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
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
Laser Induced Forward Transfer


Laser Induced Forward Transfer

Lasersonic® LIFT Process

Hennig et al, J. Laser Micro Nanoeng. 7 (2012) 299–305
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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 ± 30 Pa·s
- Ag particles size: 1-5 µm
- Donor film thickness < 100 µm
LIFT Voxel Printing

Film Thickness 30 µm

<table>
<thead>
<tr>
<th>Energy (J/cm²)</th>
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<tbody>
<tr>
<td>0.6</td>
</tr>
<tr>
<td>1.3</td>
</tr>
<tr>
<td>2.6</td>
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Film Thickness 50 µm

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- 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**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>polished c-Si</th>
<th>textured c-Si</th>
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- $E_p = 13 \, \mu J$
- $\omega_0 = 15 \, \mu m$
- Rep Rate = 20 kHz
- $v = 1800 \, \text{mm/s}$
- $h = 50 \, \mu m$
- $d = 50 \, \mu m$
**Printing of lines**

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**Graphical Representation**

- Image of polished c-Si substrate with laser marks.
- Image of textured c-Si substrate with laser marks.
- Graph showing profile and width measurements.

**Title**

LIFT for solar cell metallization
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

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

Good adherence after bending with radius down to 12 mm
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**LIFT for bio-printing**

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.

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**DIFFERENT CONCENTRATION GRADIENTS OF CHEMOKINES**

- Various colors represent different chemokine concentrations.

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**DIFFERENT TYPES OF CHEMOKINES**

- Various symbols and molecules indicate different chemokines.

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**LYMPHOID ORGAN INFLAMMATORY SITE**

- Diagram showing various cells and molecules involved in the immune response.

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**LYMPHATIC SYSTEM**

- Diagram showing the migration of cells through the lymphatic system.

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**IMMUNOLOGY**

- Diagram showing the interaction between immune cells and chemokines.

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**LASER ENGINEERING**

- Diagram showing the integration of laser technology in bio-printing.

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**CENTRO LÁSER UPM**

- Logo and name of the institute.
Centro Láser
UPM

**LIFT for bio-printing**

- ns- pulsed lasers emitting at 355 nm
- Beam scanned using a galvo scanner.
- BA-LIFT
- Donor film thickness: ~30 μm.
- Gap distance: ~500 μm.
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 ($\mu \sim 10^{-3} – 1 \text{ Pa}\cdot\text{s}$)
Cell viability after printing process

- **2% SA**
  - Live: 100%
  - Dead: 0%

- **Without SA**
  - Live: 100%
  - Dead: 0%

**LIFT for bio-printing**

- **13 µJ**
- **23 µJ**

**Scale bar 100 µm**

**CELL CONCENTRATION**

- **Without transfer**
- **Explosive range**
- **Transfer range**

The images on the left show the different stages of the printing process with varying energy levels (Ep in µJ) and cell densities. The right side of the diagram illustrates the cell viability results for both 2% SA and Without SA conditions.
Two different cell type printed in different configuration

Different S1P chemokine concentration

Scale bar 100 µm
Outlook

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

Navier-Stokes equations

\[ \rho \left( \frac{\partial \bar{u}}{\partial t} + \bar{u} \cdot \nabla \bar{u} \right) - \nabla \cdot \left( \mu \nabla \bar{u} + \nabla \bar{u}^T \right) + \nabla p = \bar{F}_{sr} \]

\[ (\nabla \cdot \bar{u}) = 0 \]

Two phase flow – level set interface

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

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

Blister Movement

Numerical simulation

Low viscosity: $\sim\text{mPa}\cdot\text{s}$
High viscosity: $\sim$Pa·s
Numerical simulation

**Dimensionless Parameters**

\[ Re = \frac{\text{inertial forces}}{\text{viscous forces}} = \frac{\rho dv}{\mu} \]

\[ We = \frac{\text{inertial forces}}{\text{cohesion forces}} = \frac{\rho dv^2}{\gamma} \]

\[ Oh = \frac{\text{viscous forces}}{\sqrt{\text{inertia forces-cohesion forces}}} = \frac{\mu}{\sqrt{\rho g d}} \quad Z = \frac{1}{Oh} \]

**Fixed Parameters**

- Laser Energy: \( E = 5.9 \ \mu J \)
- Droplet diameter: \( d = 10 \ \mu m \)

**Values**

- \( \gamma = 40.79 \ \text{mN/m} \quad \mu = 5 \ \text{mPa} \cdot \text{s} \quad (Z = 4,10) \)
- \( \gamma = 40.79 \ \text{mN/m} \quad \mu = 0.6 \ \text{mPa} \cdot \text{s} \quad (Z = 34,17) \)
- \( \gamma = 10.40 \ \text{mN/m} \quad \mu = 5 \ \text{mPa} \cdot \text{s} \quad (Z = 2,94) \)
- \( \gamma = 40.79 \ \text{mN/m} \quad \mu = 8 \ \text{mPa} \cdot \text{s} \quad (Z = 2,56) \)

** Zones**

- Too viscous: \( Z = 1/Oh < 4 \)
- Satellite droplets: \( Z = 1/Oh > 12 \)
- Insufficient energy for drop formation
- Non DOD printable
- DOD printable
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.
This work has been supported by the EUROPEAN COMISSION – APPOLO FP7-2013-NMP-ICT-FOF. 609355 and the Spanish MINECO projects SIMLASPV-MET (ENE2014-58454), HELLO (ENE2013-48629-C4-3-R), and CHENOC (ENE2016-78933-C4-4-R).
Thank You
### Printing of lines

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- **Ep = 13 µJ**
  - $\omega_0 = 15 \, \mu m$
  - Rep Rate = 20 kHz
  - $v = 1800 \, \text{mm/s}$
  - $h = 50 \, \mu m$
  - $d = 50 \, \mu m$

- **LIF** for solar cell metallization
- **Ep = 11 µJ**
  - $\omega_0 = 5 \, \mu m$
  - Rep Rate = 0.6 kHz
  - $v = 60 \, \text{mm/s}$
  - $h = 40 \, \mu m$
  - $d = 50 \, \mu m$
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

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Non-newtonian, high-viscosity fluids
Low viscosity: $\sim$mPa·s

Ink
\[ \rho = 1030 \text{ kg/m}^3 \]
\[ \mu = 1.7 \text{ mPa} \cdot \text{s} \]
\[ \gamma = 40.79 \text{ mN/m} \]

\[ E_p = 5.5 \text{ } \mu \text{J} \]
Water – glycerol, 40% weight

\[ \rho = 1103.2 \text{ kg/m}^3 \]

\[ \mu = 3.63 \text{ mPa} \cdot \text{s} \]

\[ \gamma = 70 \text{ mN/m} \]

\[ E_p = 20 \mu J \]
Ammonium alginate solution (3.37%)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Density (kg/m³)</td>
<td>1.05e3[kg/m³]</td>
</tr>
<tr>
<td>Viscosity Non-Newtonian Power Law</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\mu_1 = m(\dot{\gamma})^{n-1}$</td>
</tr>
<tr>
<td></td>
<td>$\dot{\gamma} = \max\left(\sqrt{D : D} \gamma_{\text{min}}, 0\right)$, $D = \frac{1}{2}[\nabla u + (\nabla u)^T]$</td>
</tr>
<tr>
<td>$m$ (Pa·s)</td>
<td>13</td>
</tr>
<tr>
<td>$n$</td>
<td>0.5</td>
</tr>
<tr>
<td>$\gamma_{\text{min}}$ (1/s)</td>
<td>0.01</td>
</tr>
<tr>
<td>Surface Tension (N/m)</td>
<td>40.79e-3</td>
</tr>
</tbody>
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E = 10 uJ
Thickness = 20 um
Gap = 50 um