Dept of Mechanical Engineering / Institute of Mechatronic Engineering, National Taipei University of Technology

Additive Manufacturing Center for Mass Customization Production, National Taipei University of Technology (MOE High Education Sprout Project)

Vat Photopolymerization, VP
光聚合固化技術

Presented by Prof Wang, Jia-Chang

Contents

- 3D Printing / Additive Manufacturing
- The beginning of Vat Photopolymerization
- The principle of the manufacturing process
- The development of material
- The development of machines (processes)
- Comparison between processes
- Conclusion

Rapid Prototyping/ Free Form Fabrication/ 3D Printing/ Additive Manufacturing

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- Vat Photopolymerization
  Vat Photopolymerization uses a vat of liquid photopolymer resin, out of which the model is constructed layer by layer. An ultraviolet (UV) light is used to cure or harden the resin where required, whilst a platform moves the object being made downwards after each new layer is cured.

The beginning of Vat Photopolymerization

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- Photopolymerization was developed in 1960s for the use of coating and printing.
- In 1979, a professor in Japan published a conference paper introducing an automated method to stack material layer by layer to form a 3D object.
- In 1981, Hideo Kodama of Nagoya Municipal Industrial Research Institute published his account of a functional rapid-prototyping system using. A solid, printed model was built up in layers, each of which corresponded to a cross-sectional slice in the model.
- Chuck Hull filed in 1984 " Apparatus for production of three-dimensional objects by stereolithography" (U.S. Patent 4,575,330), starts a new company 3D Systems in 1986 focusing on system development, and successful sold the first commercial (standard machine) 3D Printer in the world in 1989. The name of the system is SLA (StereoLithography Apparatus)。

The beginning of Vat Photopolymerization

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The Principle of VP Manufacturing Process

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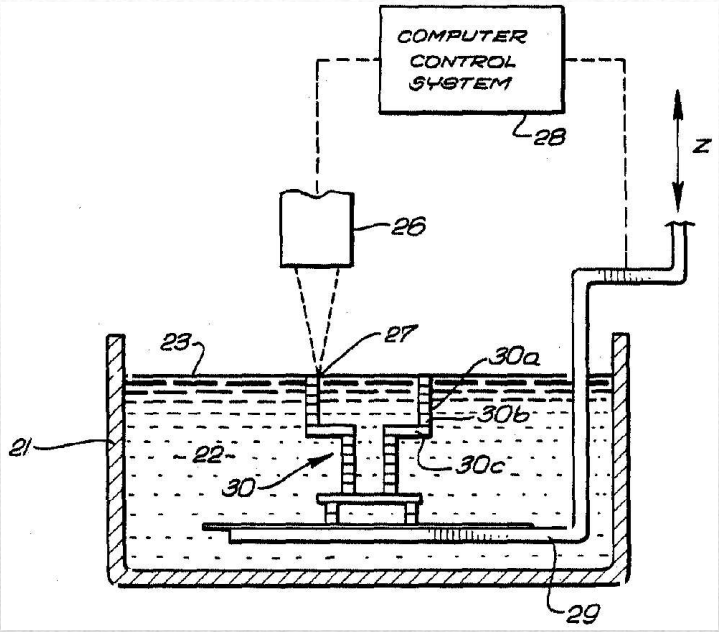
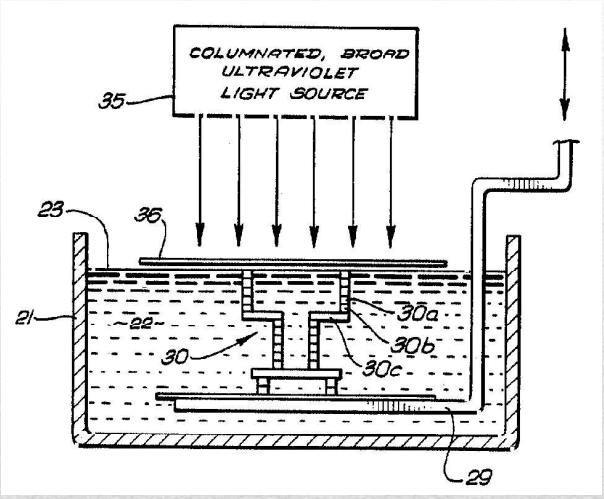
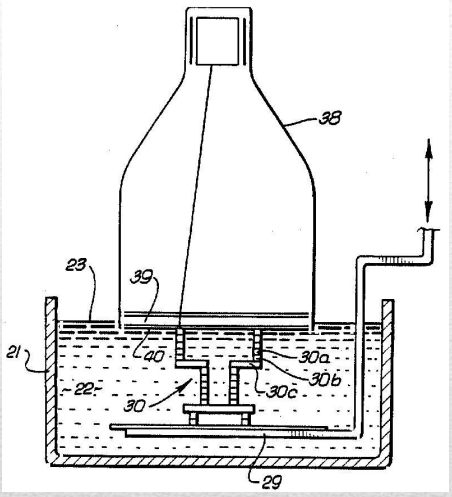


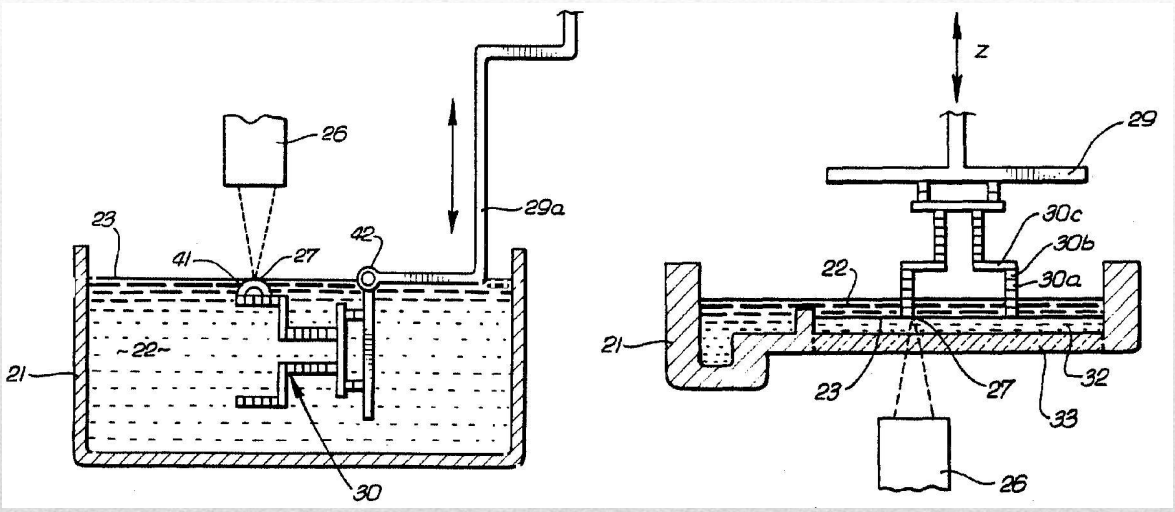
” Apparatus for production of three-dimensional objects by stereolithography” U.S. Patent 4,575,330

Original of the process

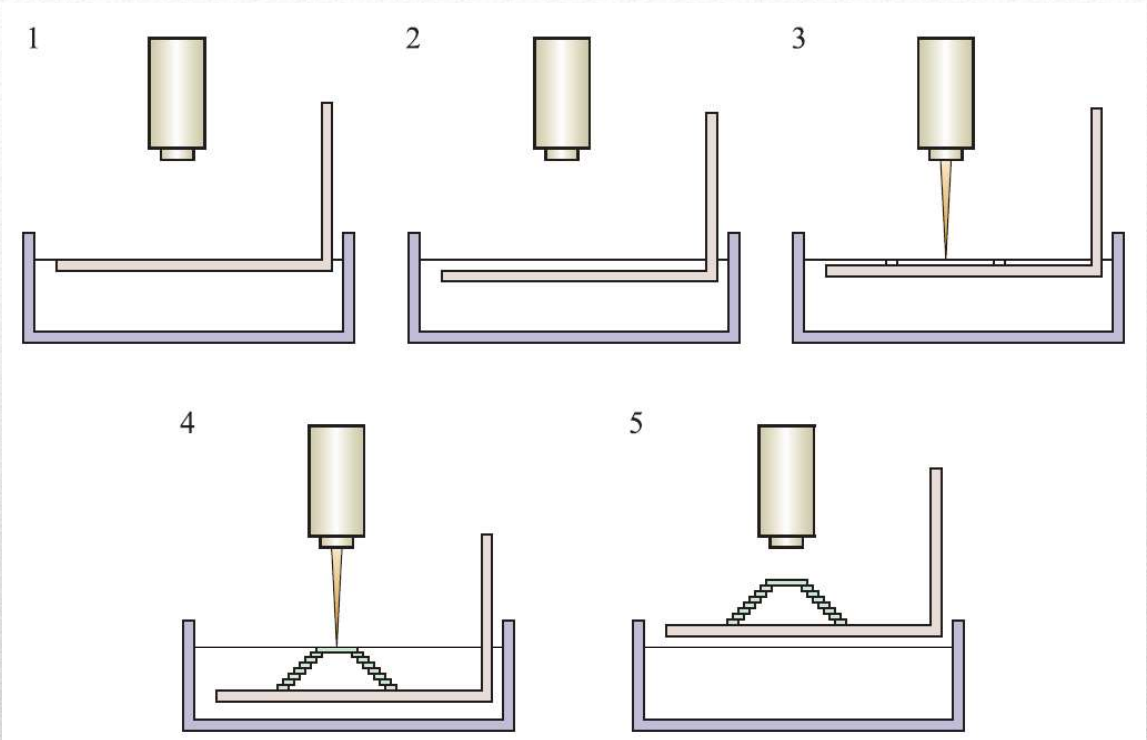




” Apparatus for production of three-dimensional objects by stereolithography” 發明專利(U.S. Patent 4,575,330)



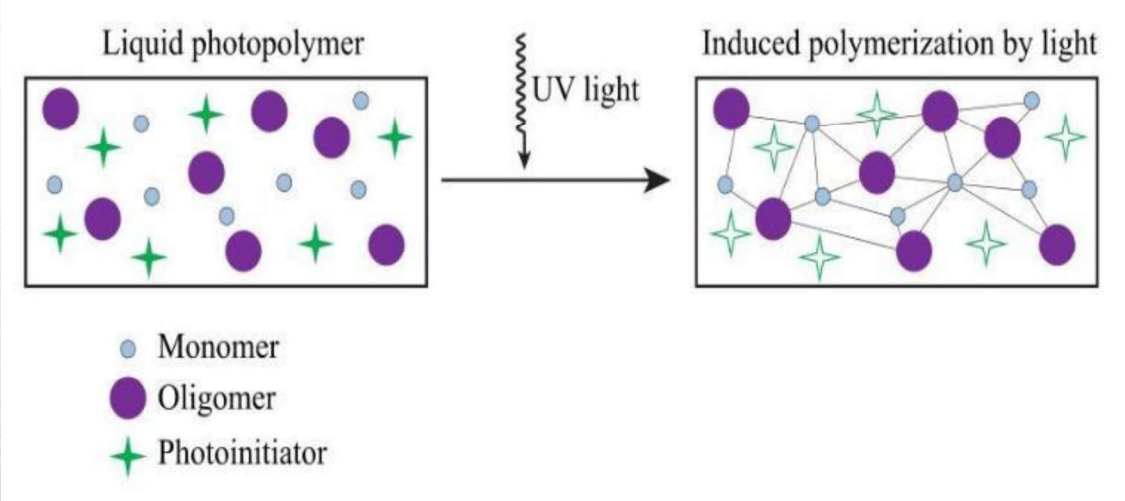
” Apparatus for production of three-dimensional objects by stereolithography” U.S. Patent 4,575,330



The process

The development of the material

- Joseph Nicéphore Niépce was a French inventor, usually credited as the inventor of photography and a pioneer in that field. Niépce developed heliography, a technique he used to create the world's oldest surviving product of a photographic process: a print made from a photoengraved printing plate in 1825。
- UV curing is the process by which ultraviolet light is used to initiate a photochemical reaction that generates a crosslinked network of polymers. Originally introduced in the 1960s, it is adaptable to printing, coating, decorating, stereolithograph, and in the assembly of a variety of products and materials.
- Curing with UV energy may be considered a low temperature process, a high speed process, and is a solventless process.
- Polymers: thermoplastic resin, thermosetting resin



Photopolymer

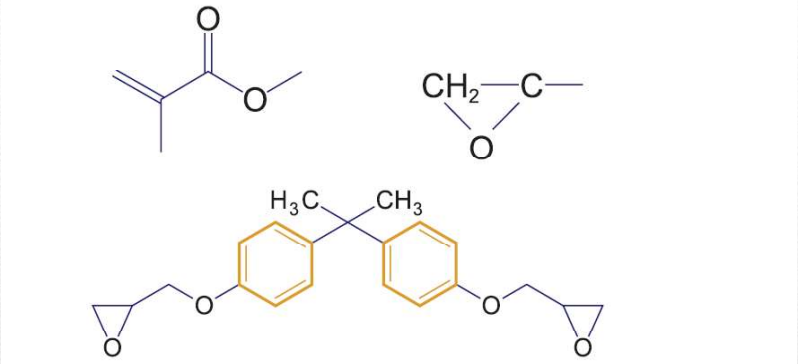
https://en.wikipedia.org/wiki/Photopolymer

- An example is shown below depicting a mixture of monomers, oligomers, and photoinitiators that conform into a hardened polymeric material through a process called curing.
- Most commonly, photopolymerized systems are typically cured through UV radiation, since ultraviolet light is more energetic; however, the development of dye-based photoinitiator systems have allowed for the use of visible light.
- Depends on the application, sometimes, we will put additives into the resin. For example, pigments, co-initiators, UV absorbers, thinner…

Photopolymer

- A monomer is a molecule that can be reacted together with other monomer molecules to form a larger polymer chain or three-dimensional network in a process called polymerization.

Monomer

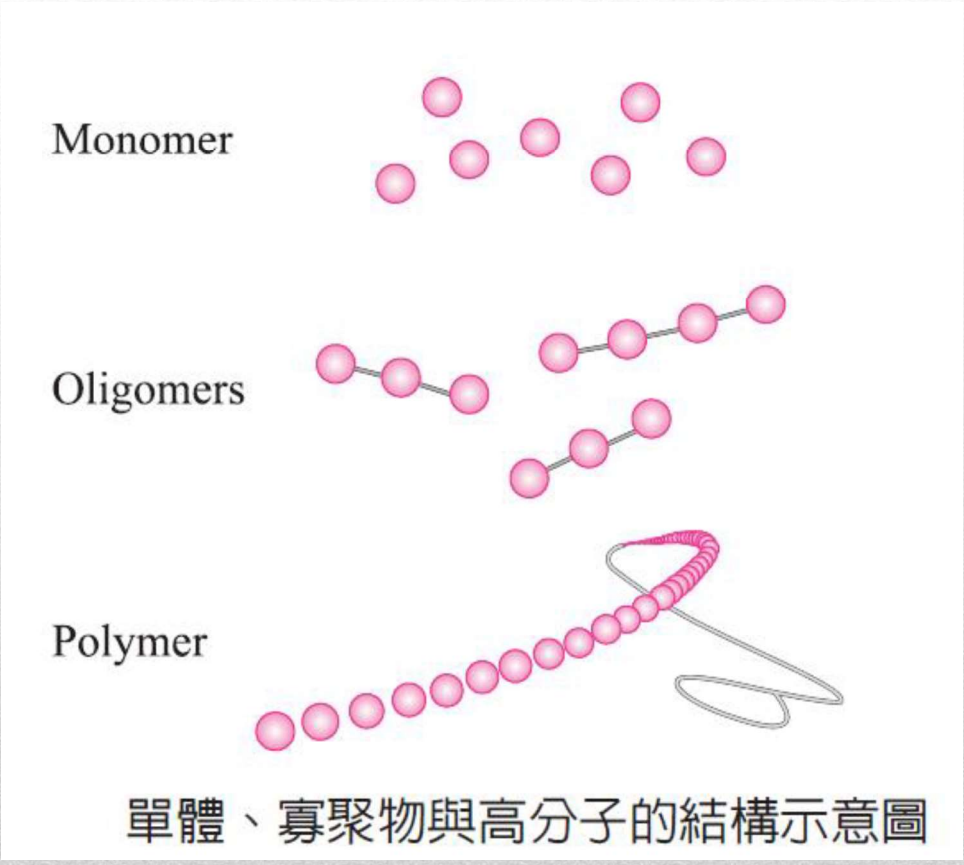


(a) 甲基丙烯酸甲酯；(b) 環氧基官能基；(c) 二酚基丙烷環氧樹脂

- 甲基丙烯酸甲酯 (Methyl Methacrylate, MMA) 是由甲基丙烯酸 (Methacrylic Acid, MAA) 與甲醇酯化反應而得，為無色液體，分子式為 CH2=C(CH3) COOCH3，是生產常見透明塑膠聚甲基丙烯酸甲酯 (PMMA) 的單體。環氧樹脂種類較多，最常見的是由二酚基丙烷 (俗稱雙酚 A) 環氧樹脂，又稱雙酚 A 二縮水甘油醚 (Bisphenol A diglycidyl ether, DGEBA)，是由雙酚 A 和環氧氯丙烷反應而得，具高透明性，實際上依據聚合分子量的大小，分成很多不同的型號，隨著相對分子量的增加，軟化點溫度亦會隨之提高。

- Oligomer molecule:
  A molecule of intermediate relative molecular mass, the structure of which essentially comprises a small plurality of units derived, actually or conceptually, from molecules of lower relative molecular mass.
  It has properties which do very significantly with the removal of one or a few of the units.
- 寡聚物(Oligomer) 或稱預聚物(Prepolymers) 或低聚物，一種分子量相對較低的感光性樹脂。固名思議，此化合物含有已部分先行聚合的單體，以及後續仍可以與單體進行光固化反應的基團，如各類之不飽和雙鍵或環氧基等。這樣一來， 才不會因為太過劇烈的反應放熱，或是聚合反應速率過快或過慢，使得最後聚合的光固化樹脂成品的品質難以掌握。
- 在樹脂成分裡，寡聚物將反映固化後樹脂的主要物理與化學性能，約佔組成中的40 ~ 50% 不等。

Oligomer



單體、寡聚物與高分子的結構示意圖

http: //www.cosmiq.de/qa/show/ 1425950/ was-bedeutet-monomer-und-welcher-kunnstoff-ist-ein-monomer-danke-schon-mal/

- 光起始劑(Photoinitiator) 是整個光固化產品中最關鍵之組分，往往也是廠商的獨家配方。光起始劑吸收光輻射能後，會形成自由基或陽離子，引發單體與寡聚物的聚合、交聯和接枝反應，它決定了整個光固化的速率

Photo-initiator

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類型	優點	缺點
自由基型樹脂	● 較普遍； ● 固化速度快、黏度低、成本低； ● 反應深度較大，大型或較厚的製品仍可適用； ● 起始劑觸發波長較廣，光源選擇多，產業利用性較佳。	● 二酚基丙烷環氧樹脂或聚氨脂丙烯酸等單體，因分子間作用力小，黏度小，硬化後硬度較低。 ● 固化後體積收縮大，易導致成品變形翹曲
陽離子型樹脂 Cationic polymerization	● 體積收縮小，黏度低；附著力強 ● 耐熱性、耐化性較佳； ● 不與空氣中的氧氣結合，固化後表面乾燥。 ● 較少刺激物質，對於安全、環境影響較低。 ● 精度高	● 固化速度較慢 ● 亦受鹼和濕氣影響； ● 價格高； ● 合適的寡聚物和活性稀釋劑選擇少。

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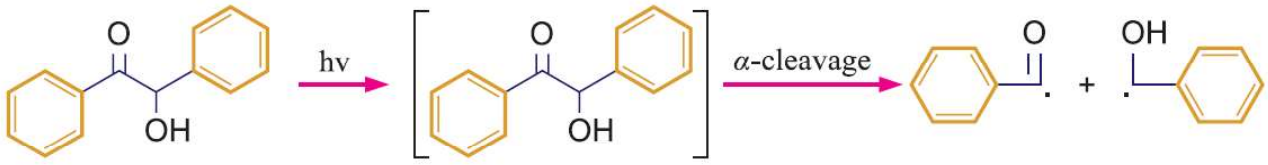
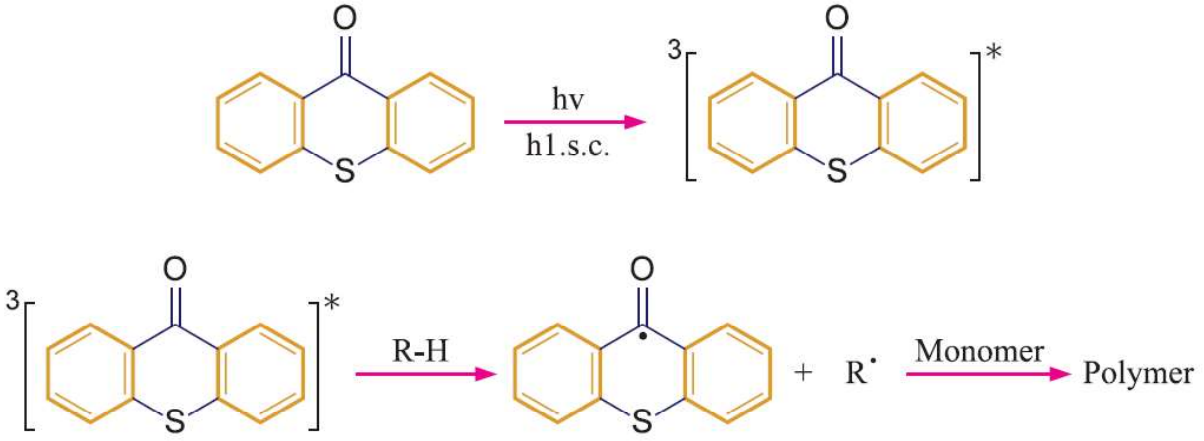


Photolytic α -cleavage of Benzoin

裂解型光起始劑(α-cleavage, Type I) ：是指光起始劑分子吸收光能後躍遷至激發單重態(Singlet state)， 經系間(Intersystem crossing) 躍遷至激發三重態(Triplet state)，在其激發態時，分子結構呈不穩定狀態，其中弱鍵或發生斷鍵，產生活性自由基與低聚物或單體進行交聯反應。



Photoinitiated free radical polymerization using Thioxanthone(TX)as the photoinitiator

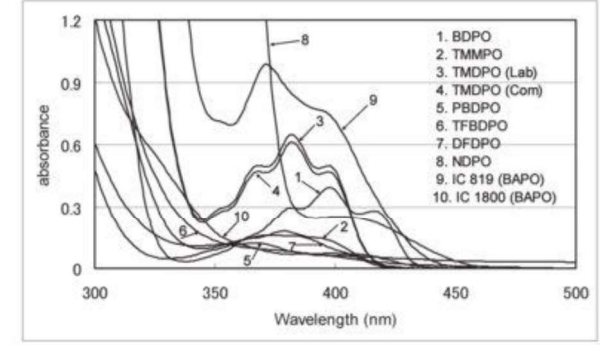
奪氫型(Type II)：是指光起始劑分子吸收光能後，經激發和系間(Intersystem crossing) 躍遷至激發三重態，與助起始劑(Co-initiator) 作為氫的供體發生雙分子作用，經電子轉移產生活性自由基，與低聚物或單體進行交聯反應。

產品名稱	物理形態	種　類*	市場應用			低氣味・低揮發・低遷移	表面固化	深層固化	快速固化	典型用量(%)
			有色油墨	白色油墨	OPV&透明					
Darocur® BP	固體	BP	■		√		√			2-4
Darocur® 1173	液體	AHK	■	■	√		√		▲	3-9
Irgacure® 4265	液體	AHK/APO		√			√	√	▲	1-6
Irgacure® 184	固體	AHK	■	■	√		√		▲	3-9
Irgacure® 250	液體	CP	▲	▲	▲		√			1-4
Irgacure® 369	固體	AAK	√			√		√	√	2-4
Irgacure® 379	固體	AAK	√			√		√	√	2-6
Irgacure® 651	固體	BDK	▲		▲		√			3-9
Irgacure® 754	液體	PG	▲		▲	√	√			3-9
Irgacure® 819	固體	APO	▲	√	■	√		√	√	1-3
Irgacure® 2022	液體	AHK/APO	■	√	▲	√	√	√	√	2-6
Irgacure® 2100	液體	APO	■	▲		▲		√	√	2-6
Irgacure® 2959	固體	AHK		■	√	√	√			3-9
Lucirin® TPO	固體	APO	■	√				√	√	2-6
Lucirin® TPO-L	液體	APO	■	√				√	√	2 -6

*AAK：α-氨基酮　AHK：α-羥基酮　APO：酰基膦氧化物　BDK：安息香二乙醚
BP：二苯甲酮　CP：陽離子光起始劑　PG：苯甲酰甲酸酯
■ 複合光起始劑
▲ 可能應用
√ 可使用

http://www.dispersions-pigments.basf.com/portal/load/fid620253/low
http://product-finder.basf.com/group/corporate/product-finder/en/brand/IRGACURE

類型	化學名	吸收光譜區間 (nm)	型態	特點
BP	Benzophenol	UV(256,340)	固體	二苯甲酮。合成容易，是價格最便宜的一種光起始劑。但其光固化速率較慢且容易使固化層泛黃，與助起始劑配合使用，使得黃變性加重。另外BP溶點較低，具有昇華性、易揮發，不利於使用
CQ	Camphorequinone	UV(<300,375) Vis(475)	固體	黃色粉末，常使用於牙科。
PPD	1-Phenyl 1,2-propanedione	UV(393)	固體	較白，常與CQ混合使用，但聚合較慢。
TPO (Lucirin® TPO)	2,4,6-Trimethylbenzoyl-diphenylphosphine oxide	UV (290,380,393)	固體	攜基膦氧化物。溶解性高，氣味低，少黃變，穿透深度較淺。
Irgacure® 184	1-hydroxy-cyclohexyl-phenyl-ketone	UV (246,280,333)	固體	α- 羥基酮。低黃變，中度揮發性，表面固化佳。
Irgacure® 651	2,2-dimethoxy-1,2-diphenylethan-1-one	UV(254,337)	固體	安息香二乙醚。易黃變
Irgacure® 819	bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide	UV(360,365) Vis(405)	固體	攜基膦氧化物。氣味低，揮發性少，對於可見光略有光敏性
Irgacure® PGA 290	tetralis(2,3,4,5,6-pentafluorophenyl) boranuide; tris[4-(4-acetylphenyl) sulfanylphenyl]sulfonium	UV(293,318)	固體	陽離子型，高活性，可用於3D列印，保存期長。



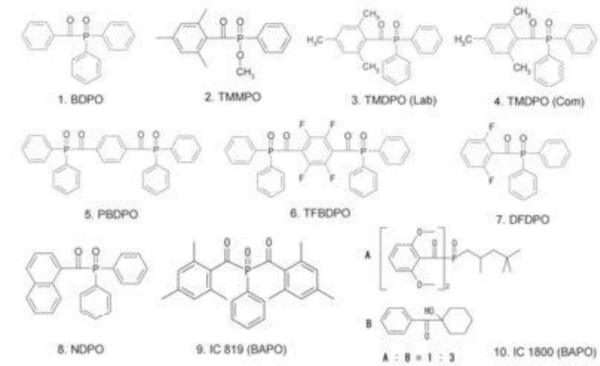
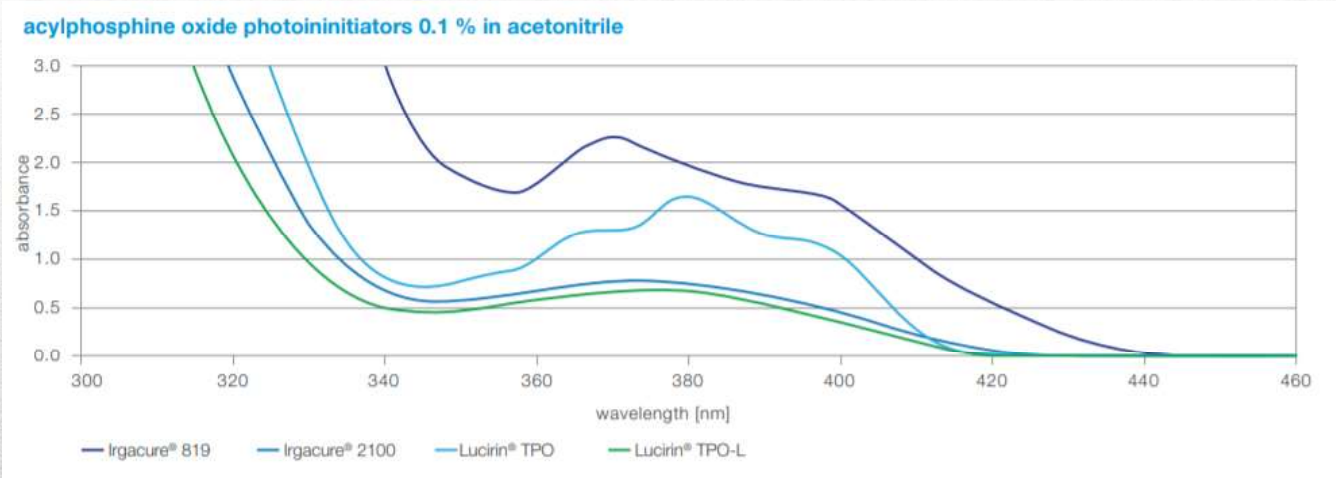


Photo initiator

http://3dprinter.wikidot.com/photoactive-resins



http://www.dispersions-pigments.basf.com/portal/load/fid620253/low page 42

Invicta

Invicta 915

ABS-like, white colour. High impact resistant, functional prototypes, casings, snap-fit parts and assembly applications.

Invicta

Invicta 917

ABS-like, anthracite gray colour. High impact resistant, functional prototypes, casings, snap-fit parts and assembly applications.

Invicta

Invicta 977

Polypropylene-like. Flexible, for snap-fit prototypes of mechanical components, lab equipment, appliance parts and casings.

Precisa

Precisa 779

Rigid opaque, gray colour. For prototypes, toys, high detailed models, marketing samples and patterns for silicon molds.

Vitra

Vitra 413

Standard acrylic, amber colour. General applications.

Vitra

Vitra 429

Transparent. For clear prototypes, liquid flow visualization, lighting, equipments.

Therma

Therma 289

Nanoceramic, light green colour. For thermal resistance tests and high definition models for vulcanized rubber molds.

Flexa

Flexa 692

Rubber-like, black colour. For prototypes of handles, gaskets, ergonomic tests, functional parts, footwear, wearable devices.

Flexa

Flexa 693

Rubber-like, transparent. For prototypes of functional parts, gaskets, wearable accessories and prototype molds.

Vesta

Vesta 443

Wax-like. For lost-wax casting applications.

Material- Photopolymer

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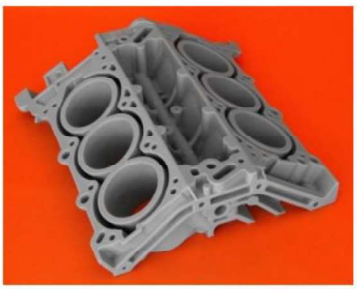
http://www.dwslab.com/materials-range/?v=3d9975706be3

3SP® 3D PRINTING MATERIALS



PERFACTORY® 3D PRINTING MATERIALS

MICRO 3D PRINTING MATERIALS

DENTAL

JEWELRY

HEARING AID

Material- Photopolymer

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http://envisiontec.com/3d-printing-materials/

Systems

光聚合固化技術是以光進行選擇性的照射，將低分子量的液態樹脂以光聚合方式結合成高分量的固態工件，而如何將光進行選擇性的照射，是其關鍵的技術之一。依不同光照射的方式進行分類，可分為點掃描及面曝光兩大方法，而點掃描的點光源都是運用雷射，而掃描方式可分為振鏡掃描、XY平面運動掃描、及平台運動掃描；而面曝光的面影像可分為LCD (Liquid Crystal Display) 動態光罩、DLP (Dynamic Light Processing) 動態光罩、及實體靜態光罩等。另外從照射的方向又可分為上往下照(簡稱上照式)、下往上照(簡稱下照式)兩大類，而面曝光的方式又再可分為面投射式及面成像式。

點掃描			面曝光		
雷射振鏡	雷射XY運動	雙光子平台運動	LCD	DLP	實體光罩
SLA/Nobel	SLP	Photonic Professional GT	Smartphone 3D Printer	MiiCraft/CLIP/3S	SGC

設備之發展

Vat Photopolymerization is curing the resin selectively be control the light to expose to the designed area. The polymerization process will crosslink the low molecule weight of monomer or oligomer together into a huge molecule weight polymer. It will turn the liquid form of resin into solid.
The key of the process is to control the light selectively exposure to the resin. We can classify the way of exposure into 2 types: point scan and area scan.
The light can either exposure from the top surface or bottom surface of the vat, which we call top-down and bottom-up to the process. There is also a method to cure the resin not on the surface but inside the resin.

Point scan			Area mask		
Galvanometer	XY table	Two photon	LCD	DLP	Physical mask
SLA/Nobel	SLP	Photonic Professional GT	Smartphone 3D Printer	MiiCraft/CLIP/3S	SGC

The development of VP systems

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PolyRay Print Technology	
Lasers	Solid-state frequency tripled Nd: YVO_4 with SteadyPower™
Wavelength	354.7 nm
Power (nominal) - at head	1450 mW (1000 mW at material surface under nominal optical path condition)
Laser Warranty	10,000 hours or 18 months (whichever comes first), replacement at 800 mW
Zephyr™ Recoating System	
Process	Removable applicator
Adjustment	Self-leveling; self-correcting
Layer thickness	Min -0.05 mm (0.002 in); Max -0.15 mm (0.006 in)
ProScan™ Scanning System	
Border spot (diameter @ $1/e^2$)	0.13 mm (0.005 in)
Large hatch spot	Nominal 0.76 mm (0.030 in)
Maximum part drawing speed*	
Border spot	3.5 m/sec (150 ips)
Large hatch spot	25 m/sec (1000 ips)
Build Envelope Capacity	
MDM 950 (ProX 950)	1500 x 750 x 550 mm (59 x 30 x 22 in)
Maximum part weight	150 kg (330 lbs)

System-SLA

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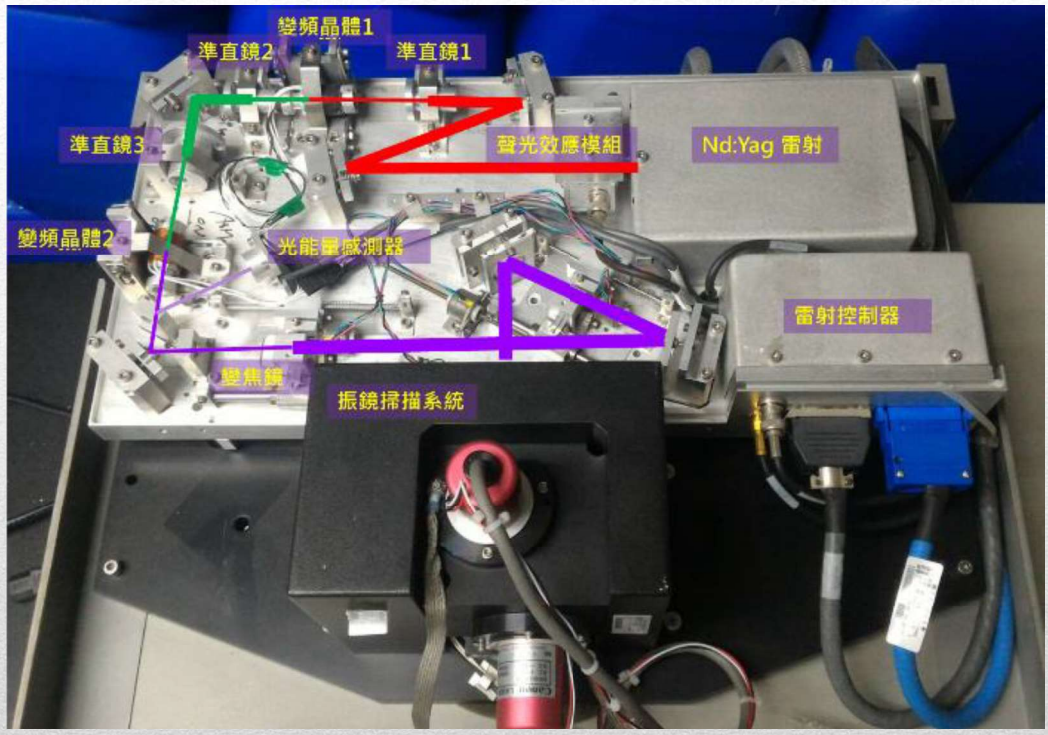
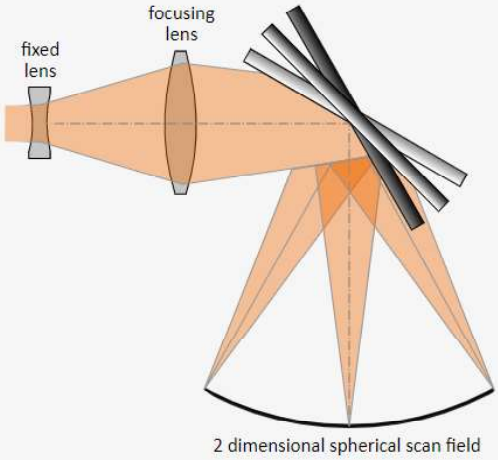
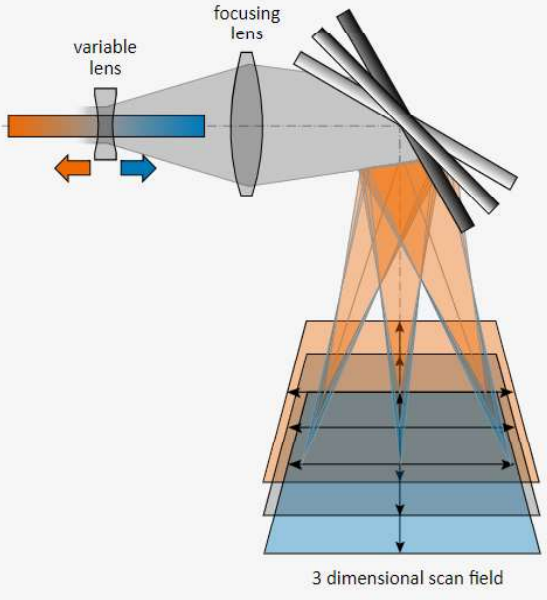
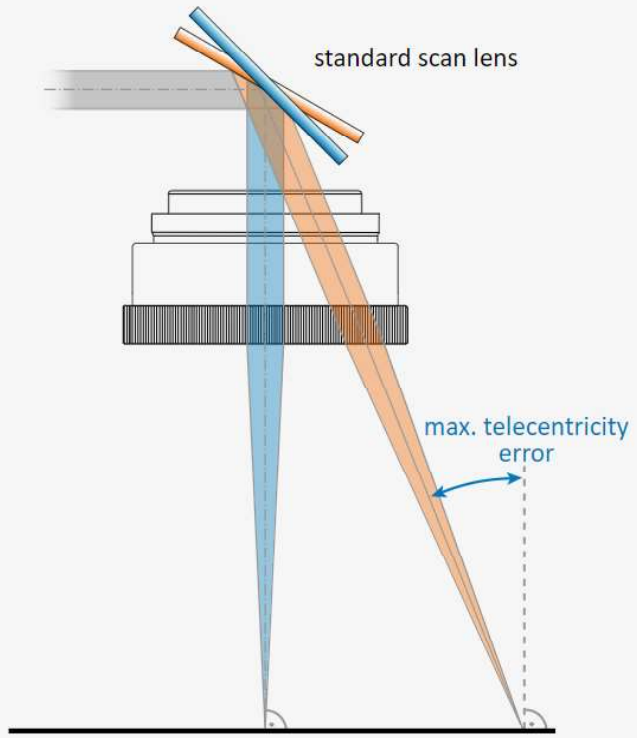
Images from http://www.3dsystems.com/3d-printers/production/prox-950

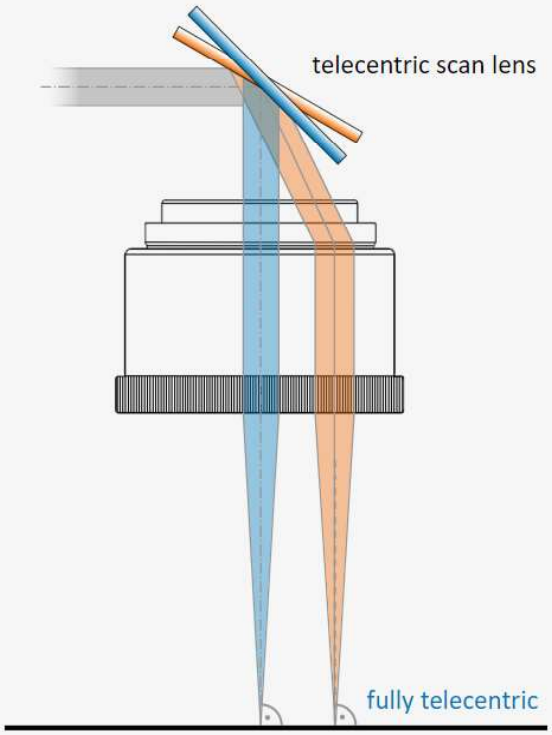


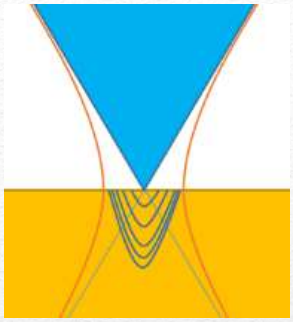
System-SLA optical system



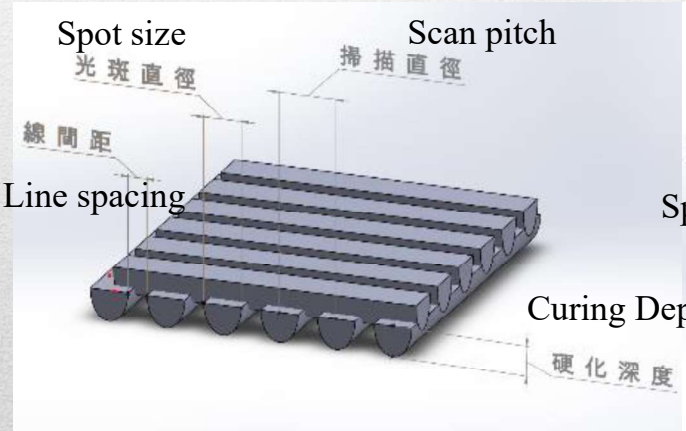


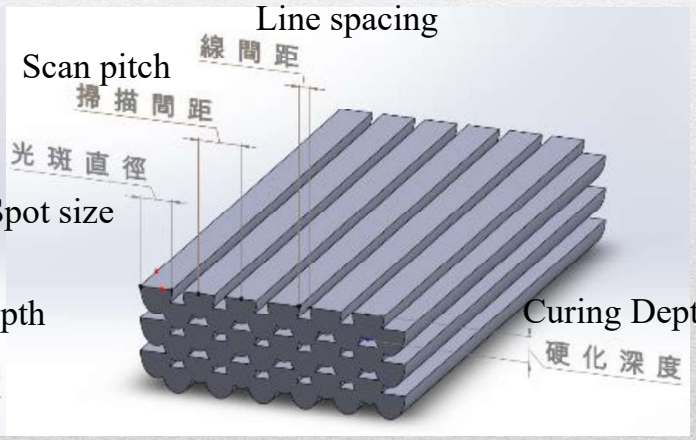




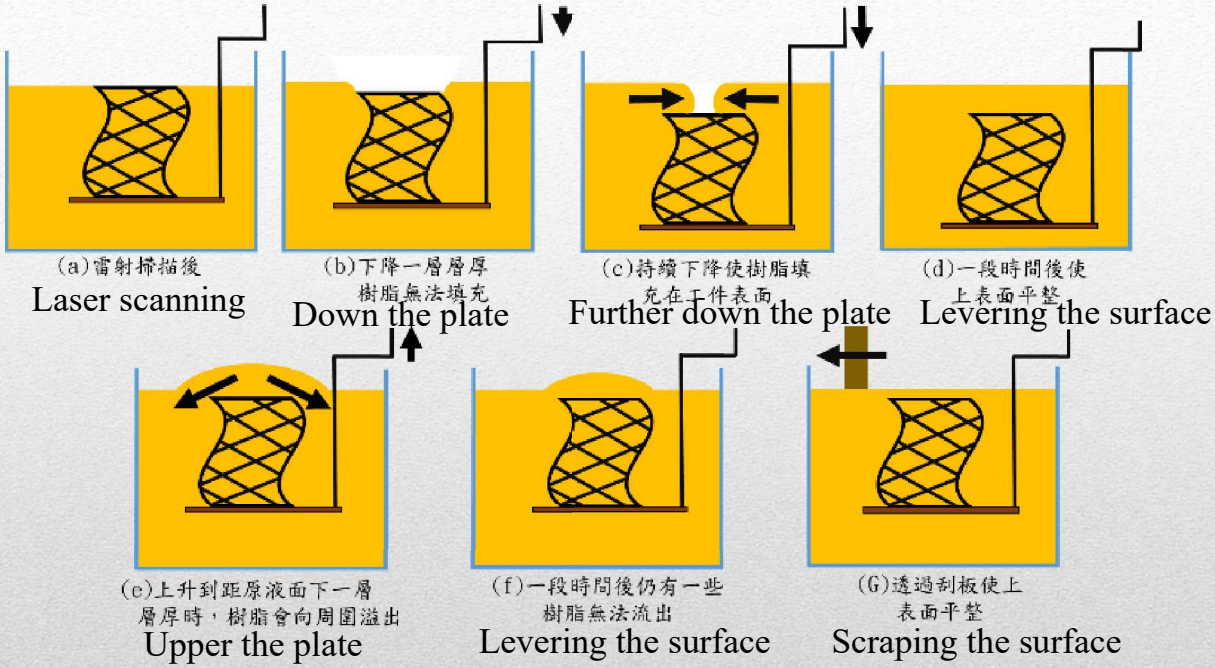


$$C_d = D_p \ln\left(\frac{E_{max}}{E_c}\right)$$

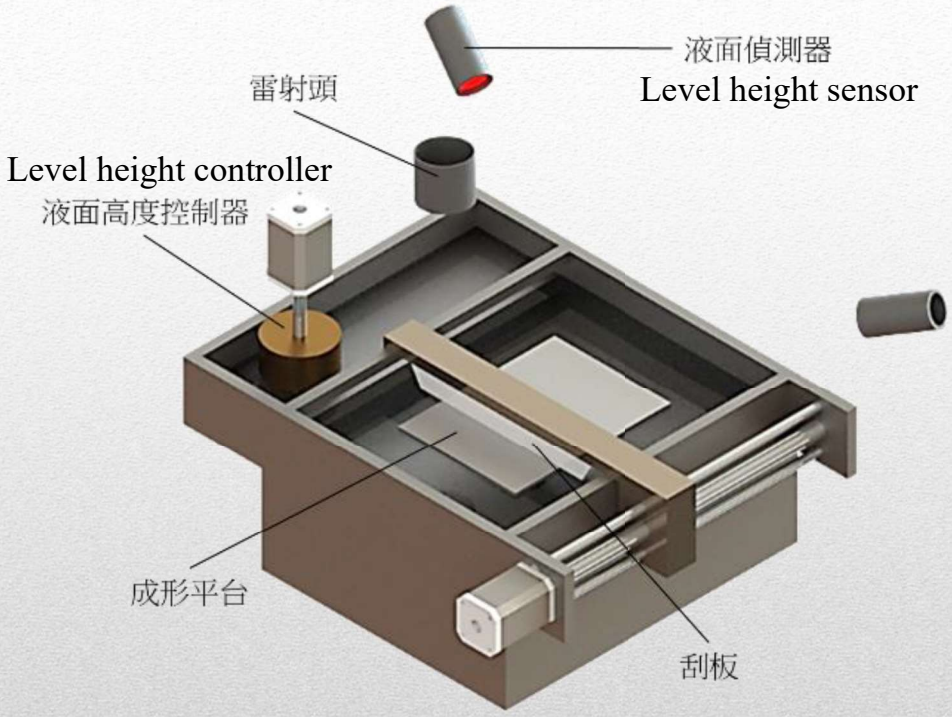




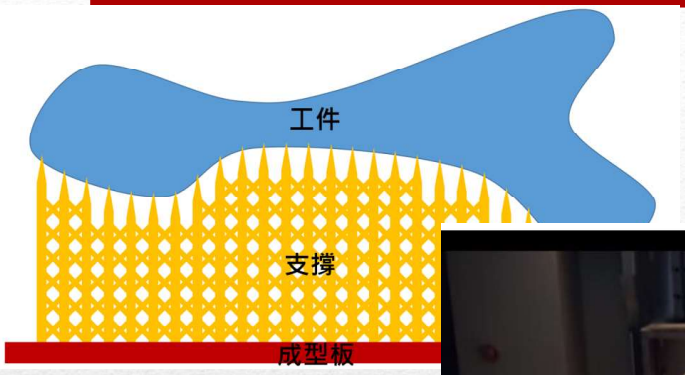
System-SLA scanning



System-SLA Process

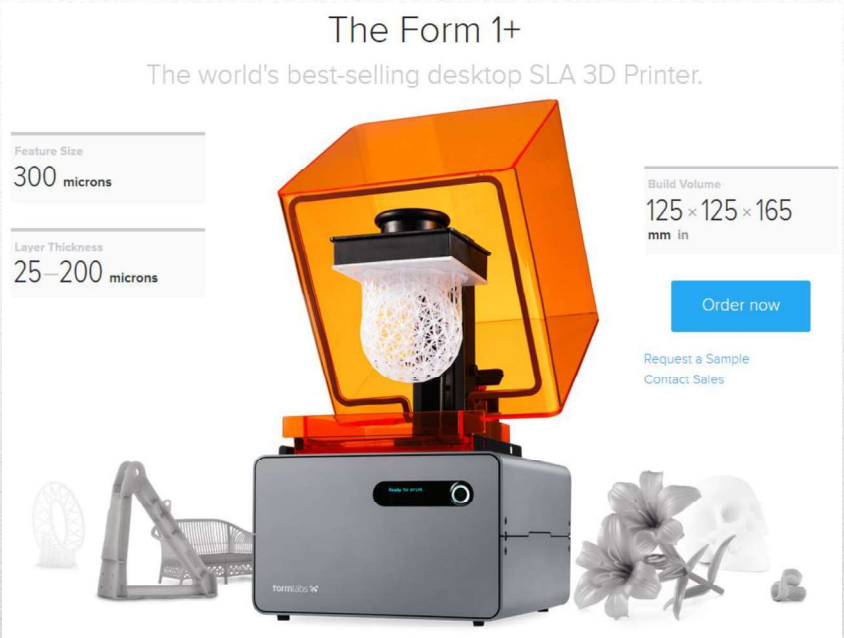


System-SLA level control



System-SLA Support structure

https://www.youtube.com/watch?v=EKU6RRkjM6E

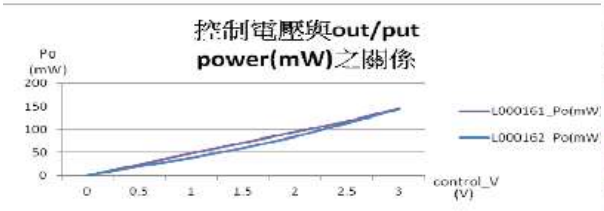


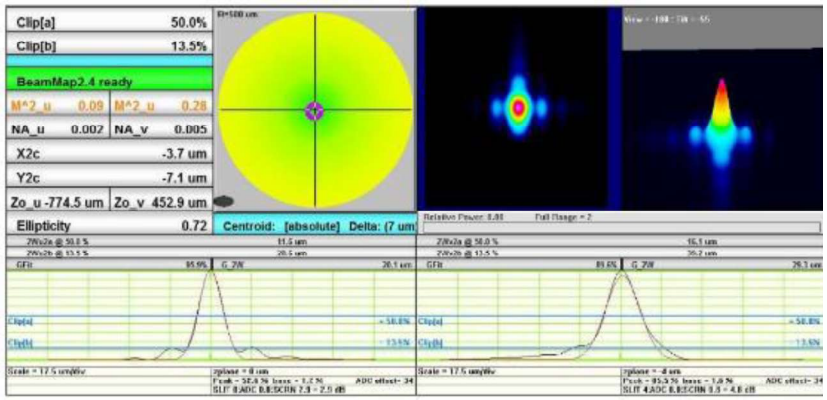
System- Form1

LECC TECHNOLOGY CO., LTD.
SHANGHAI LECC OPTO. CO., LTD.

System-Laser diode

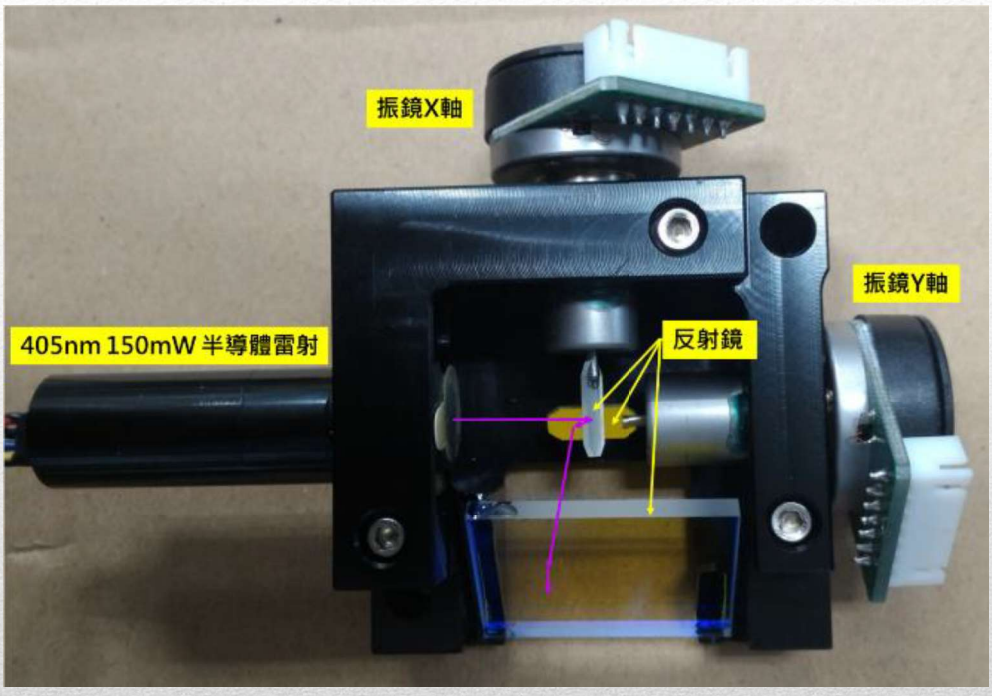
SPECIFICATION:					
SYMBOL	PARAMETER	MIN.	TYPICAL	MAX.	UNIT
PO	CW OPTICAL POWER	140			mW
IOP	OPERATING CURRENT			250	mA
VOP	OPERATING VOLTAGE		5	5.5	V
	VOLTAGE CONTROL	0		3.3	V
λP	WAVELENGTH AT PEAK EMISSION	400	405	410	nm
TOP	OPERATING TEMP. RANGE	-10		50	°C
TSTG	STORAGE TEMP. RANGE	-20		80	°C
SPOT SIZE	BEAM AT 30mm@FWHM		15	30	um
DRIVING CIRCUIT	APC CIRCUIT OR VOLTAGE CONTROL				
LENS	GLASS LENS				



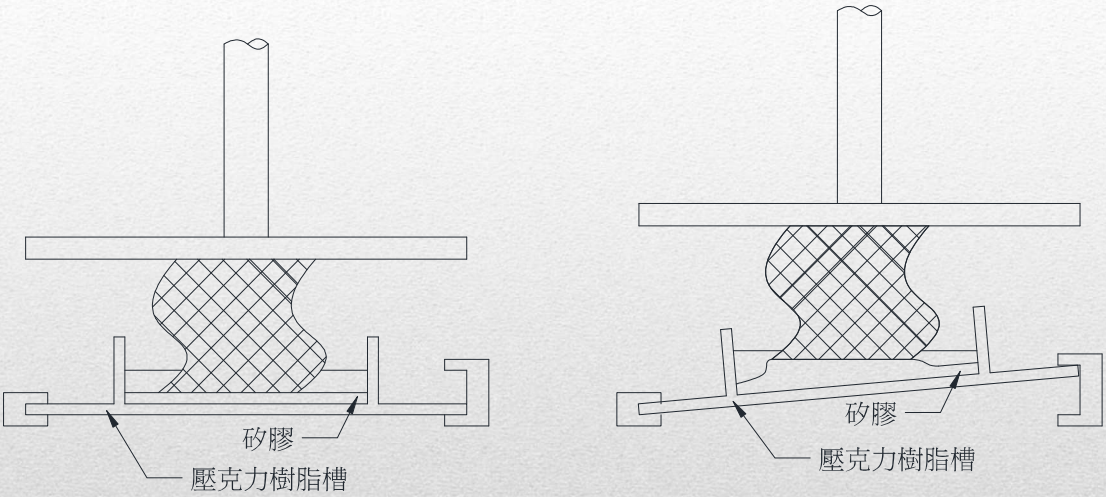


System-Laser diode

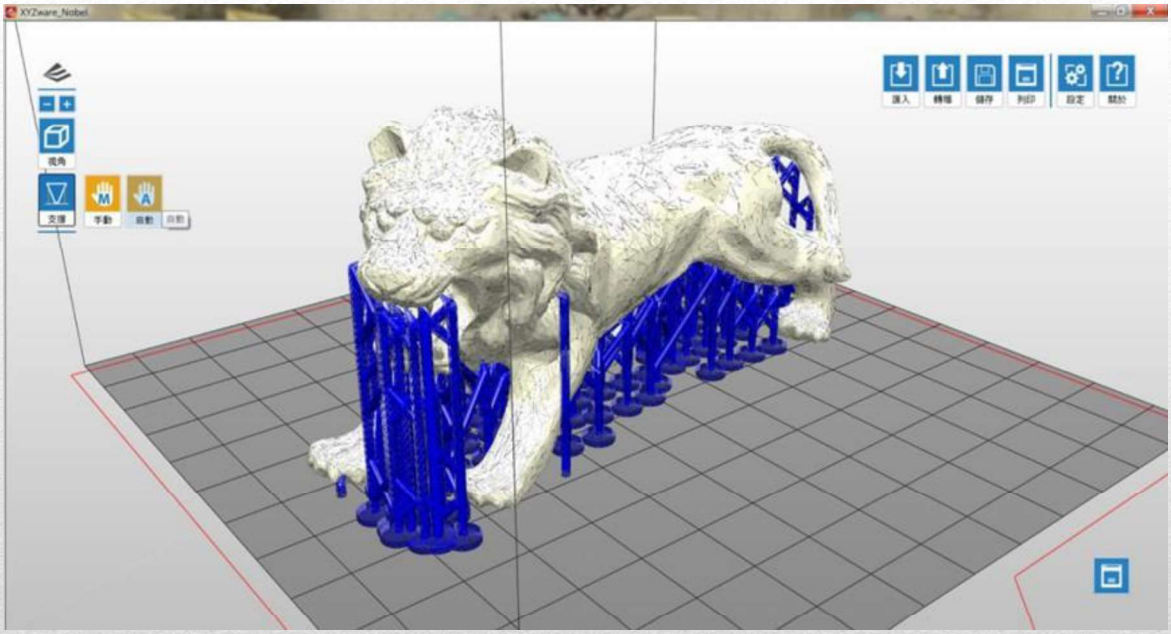
TAIPEI TECH



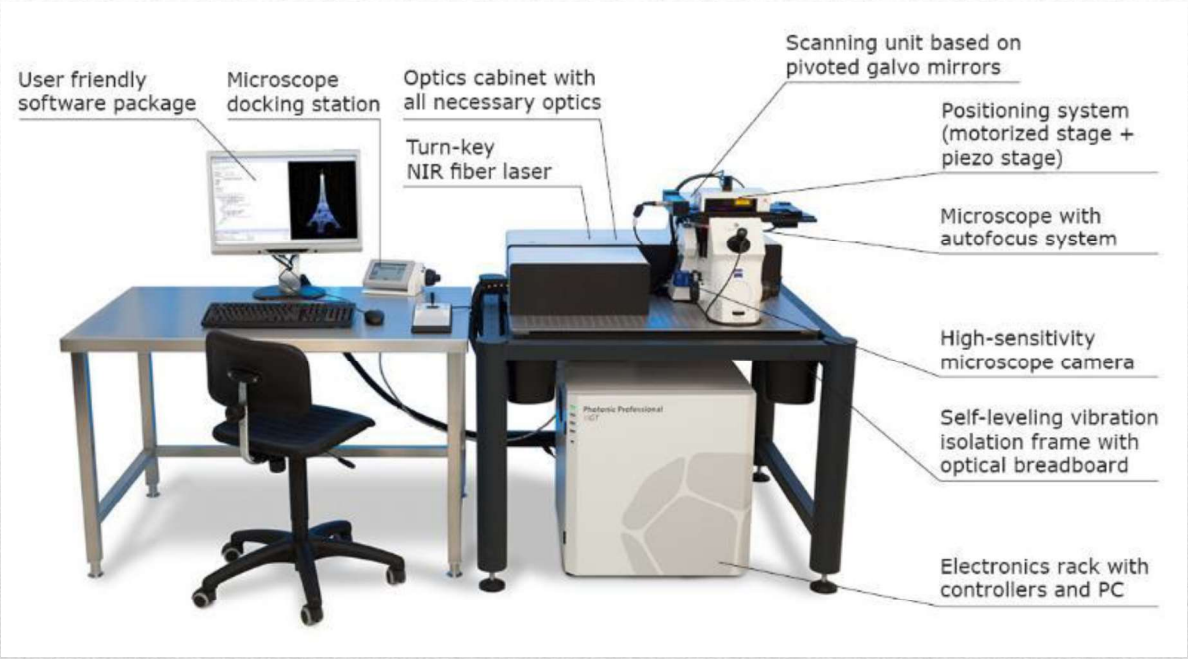
System-Scanning (Galvanometer)



System-forming direction



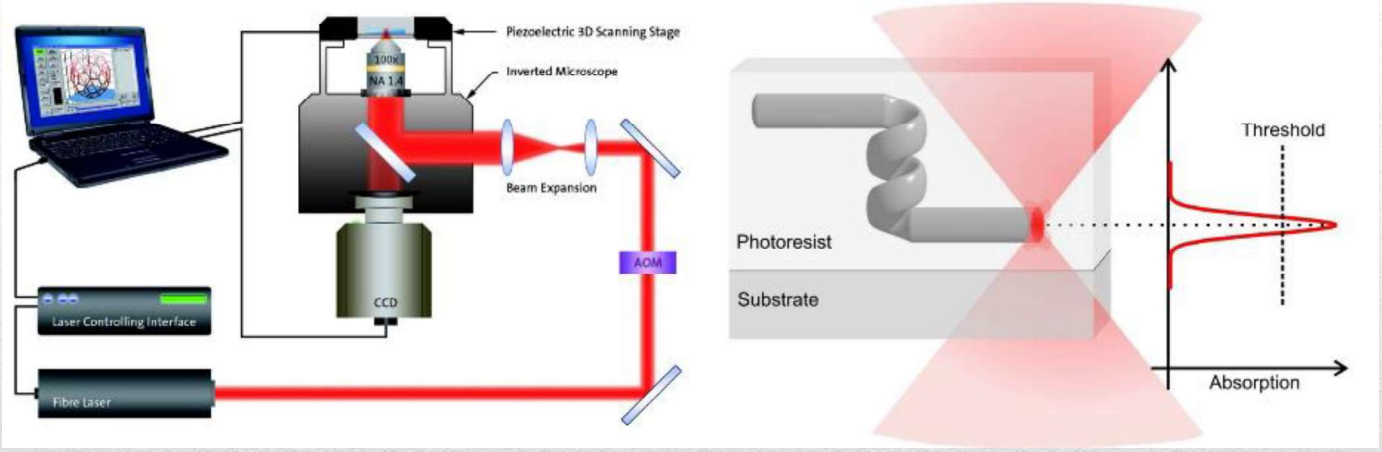
System-Support design



http://www.nanoscribe.de/files/5014/2062/6360/Flyer_PPGT_web.pdf

System-

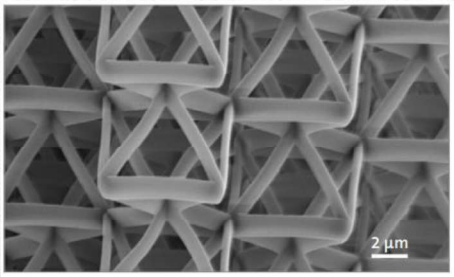
two-photon photopolymerization



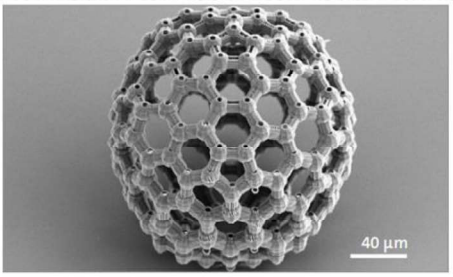
http://detallesimpresoras3d.blogspot.tw/p/blog-page_11.html

System-

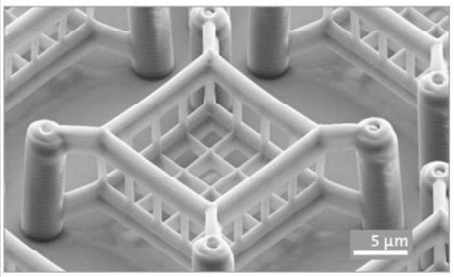
two-photon photopolymerization



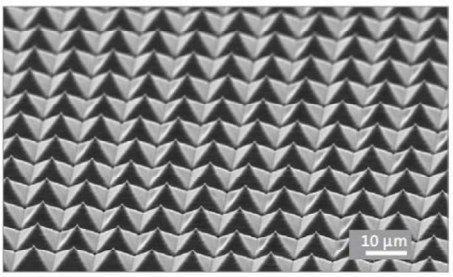
3D polymer micro-truss serving as ultralight material. Along T. A. Schaedler et al., Science 334, 962 (2011).



C180 fullerene-like polymer microstructure for rheology and cell scaffold research.



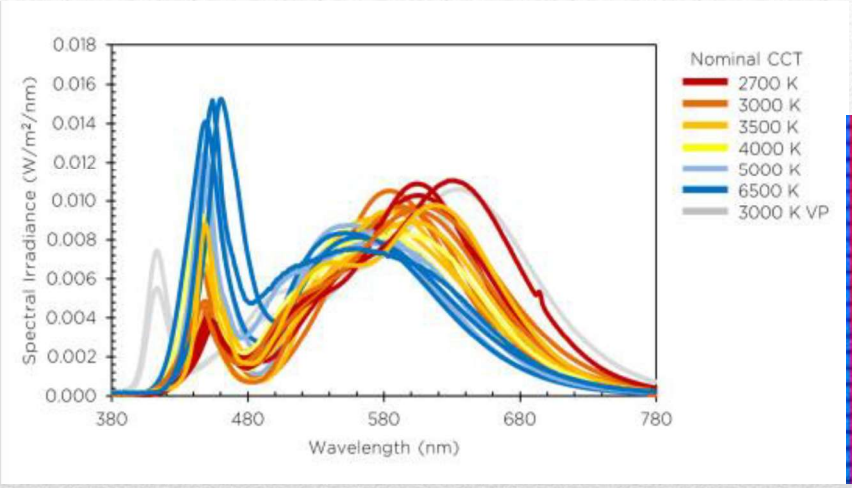
Biocompatible cell scaffold. Courtesy of T. Striebel, M. Bastmeyer, CFN, KIT (Germany).

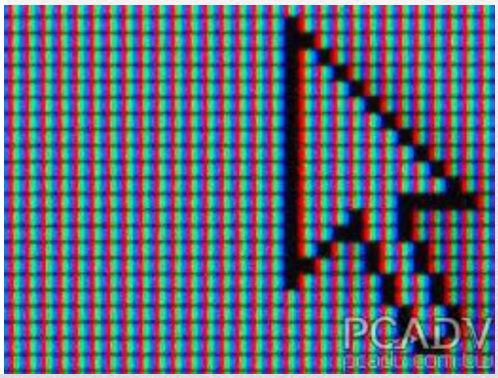


Beyond gray scale lithography: Large-area micro-optical pyramid array.

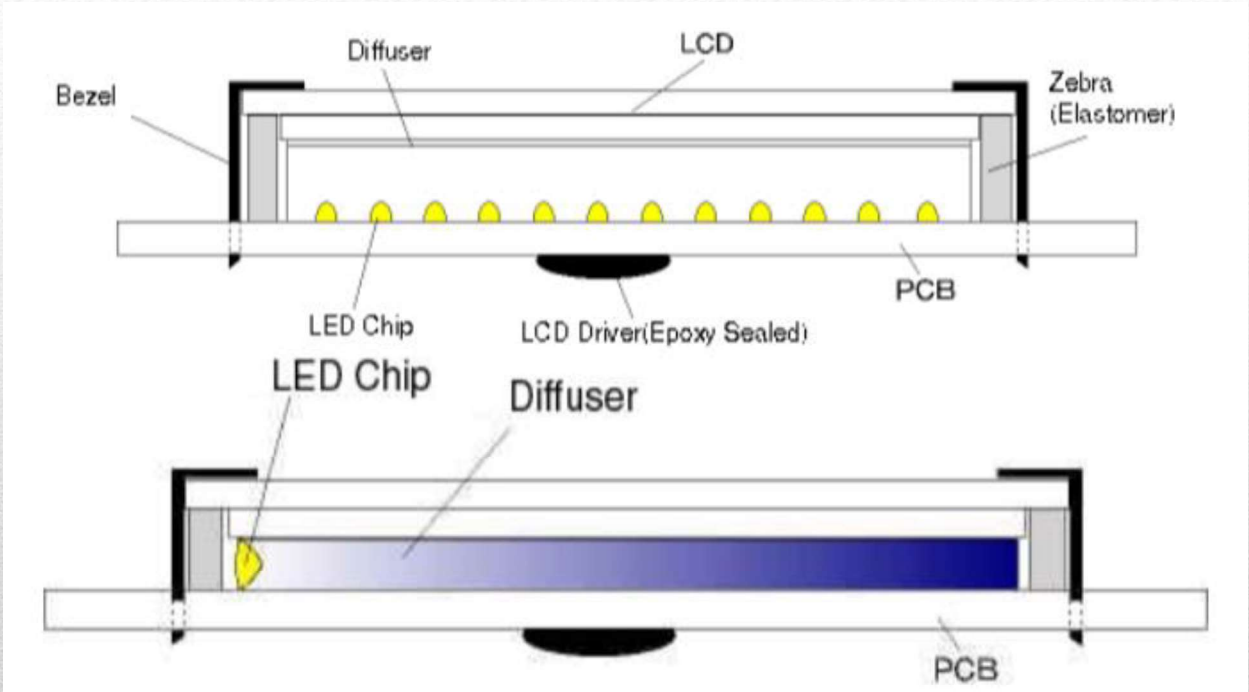
http://www.nanoscribe.de/files/5014/2062/6360/Flyer_PPGT_web.pdf

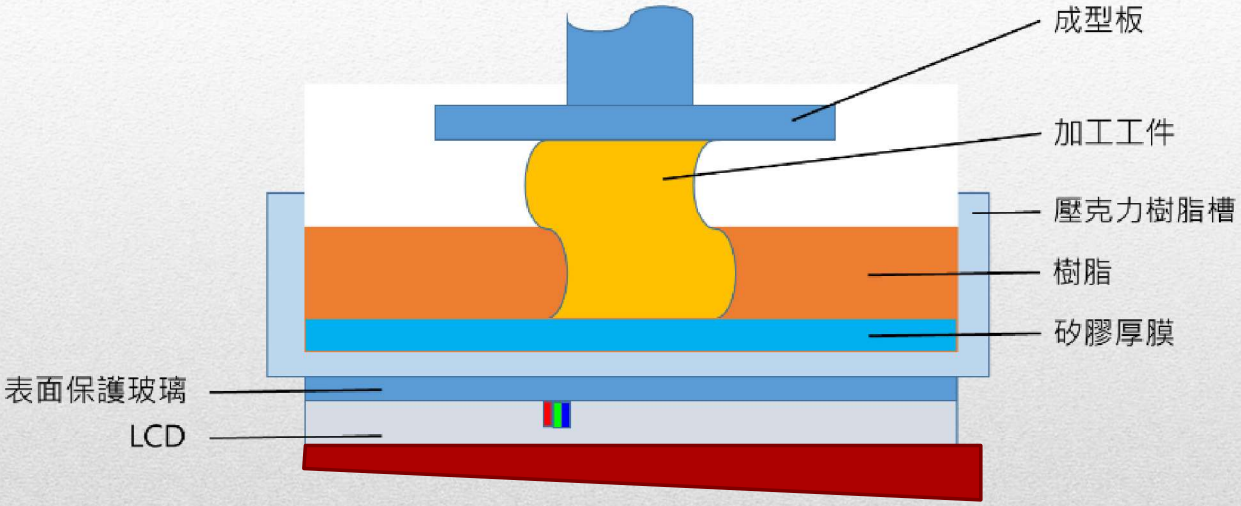
System- Smart Phone



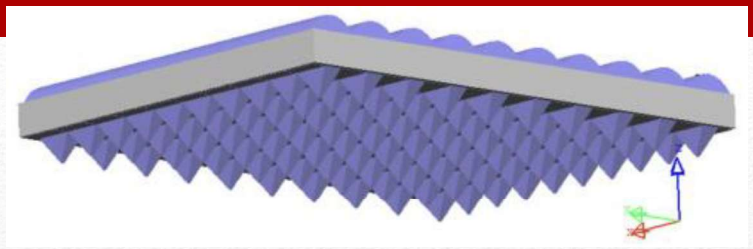


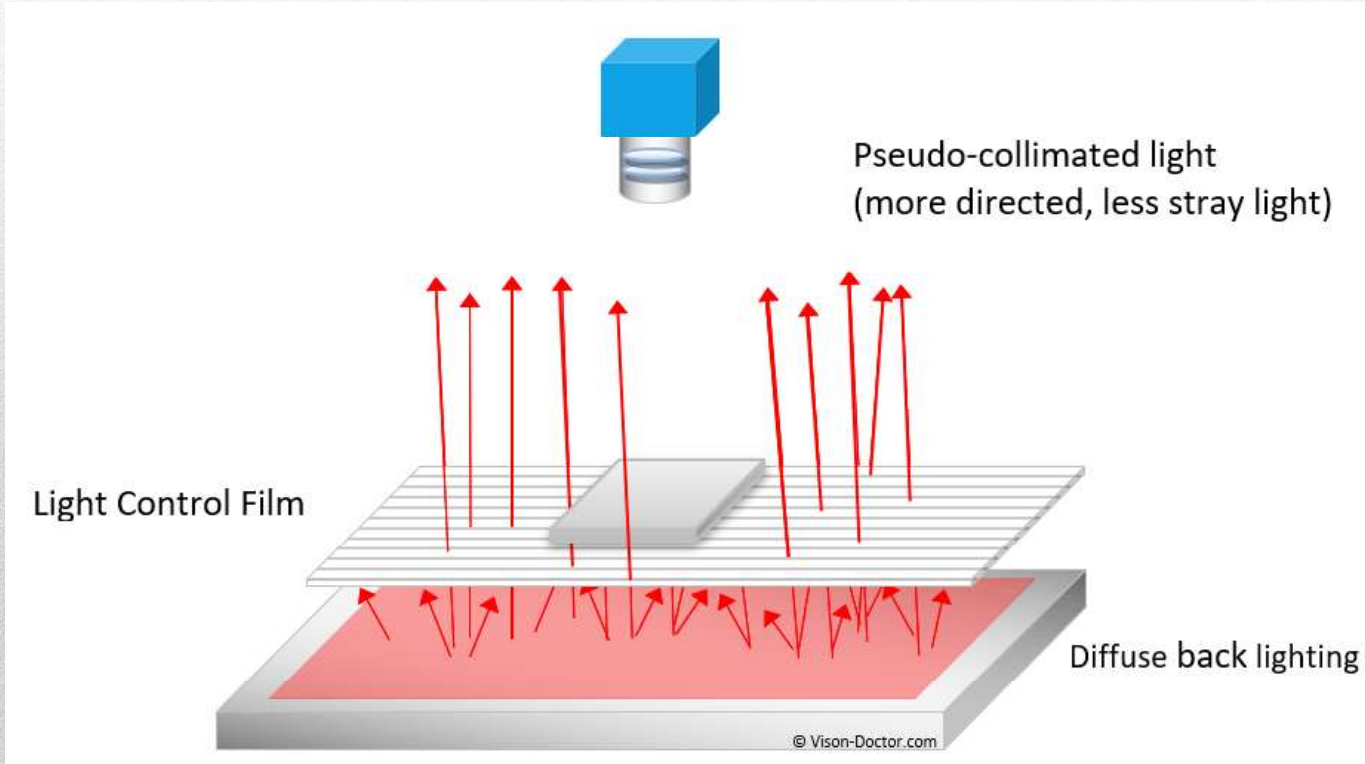
System-Smart Phone LED backlight





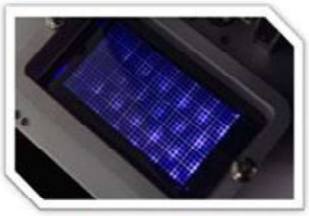
System- Smart Phone





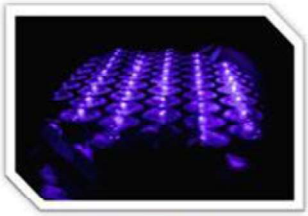
phrozen

極速列印 窺視Sonic極速成形的秘密



Mono-LCD
採3D列印專用螢幕

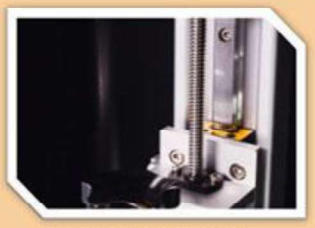
在405nm波長光源投射下
可達4倍透光率



ParaLED™ 3.0
陣列式平行光源再升級

Mono-LCD專用光源
鋁基散熱電路板
搭載高效UV-LED

最快每層0.5秒可成形



極速單線性滑軌
全鋁合金CNC加工製造

提高50%載台移動速度

運作循環
更為快速

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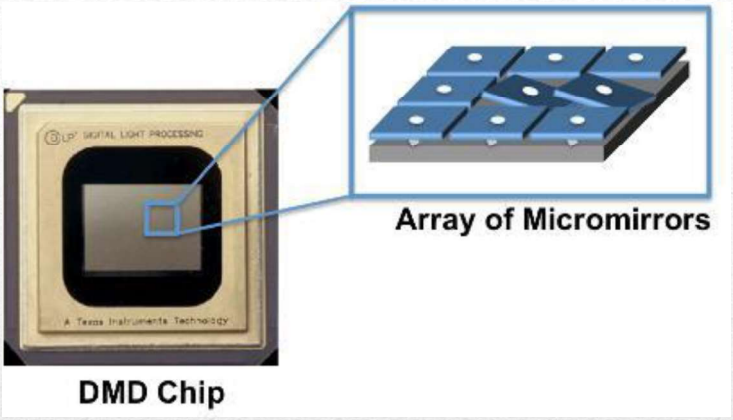
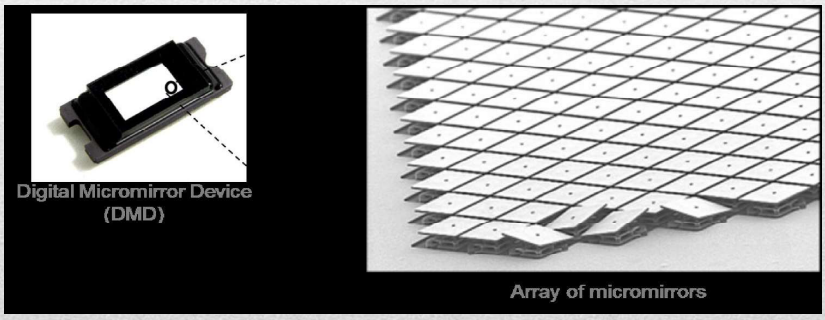
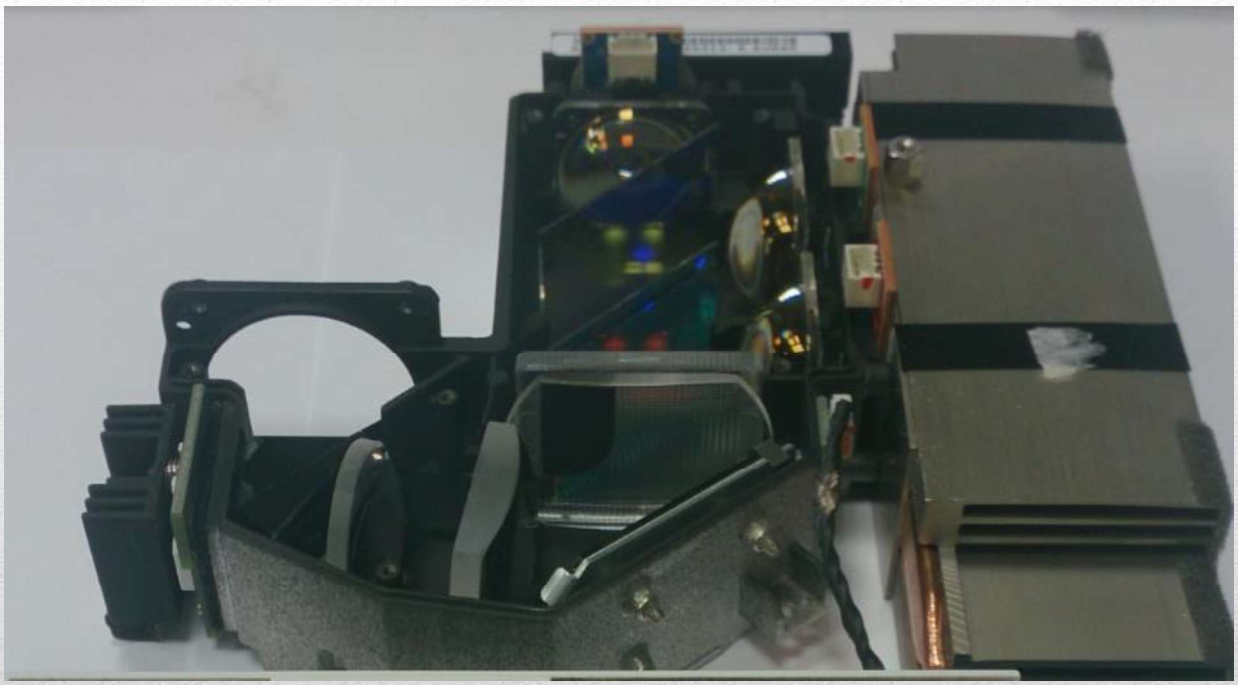
System-DLP

TAIPEI TECH

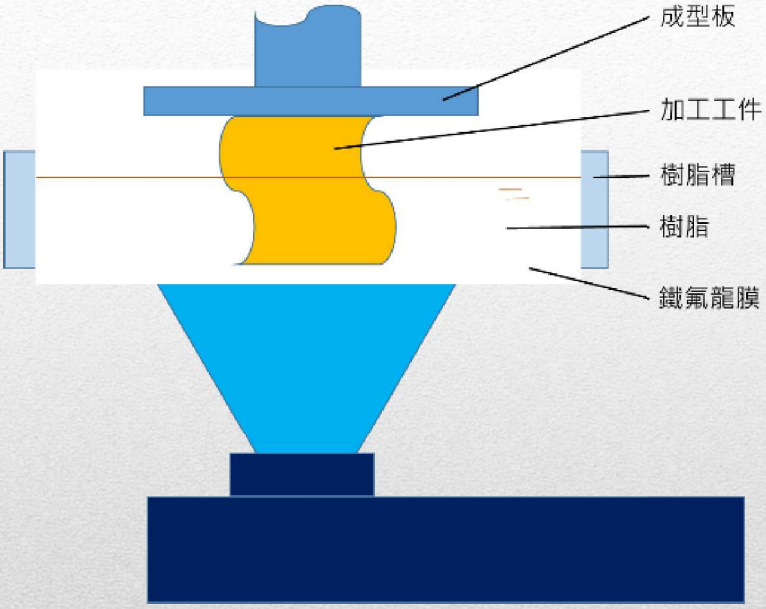




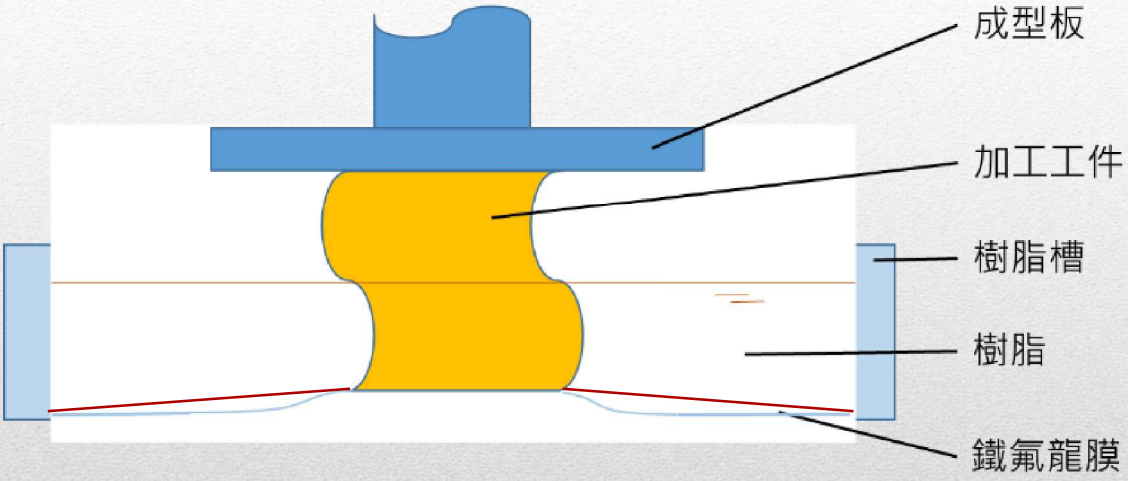
System-DMD Chip



System-DLP engine



System- Projet 1200

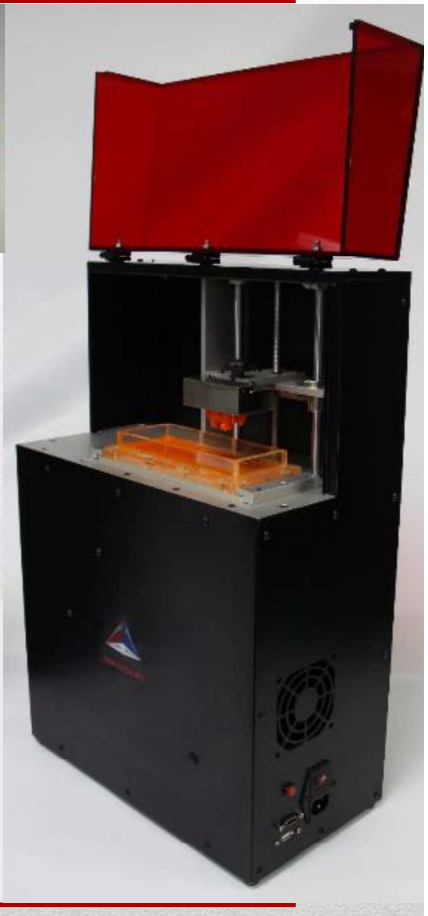


System- Projet 1200

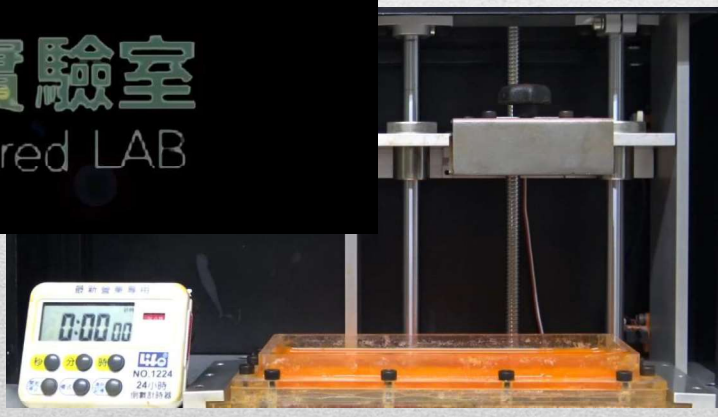
TAIPEI TECH

System- Projet 1200 supports

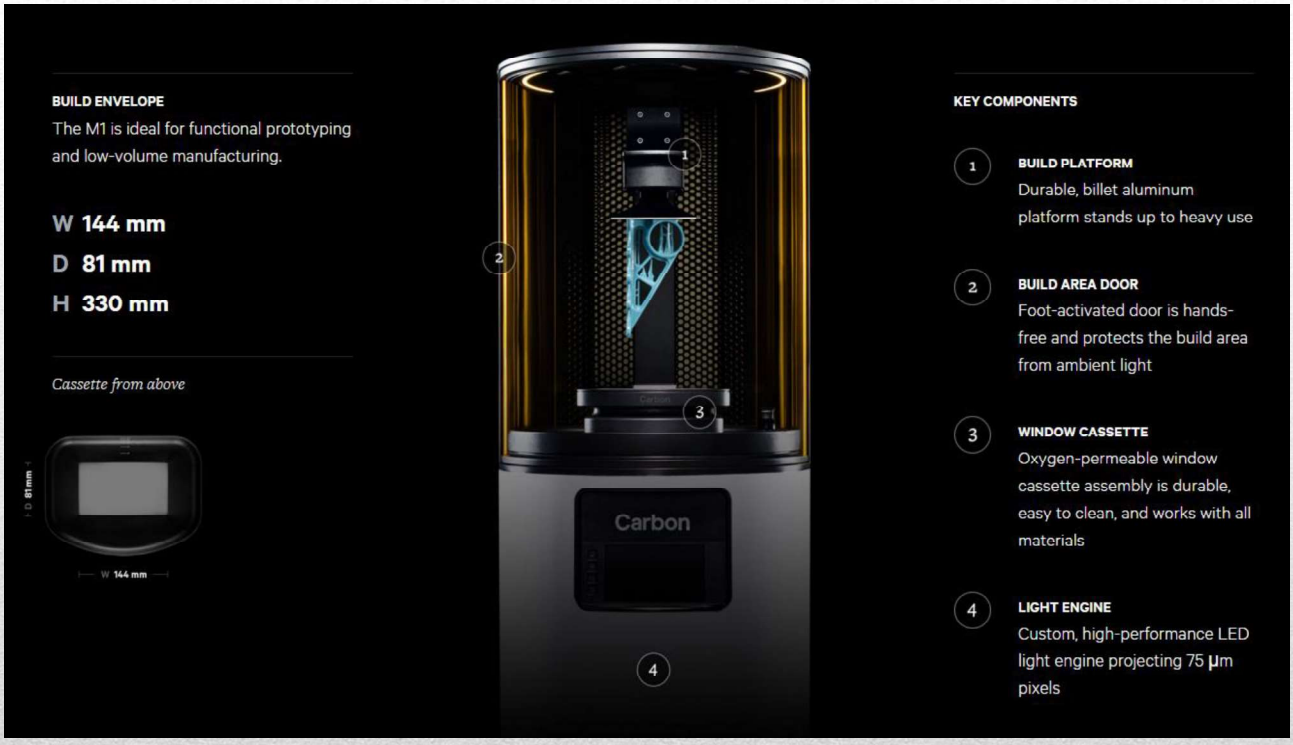
High precision VP resin type 3D printer. Bottom exposure design, low pulling force, high precision and speed. Layer thickness adjustable between 0.01-0.2mm, Full-HD resolution and 30μm pixel size.



System-3DT Lab bottom up system



TAIPEI TECH



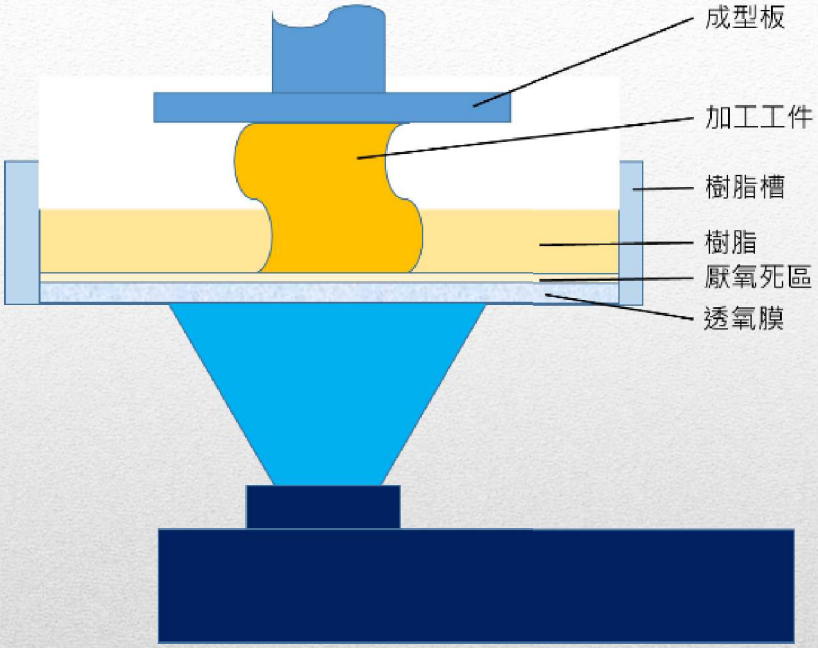
System- CLIP

http://carbon3d.com/

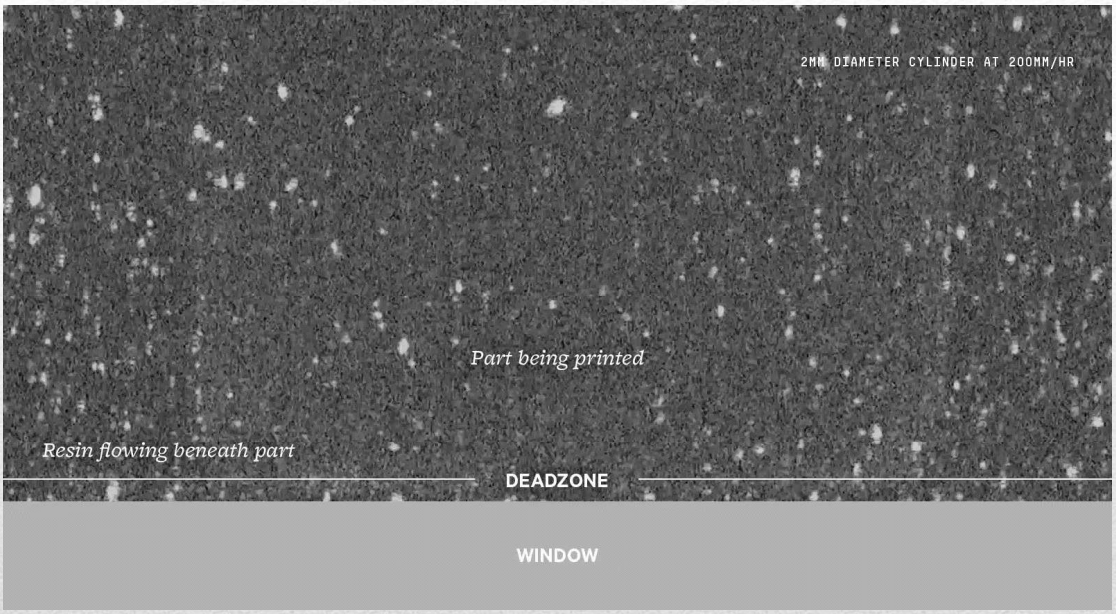
TAIPEI TECH

System- CLIP

https://www.youtube.com/watch?v=VTJq9Z5g4Jk

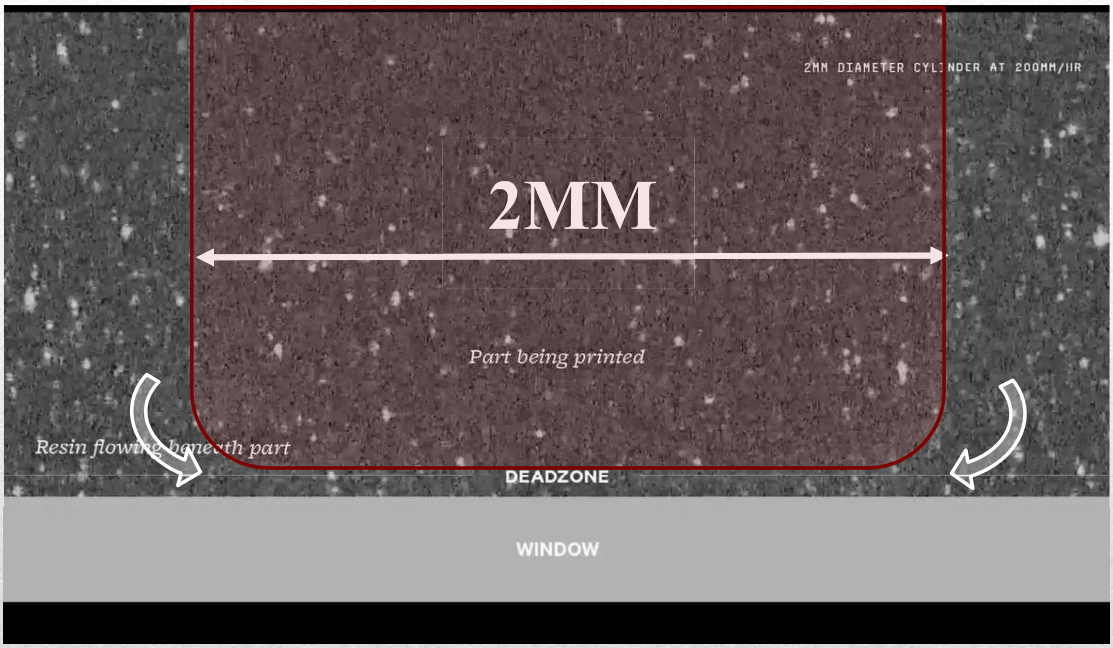


System- CLIP原理



System- CLIP

http://carbon3d.com/clip-process



System- CLIP separation

System- CLIP production

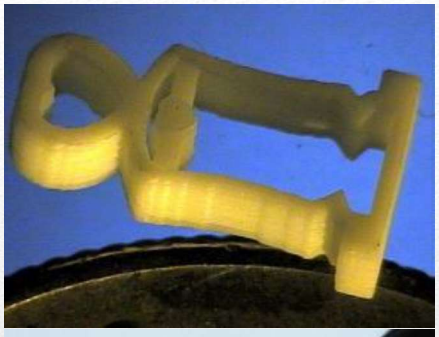
http://carbon3d.com/stories/clip-and-the-future-of-additive-manufacturing-in-automotive

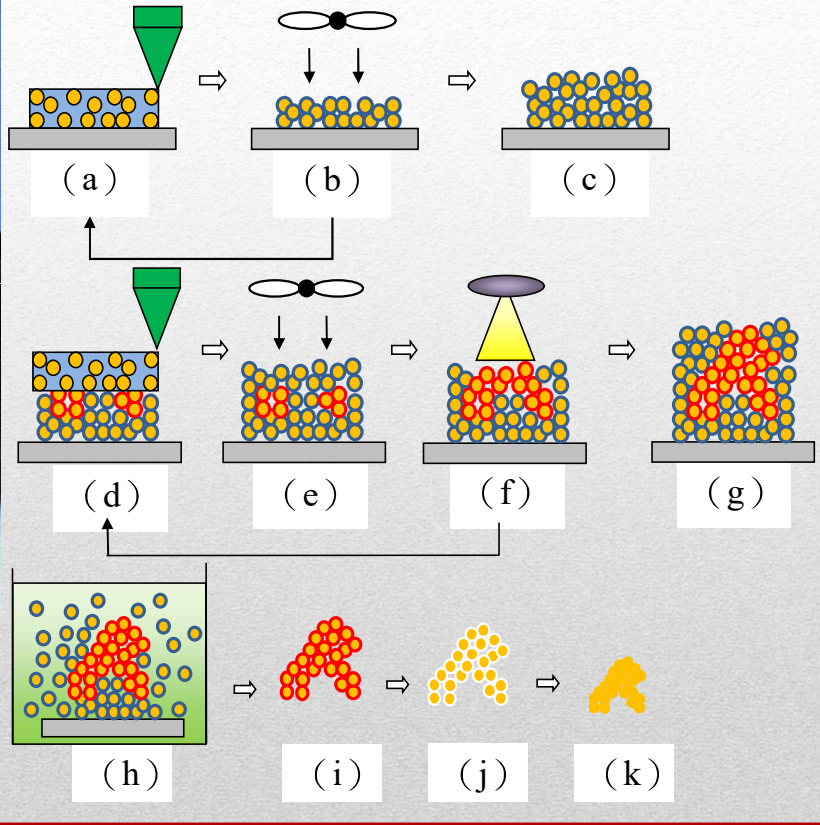
Computed Axial Lithography (Tomographic reconstruction)

Kelly, Brett E., et al. "Volumetric additive manufacturing via tomographic reconstruction." *Science* (2019): eaau7114.
DOI: 10.1126/science.aau7114

System-

3S (Solvent-based Slurry Stereolithograph)





Solvent-based Slurry Stereolithography

A Very Unique Process to fabricate High-Performance Ceramic

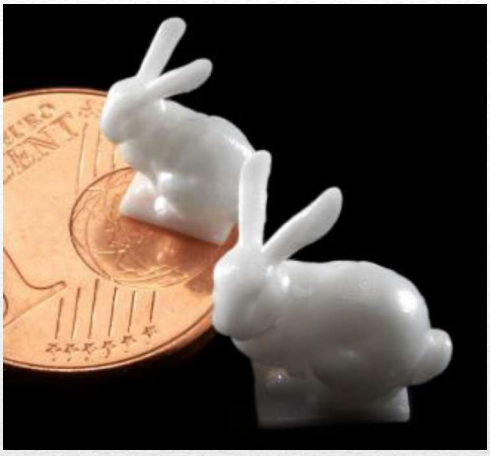
Compare to world leading ceramic 3D printing technology

The well know high-performance ceramic 3D printing process is developed by Lithoz in Vienna

- Founder and CEO of EOS starts to invest this company
- The drawback of the process by Lithoz is the pulling force and the support building up, it limits the freedom of the 3D shape.
- Our 3S process DON'T NEED SUPPORT DESIGN

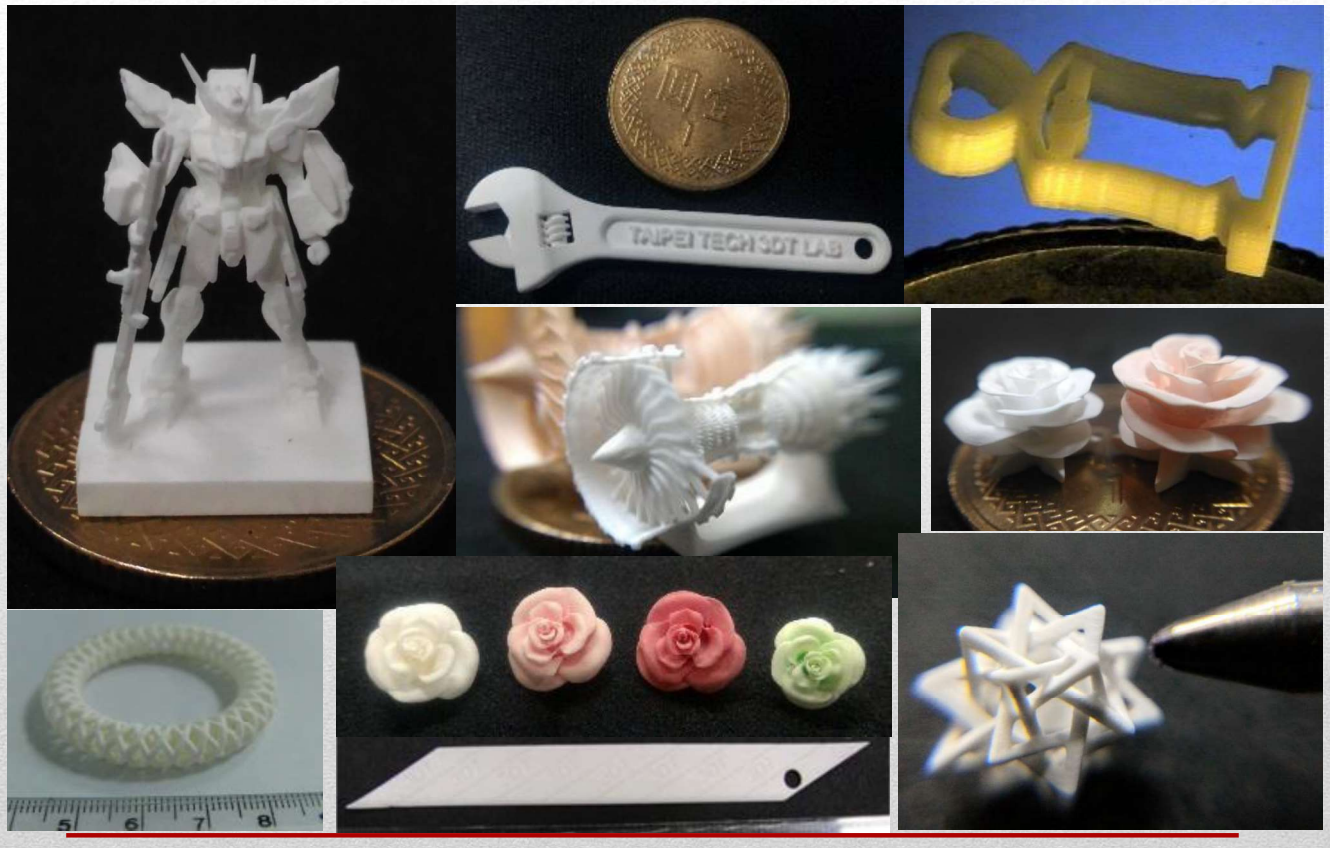
3S's sample with fine features and free shape design

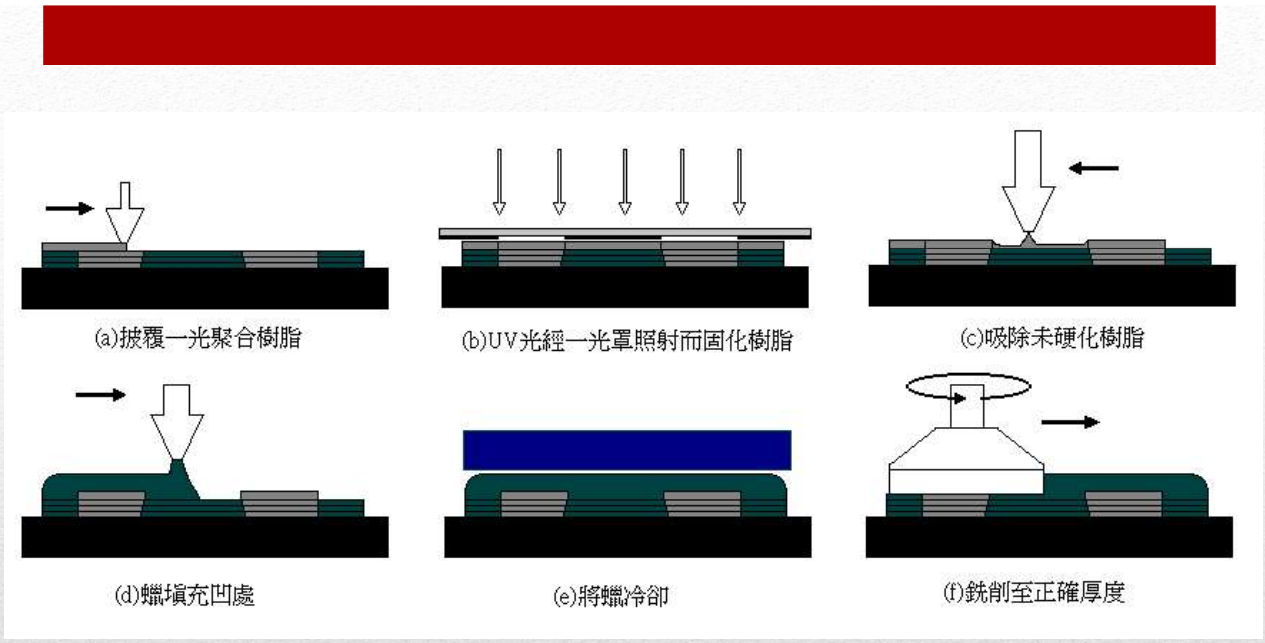
Lithoz's sample, there is a building plate on the bottom



Top left: picture from Formatec web site. The shape of the rabbit has to be standing on a plate.
Others are our results. Bottom left are two lions with different material: one is Zirconia, the other is alumina. Bottom right is showing the precision and accuracy of the result.

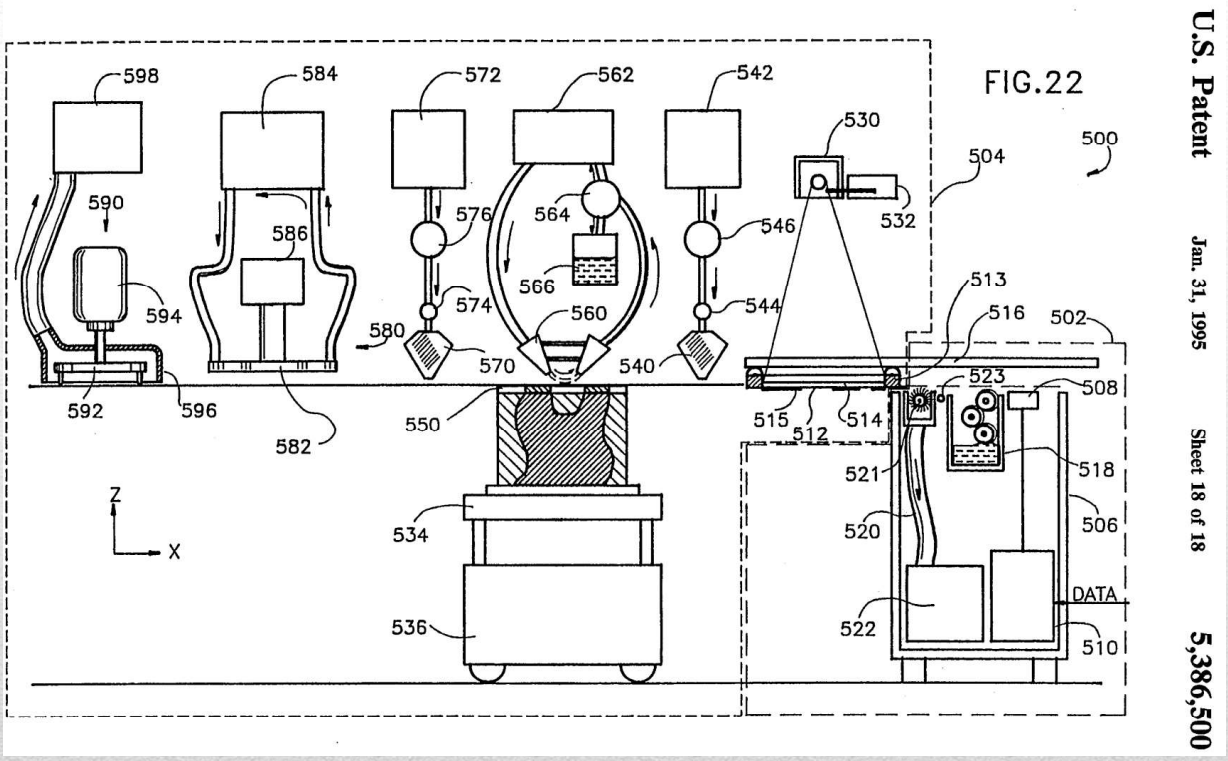
results



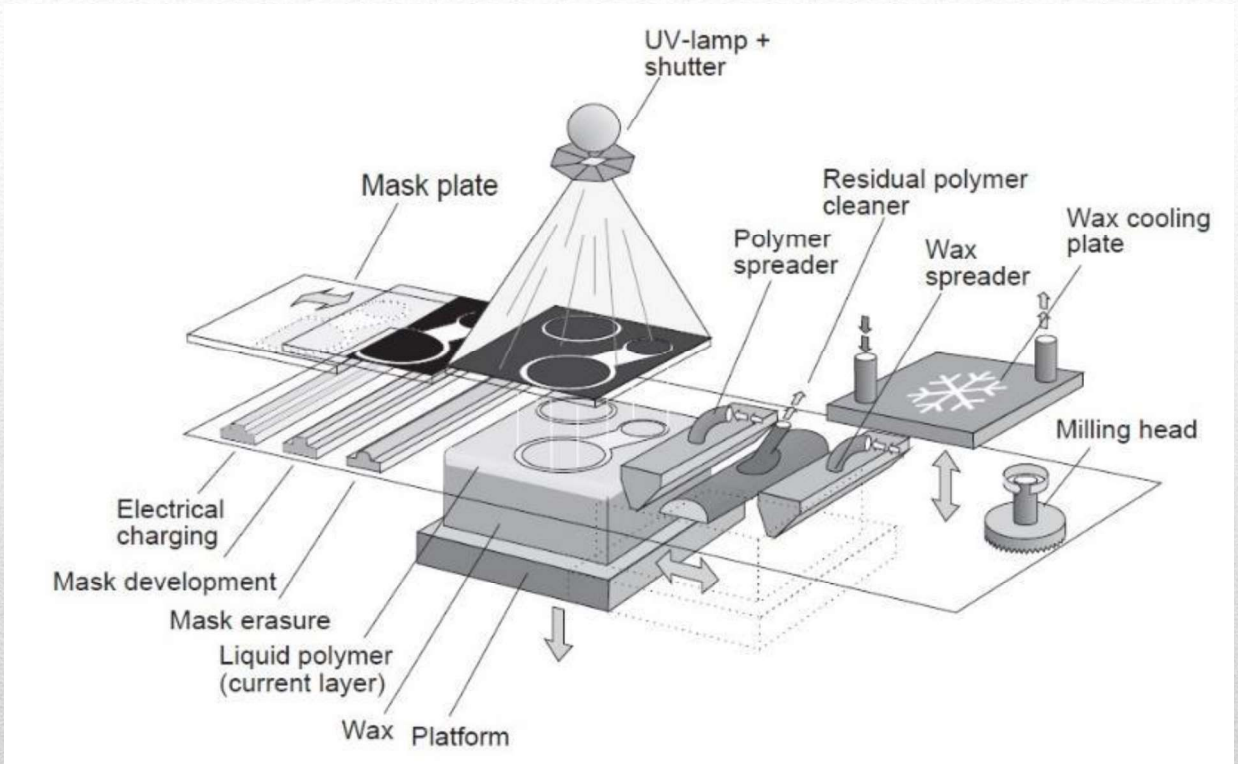


SGC(Solid Ground Curing)為以色列所開發出的，雖然現在已經沒有繼續生產，但其技術方法對現代的積層製造技術仍有很大的貢獻。這是第一個導入雙材料的光聚合固化技術，也是第一個以光罩面曝光成型的技術。

System-SGC



Three dimensional modeling apparatus US 5386500 A



SGC

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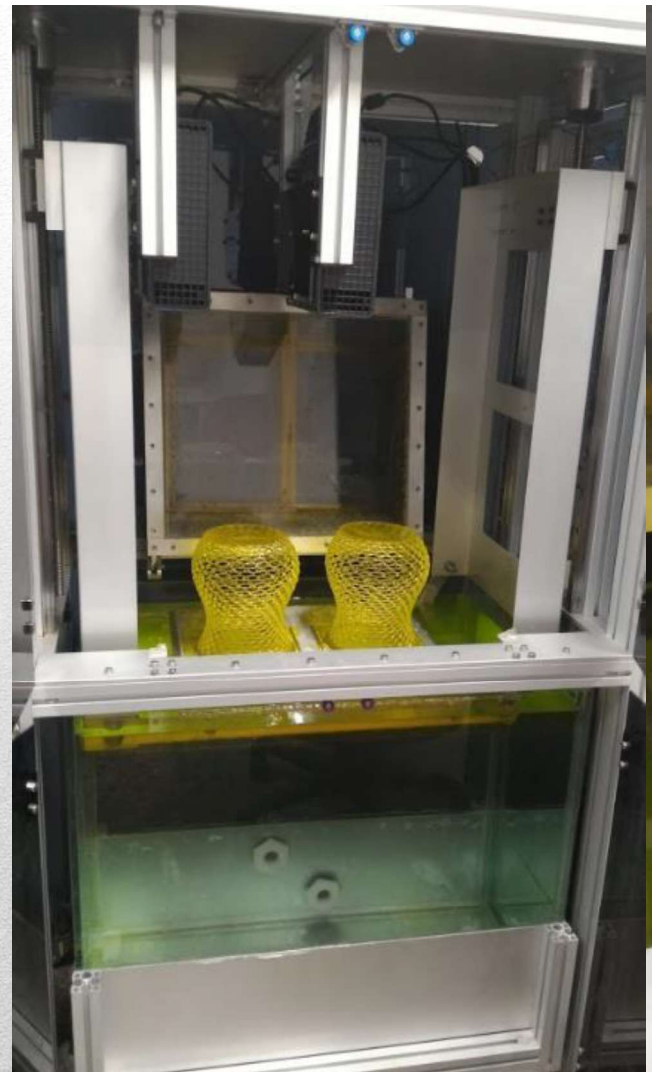
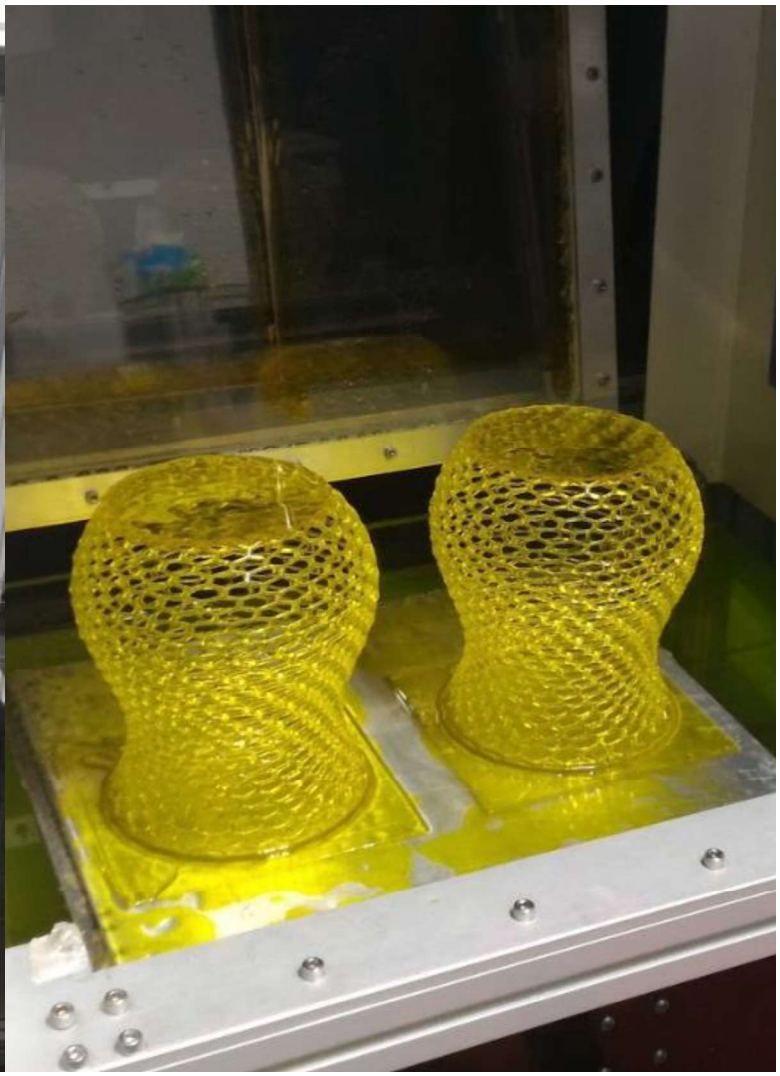
- 光聚合固化技術是以光進行選擇性的照射，將低分子量的液態樹脂以光聚合方式成為高分子量的固體，本章節是以不同光照射方式之光聚合固化技術分類，區分出了點掃描及面固化兩大類，其中又有上照與下照，甚至還有在中間固化的多種方式。一般而言，光聚合固化可以藉由光的調整，而有不同的精細程度，此較不會因為物理上的熱傳導、材料本身的顆粒大小、噴頭本身的孔洞尺寸等等的限制，而受到細緻度上的限制。有的製造方式可以不用支撐的設計，這對未來全自動化的實現具有一定的優勢。加工速度也是一大重點，現今的積層製造還無法全面的應用在生產上，速度也是一大原因，但在如CLIP的連續拉拔方式，如果把傳統製造還要前置的模具時間考慮進來，積層製造可以立即滿足市場變化的特性，也是有機會直接導入到生產之中的。另外一大重點為材料，光聚合固化的材料特性與傳統常用的材料還是不一樣，如何開發出各式先進的材料，滿足日亦嚴格的產品物性要求，也是一大研究的重點。

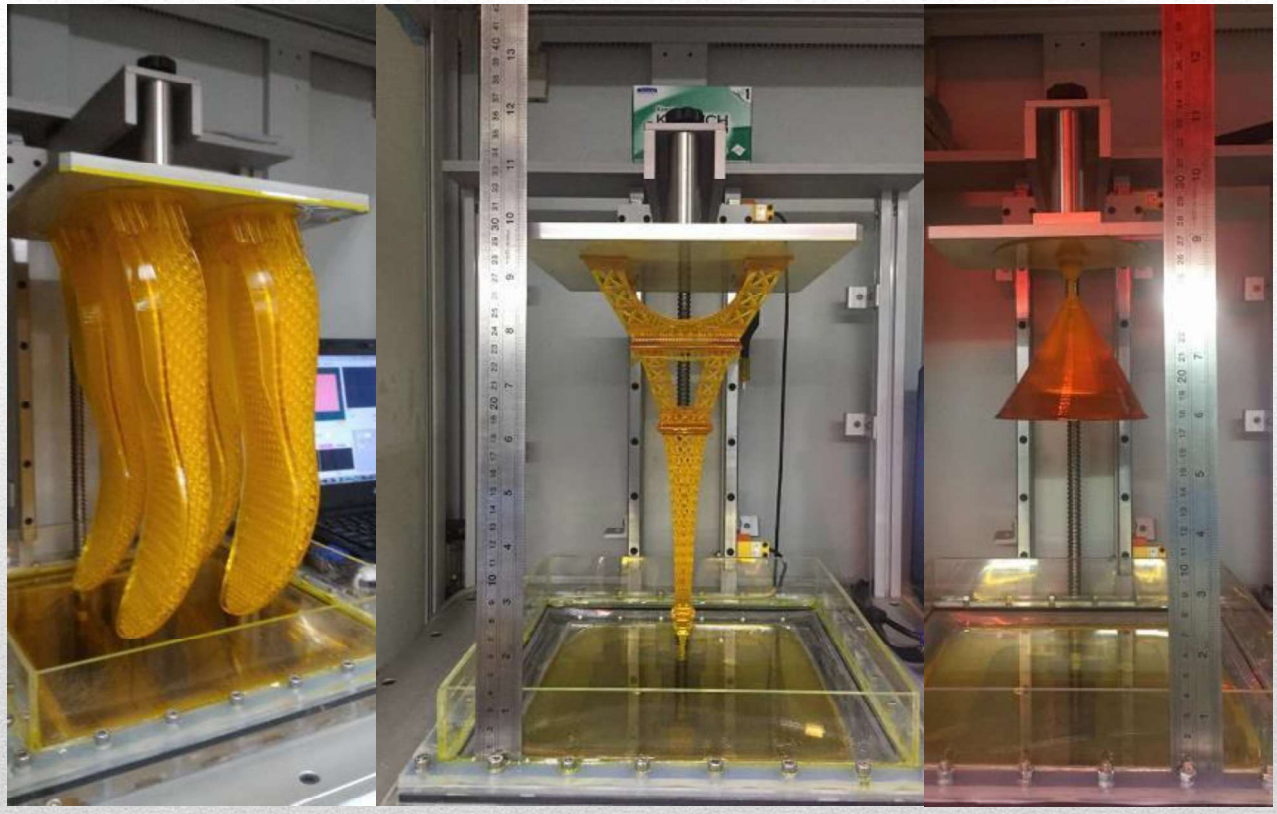
製程優缺點分析

TAIPEI TECH

Album





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