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

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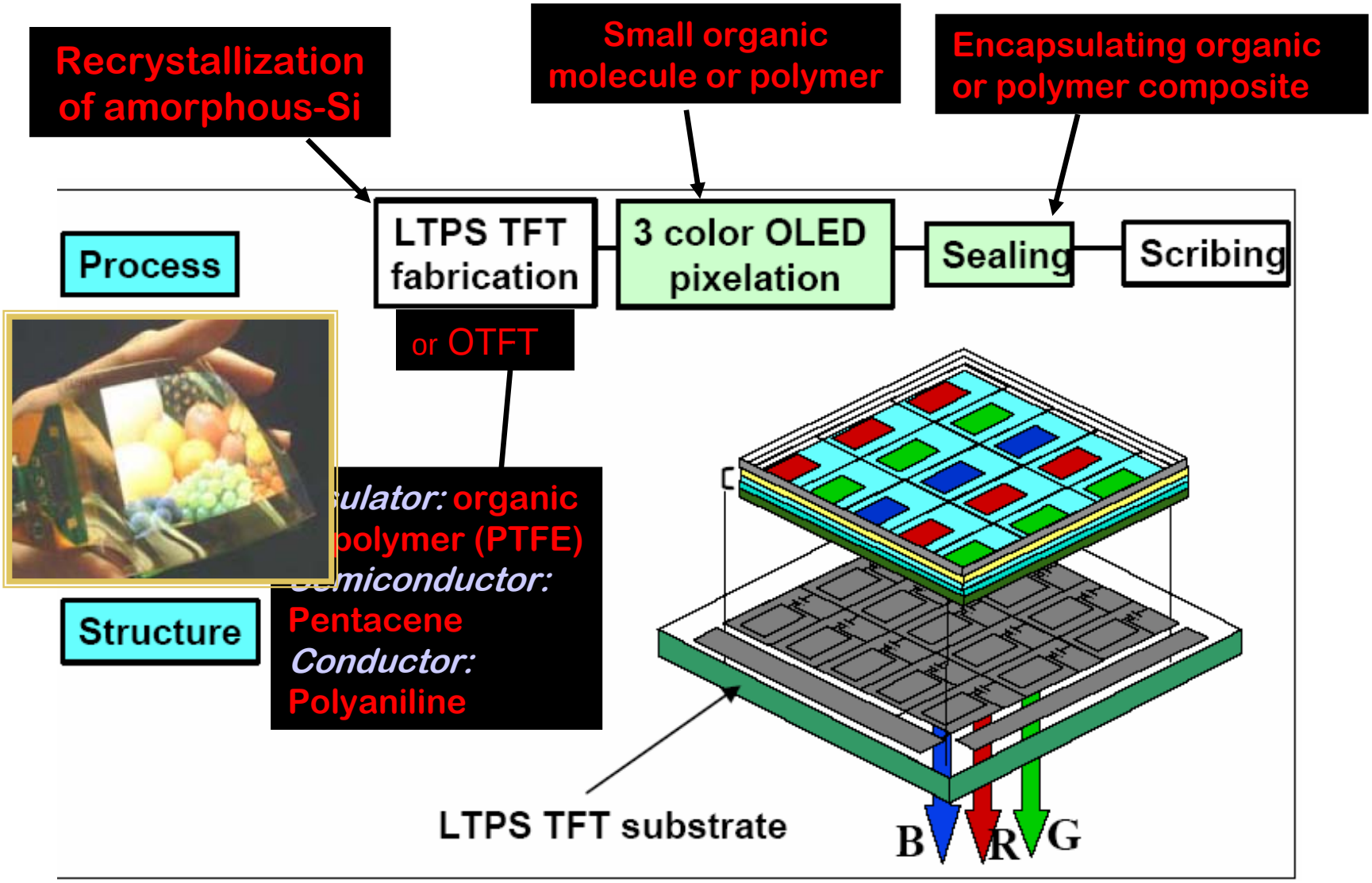
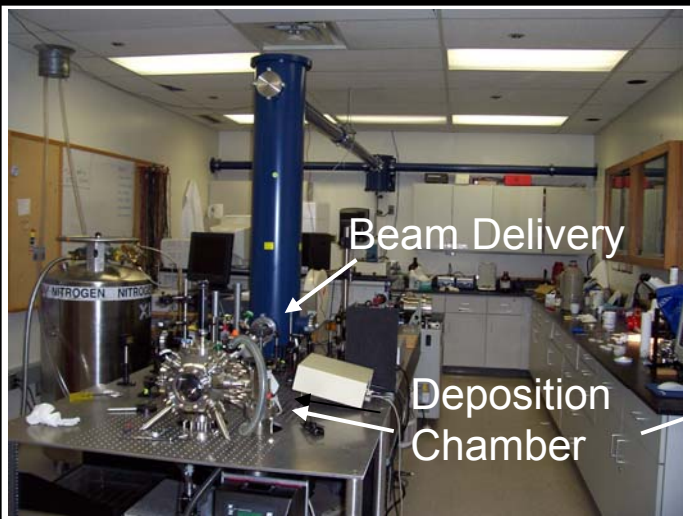
In the next fifteen minutes …

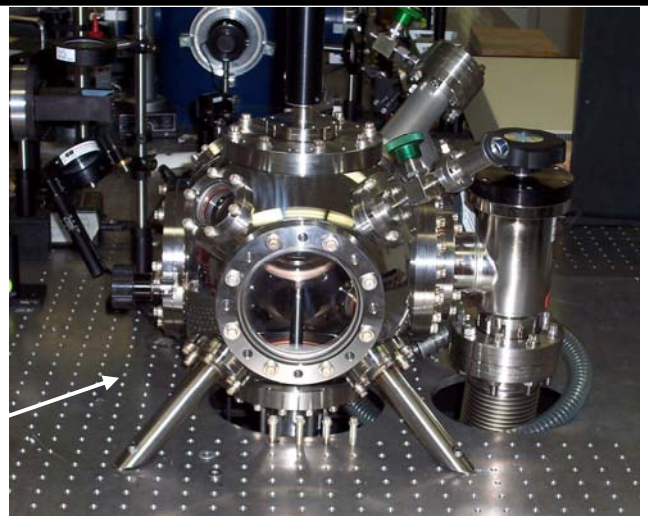
- Motivation: Find a vacuum deposition process for organic, polymeric and nanoscale materials for opto-electronics, sensors and smart coatings
- Mid-infrared laser vaporization for thin-film deposition of organics and polymers
- Evidence for low-temperature IR vaporization … and some thoughts about how and why it works
- … and why it matters for a variety of laser-based fabrication processes.

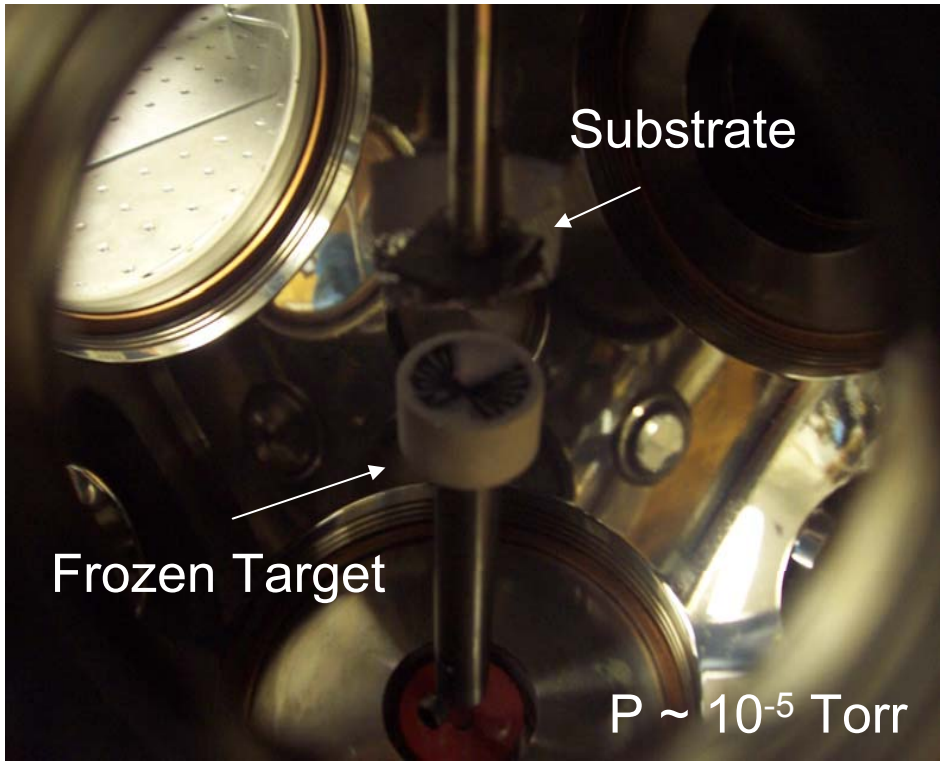
Laser vaporization in OLED processing …



Experimental procedure: conducting polymer

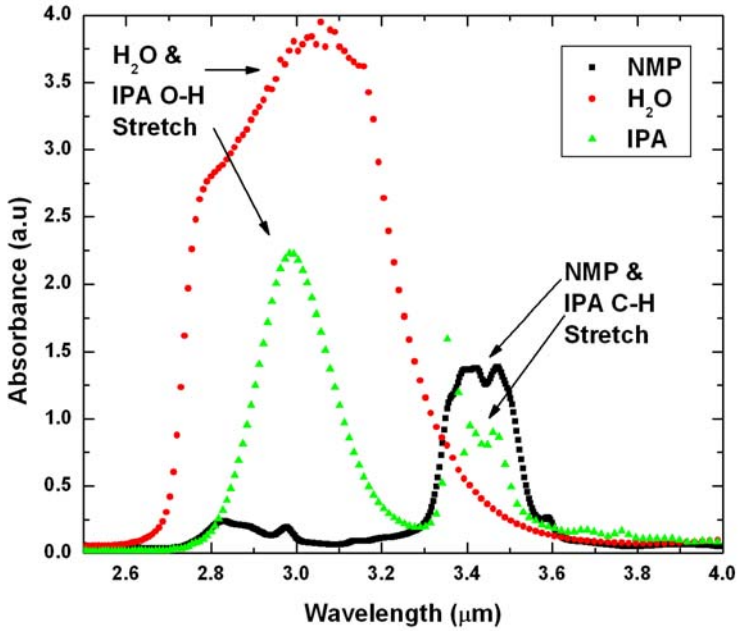




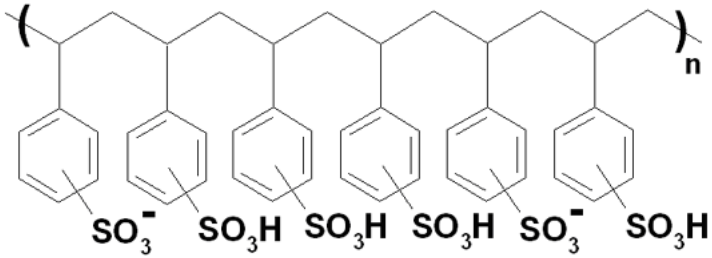


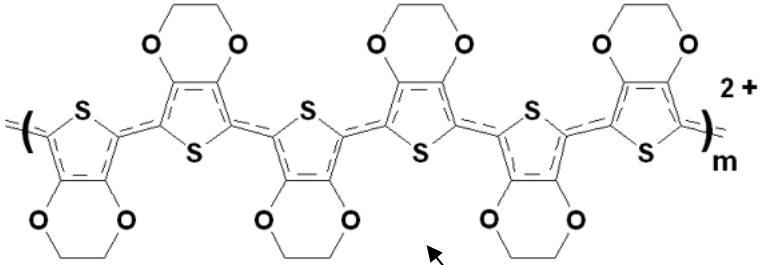
- FEL tuned to 3.05 μm (O-H stretch of H_2O) …
- …or 3.45 μm (C-H stretch mode of NMP, IPA)
- Laser Fluence ~2 J/cm^2
- Exposure ~5 minutes

Depositing PEDOT:PSS by RIR-LVD



PSS::poly(styrene sulfonate)

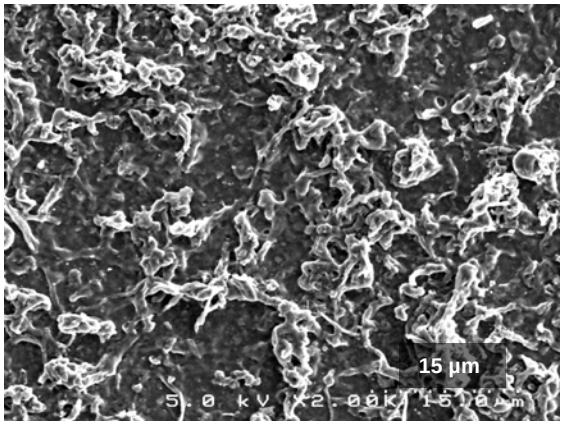




PEDOT::poly(3,4-ethylene dioxythiophene

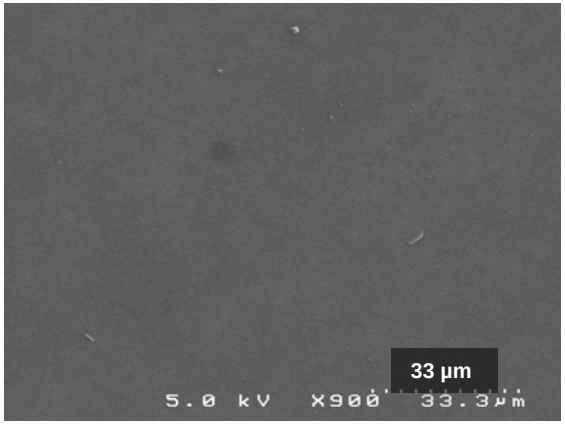
- Common HTL in OLEDs, used in anti-static coatings
- Good conductivity, optically transparent
- Baytron® P: PEDOT with PSS added for solubility
- Decomposes thermally …and may poison OLEDs.

PEDOT:PSS films by resonant IR laser ablation



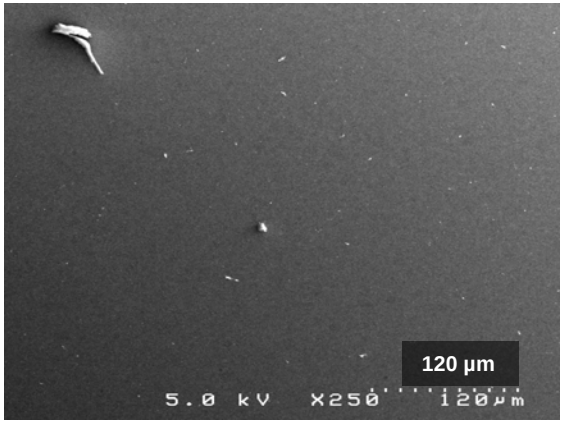
PEDOT:PSS IN H_2O irradiated at 3.05 µm (O-H resonance)

- Film very rough
- Not conductive



PEDOT:PSS in H_2O with 10-40% NMP irradiated at 3.05 µm or 3.47 µm (C-H resonance in NMP)

- Film very smooth
- Conductive

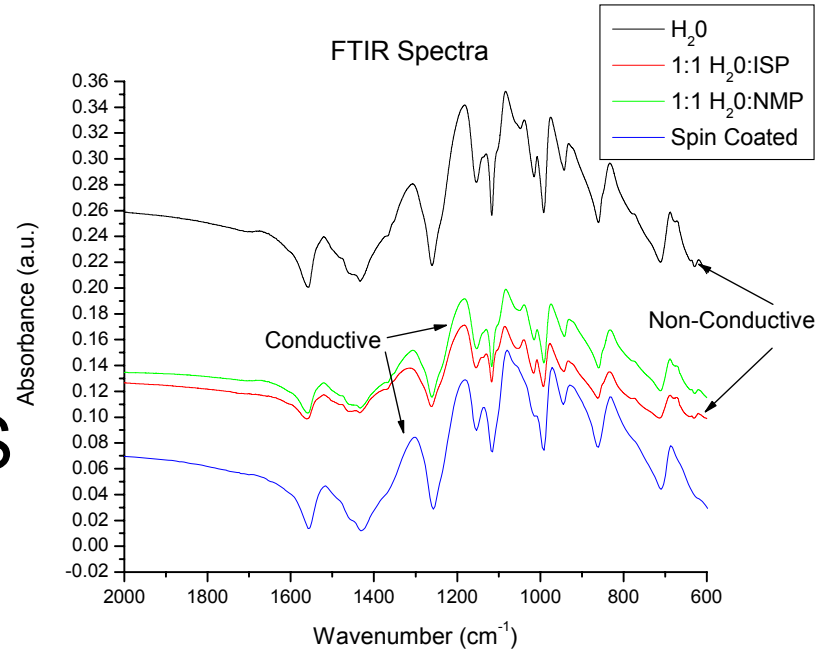


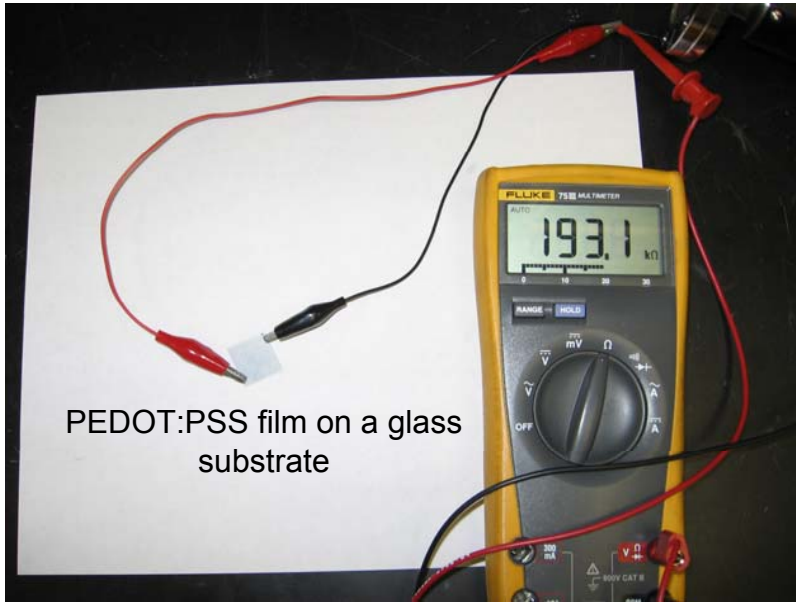
PEDOT:PSS in H_2O with ISP irradiated at 3.05 µm and 3.47 µm

- Film fairly smooth
- Not conductive at 3.05 µm

FTIR and Conductivity

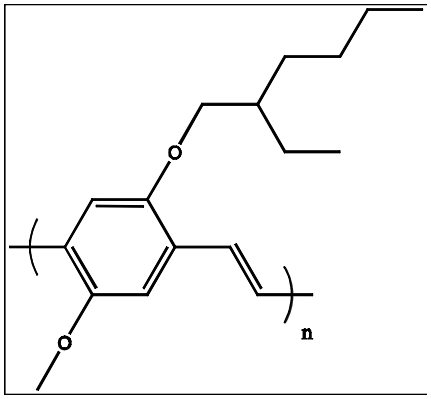
- FTIR shows only that local bonding structure preserved
- Resistivity compares to spin-coated PEDOT:PSS

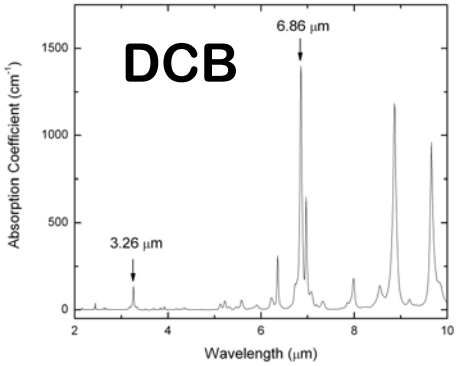




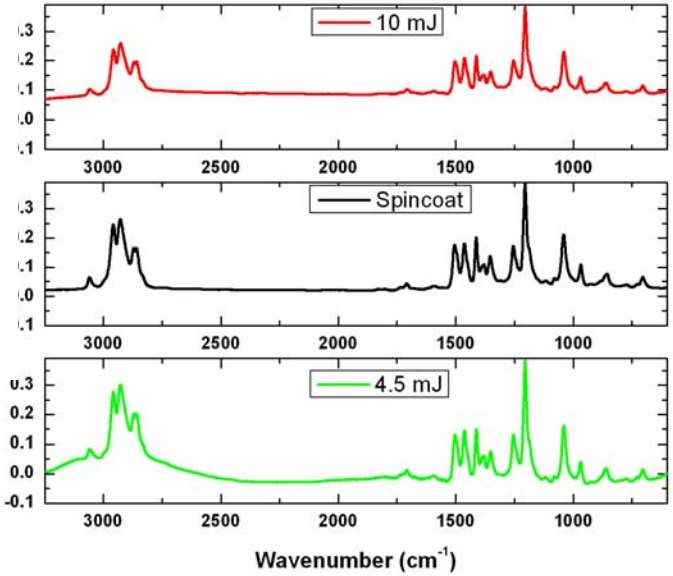
Wavelength (µm)	% NMP	Resistivity (Ω-cm)
Spin Coat	0%	14.7 ± 2.9
3.05	0%	N/A
3.05	10%	39.5 ± 22
3.05	50%	11.7 ± 8.9
3.47	10%	5.65 ± 0.5
3.47	50%	5.2 ± 1.7

Deposition of electroluminescent MEH-PPV





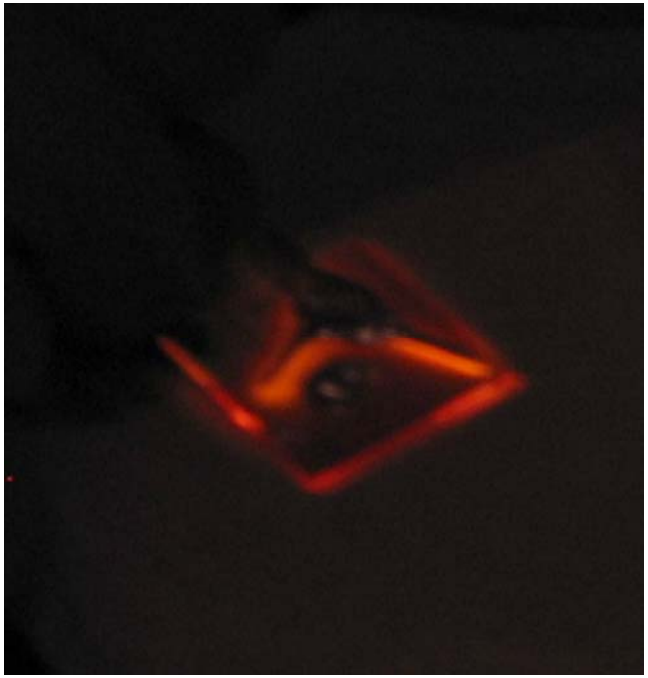
Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4 phenylene vinylene] — MEH-PPV

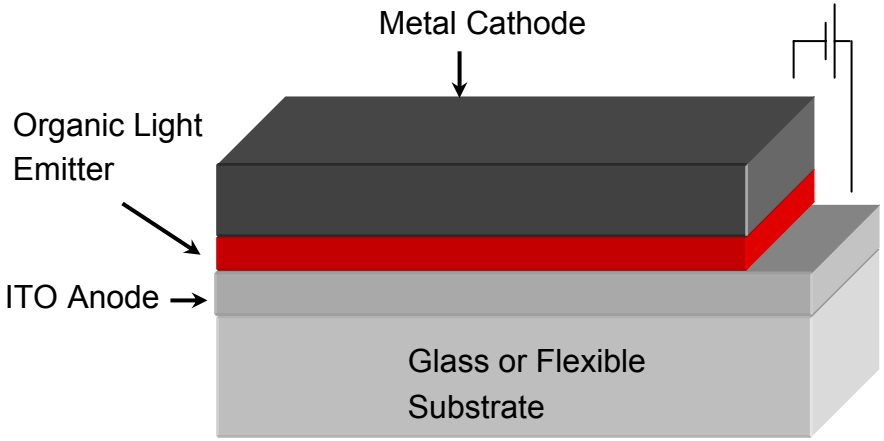


QuickTime™ and a
Motion JPEG OpenDML decompressor
are needed to see this picture.

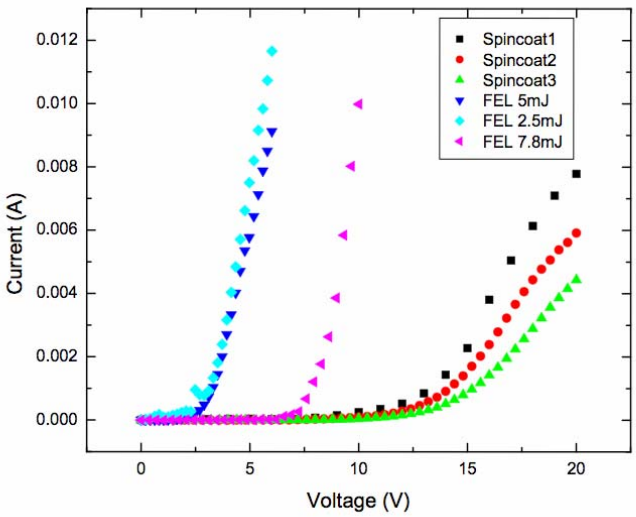
- Works at 2.94 μm
- Better at 6.68 μm
- Electroluminescent
- … but droplets are still a problem.

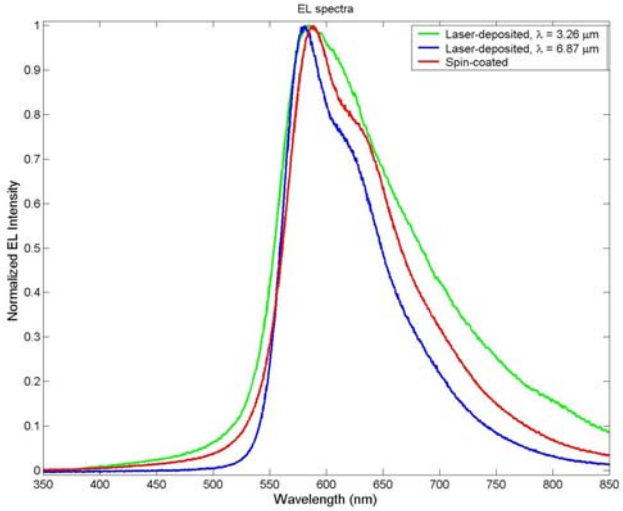
Electroluminescence!





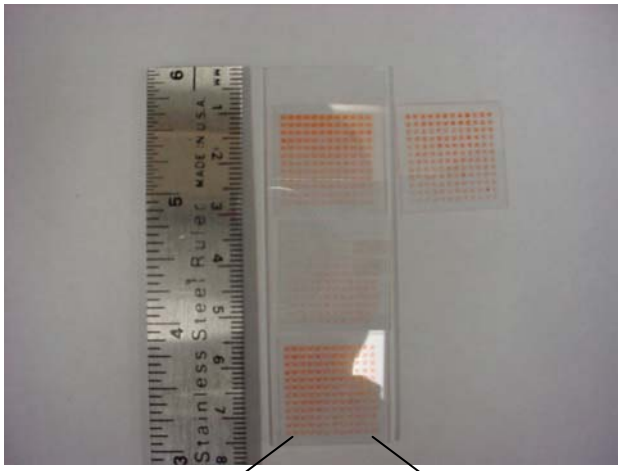
Left: PLED made with additional layer of PEDOT:PSS as hole-transport layer between anode and MEH-PPV light emitter

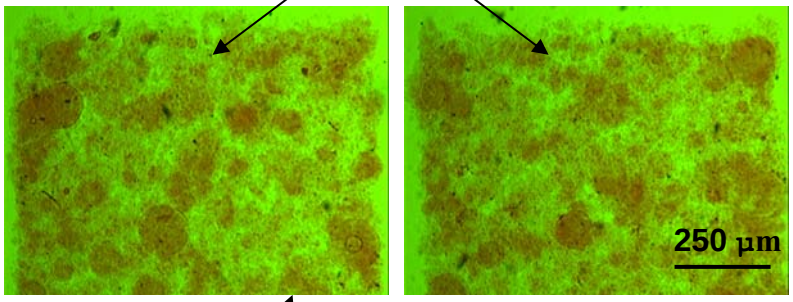




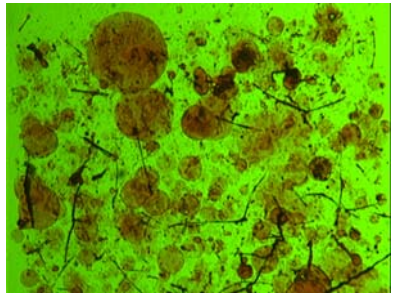
Initial results on multi-pixel devices

- 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.





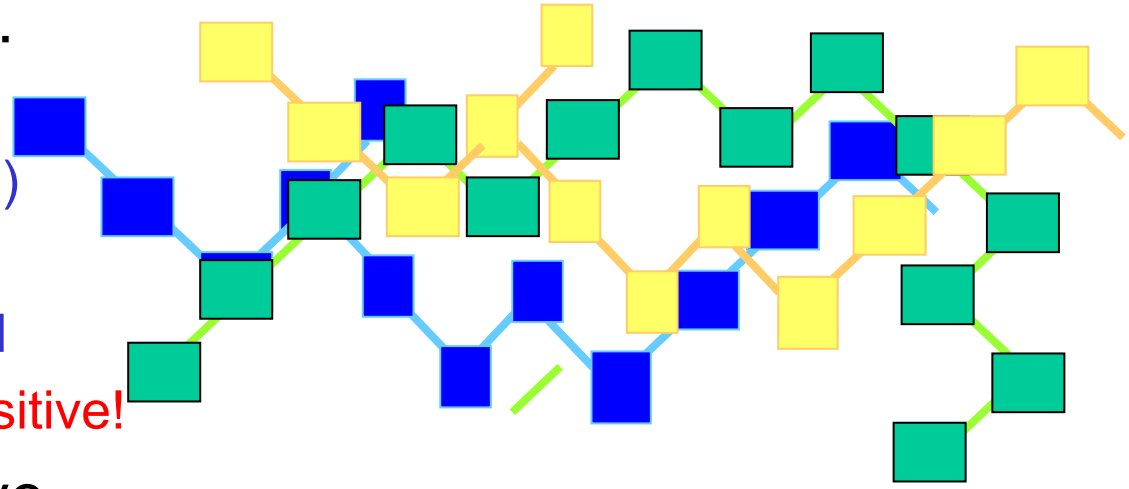
Focal spot <1mm



Focal spot >1mm

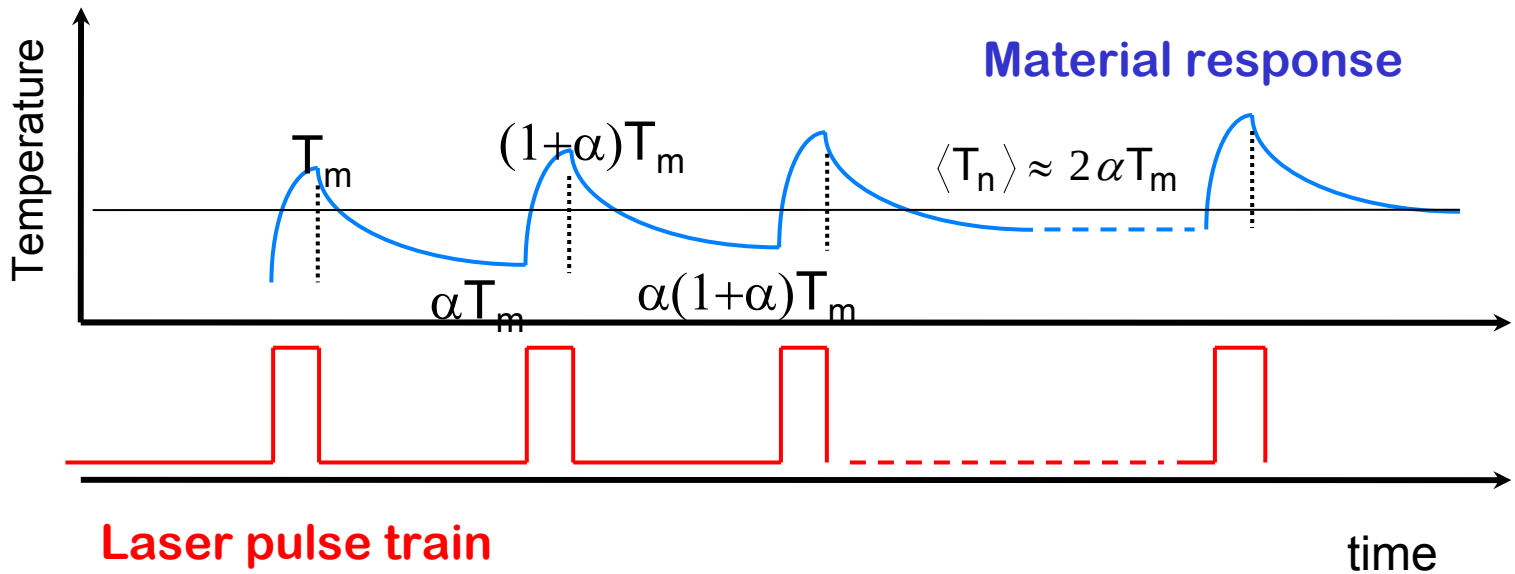
Spherical cow model of polymer melt

- Polymer melt is …
  - Polydisperse
  - Entangled (n≥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 ~0.3 eV

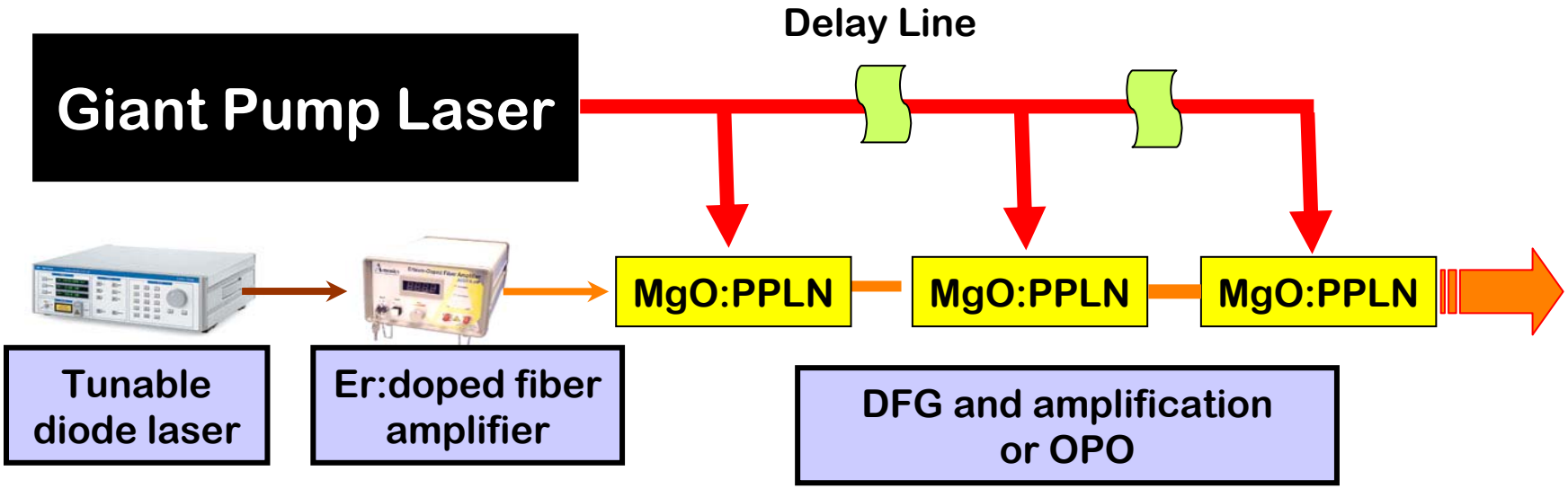
Resonant ps IR laser ablation works because



- Anharmonic, localized ***monomer*** excitation
- Micropulse excitation density 1 photon/nm^3!
- Stress confinement: $\tau_{micro} \leq L_{opt} / C_s \sim 0.01 - 0.1\ \mu s$
- Thermal confinement: $\tau_{macro} < L_{opt}^2 / D_T \sim 0.1 - 1\ \mu s$

Gamaly, Rode, Luther-Davies, J. Appl.Phys. **85**, 4213 (1999)

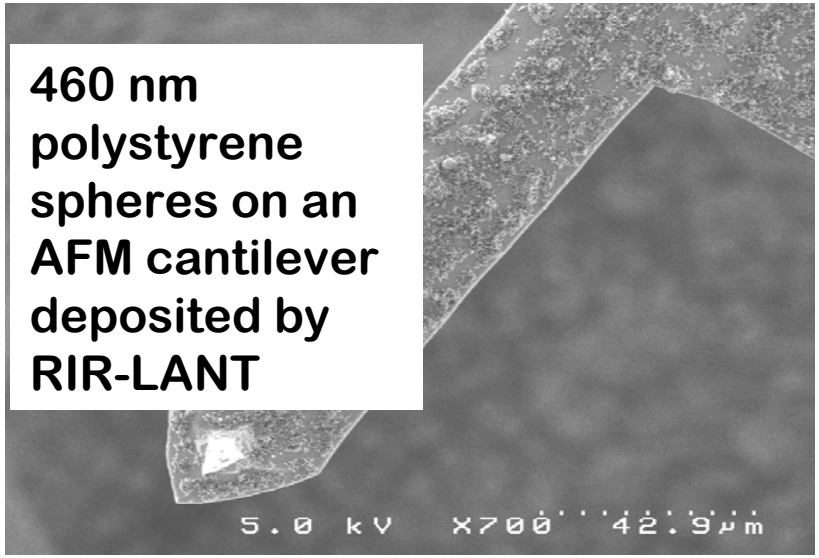
Now about that free-electron laser …



- 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!**

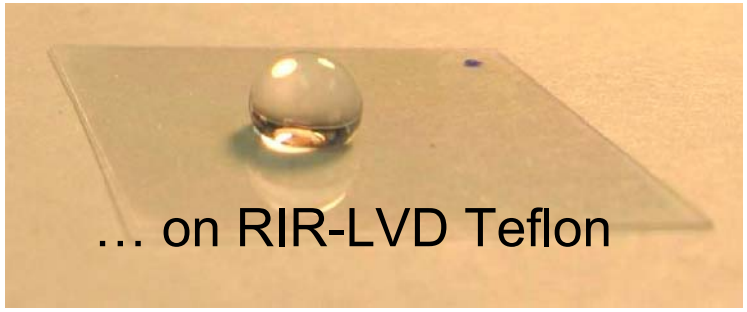
Broader implications?

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

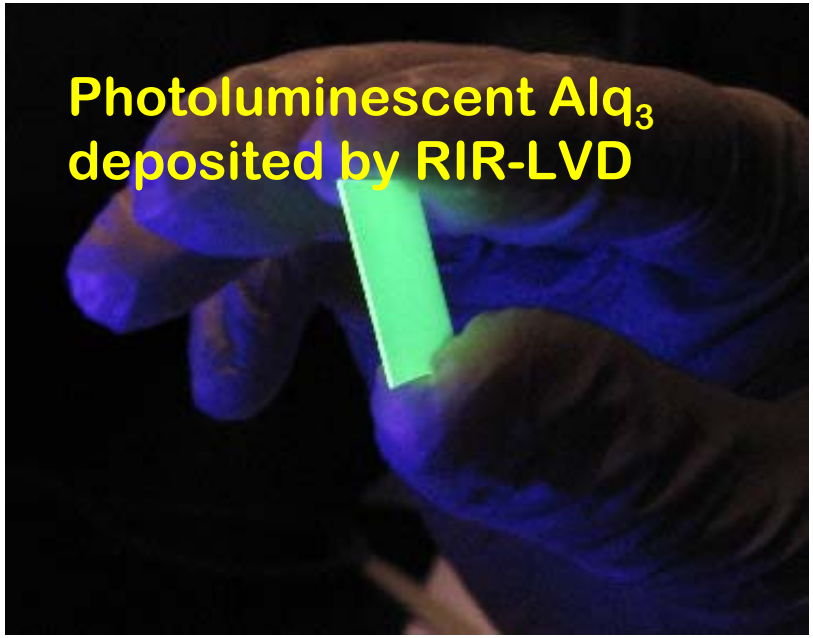


460 nm polystyrene spheres on an AFM cantilever deposited by RIR-LANT

Water droplet on glass and



… on RIR-LVD Teflon



Photoluminescent Alq_3 deposited by RIR-LVD

Summary and outlook …

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

Thanks to the heavy lifters …

Nicole Dygert

Stephen Johnson

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

Hee Park

$$upported 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*)