First Light: a Polymer LED Fabricated in Vacuum by Resonant IR Laser Ablation

Stephen Johnson¹, Nicole Dygert,¹ Hee Park²
and Richard Haglund¹,²

¹Vanderbilt University  ²AppliFlex LLC
In the next fifteen minutes …

• Motivation: Find a vacuum deposition process for organic, polymeric and nanoscale materials for opto-electronics, sensors and smart coatings

• Mid-infrared laser vaporization for thin-film deposition of organics and polymers

• Evidence for low-temperature IR vaporization … and some thoughts about how and why it works

• … and why it matters for a variety of laser-based fabrication processes.
Laser vaporization in OLED processing …

- Recrystallization of amorphous-Si
- Encapsulating organic or polymer composite
- Small organic molecule or polymer
- Process
- LTPS TFT fabrication or OTFT
- 3 color OLED pixelation
- Sealing
- Scribing
- Structure
- LTPS TFT substrate
- B, R, G
- Insulator: organic or polymer (PTFE)
- Semiconductor: Pentacene
- Conductor: Polyaniline
Experimental procedure: conducting polymer

- FEL tuned to 3.05 μm (O-H stretch of H₂O) …
- …or 3.45 μm (C-H stretch mode of NMP, IPA)
- Laser Fluence ~2 J/cm²
- Exposure ~5 minutes
Depositing PEDOT:PSS by RIR-LVD

- Common HTL in OLEDs, used in anti-static coatings
- Good conductivity, optically transparent
- Baytron® P: PEDOT with PSS added for solubility
- Decomposes thermally …and may poison OLEDs.
PEDOT:PSS films by resonant IR laser ablation

PEDOT:PSS in H$_2$O irradiated at 3.05 µm (O-H resonance)
- Film very rough
- Not conductive

PEDOT:PSS in H$_2$O with 10-40% NMP irradiated at 3.05 µm or 3.47 µm (C-H resonance in NMP)
- Film very smooth
- Conductive

PEDOT:PSS in H$_2$O with ISP irradiated at 3.05 µm and 3.47 µm
- Film fairly smooth
- Not conductive at 3.05 µm
- FTIR shows only that local bonding structure preserved
- Resistivity compares to spin-coated PEDOT:PSS

**FTIR and Conductivity**

- **FTIR Spectra**
  - H₂O
  - 1:1 H₂O:ISP
  - 1:1 H₂O:NMP
  - Spin Coated

- **Conductive**
- **Non-Conductive**

<table>
<thead>
<tr>
<th>Wavelength (µm)</th>
<th>% NMP</th>
<th>Resistivity (Ω-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin Coat</td>
<td>0%</td>
<td>14.7 ± 2.9</td>
</tr>
<tr>
<td>3.05</td>
<td>0%</td>
<td>N/A</td>
</tr>
<tr>
<td>3.05</td>
<td>10%</td>
<td>39.5 ± 22</td>
</tr>
<tr>
<td>3.05</td>
<td>50%</td>
<td>11.7 ± 8.9</td>
</tr>
<tr>
<td>3.47</td>
<td>10%</td>
<td>5.65 ± 0.5</td>
</tr>
<tr>
<td>3.47</td>
<td>50%</td>
<td>5.2 ± 1.7</td>
</tr>
</tbody>
</table>
Deposition of electroluminescent MEH-PPV

Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4 phenylene vinylene] — MEH-PPV

- Works at 2.94 µm
- Better at 6.68 µm
- Electroluminescent
- … but droplets are still a problem.
Electroluminescence!

Left: PLED made with additional layer of PEDOT:PSS as hole-transport layer between anode and MEH-PPV light emitter.
- Problem with droplets arriving at substrate surface.
- Film properties depend strongly on laser fluence (spot size).
- Seems to vary with viscosity of matrix and co-matrix, rather than boiling point.
- Using different solvents with different thermal properties might reduce droplet formation.
Spherical cow model of polymer melt

- Polymer melt is ...
  - Polydisperse
  - Entangled ($n \geq 100$)
  - Disordered
  - Hydrogen-bonded
  - Temperature-sensitive!

- UV light can cleave
  - Inter-monomer bonds
  - Intra-monomer bonds
  - Hydrogen bonds

- mid-IR light can only
  - Break hydrogen bonds
  - Excite intra-monomer vibrations

- Polymer energetics
  - Covalent bonds 2-6 eV
  - Localized anharmonic modes 0.5-0.05 eV (mostly stretching and bending modes)
  - Hydrogen bonds $\sim 0.3$ eV
Resonant ps IR laser ablation works because

- Anharmonic, localized *monomer* excitation
- Micropulse excitation density 1 photon/nm³!
- Stress confinement: \[ \tau_{\text{micro}} \leq \frac{L_{\text{opt}}}{C_s} \sim 0.01 - 0.1 \, \mu s \]
- Thermal confinement: \[ \tau_{\text{macro}} < \frac{L_{\text{opt}}^2}{D_T} \sim 0.1 - 1 \, \mu s \]

Now about that free-electron laser …

- The “black box” - a.k.a. Giant Pump Laser
  - ANU: 35 W, 1064 nm, 1.5 MHz, 13 ps
  - Jena: 21 W, 1030 nm, 17 MHz, 750 fs
  - Concept: 200 W, 1030 nm, 1 GHz, 1 ps, 1 µs macropulse

- Demonstrated tunable IR output …
  - ANU: 3 W, 2-4 µm, 13 ps etc. now going to 28 MHz
  - Jena and ETH: sub-ps, 60-80 MHz, 8-9 W at 3.5 µm
  - Vanderbilt FEL: 1.5 W, 2-10 µm

- The challenge: nonlinear mid-infrared materials!
Broader implications?

- μfabrication needs ...
- polymer coatings for ...
- ... added functionality
- ... and protection.

460 nm polystyrene spheres on an AFM cantilever deposited by RIR-LANT

Photoluminescent Alq₃ deposited by RIR-LVD

Water droplet on glass and ...

... on RIR-LVD Teflon
• PLED fabrication by IR-LVD is a major breakthrough
  o PEDOT:PSS hole transporter for OLEDs, now has to be spin-coated
  o Demonstrated functional multilayer OLED with IR-LVD
  o LVD PEDOT:PSS gives conductivities at least as good as spin-coating
• Mechanism: IR-LVD is intrinsically a low-temperature process
  o Sensitive to choice of IR wavelength and pulse duration
  o Modest temperature rise, but large viscosity change
  o Mode selectivity influences fragmentation, multi-photon excitation
  o Deposition sensitive to material preparation (e.g., co-matrix, viscosity)
• Future holds technical and scientific challenges
  o Need to understand mechanism: e.g., ultrafast pulses required?
  o Photoacoustics, schlieren plume photography ready soon
  o Need to understand macropulse-micropulse optimization
  o Finding a table-top replacement for the FEL is also a high priority!
Thanks to the heavy lifters ...

Nicole Dygert            Stephen Johnson            Hee Park

Supported by the Naval Research Laboratory, the National Science Foundation (IGERT program), AppliFlex LLC and the Department of Defense Medical Free-Electron Laser Program administered by the Air Force Office of Scientific Research,

And about wavelength-selective infrared laser vapor deposition: “It warn’t so much what I didn’t know what hurt me, but what I knowed that warn’t so.”

(Huck Finn, *The Adventures of Tom Sawyer*)