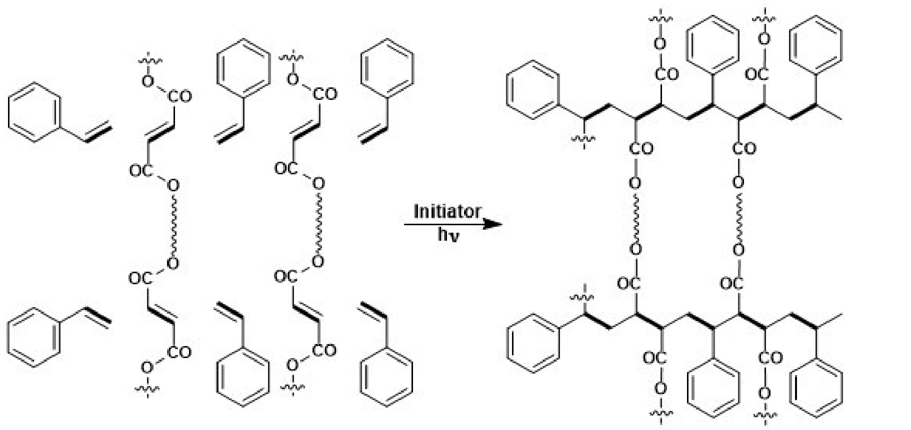


Photopolymerization (recap)

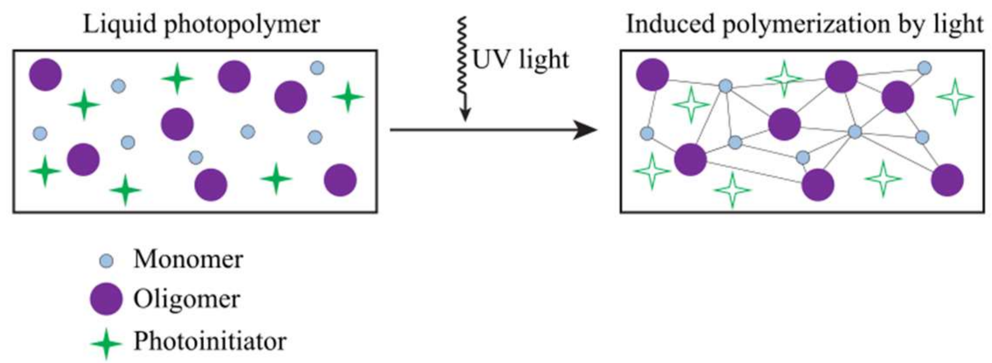
Photon absorption can cause **Photopolymerization** reactions (cross linking):

Chain-growth polymerizations is initiated via absorption:

Directly by the monomer Or Photo active compound (PAC)



Monomeric styrene and oligomeric acrylates can be used to produce crosslinked polymeric structures through photopolymerization



Several forms of 3D printing use photopolymerization:

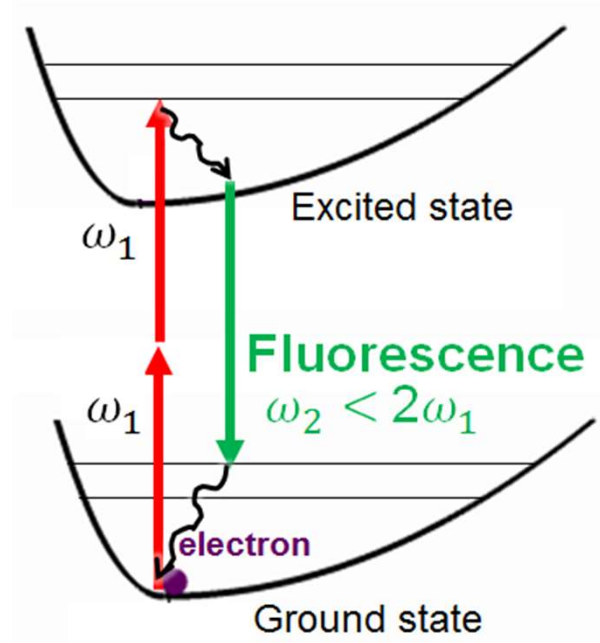
- ❖ Two-photon absorption (TPA); 3D photopolymerization
- ❖ Layer-by-layer stereo lithography (SLA)

Nano scale 3DP
Two-photon absorption

Two-photon absorption (**TPA**) process:

Two photons of identical (or different) frequencies are absorbed by a molecule, resulting in molecular excitation.

Two-photon absorption is a second-order process, several orders of magnitude weaker than linear absorption.



Linear absorption ← → TPA

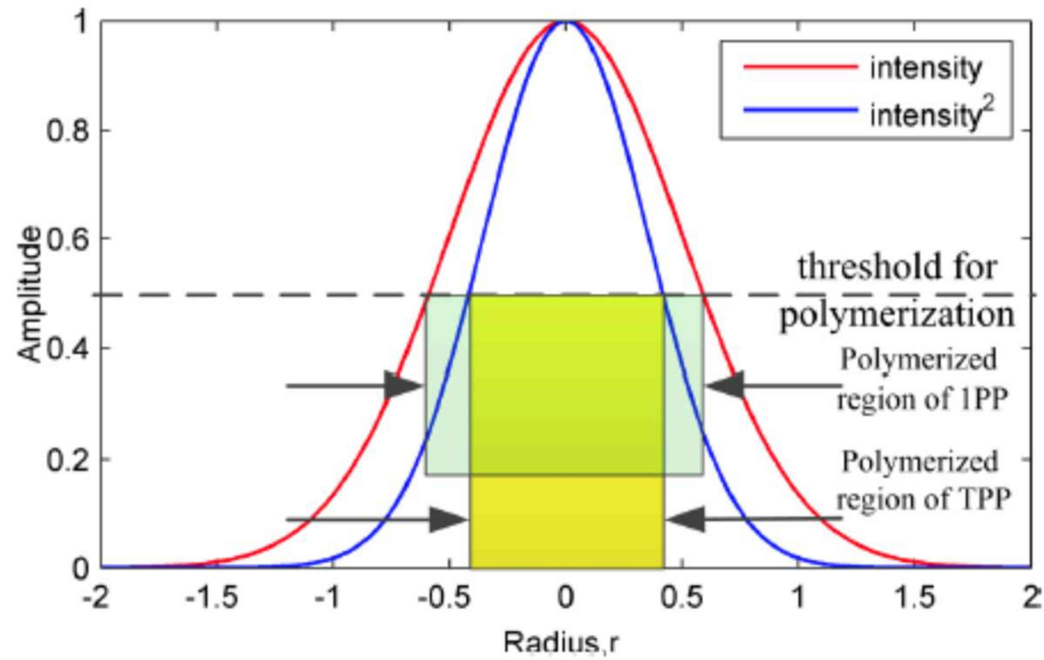
The atomic transition rate in **TPA** depends on the **square** of the light intensity:

A nonlinear optical process

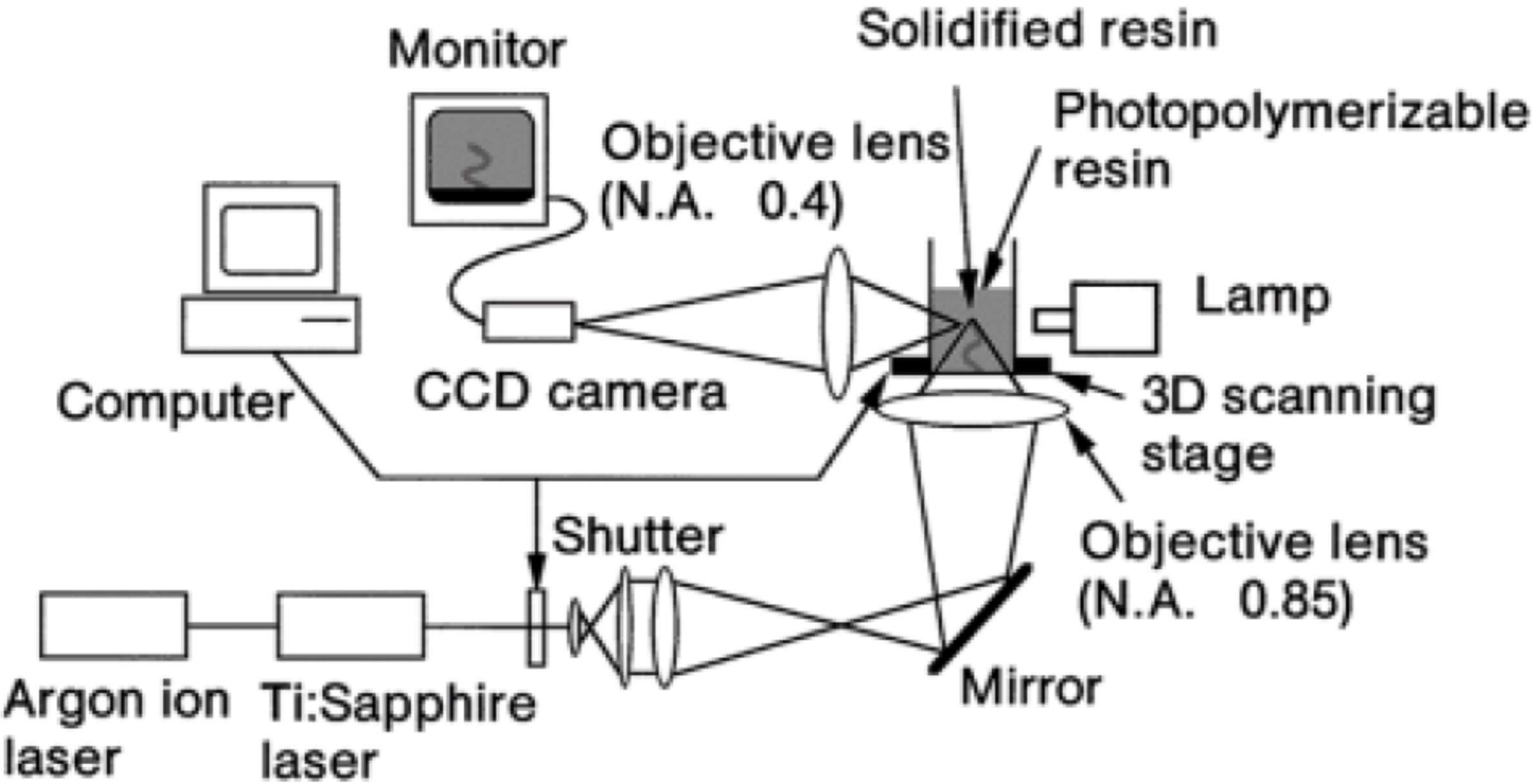
Therefore it can result in finer features!

Compared to SLA

TPA can dominate over linear absorption at **high intensities**



Nano scale 3DP
Two-photon absorption System



S. Maruo et al., Opt Lett
22 (2), 132 (1997)

For info

Nano scale 3DP
Methods to improve the resolution in TPA

Quenching

In 2006, Park et al. studied the quenching effect
➔ Improved lateral resolution approaching 100 nm using a radical quencher (2,6-di-tert-butyl-4-methylphenol (DBMP))

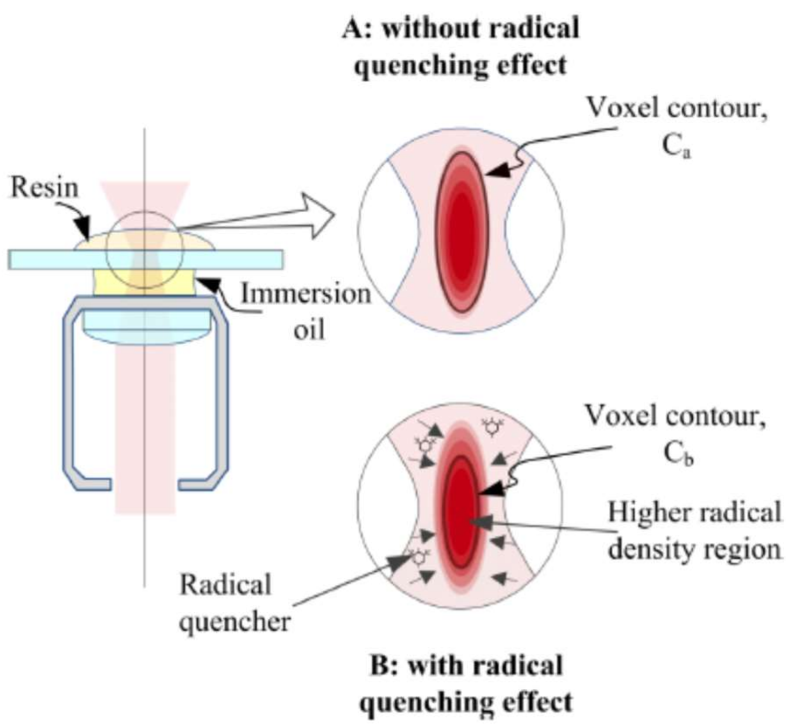
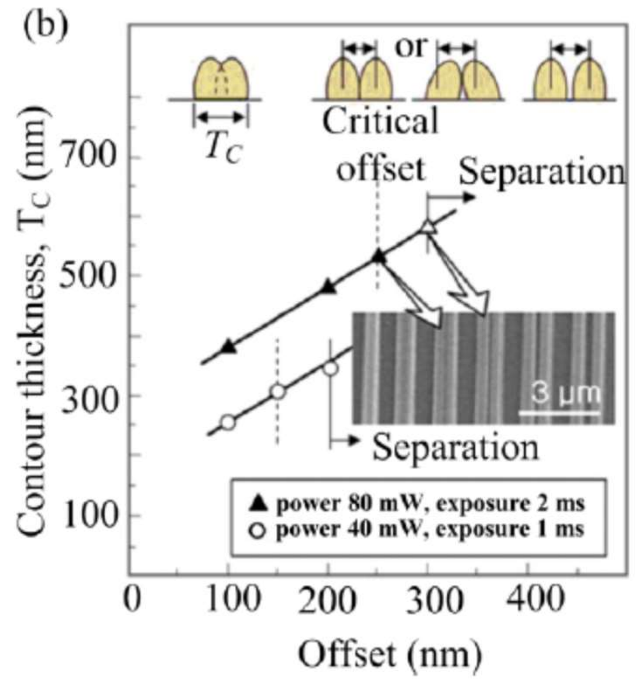


FIG. 9. Schematic illustration of radical quenching mechanism. In case the radical quencher is mixed into the original resin the voxel size (C_b) is reduced comparing to the case of the original resin only used (C_a). Reprinted with permission from S. H. Park et al., Macromol Res **14** (5), 559 (2006). Copyright 2006 Springer.

Quenching effect reduces the mechanical strength of polymerized structures due to their short chain lengths.

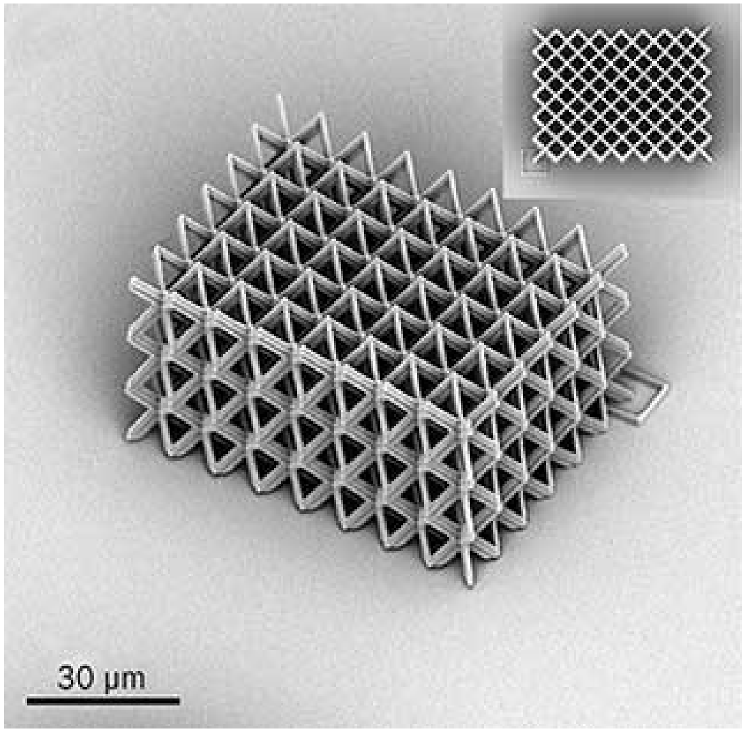
Exposure strategy

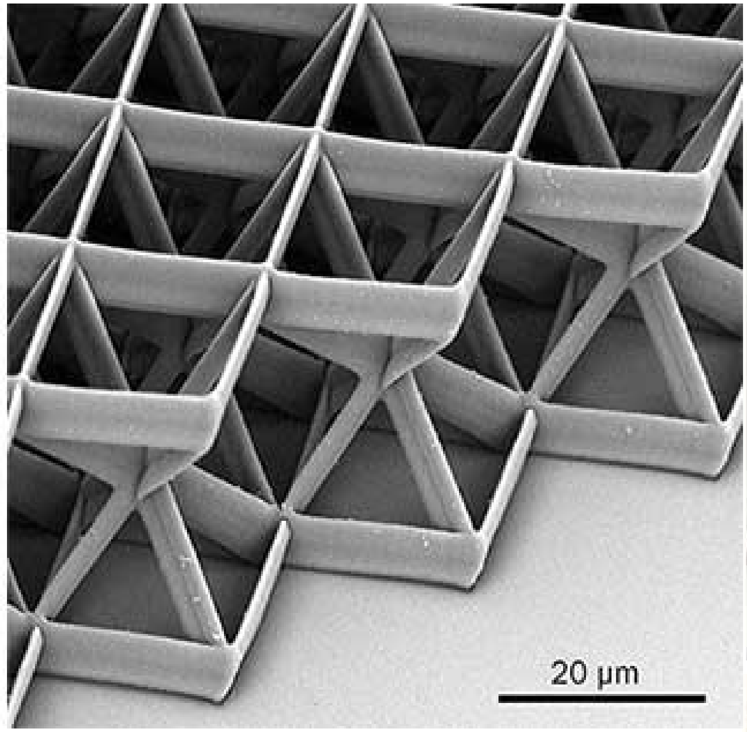
In 2007 Yang et al varied exposure strategies in TPA

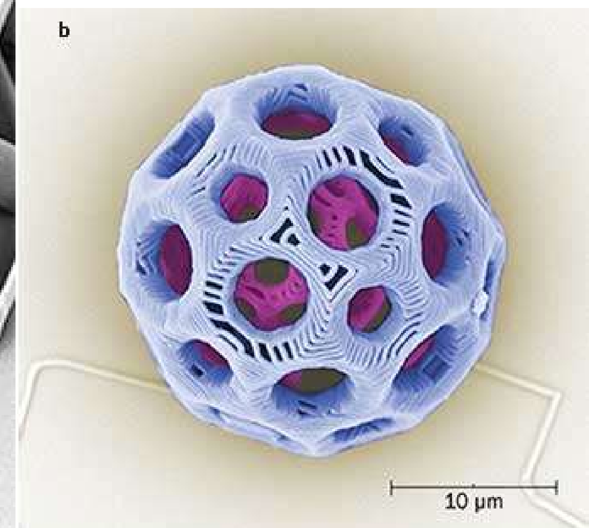


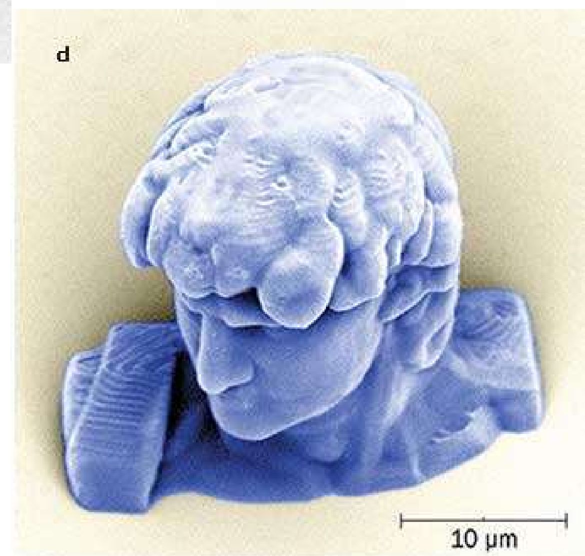
D.-Y. Yang et al., Applied Physics Letters 90 (7), 079903 (2007)

Nano scale 3DP
Two-photon polymerization manufacturing









There are two key reasons that render TPA an attractive solution for the fabrication of microstructures:

1) TPA is intrinsically a 3D writing technique; it does not require a layer-by-layer approach to create complex objects
2) TPA can also create microstructures with submicron feature sizes in a straightforward manner. *These characteristics originate from the nonlinear optical nature of light absorption in TPA and from the chemistry of the polymerization.*

Forms of 3DP

Stereo lithography (SLA)

SYSTEMS

1984-1988

1984
Charles W. Hull developed the first 3D printing technique and named it as **Stereo Lithography (SLA)**

- 1986
  Charles W. Hull and entrepreneur Raymond S. Freed found **3D Systems Inc.**(USA)

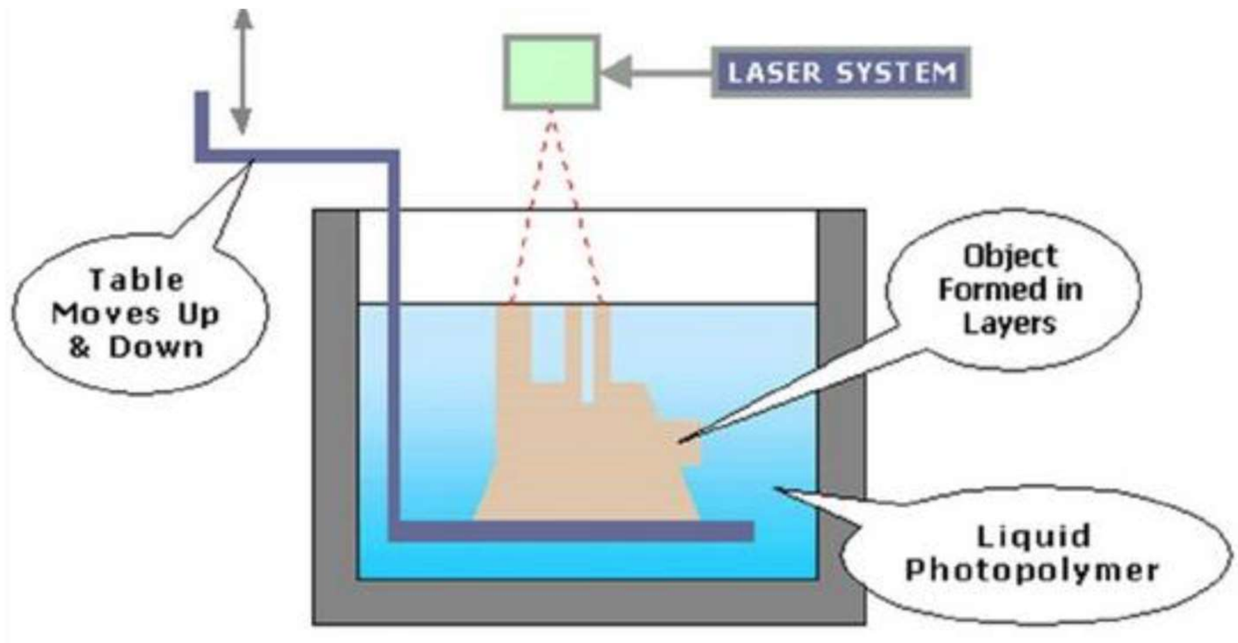
- 1988
  The **first** commercial system marketed

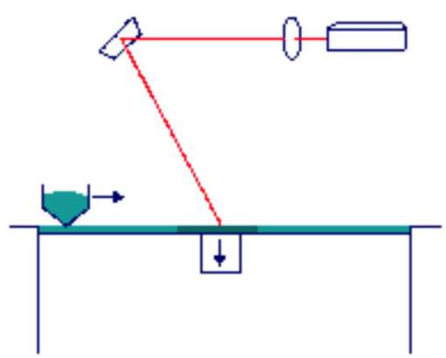
Forms of 3DP

Stereo lithography (SLA)

SLA builds 3D models from **liquid photosensitive polymers** that solidify when exposed to **ultraviolet light or laser**.

- Capable of creating **high accuracy** parts (+/-50 um)
- **Good surface finish**





Forms of 3DP

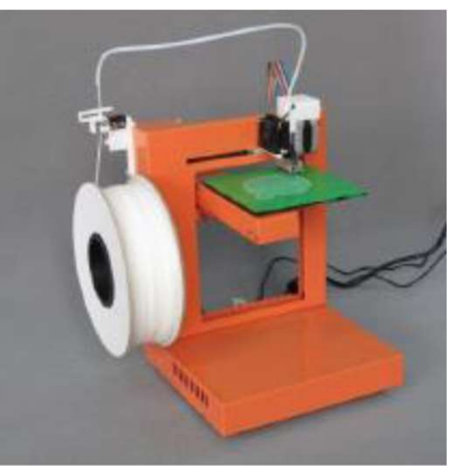
Fused (filament) Deposition Modeling (FDM)

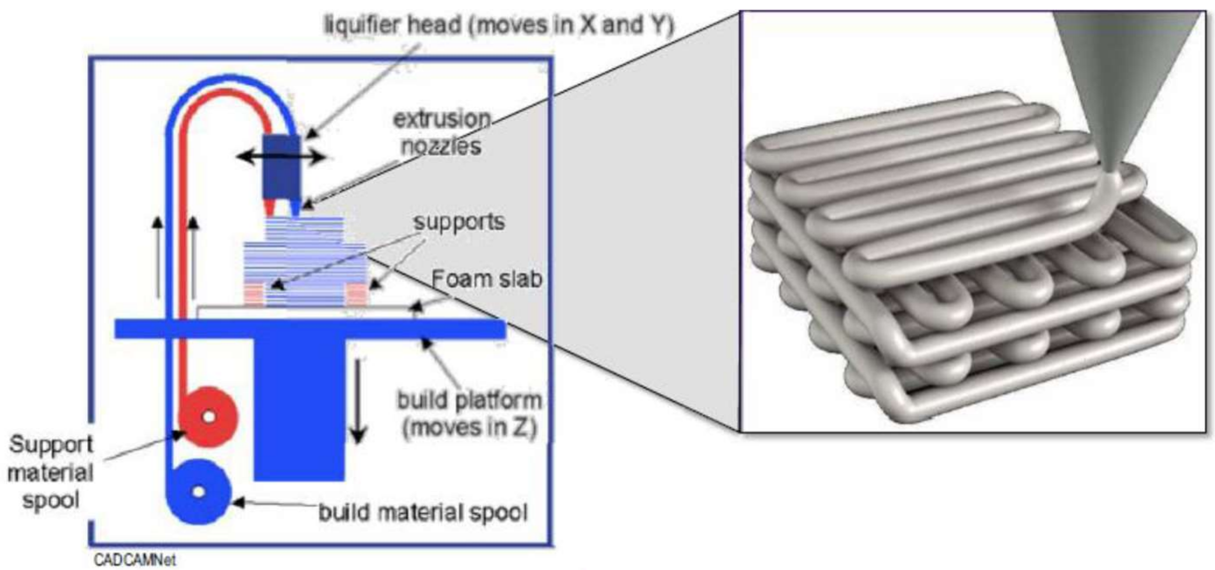
FDM is a method that extrudes **solid thermoplastic** material (such as ABS, PC, PLA, PPS), layer-by-layer, to build a model.

•A thread of plastic is fed into an **extrusion head**, where it is heated into a **semi-liquid state** and extruded through a very small hole onto the precious layer of material

•Support material is also laid down in a similar manner

Temperature of work piece and extrusion nozzle have to be tuned such that the thermoplastic can melt during extrusion and solidify when deposited but still gives good adhesion to the next layer without compromising the earlier layers …





For info

Forms of 3DP

Fused Deposition Modeling (FDM)

Differences in physical and chemical properties cause weak bond strength between dissimilar materials in multi-material FDM parts.

Properties of PLA and PCL filaments.

	Symbol	PLA	PCL
Tensile strength (MPa)	σ_b	60	18
Elongation at break (%)	δ	3.0	11
Flexural strength (MPa)	σ_{bb}	97	29
Flexural modulus (MPa)	E	3600	940
Density (g/cm^3)	ρ	1.25	1.16
Melting temperature (°C)	T_m	180	60
Glass transition temperature (°C)	T_g	60	−60
Decomposition temperature (°C)		280	230

The bonding-layer temperature effects on the tensile strength of polycaprolactone (PCL)/polylactic acid (PLA)

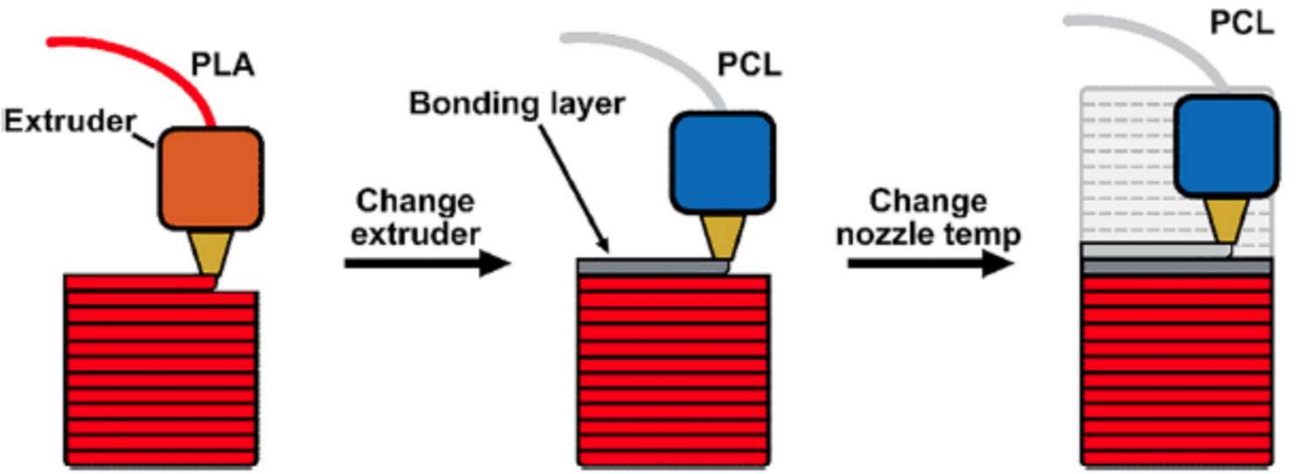


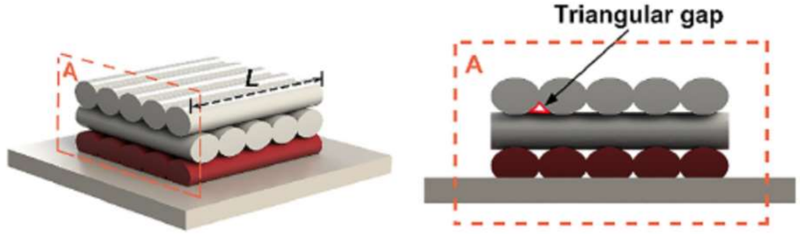
Fig. 2. Schematic of the principle of the SLTAT method.

PCL/PLA parts prepared with this method had 28% higher tensile strength than unprocessed parts when the bonding-layer temperature was 130 °C.

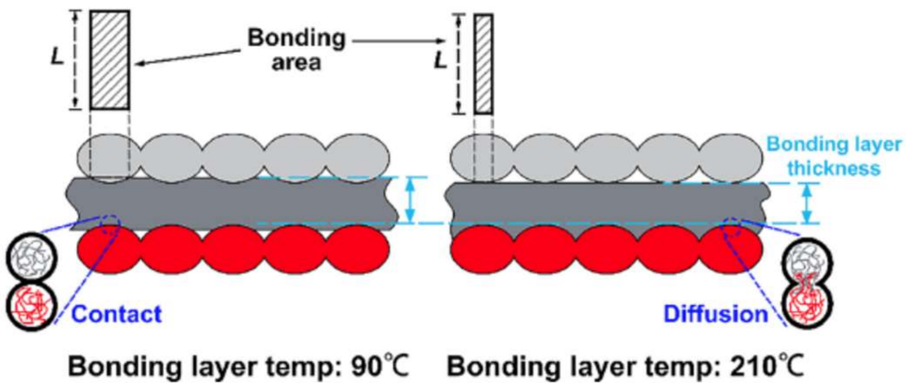
Composites Part A 115 (2018) 22–30

For info

Forms of 3DP
Fused Deposition Modeling (FDM)



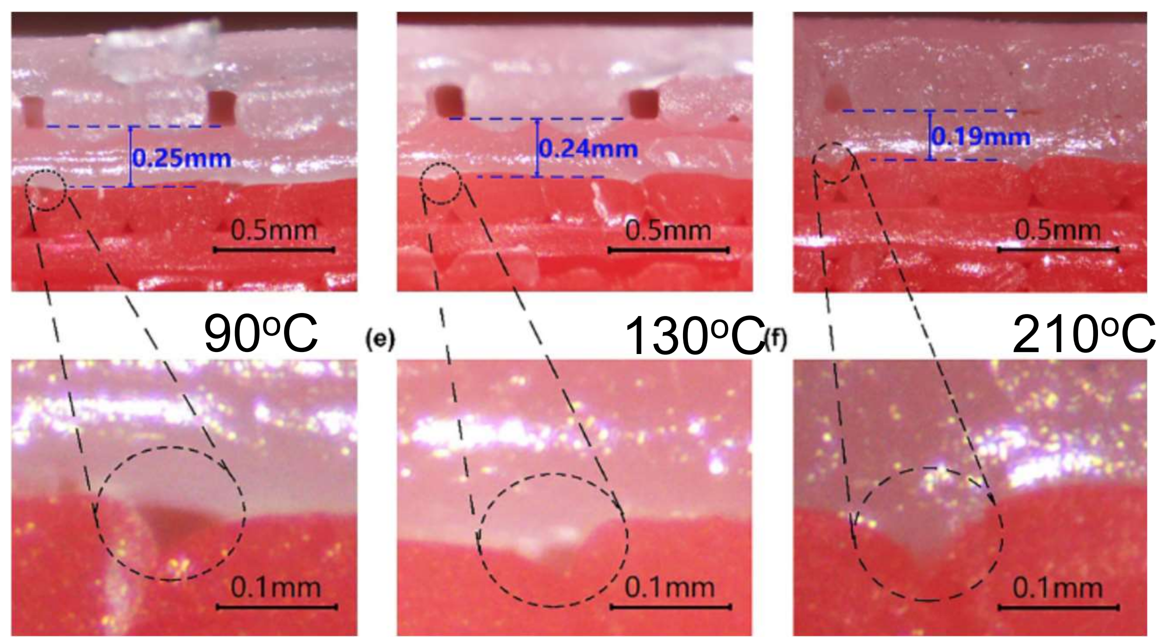
Ideal cross section of FDM



Cross section of PCL/PLA parts with different bonding layer temperature

Freeze-fractured test samples

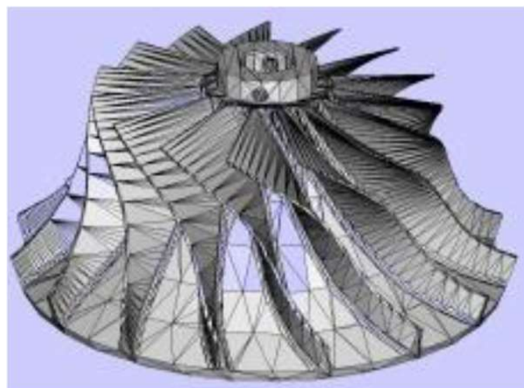
Bonding layer

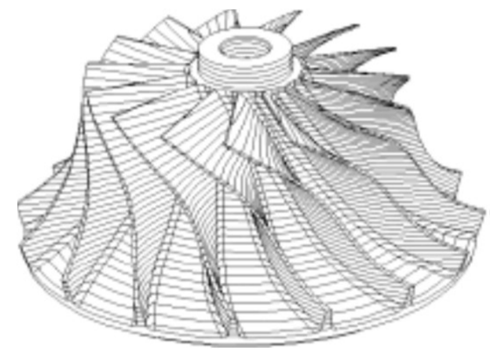


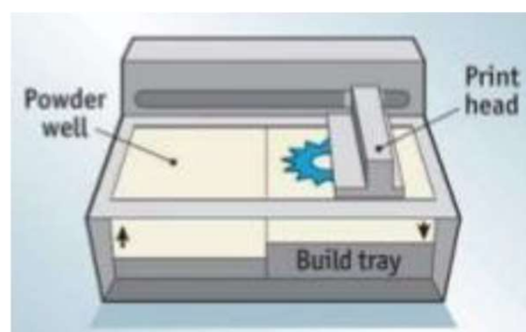
Forms of 3DP

Typical steps of the 3D printing process

1. **3D CAD Modeling**
2. **Convert to STL file**
3. **Transfer to 3DP machine and slice STL file**
4. **Build**
5. **Remove & post-processing**







For info

Forms of 3DP

Fused Deposition Modeling (FDM)

Q = volumetric flow rate of extruded material
P_{max} = maximum system pressure
t_{layer} = time to deposit a single layer
D_E = diameter at the exit of the extrusion head
L_E = length of the extruder exit region
D_n = diameter of the nozzle leading up to the extruder exit
L_n = length of the nozzle leading up to the extruder exit
T_{amb} = ambient temperature of the build chamber
T_{dep} = deposition temperature
T_{sub} = substrate temperature of successive deposited beads
h = deposited bead height
w = deposited bead width
H = height of the overall structure
L = length of the overall structure

Nozzle clogging is one of the most significant process errors in 3D printers, and it affects the quality of the prototyped parts in terms of geometry tolerance, surface roughness, and mechanical properties.

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Fused Filament Fabrication (FFF)
Big Area Additive Manufacturing (BAAM)
Direct Write (DW)

Table 1
Typical printing parameters for each printing platform.

Parameter	FFF	BAAM	DW	Units
Volume Flow Rate (Q)	1.18×10^{-3}	5.25	7.88×10^{-4}	cm^3/s
Max Pressure (P_{max})	0.57*	6.89	1.38	MPa
Layer Time (t_{layer})	60	60	60	s
Exit Diameter (D_E)	0.04	0.76	0.02	cm
Exit Length (L_E)	0.08	0.86	1.0	cm
Nozzle Diameter (D_n)	0.175	1.02	1.0	cm
Nozzle Length (L_n)	1.0	6.4	5.0	cm
Bead Height (h)	0.02	0.38	0.01	cm
Bead Width (w)	0.03	0.84	0.02	cm
Structure Height (H)	0.40	7.6	0.20	cm

* Material dependent.

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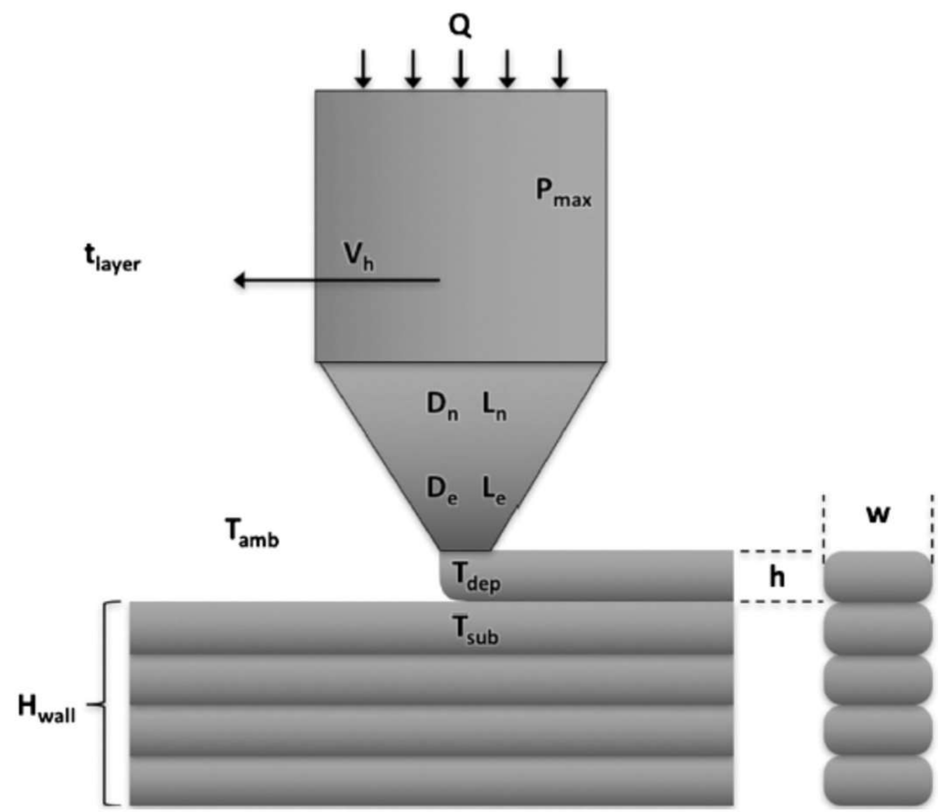


Fig. 1. Deposition parameters for typical extrusion-based deposition platforms.

Forms of 3DP

Major 3D (Rapid) Prototyping Systems

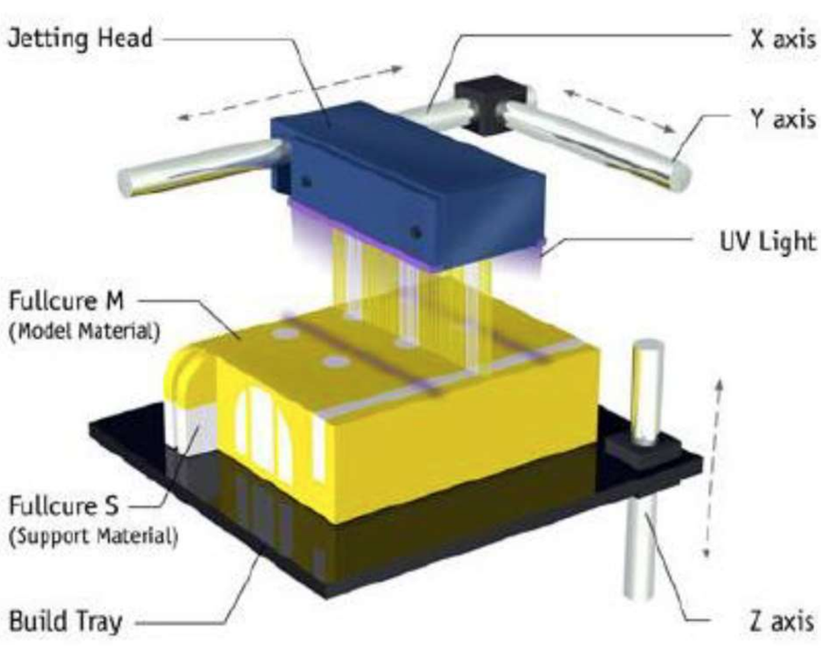
- Stereolithography Apparatus (SLA) –*liquid*
  (Chuck Hull, 3D System, 1986)
- Solid Ground Curing (SGC) –*liquid*
- Two photon absorption (TPA) – *liquid (Nano scale possible)*
- Laminated Object Manufacturing (LOM) -*solid*
- Fused Deposition Modeling (FDM) -*solid*
- Selective Laser Sintering (SLS) –*powder*
- 3D Printing (3DP), -*powder*

Forms of 3DP

PolyJet Technology

PolyJet technology is a method in which droplets of a **liquid photo-sensitive resin** are selectively deposited, and simultaneously solidified by a **UV lamp**.

- **Multiple nozzles** to speed up the process
- **Multiple materials** can be used to construct the same part for added functionality or aesthetics

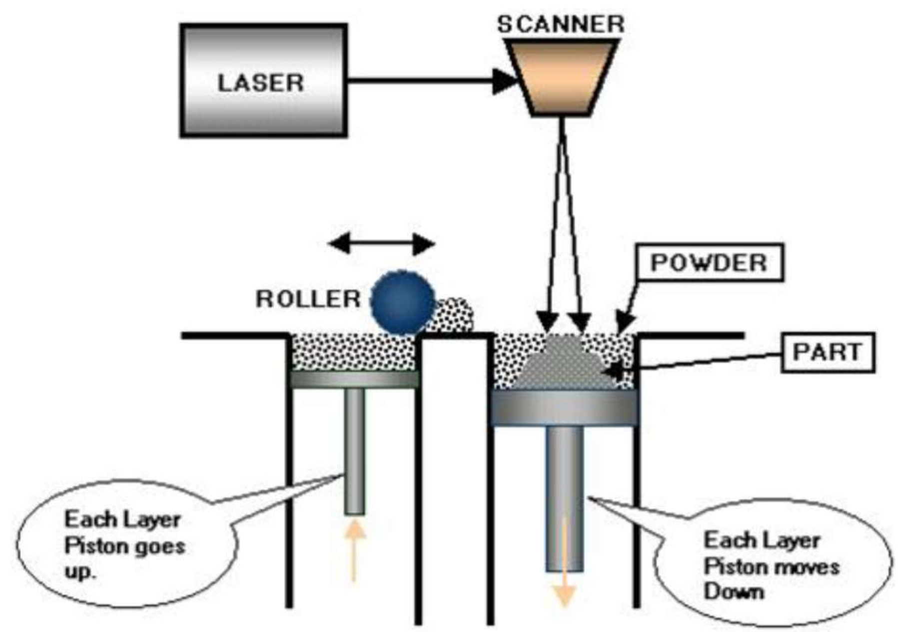


The Objet PolyJet Process

Selective Laser Sintering (SLS)

SLS is a process in which **powder** particles are selectively sintered (fused) together by heating with a **laser**.

- A very thin layer of powder is applied to the building platform
- A carbon dioxide laser melts the desired pattern into the powder and another thin layer of power is added to the platform
- The material can be **polymers, metals, ceramics or sand**
- No need to create a structure to support the part



Forms of 3DP

	NAME	TITLE	FILED	COUNTRY
	Housholder	Molding process	December 1979	U.S.
	Murutani	Optical molding method	May 1984	Japan
	Masters	Computer automated manufacturing process and system	July 1984	U.S.
	André et al.	Apparatus for making a model of an industrial part	July 1984	France
SLA	Hull	Apparatus for making three-dimensional objects by stereolithography	August 1984	U.S.
	Pomerantz et al.	Three-dimensional mapping and modelling apparatus	June 1986	Israel
LOM	Feygin	Apparatus and method for forming an integral object from laminations	June 1986	U.S.
	Deckard	Method and apparatus for producing parts by selective sintering	October 1986	U.S.
	Fudim	Method and apparatus for producing three-dimensional objects by photosolidification; radiating an uncured photopolymer	February 1987	U.S.
	Arcella et al.	Casting shapes	March 1987	U.S.
FDM	Crump	Apparatus and method for creating three-dimensional objects	October 1989	U.S.
	Helinski	Method and means for constructing three-dimensional articles by particle deposition	November 1989	U.S.
	Marcus	Gas phase selective beam deposition: three-dimensional, computer-controlled	December 1989	U.S.
3DP	Sachs et al.	Three-dimensional printing	December 1989	U.S.
	Levent et al.	Method and apparatus for fabricating three-dimensional articles by thermal spray deposition	December 1990	U.S.
	Penn	System, method, and process for making three-dimensional objects	June 1992	U.S.