



Laser Induced Forward Transfer of High Viscosity Fluids. Application To Solar Cell Metallization and Bio-Printing

M. Morales, D. Munoz-Martin, S. Lauzurica, A. Márquez, Y. Chen, D. Canteli, C. Molpeceres

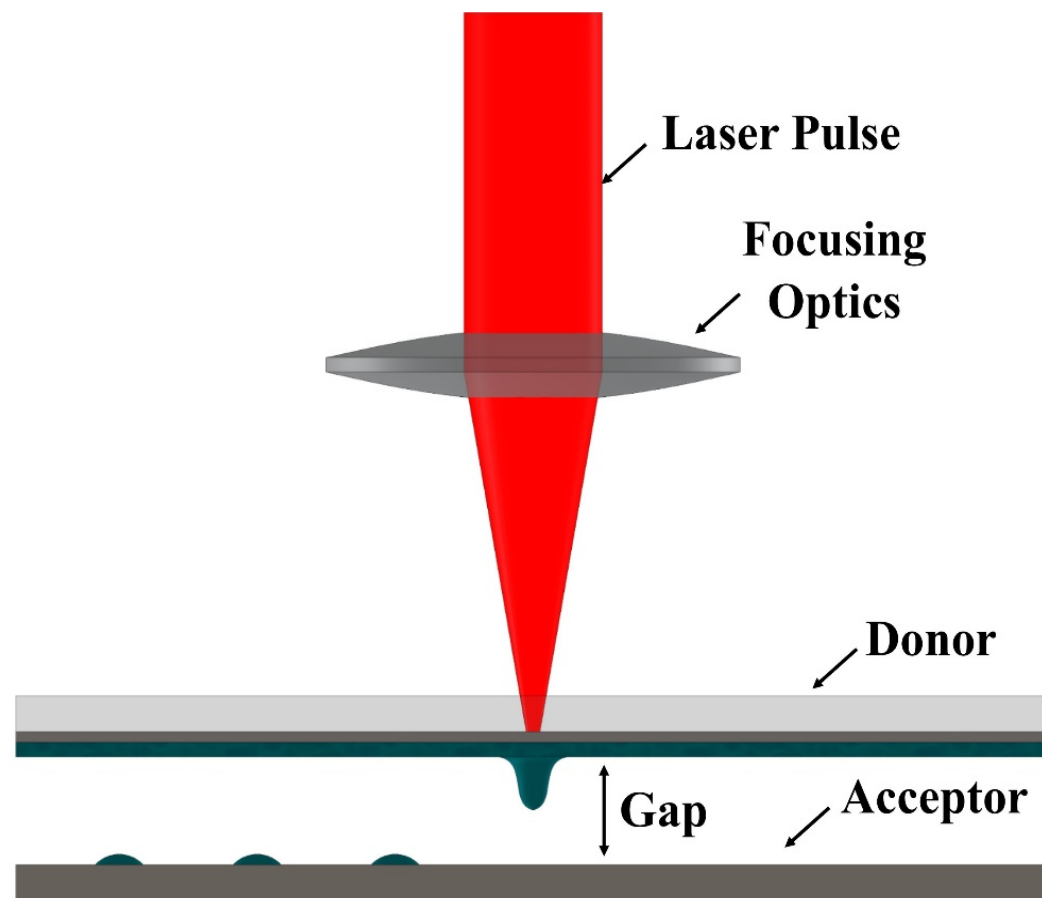


Hub of Application Laboratories for Equipment Assessment
in Laser Based Manufacturing



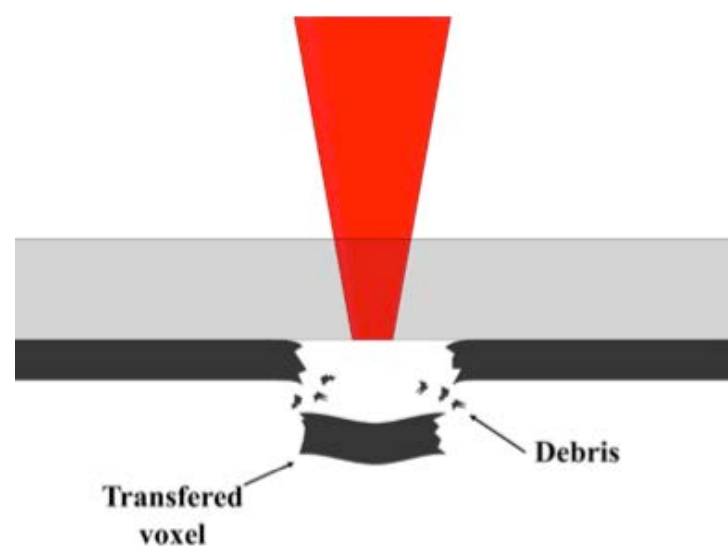
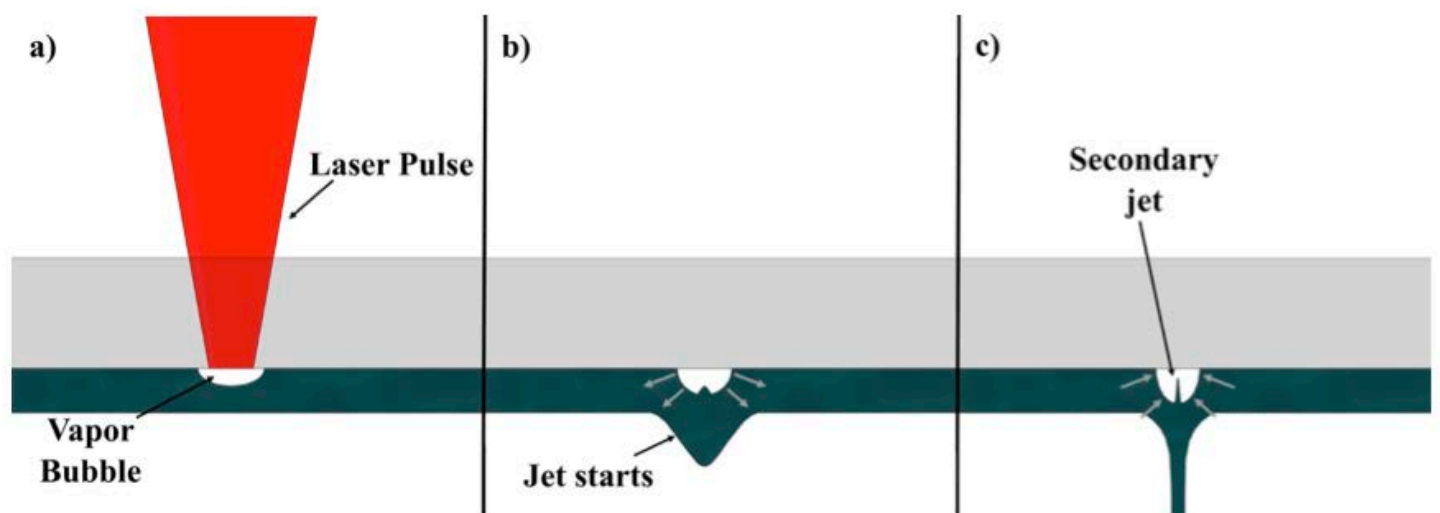


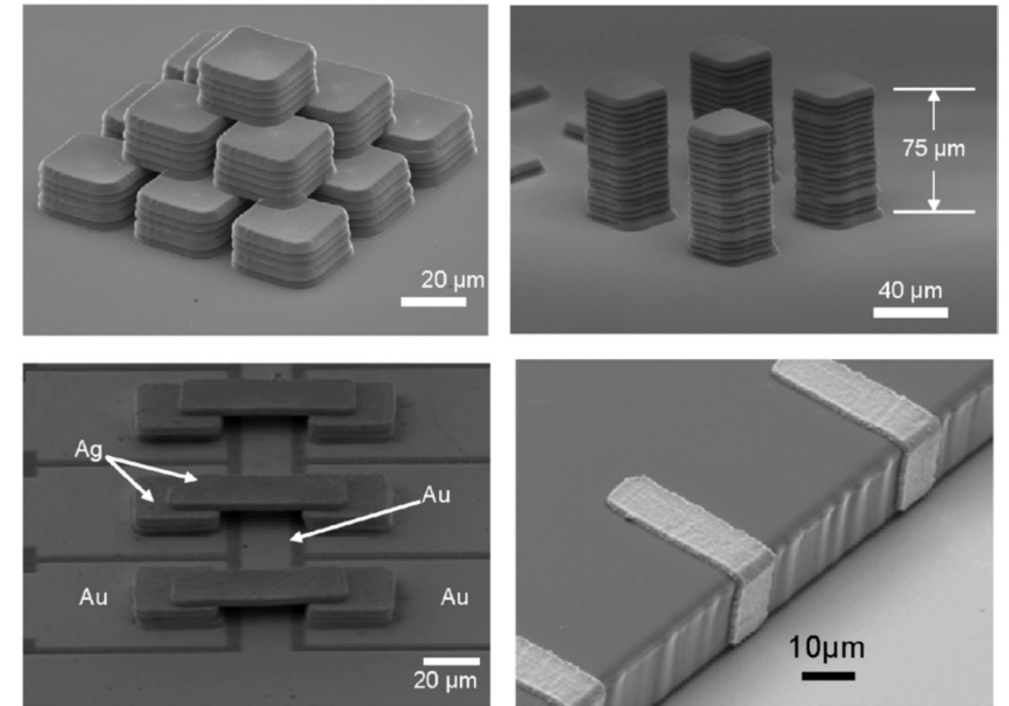
1. Introduction to Laser Induced Forward Transfer (LIFT)
2. Application to PV industry: solar cell metallization
3. Application to bio-printing
4. Understanding the printing process: numerical simulation
5. Summary & Acknowledgements



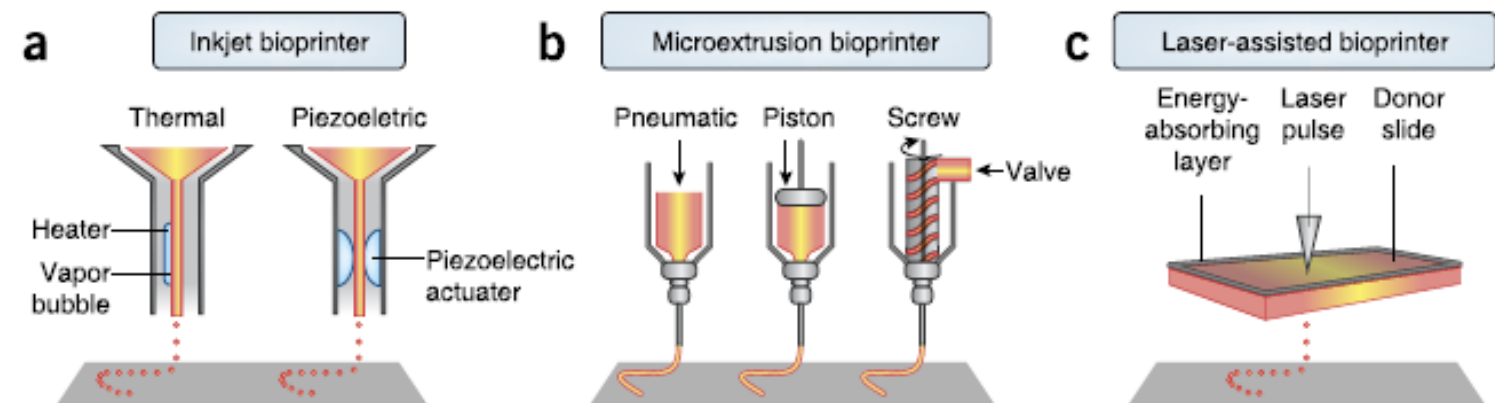
Some materials deposited using LIFT:

- Metals
- Oxides
- Nanopowders
- Organic polymers
- Biomaterials & living cells
- Conductive inks
- Ag nanoparticles pastes





Piqué et al, J. Phys. D: Appl. Phys. 49 (2016) 223001

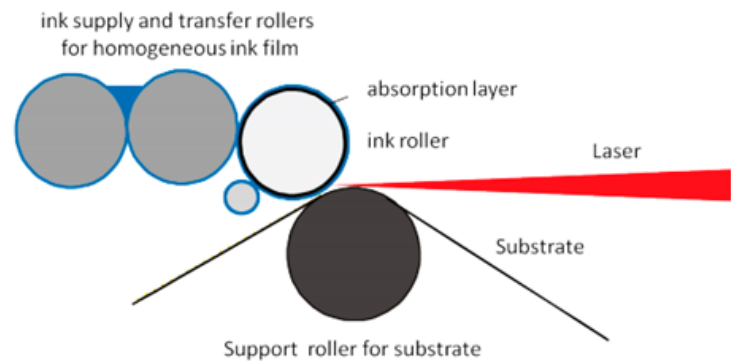


Murphy & Atala, Nat. Biotechnol. 32 (2014) 773-785

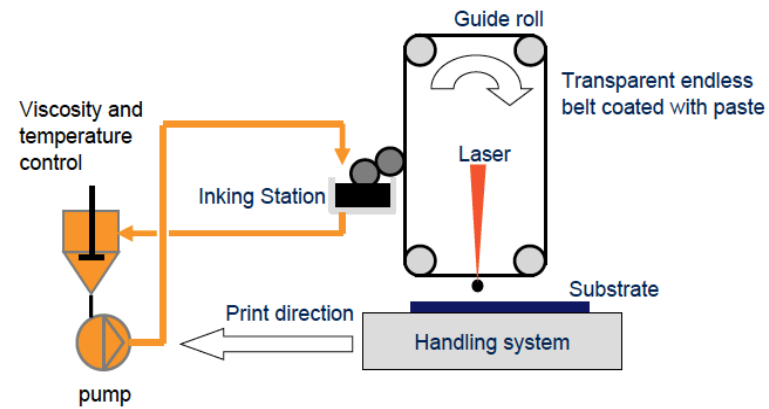


Laser Induced Forward Transfer

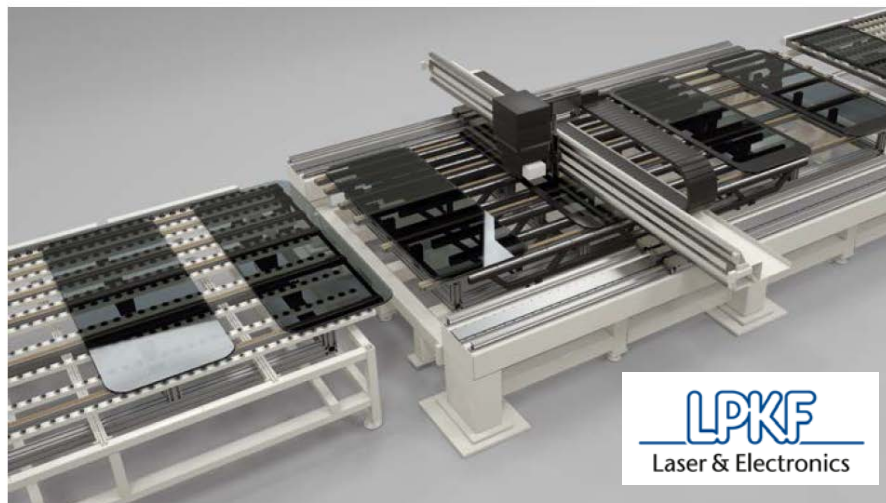
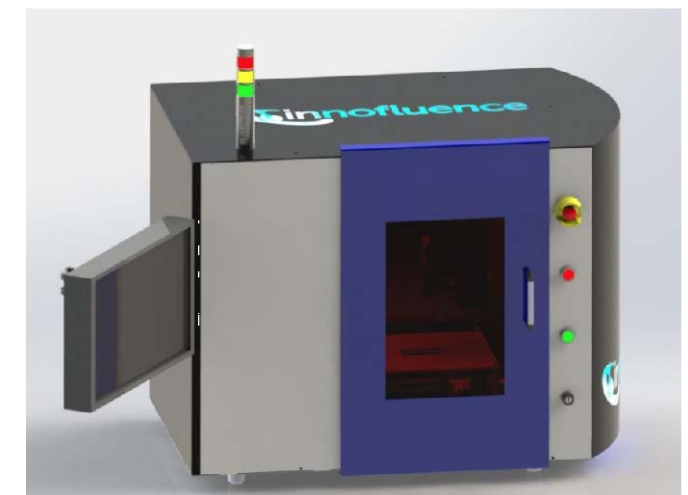
Lasersonic® LIFT Process



Hennig et al, J. Laser Micro Nanoeng. 7
(2012) 299–305



Fraunhofer ILT



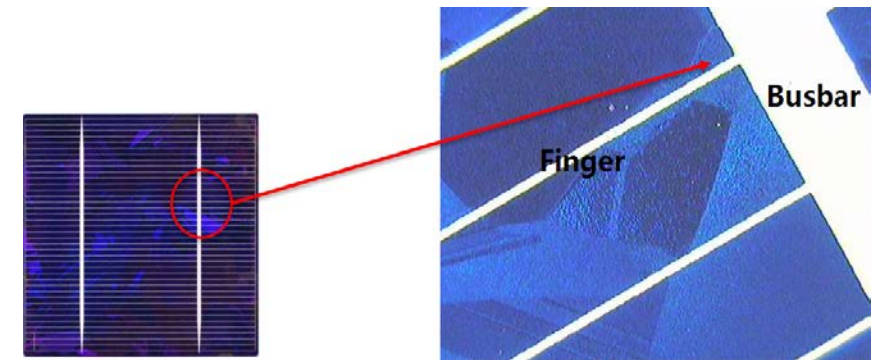


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Front-side metallization: key process for enhancing efficiency in a cost effective way. It comprises different steps:

1. Pre-metallization processes
2. Metallization
3. Curing, sintering and firing

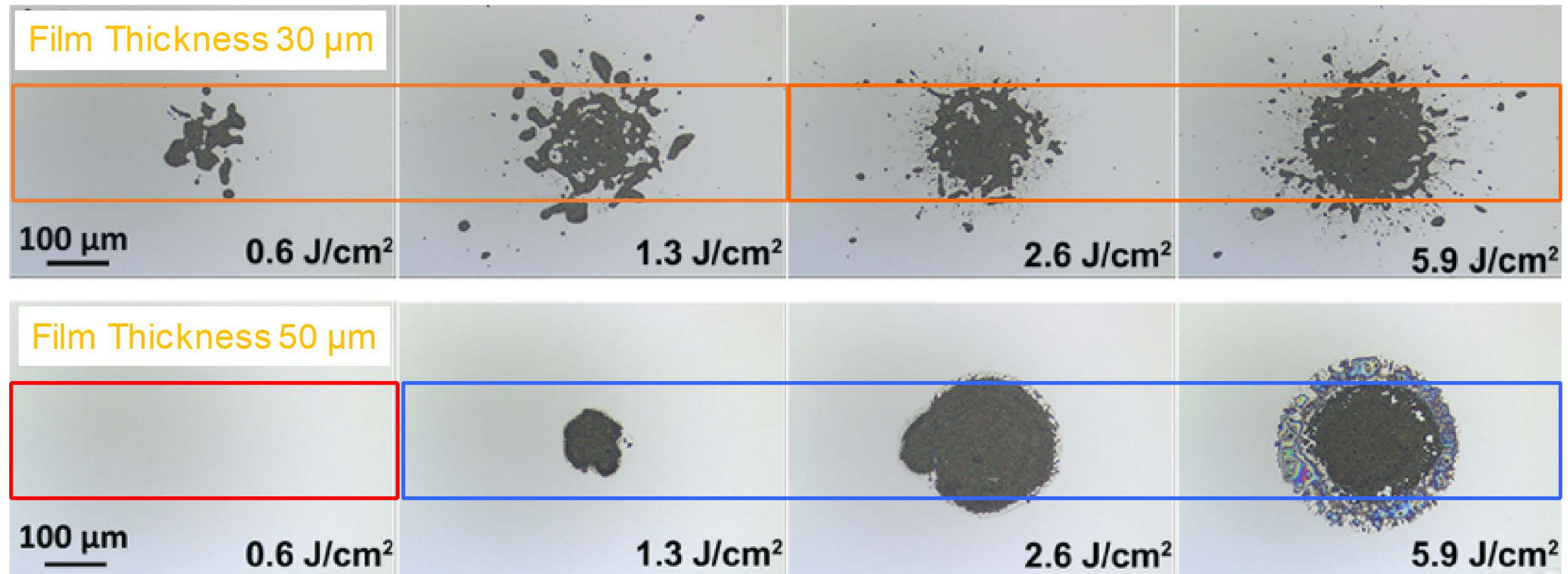


- ns- & ps- pulsed lasers emitting at 532 nm
- Beam scanned using motorized axis, galvo and polygon scanners.
- Basic LIFT configuration (no intermediate absorbing layer or assisting liquid matrix). Gap distance: in de order of tens of μm .

- DuPont PV17F & PV19B commercial screen printing Ag pastes.
- Non-newtonian, pseudoplastic, thixotropic fluids
- μ up to $250 \pm 30 \text{ Pa}\cdot\text{s}$
- Ag particles size: $1\text{-}5 \mu\text{m}$
- Donor film thickness $< 100 \mu\text{m}$



LIFT Voxel Printing



No transfer

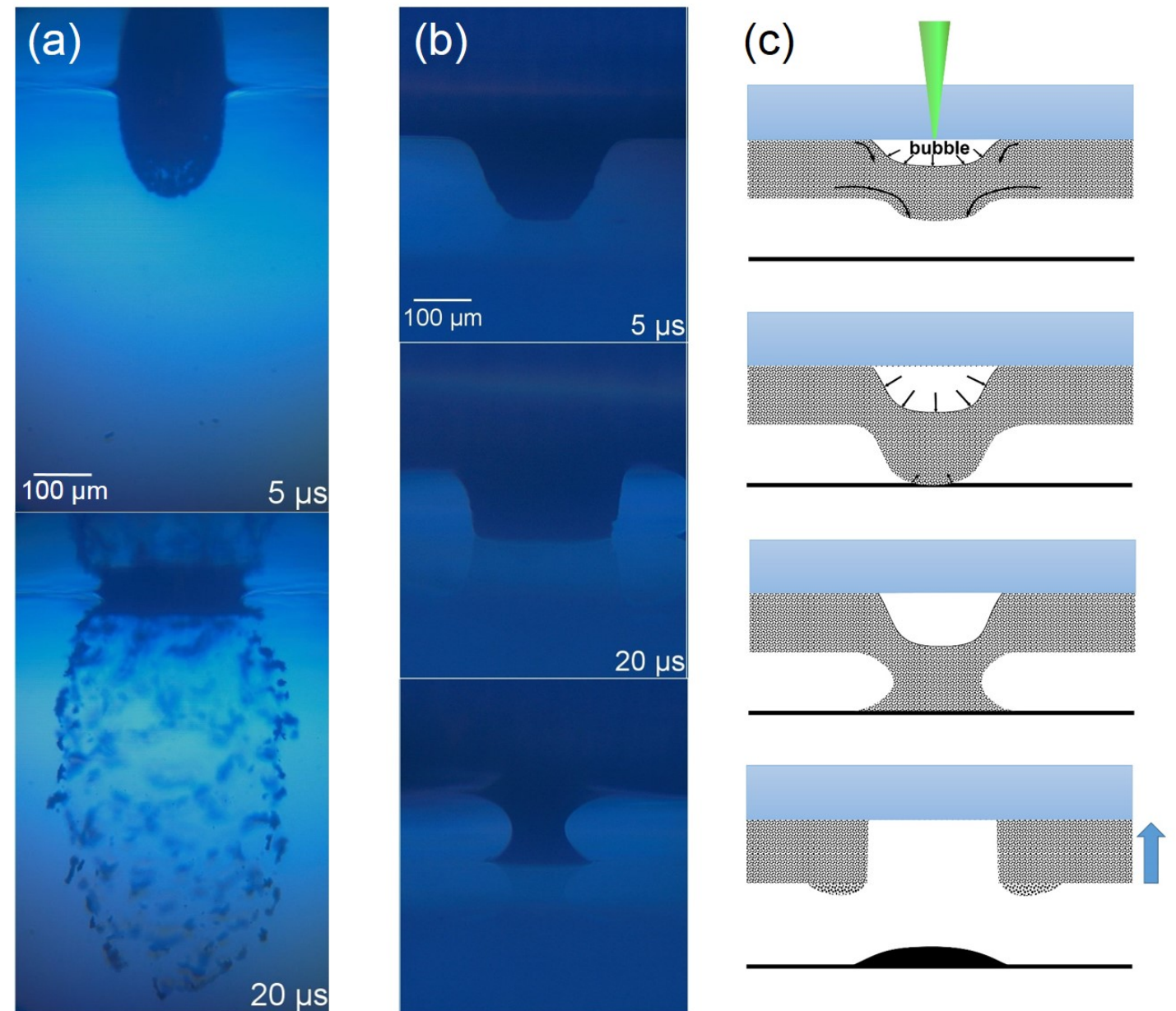
Cluster transfer

Explosive transfer

Concrete-dot transfer

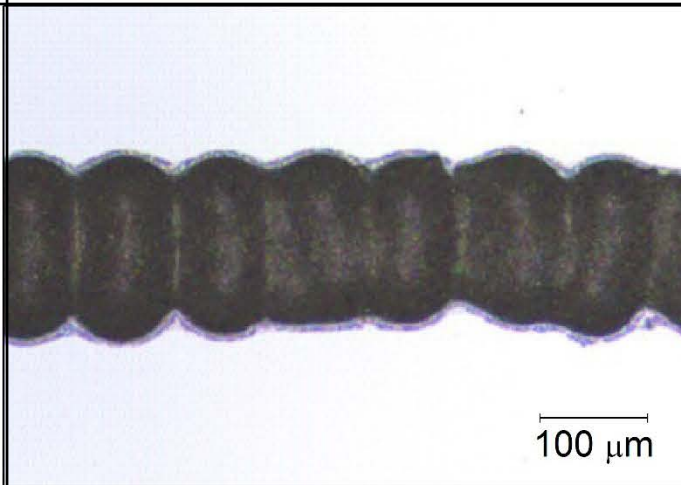
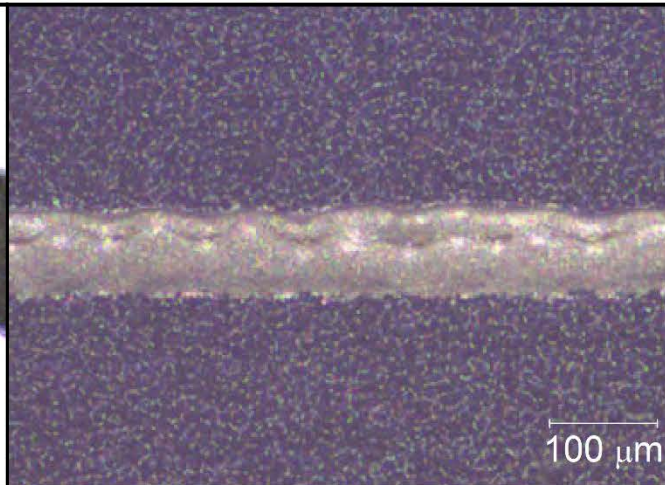
High viscosity paste transfer mechanisms

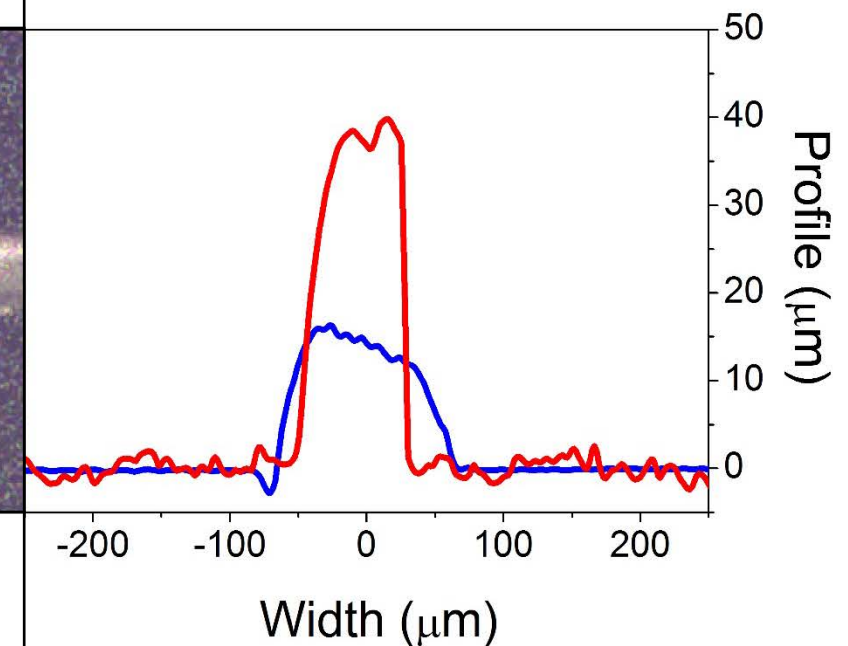
- Morphology of the transferred voxel depends on laser fluence (F), donor film thickness (h) and gap distance (d)
- Voxels transferred using large F consist of non-continuous clusters of paste (cluster-dot transfer)
- F just larger than the transfer threshold allows printing single dots of paste with large aspect ratio (concrete-dot transfer)
- **Effect of the substrate:** formation of a continuous pillar between donor and acceptor





Printing of lines

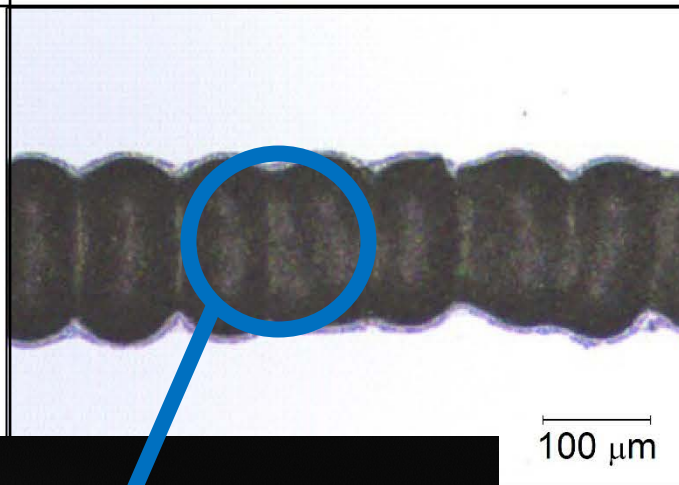
Substrate	polished c-Si	textured c-Si
Laser	ns-laser	
		
	$E_p = 13 \mu\text{J}$ $\omega_0 = 15 \mu\text{m}$ Rep Rate = 20 kHz $v = 1800 \text{ mm/s}$ $h = 50 \mu\text{m}$ $d = 50 \mu\text{m}$	



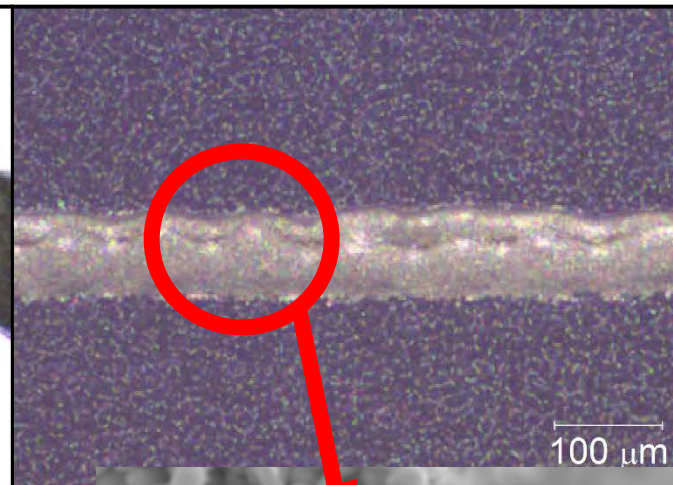


Printing of lines

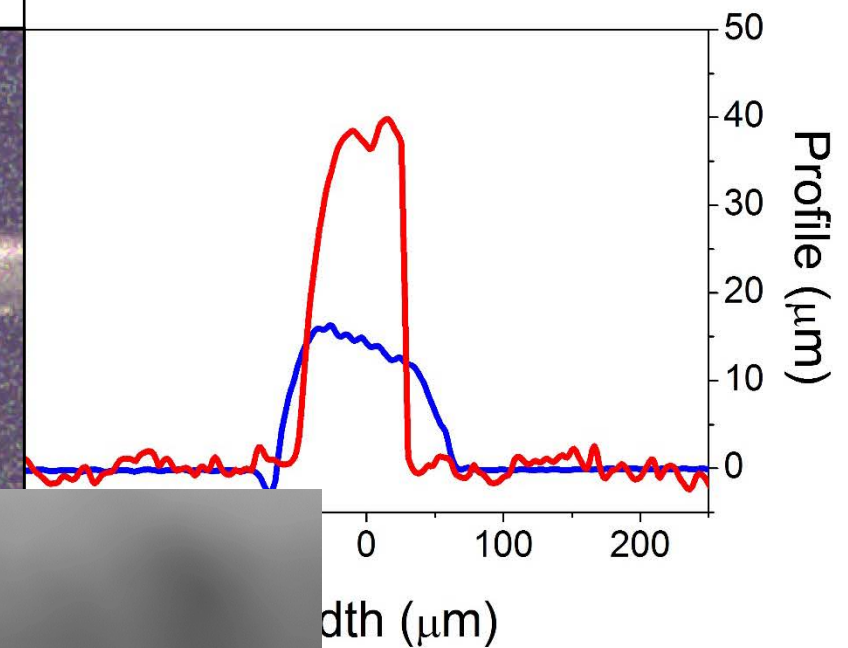
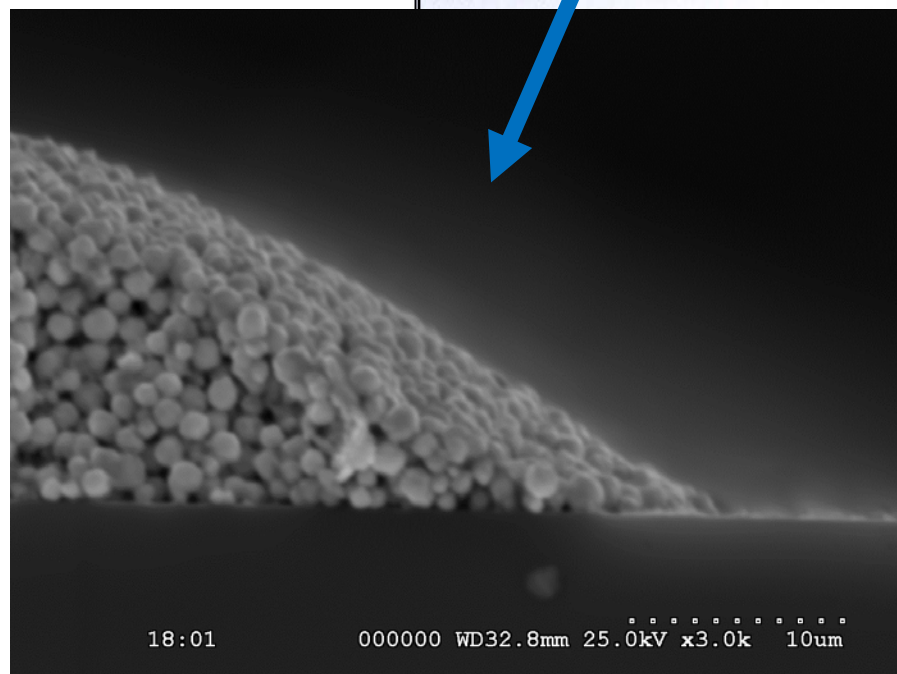
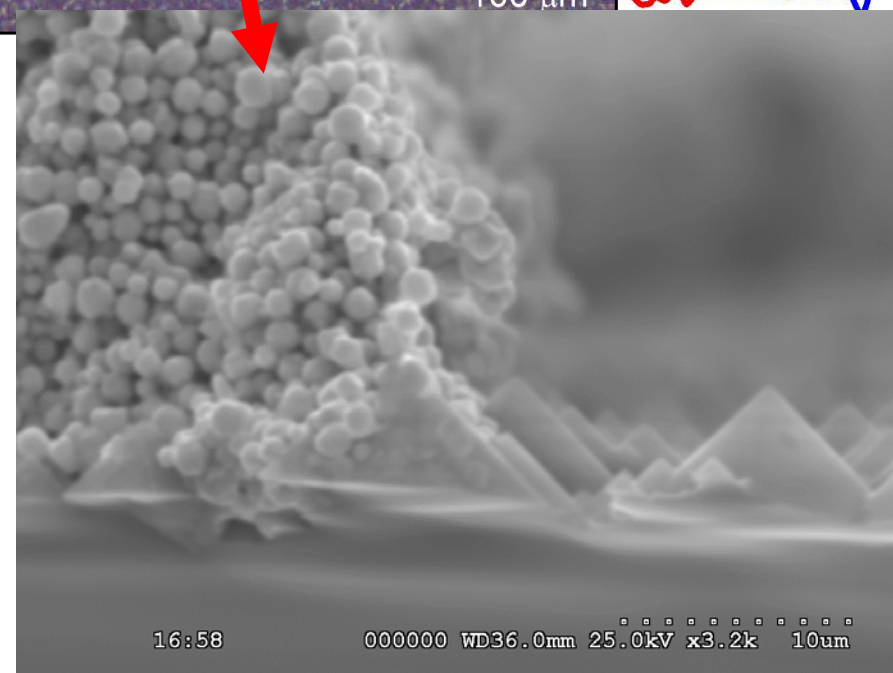
Substrate	polished c-Si	textured c-Si
Laser	ns-laser	



100 μm



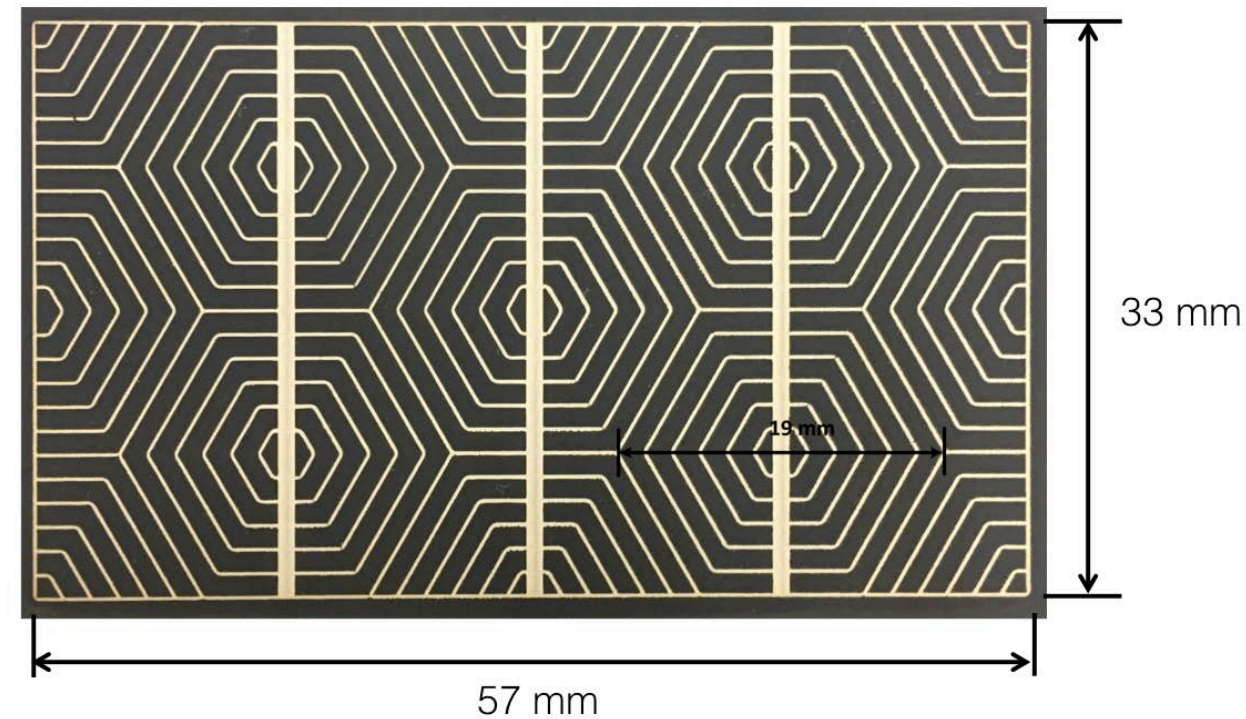
100 μm





Printing of lines: design flexibility

- Optical scanners allows fast processing and flexible design to print large areas.
- Very versatile, allowing any freeform design for the solar cells personalization.
- Application in Building integrated PV.





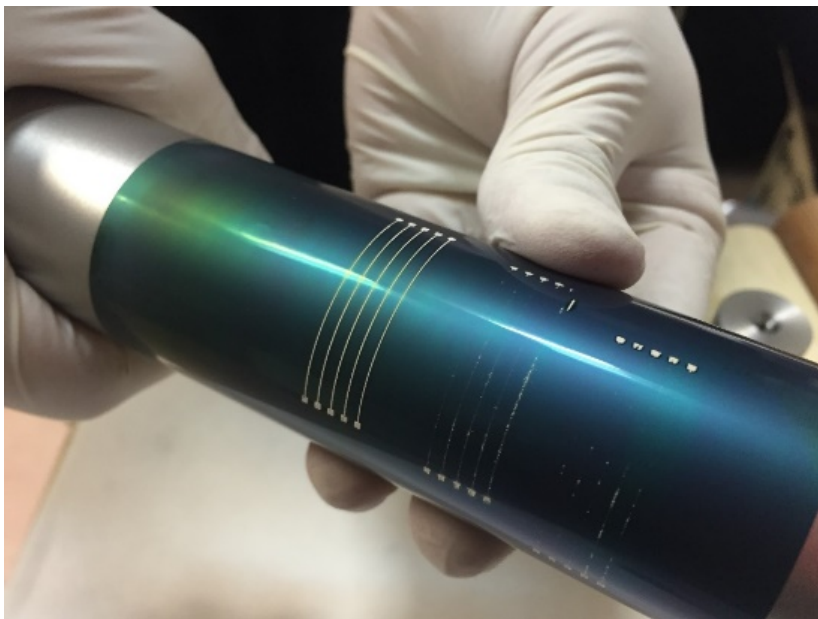
Proof of concept: full metallization of a CIGS solar cell on steel flex substrate

appolo

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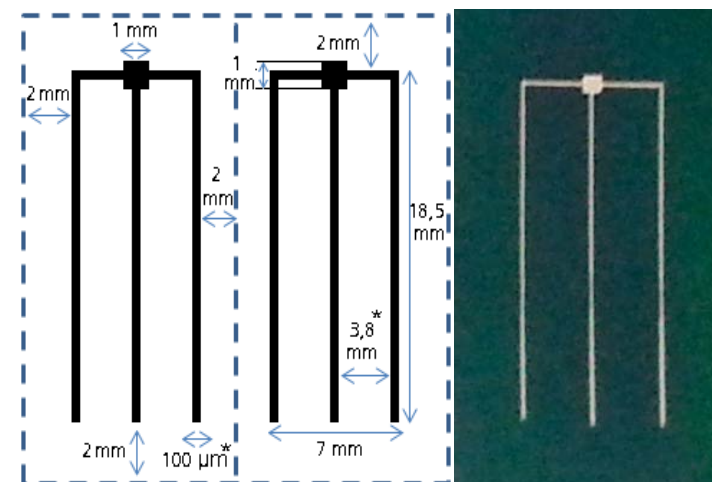
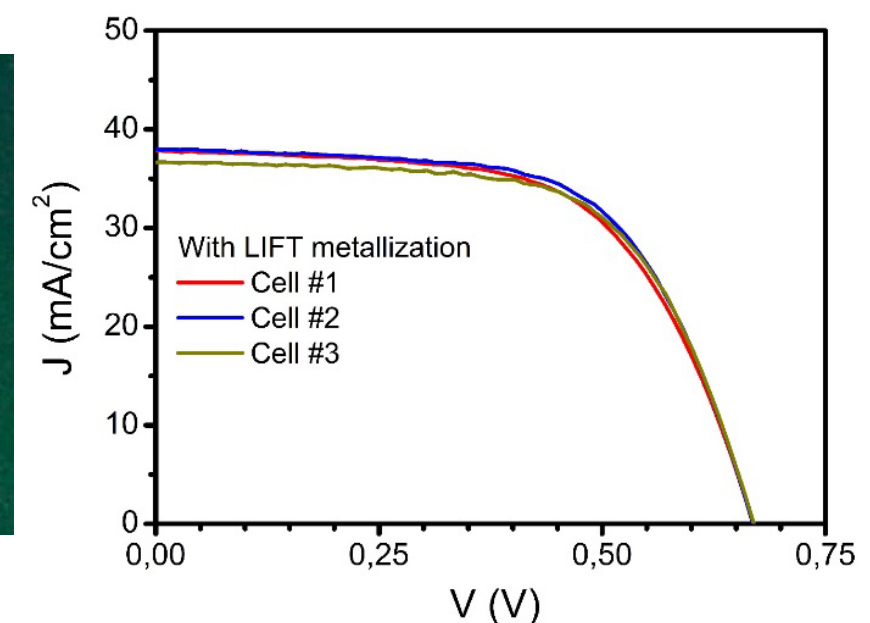


ABENGOA SOLAR



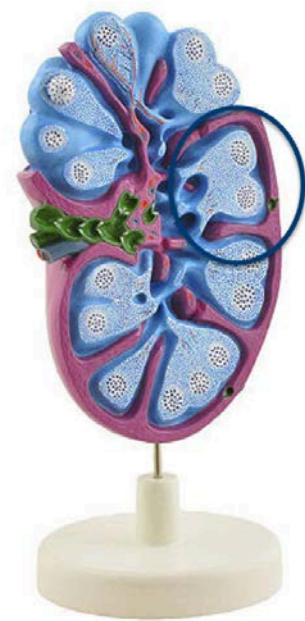
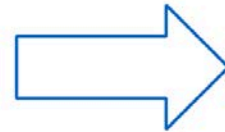
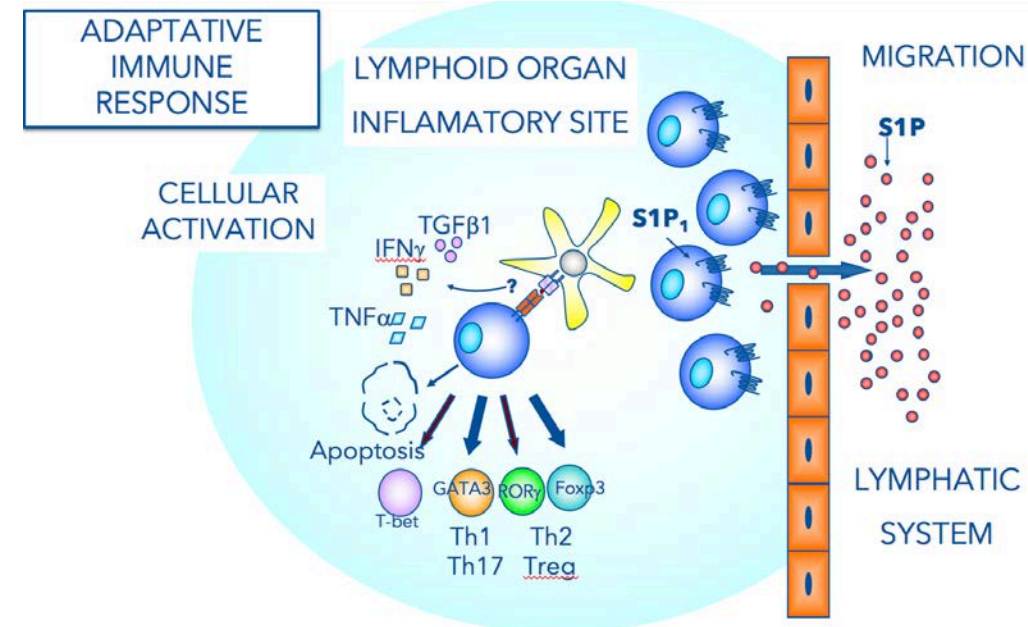
Good adherence after bending
with radius down to 12 mm

Resistivity	40 $\mu\Omega\cdot\text{cm}$
Specific contact resistance	50 $\text{m}\Omega\cdot\text{cm}^2$





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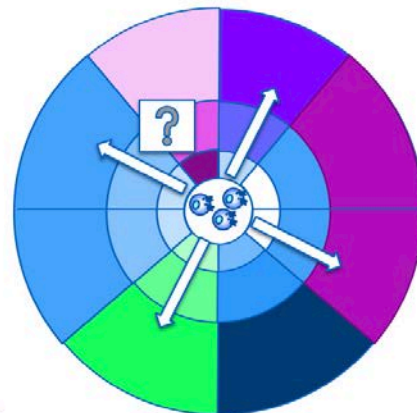
1. PRINTING different size of droplets with different cell concentration in order to control the number of cells inside them.

2. PRINTING different type of cells as close as possible.

3. Cell Activation, the interaction between different cell types is measured by cytokine reporters.

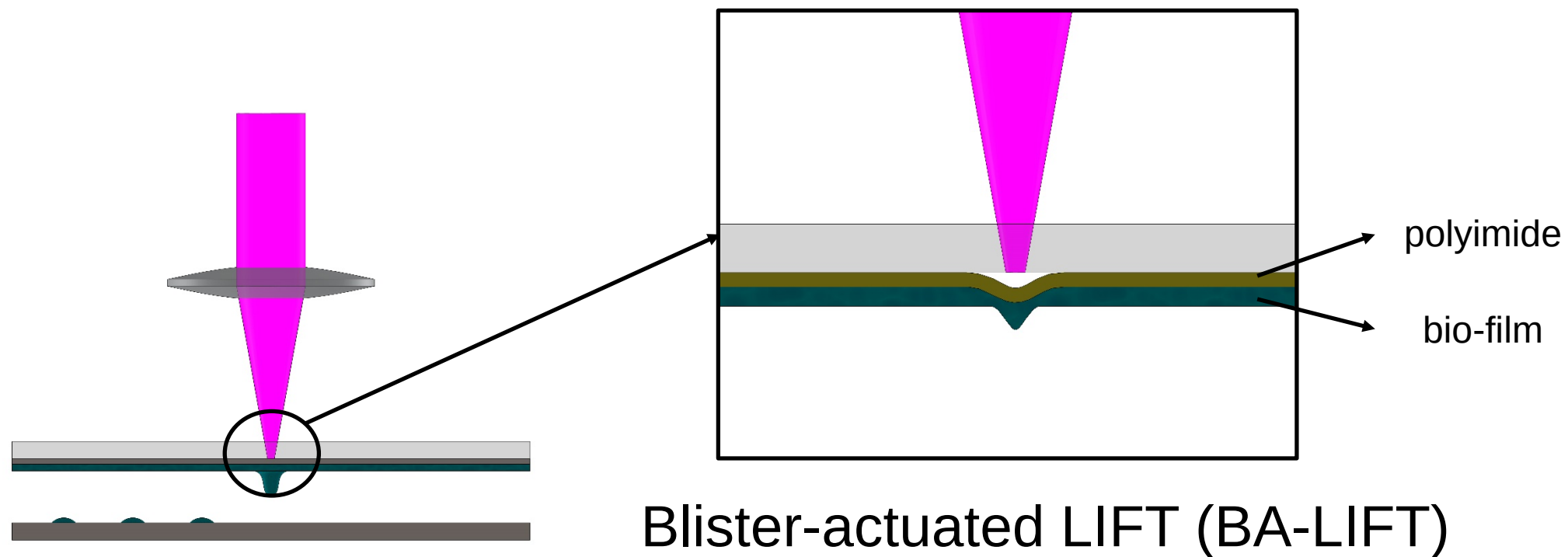
4. Study of cellular migration by means of different chemokine gradients

Different concentration gradients of chemokines



Different types of chemokines



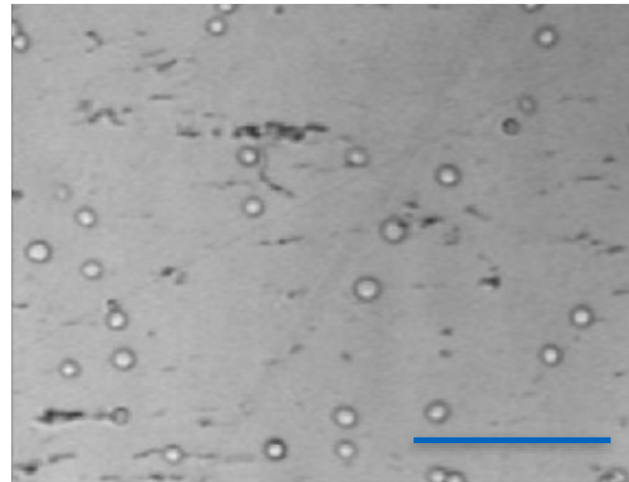
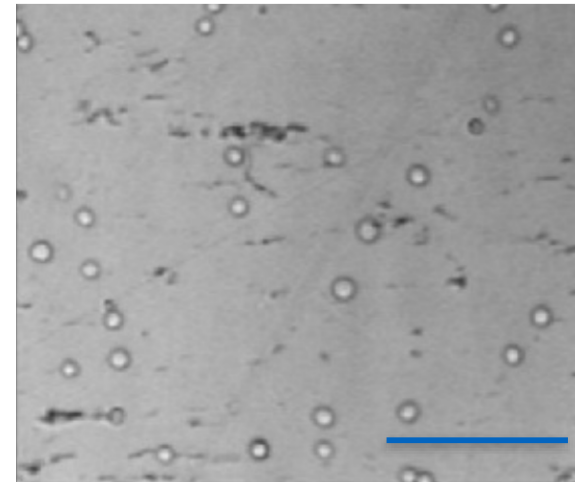


- ns- pulsed lasers emitting at 355 nm
- Beam scanned using a galvo scanner.
- BA-LIFT
- Donor film thickness: $\sim 30 \mu\text{m}$.
- Gap distance: $\sim 500 \mu\text{m}$.



Two different cell types were used:

Dendritic cells
(antigen presenting
cells)



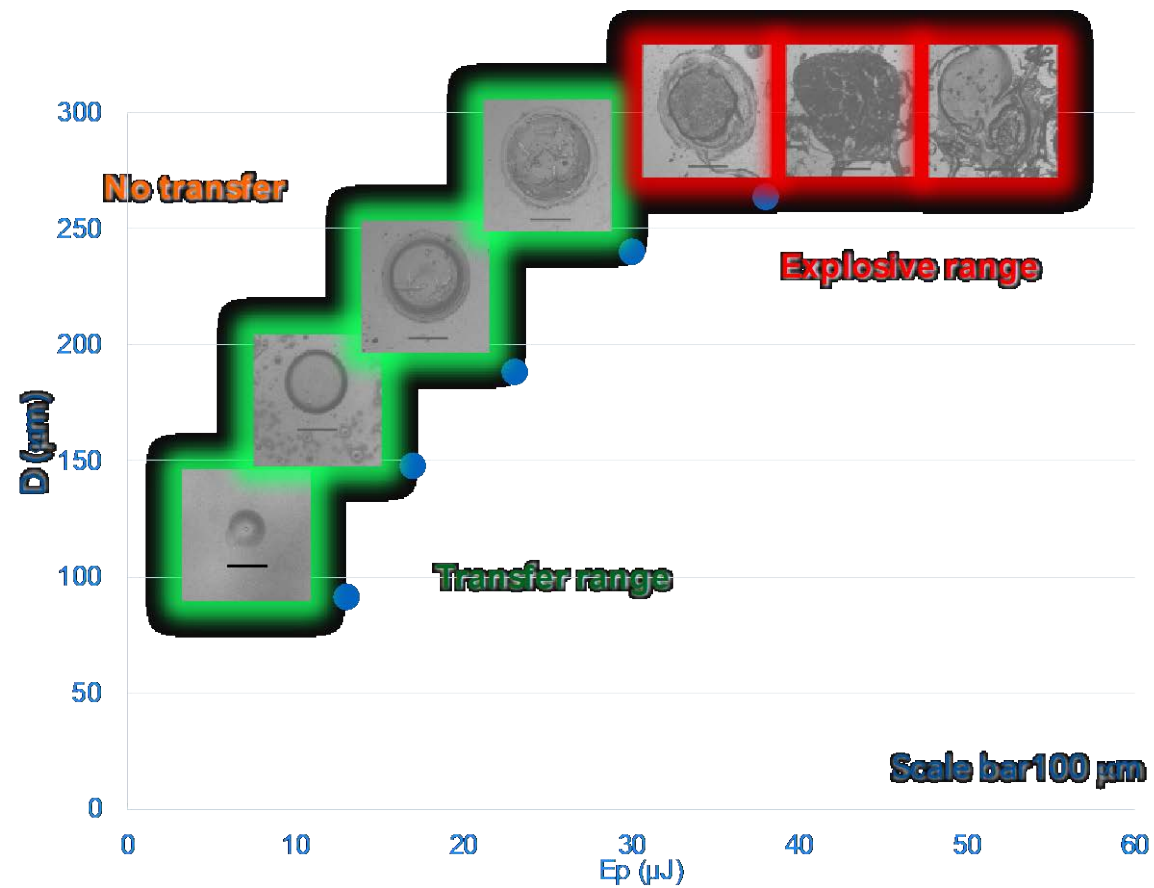
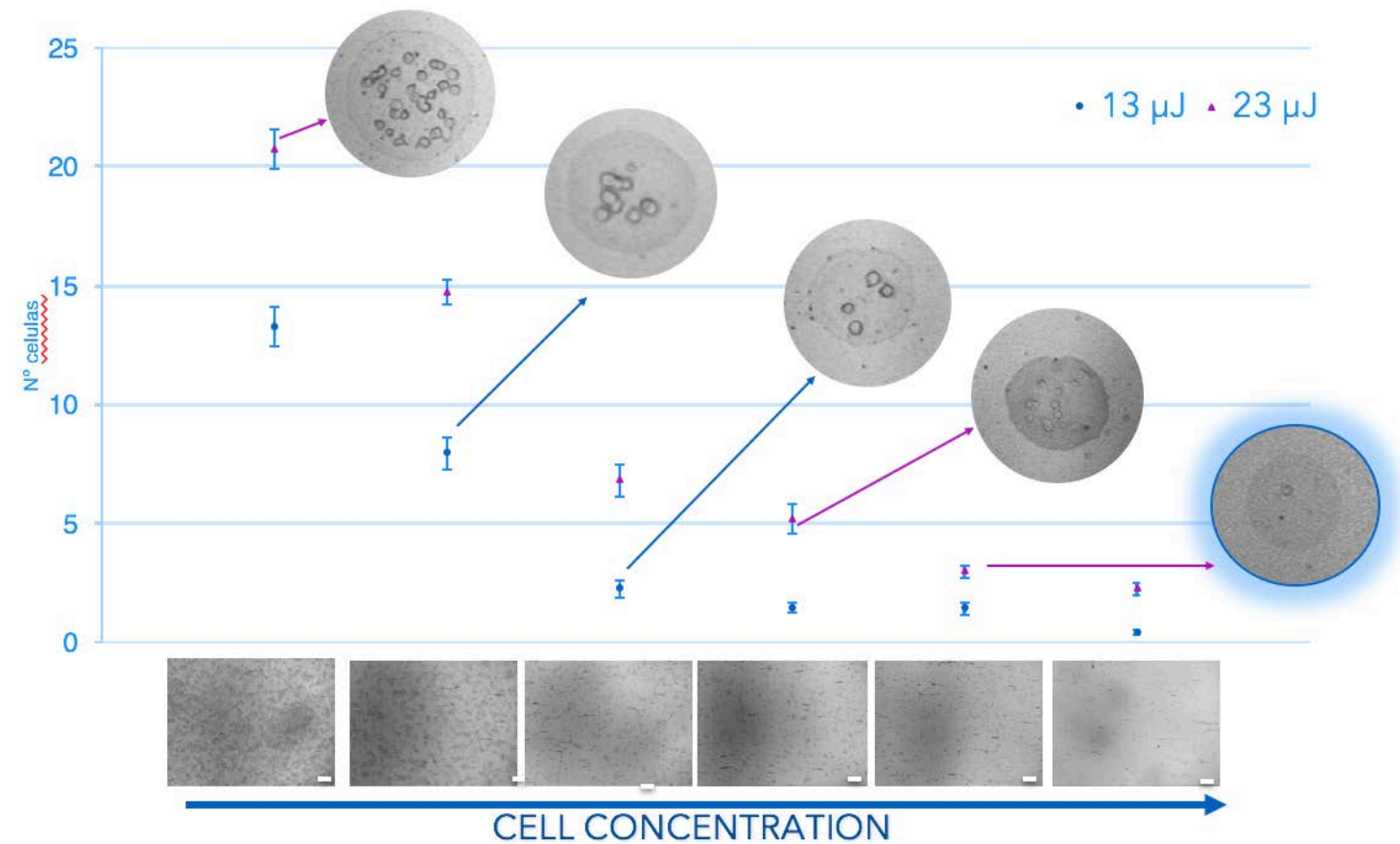
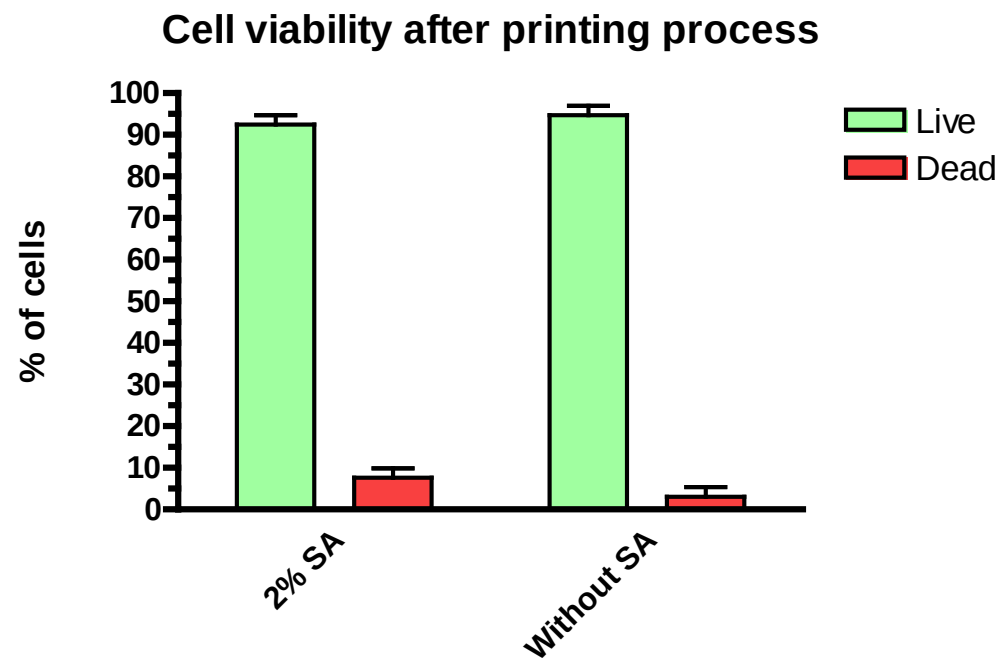
T lymphocytes from both
human (jurkat cell line) and
mouse (RMA/S cell line)

Cells need to be in a **matrix** that:

- allows keeping cells alive
- acts as a carrier during the cell printing process
- allows the formation of 3D structures once printed

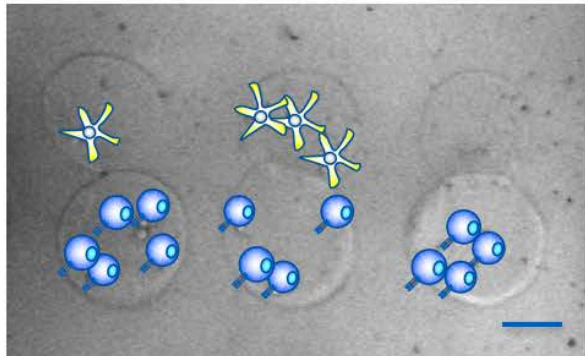
Different media can be used (sodium alginate solution in water and hydrogels)

Non Newtonian fluids with viscosities strongly dependent on the concentration and the temperature ($\mu \sim 10^{-3} - 1 \text{ Pa}\cdot\text{s}$)

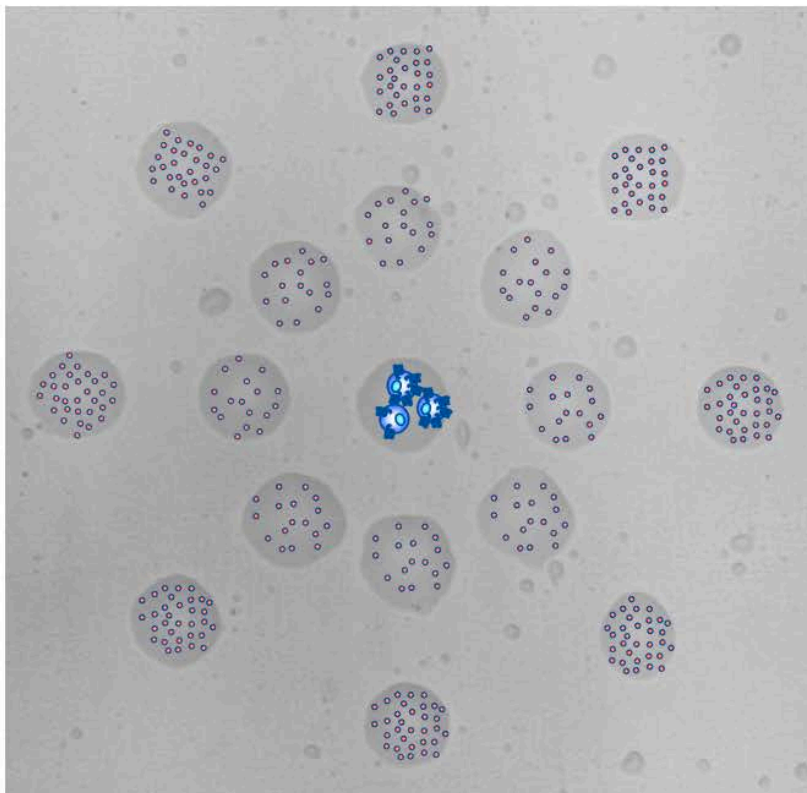
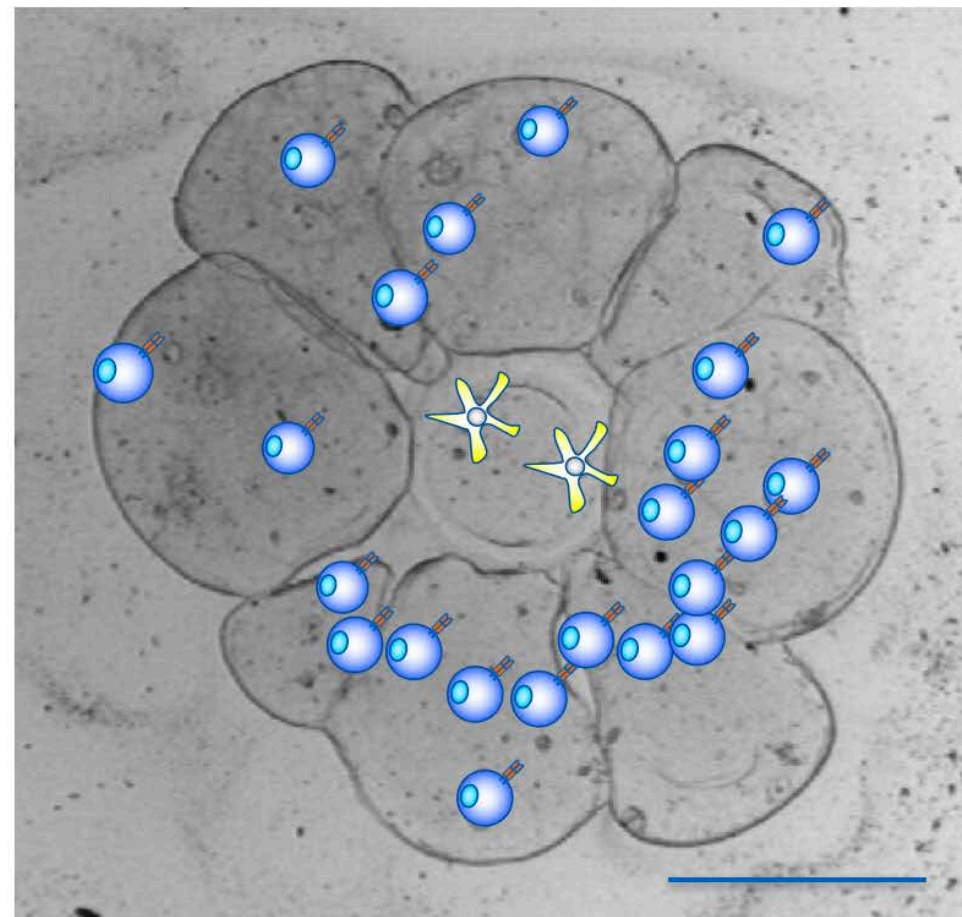




Two different cell type printed in different configuration



Different S1P chemokine concentration



Scale bar 100 μm



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Numerical simulation of the expansion of low and high viscosity fluids using BA-LIFT



Navier-Stokes equations

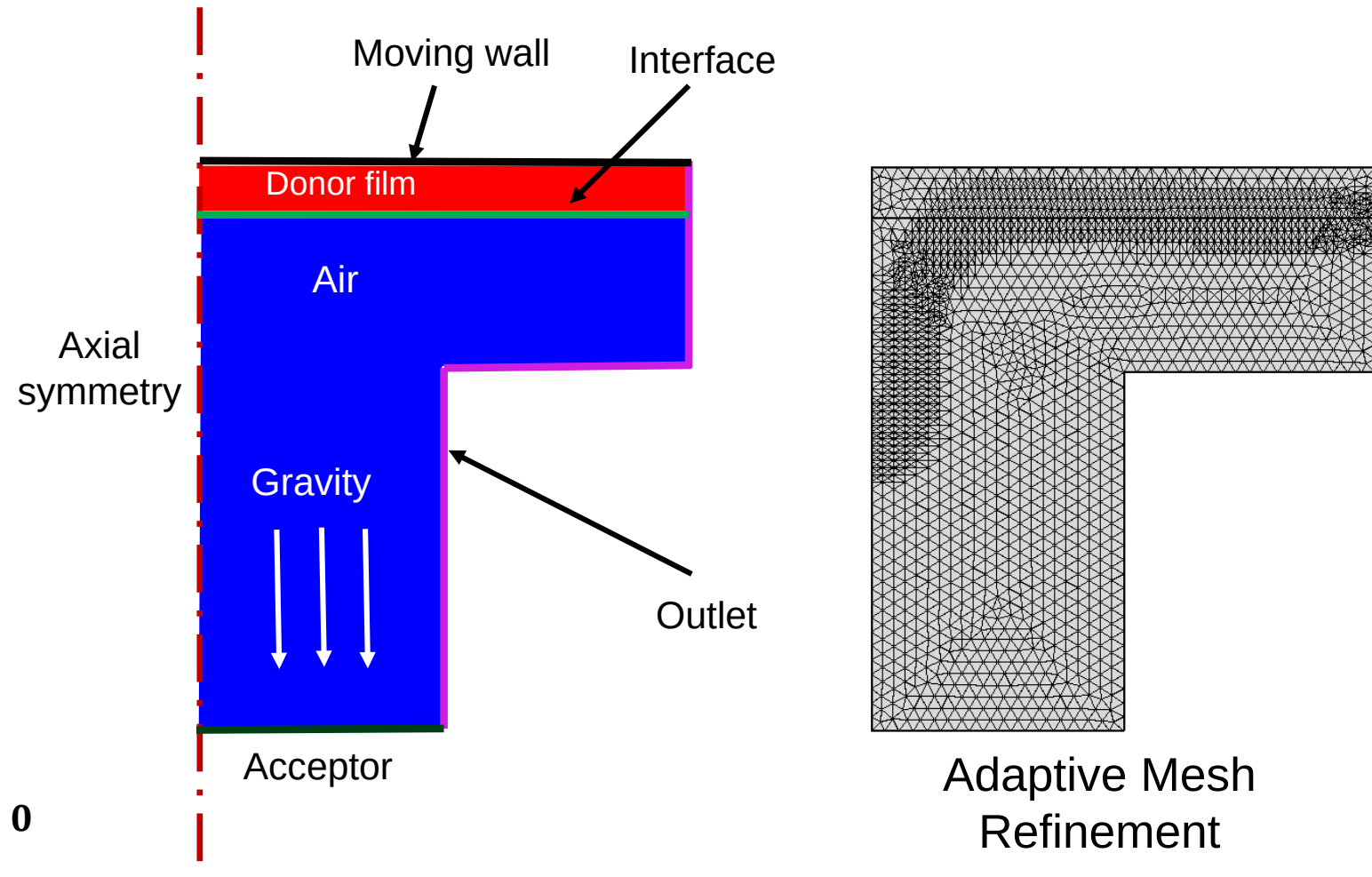
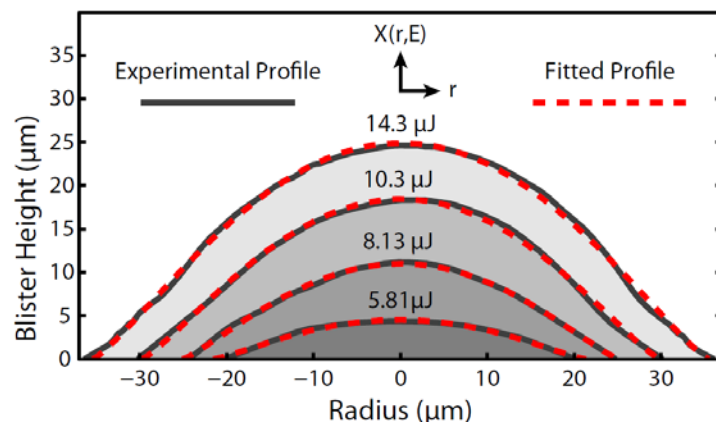
$$\rho \left(\frac{\partial \vec{u}}{\partial t} + \vec{u} \cdot \nabla \vec{u} \right) - \nabla \cdot (\mu (\nabla \vec{u} + \nabla \vec{u}^T)) + \nabla p = \vec{F}_{ST}$$

$$(\nabla \cdot \vec{u}) = 0$$

Two phase flow – level set interface

$$\phi = \begin{cases} \phi = 0 & \text{air} \\ 0 < \phi < 1 & \text{interface} \\ \phi = 1 & \text{film} \end{cases}$$

$$\frac{\partial \phi}{\partial t} + \nabla \cdot (\phi \vec{u}) + \gamma \left[\left(\nabla \cdot \left(\phi (1 - \phi) \frac{\nabla \phi}{|\nabla \phi|} \right) \right) - \epsilon \nabla \cdot \nabla \phi \right] = 0$$



Blister Movement

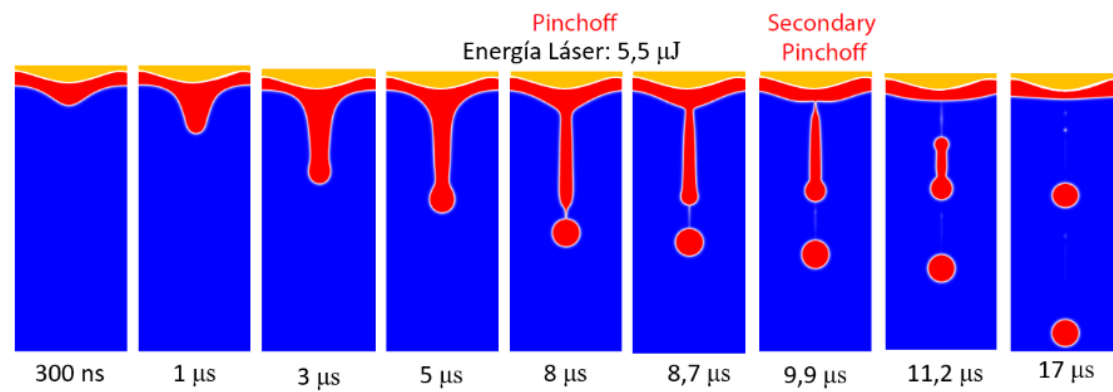
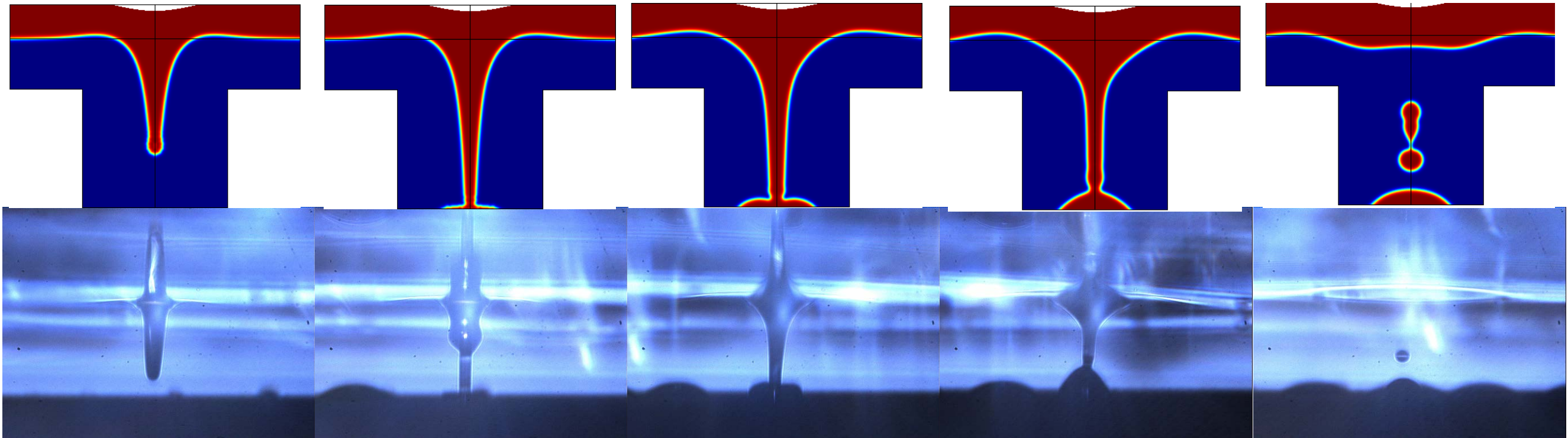
Brown, PhD Thesis (2011)





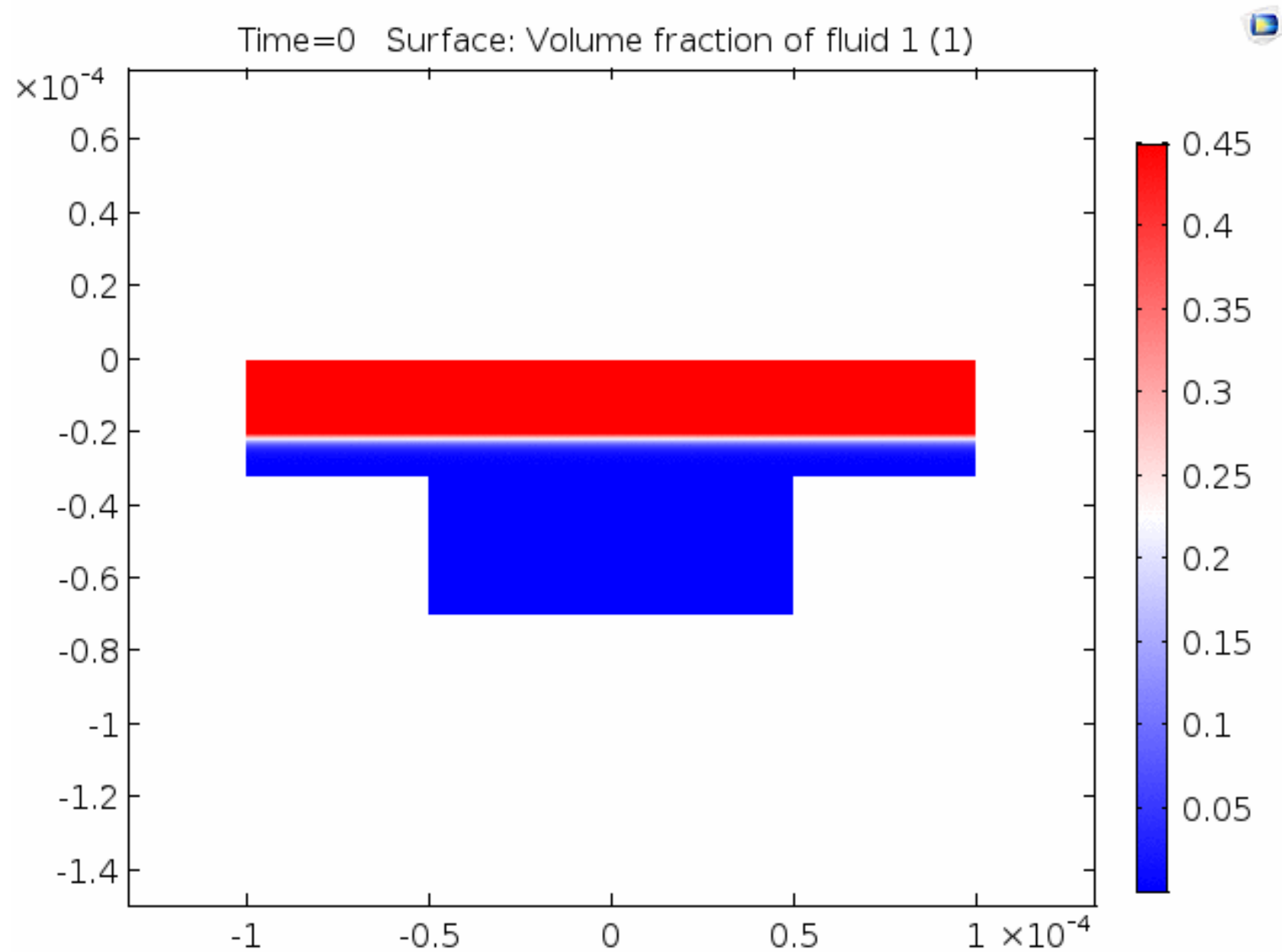
Low viscosity: $\sim \text{mPa}\cdot\text{s}$

Time=0 Isosurface: Volume fraction of fluid 1 (1)





High viscosity: $\sim \text{Pa}\cdot\text{s}$

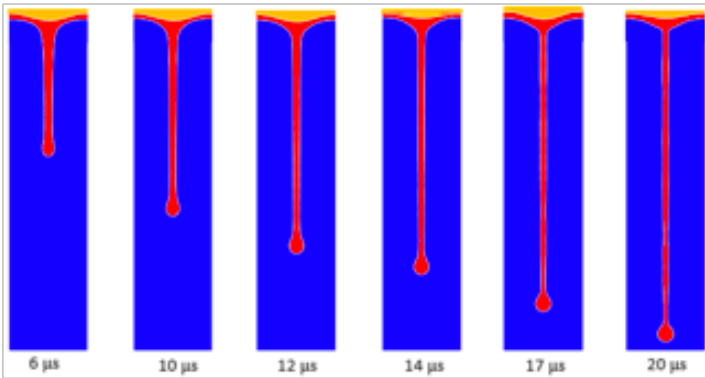




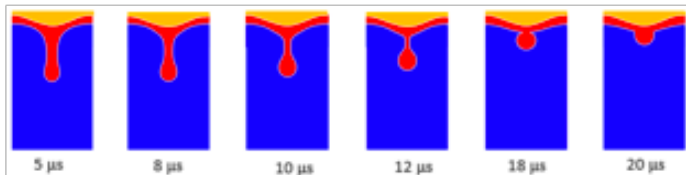
Dimensionless Parameters

$$\text{Re} = \frac{\text{inertial forces}}{\text{viscous forces}} = \frac{\rho dv}{\mu} \quad \text{We} = \frac{\text{inertial forces}}{\text{cohesion forces}} = \frac{\rho dv^2}{\gamma}$$
$$\text{Oh} = \frac{\text{viscous forces}}{\sqrt{\text{inertia forces} \cdot \text{cohesion forces}}} = \frac{\mu}{\sqrt{\rho \gamma d}} \quad Z = \frac{1}{\text{Oh}}$$

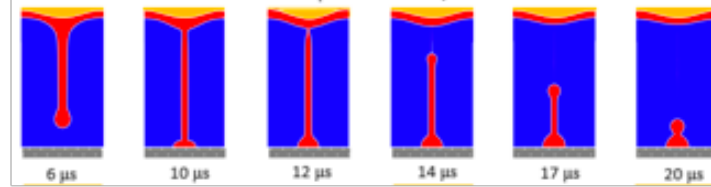
$\gamma = 10.40 \text{ mN/m}$ $\mu = 5 \text{ mPa}\cdot\text{s}$ ($Z = 2,94$)



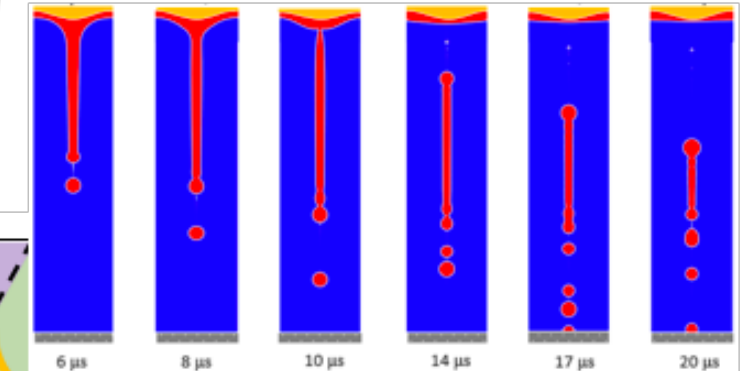
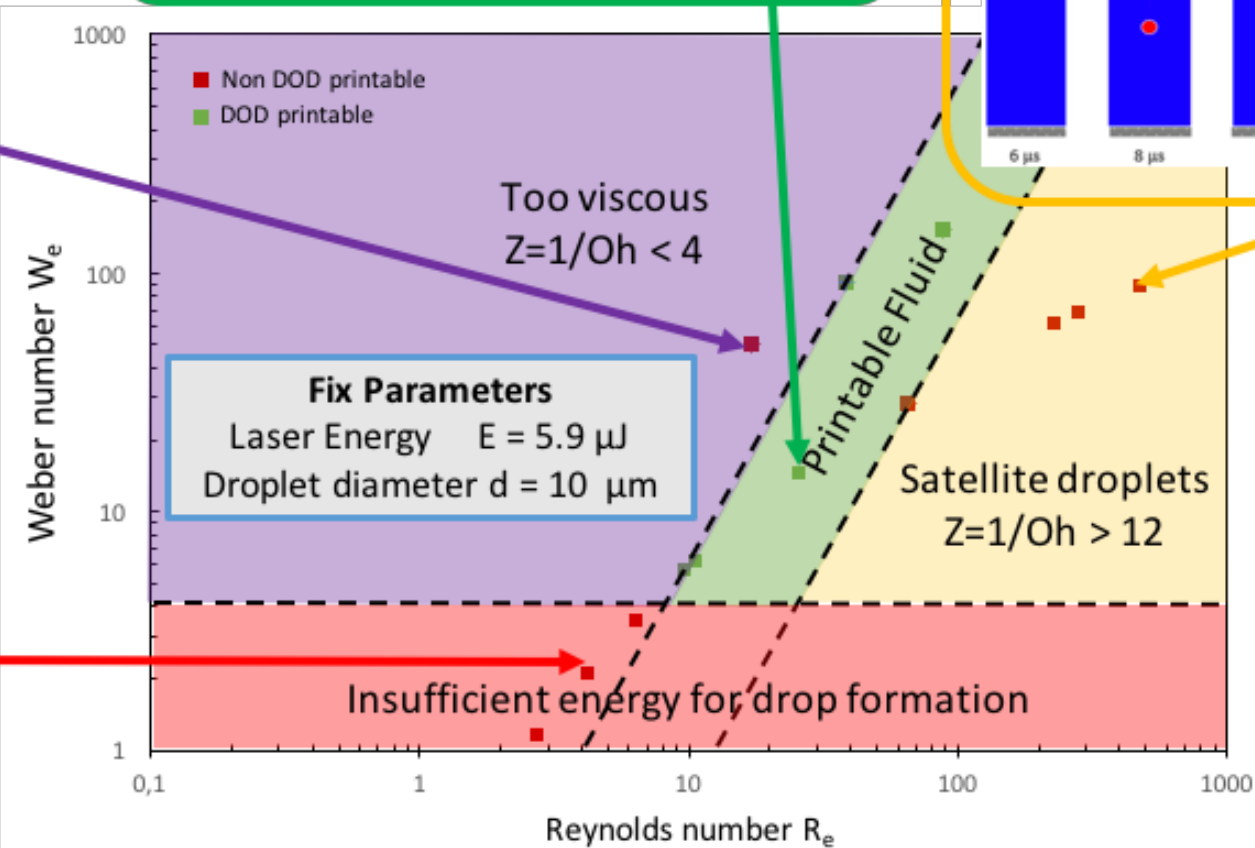
$\gamma = 40,79 \text{ mN/m}$ $\mu = 8 \text{ mPa}\cdot\text{s}$ ($Z = 2,56$)



$\gamma = 40.79 \text{ mN/m}$ $\mu = 5 \text{ mPa}\cdot\text{s}$ ($Z = 4,10$)



$\gamma = 40.79 \text{ mN/m}$ $\mu = 0.6 \text{ mPa}\cdot\text{s}$ ($Z = 34,17$)





- 1) LIFT is laser direct writing technique very promising for printing high viscosity fluids, since it allows printing fully personalized, customized designs.
- 2) Two different applications of LIFT have been shown:
 - Using LIFT is possible to print the front metallization pattern of solar cells in a single step from standard silver pastes. The lines obtained have large aspect ratios, low electrical resistance, and show good mechanical adherence. Lab CIGS cells are functional.
 - LIFT is a tool for bio- researchers, since it allows printing living cells with controlled 2D and 3D geometries, for example, for studying the immune response.
- 3) Numerical models are been developed for understanding the transfer mechanisms and predict the best parametric window for printability.



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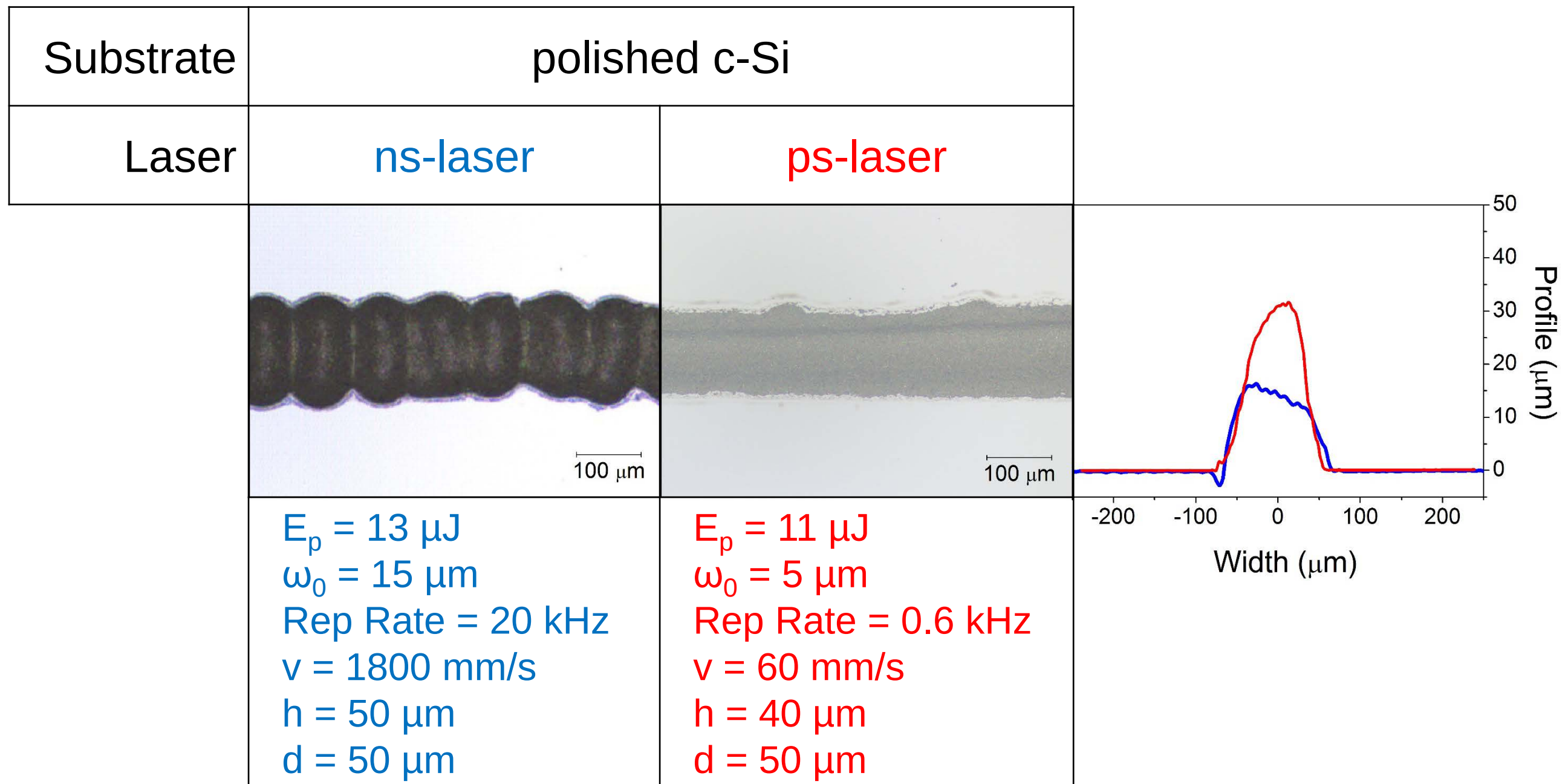
GOBIERNO
DE ESPAÑA

MINISTERIO
DE ECONOMÍA
Y COMPETITIVIDAD

תודה
Dankie Gracias
Спасибо شكرًا
Merci Takk
Köszönjük Terima kasih
Grazie Dziękujemy Děkojame
Ďakujeme Vielen Dank Paldies
Kiitos Täname teid 谢谢
Thank You Tak
感謝您 Obrigado Teşekkür Ederiz
Σας ευχαριστούμε 감사합니다
ขอบคุณ
Bedankt Děkuje vám
ありがとうございます
Tack



Printing of lines



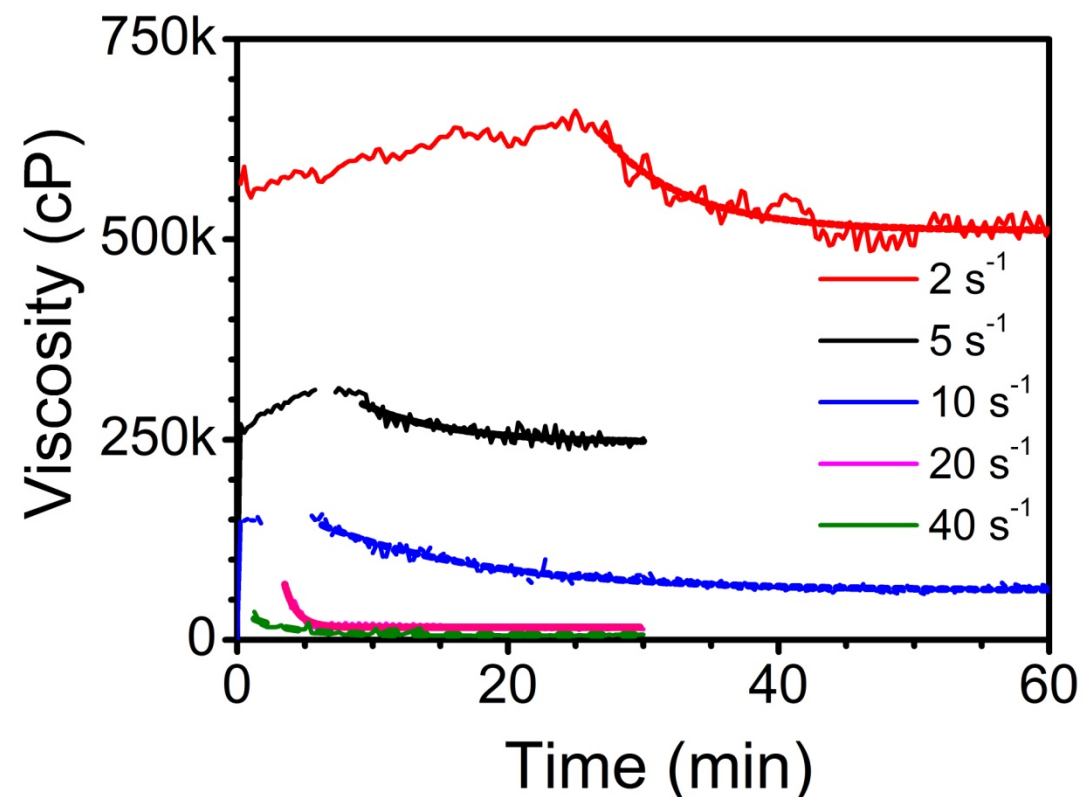
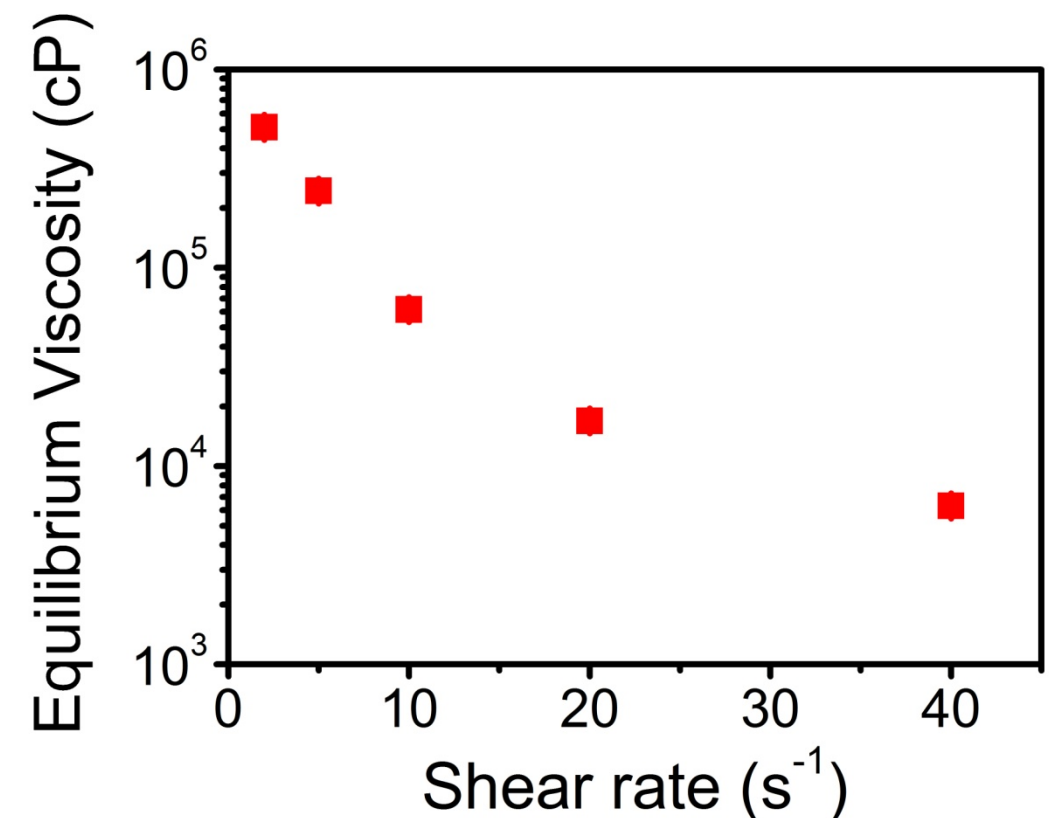


DuPont PV17F

Viscosity (Brookfield HBT, 10 rpm SC4-14/6R utility cap and spindle, 25°C)	280 - 400 Pa·s
Solid Content at 750 °C	89.5 - 91.0 %
Resistivity	< 5 mΩ/sq/μm
Silver grain	1-5 μm
Organic carrier	N,N'-Ethane-1,2-diylbis(decanamide) 12-Hydroxy-N-[2-[1-oxydecyl)amino]ethyl]octadecanamide N,N'-Ethane-1,2- diylbis(12-hydroxyoctadecanamide)
Thinner	9450

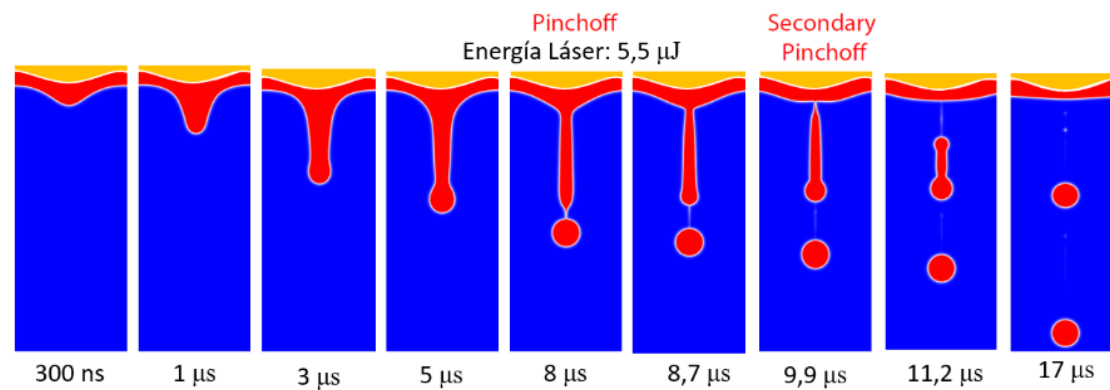


Non-newtonian, high-viscosity fluids





Low viscosity: $\sim \text{mPa}\cdot\text{s}$



Time=0 Isosurface: Volume fraction of fluid 1 (1)



Ink

$$\rho = 1030 \text{ kg/m}^3$$

$$\mu = 1,7 \text{ mPa}\cdot\text{s}$$

$$\gamma = 40,79 \text{ mN/m}$$

$$E_p = 5,5 \text{ μJ}$$



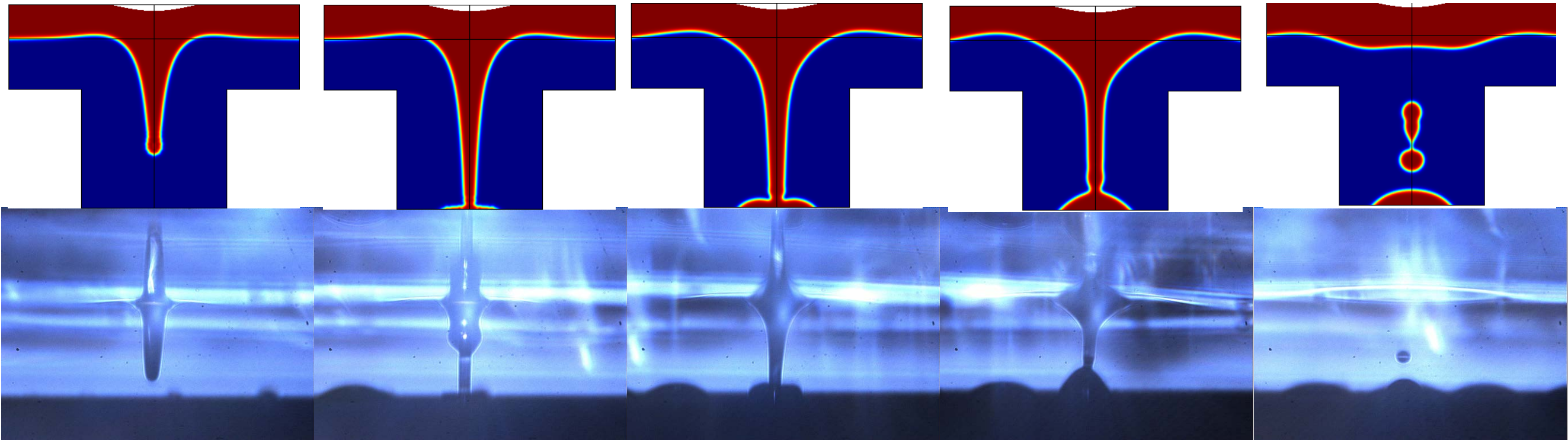
Water – glycerol, 40%weight

$$\rho = 1103,2 \text{ kg/m}^3$$

$$\mu = 3,63 \text{ mPa}\cdot\text{s}$$

$$\gamma = 70 \text{ mN/m}$$

$$E_p = 20 \text{ }\mu\text{J}$$





Ammonium alginate solution (3.37%)		
Density (kg/m ³)	1.05e3[kg/m ³]	
Viscosity Non-Newtonian Power Law	$\mu_1 = m(\dot{\gamma})^{n-1}$ $\dot{\gamma} = \max(\sqrt{\mathbf{D} : \mathbf{D}}, \dot{\gamma}_{\min}), \quad \mathbf{D} = \frac{1}{2}[\nabla \mathbf{u} + (\nabla \mathbf{u})^T]$	
	m (Pa·s)	13
	n	0.5
	$\dot{\gamma}_{\min}$ (1/s)	0.01
Surface Tension (N/m)	40.79e-3	

$E = 10 \text{ uJ}$
Thickness = 20 μm
Gap = 50 μm

