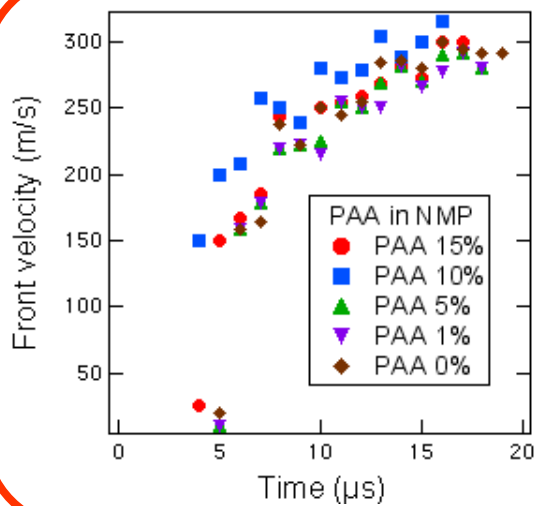
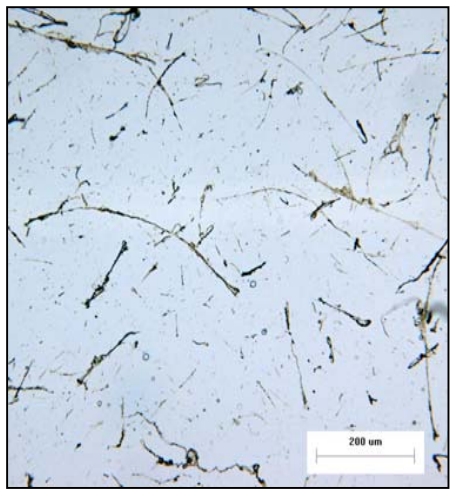
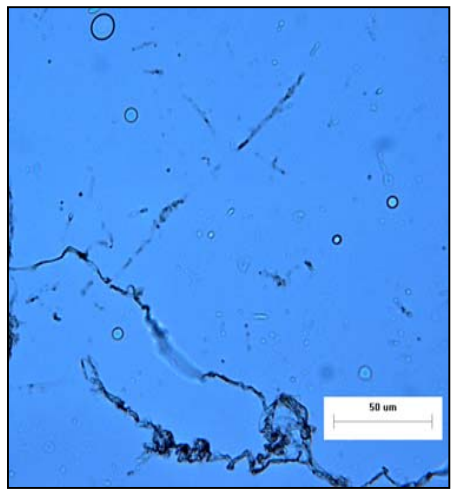
Infrared laser vaporization of polymers: update on mechanisms and applications



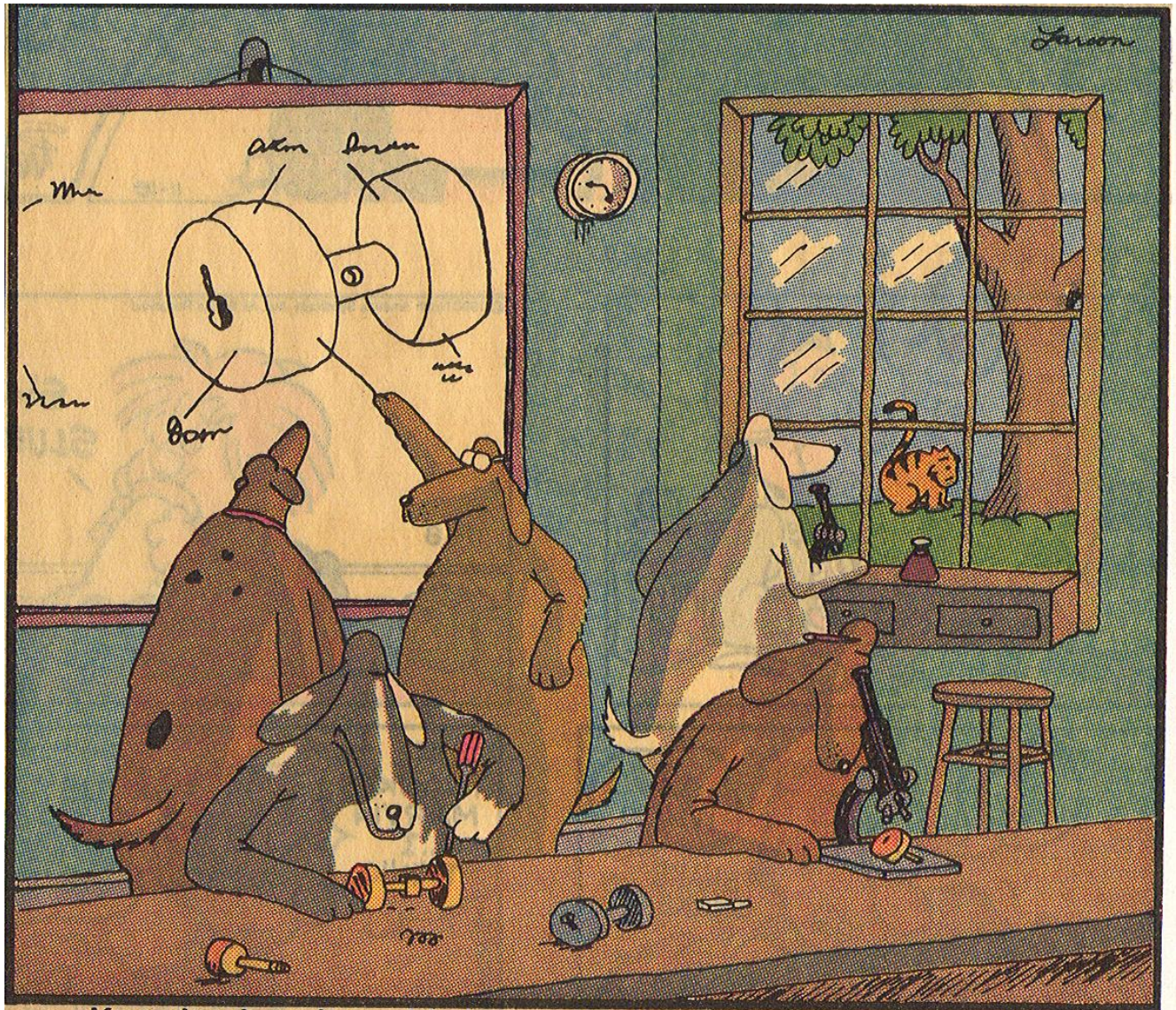




What you are about to hear …

- A new paradigm: resonant infrared pulsed laser deposition (RIR-PLD) of polymer films
- Two case studies …
  - Successful deposition of thermoset polymer: polyamic acid in *n*-methyl pyrrolidinone
  - Successful deposition of a hole-transport polymer: 3,4 poly(ethylene dioxythiophene):poly(styrene sulfonate) … PEDOT:PSS
- New evidence for low-temperature, non-thermal character of RIR-PLD … and some new thoughts about the mechanism

Is ps IR laser ablation a thermal process?

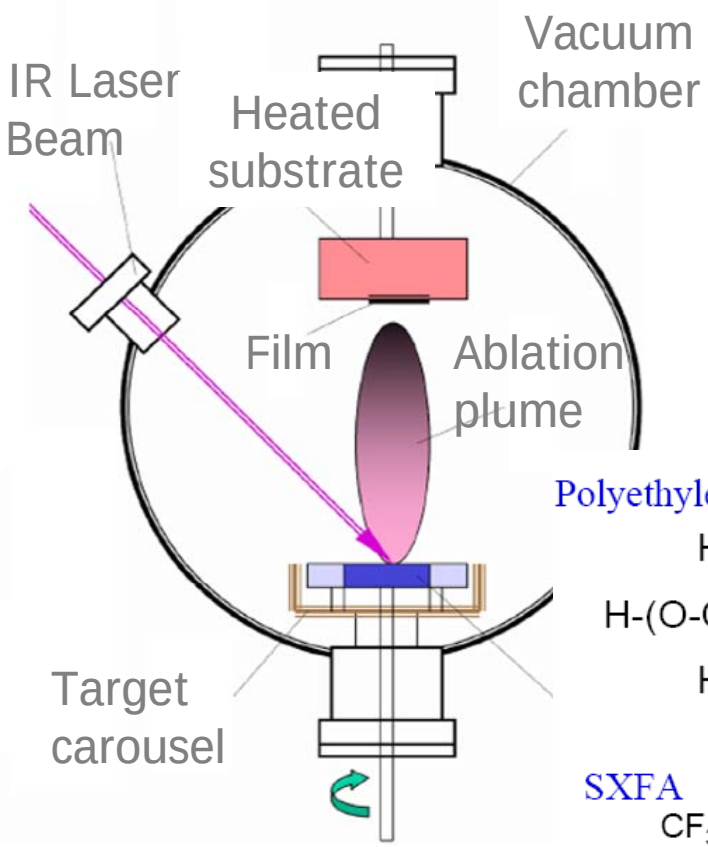


Knowing how it could change the lives of canines everywhere, the dog scientists struggled diligently to understand the Doorknob Principle.

What you are about to hear …

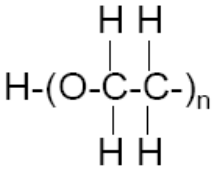
- A new paradigm: resonant infrared pulsed laser deposition (RIR-PLD) of polymer films
- Two case studies …
  - Successful deposition of thermoset polymer: polyamic acid in *n*-methyl pyrrolidinone
  - Successful deposition of a hole-transport polymer: 3,4 poly(ethylene dioxythiophene):poly(styrene sulfonate) … PEDOT:PSS
- New evidence for low-temperature, non-thermal character of RIR-PLD … and some new thoughts about the mechanism

RIR-PLD demonstrated on …



RIR-PLD collaboration (Bubb, Haglund et al., Horwitz) at the Vanderbilt FEL has demonstrated successful low-temperature deposition of a variety of thermally labile thermoplastic polymers

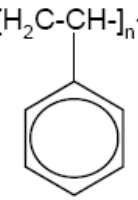
Polyethylene Glycol

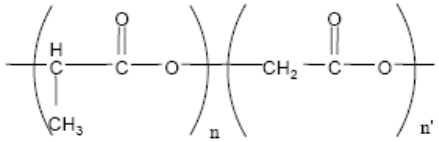


Teflon

$-(CF_2)_n-$

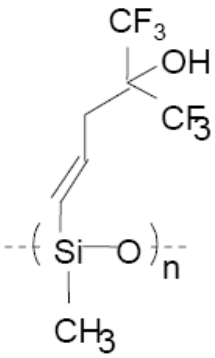
Polystyrene

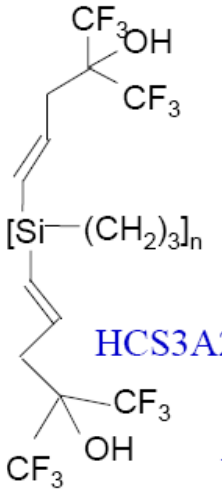




poly(DL-lactide-co-glycolide) (PLGA)

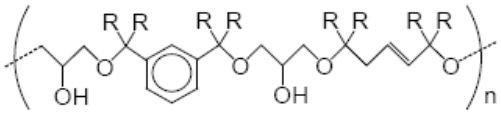
SXFA





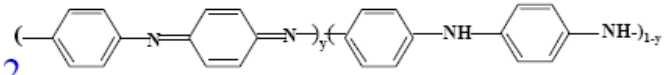
HCS3A2

Fluoropolyol



R = CF_3

Polyaniline

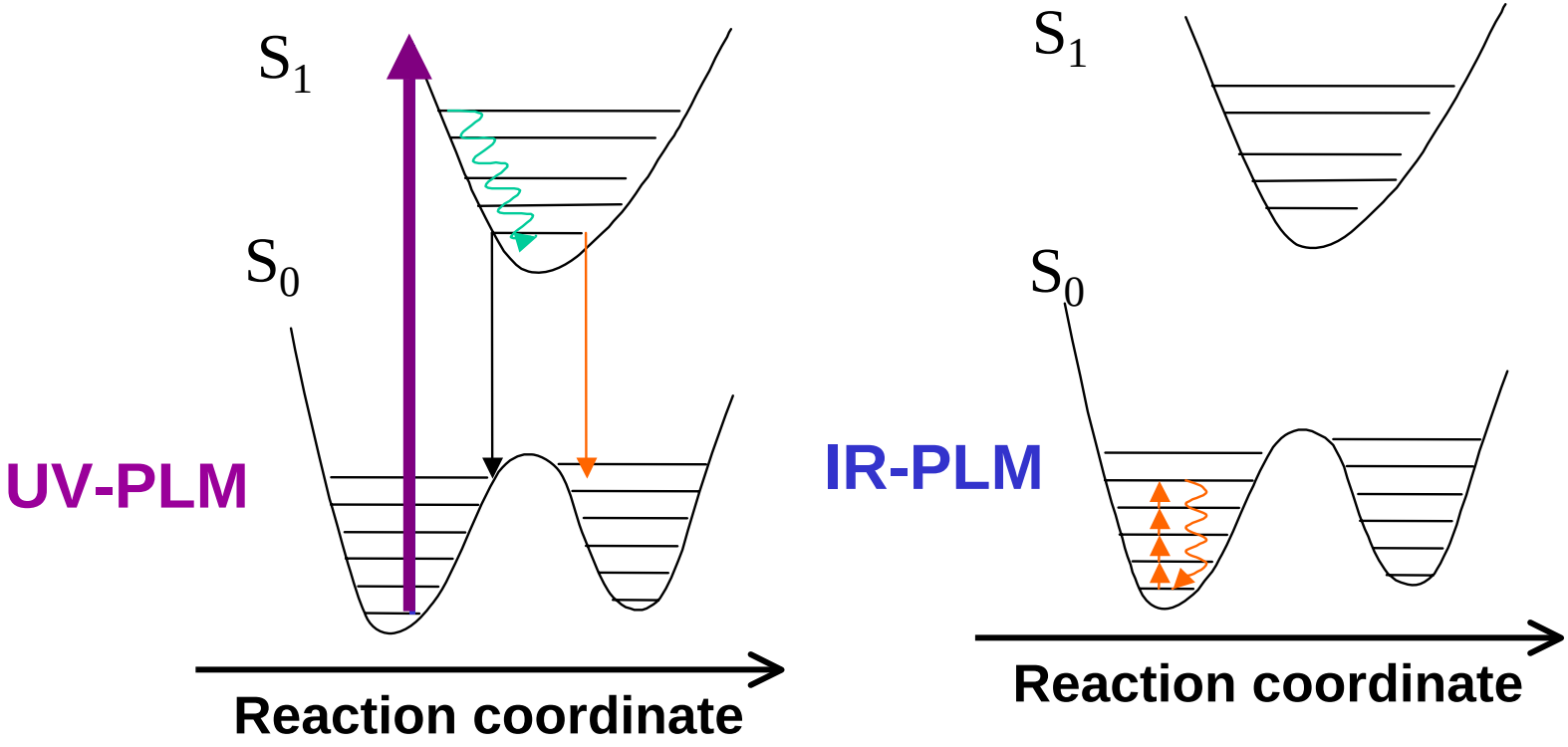


Versatile technique which preserves chemical structure and function

Electroluminescent polymers for OLEDs

A novel paradigm

- UV-visible-NIR processing begins with electronic excitation. Many materials modifications require *vibrational* energy.
- Relaxation of UV-visible-NIR energy often leads to undesirable, photolytic or photochemical products.



Efficient laser deposition

- Requires an ablation process which
  - Produces vapor, rather than particulates or clusters
  - Localizes vibrational energy long enough to break bonds
  - Converts photon energy into desired material modification
- Efficiency requires spatio-temporal energy localization:
  - Thermal confinement $\tau_L < L_{opt}^2 / D_T$ and/or
  - Mechanical or stress confinement $\tau_L \leq L_{opt} / C_s$
  - Minimal "leakage" of energy into heat (phonons), defect formation
- The processing rate and total yield are

$$\frac{dn_{\text{proc}}}{dt} = \eta n_{\text{target}} \sigma_{(\text{k})} I^{\text{k}} \Rightarrow n_{\text{proc}} \propto \frac{E_{\text{abs}}}{\text{V}} \propto F_{\text{abs}} \alpha(\omega, I)$$

- In the IR, the process yield is frequency and intensity-dependent!

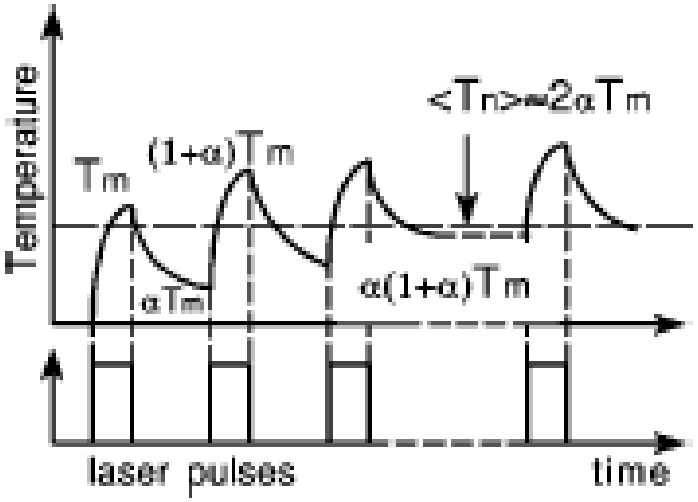
Why high repetition rate?

- Over an FEL macropulse, thermal equilibrium is established within the thermal confinement time - but …
- Each 1-ps micropulse (3-15 μJ) generates a high density of vibrationally excited states, depending on absorption length
- Materials modification is initiated by resonantly enhanced absorption in anharmonic vibrational modes.

$$T_{\max} = \sqrt{\frac{2}{\pi}} \frac{I_{\text{abs}} (D_{\text{therm}} \tau_{\text{L}})^{1/2}}{\kappa}$$

After n pulses, *T is*

$$T_{\text{n}} = 2T_{\max} \sqrt{\tau_{\text{L}} \cdot \nu_{\text{PRF}}}$$



Ergo, low temperature, high yield!

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

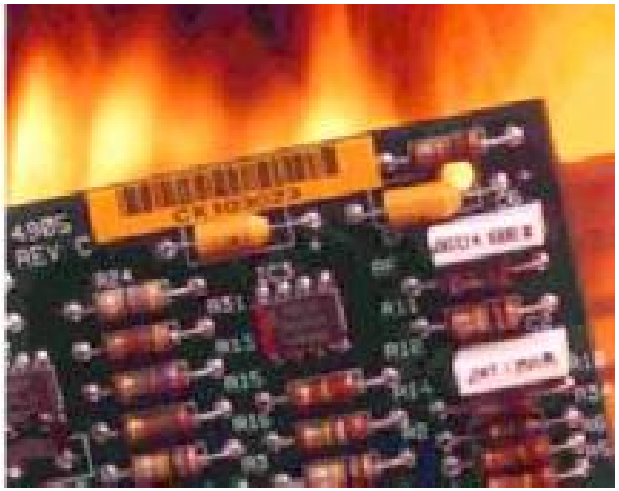
What you are about to hear …

- A new paradigm: resonant infrared pulsed laser deposition (RIR-PLD) of polymer films
- Two case studies …
  - Successful deposition of thermoset polymer: polyamic acid in *n*-methyl pyrrolidinone
  - Successful deposition of a hole-transport polymer: 3,4 poly(ethylene dioxythiophene):poly(styrene sulfonate) … PEDOT:PSS
- New evidence for low-temperature, non-thermal character of RIR-PLD … and some new thoughts about the mechanism

Polyimide - a thermoset polymer

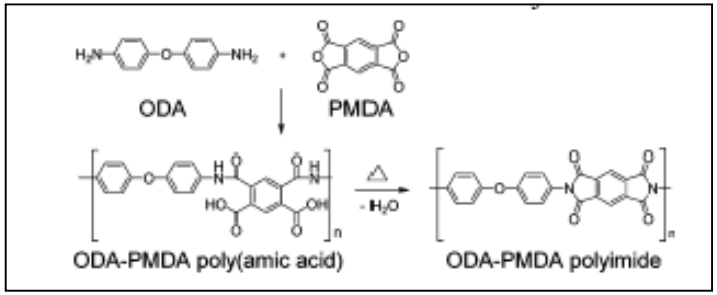
DUPONT

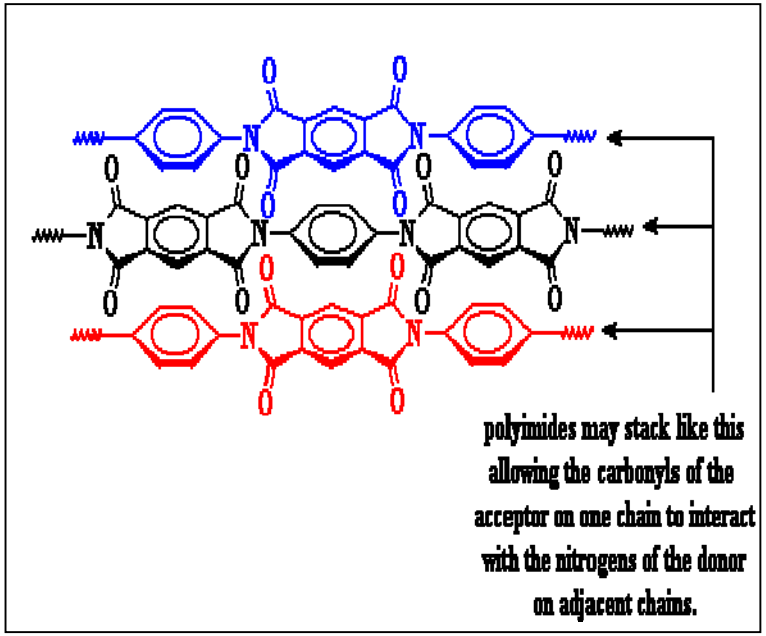
Kapton®
polyimide film



- Withstands huge extremes of temperatures
- Can be fabricated in many different forms
- Excellent insulating properties
- Chemically inert, mechanically hard
- Widely used in electronics industry

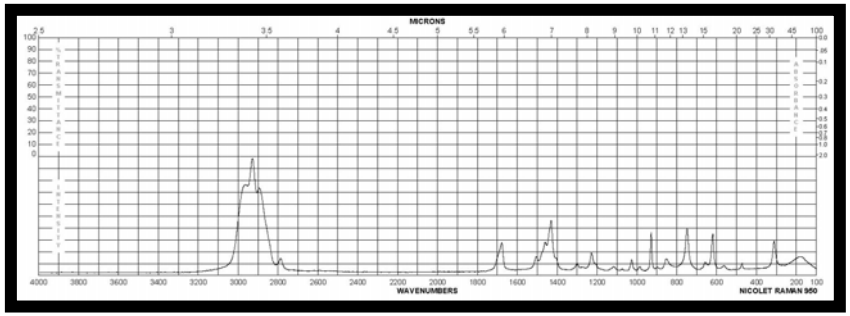
Synthesis and IR-PLD of PAA



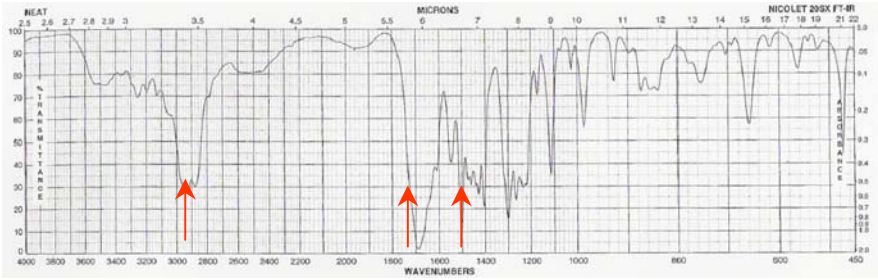


- Normal synthesis requires heating to make "thermoset"
- RIR-PLD with FEL attempted at 3.45, 5.95 and 6.67 µm (see arrows)

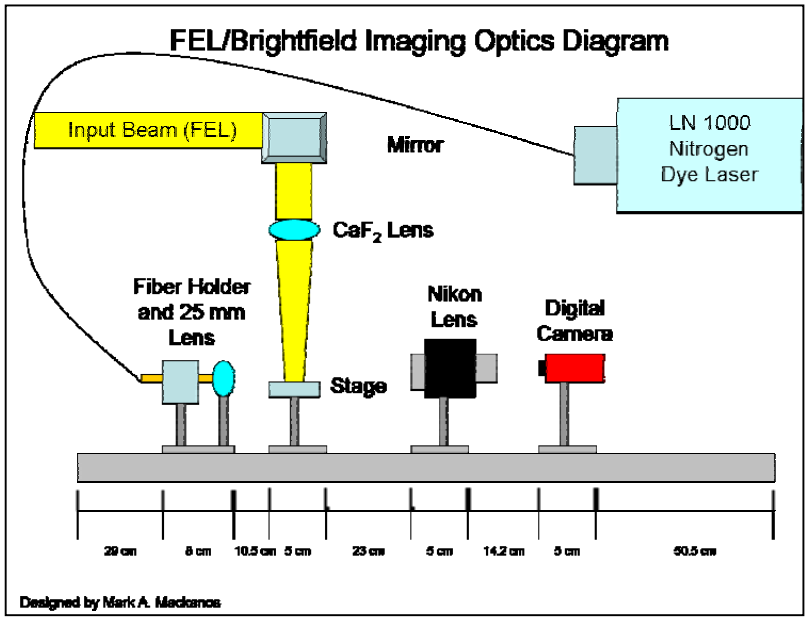
n-methyl pyrrolilidone (NMP)



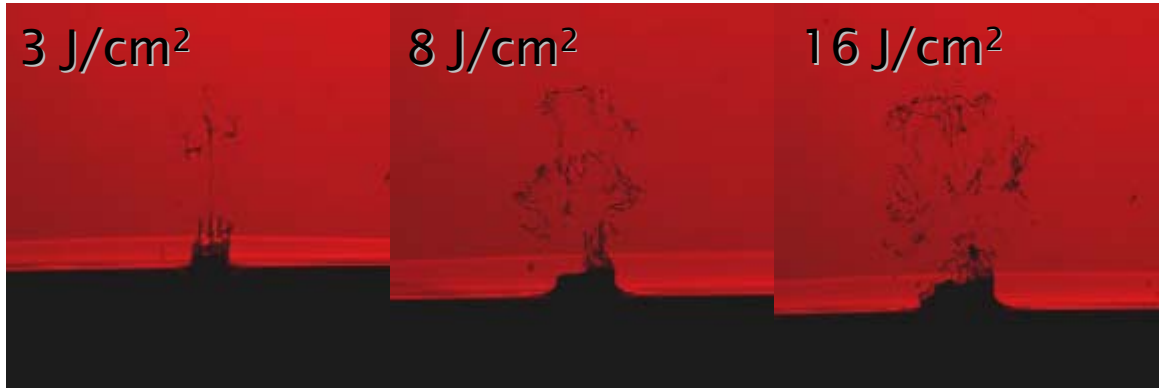
FTIR spectrum of PAA in MNP



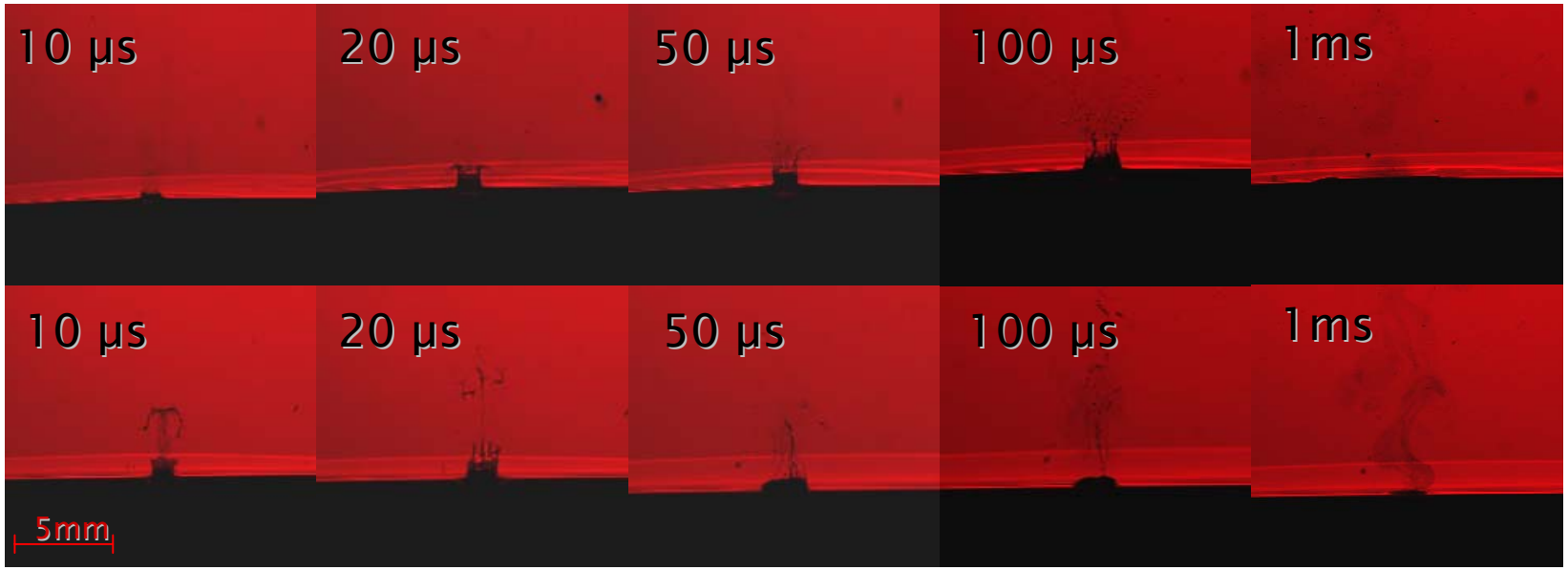
Bright-field shadowgraphy



- Use N_2-laser-pumped dye (rhodamine 6G) for bright-field shadowgraphy
- Zero-time trigger signal set on leading edge of the FEL macropulse
- Functions in air and in vacuum, permits extraction of material and shockwave velocities



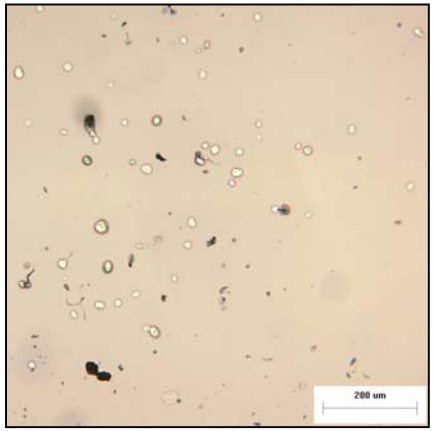
Plume photography of MNP and PAA-MNP



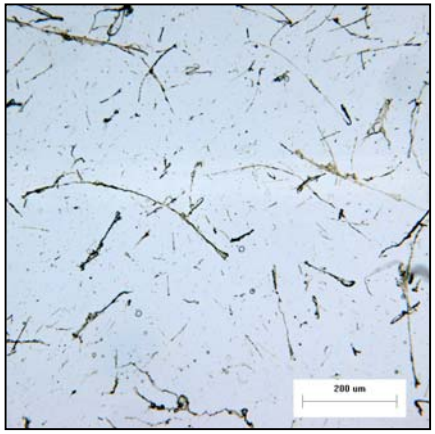
Ablation plume evolution, FEL wavelength 3.45 µm fluence ~3J/cm^2: Top NMP; bottom, PAA solution

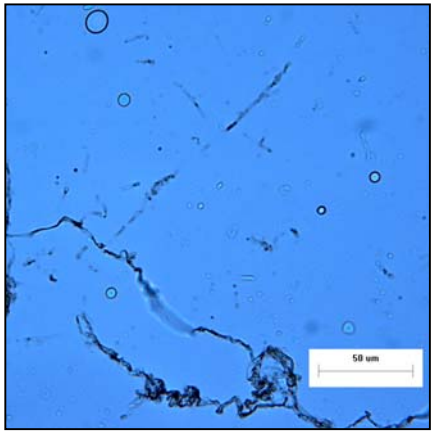
- Clear difference between the NMP matrix solution, and the more viscous NMP-PAA solution.
- Ablation phenomenology strongly resembles the behavior of liquids (*á la* Vogel, Jansen, Venugopalan)
- Suggests an important role for viscosity in the non-destructive ablation of polymers …

Results of RIR-PLD of PAA in nMP



RIR-PLD in air

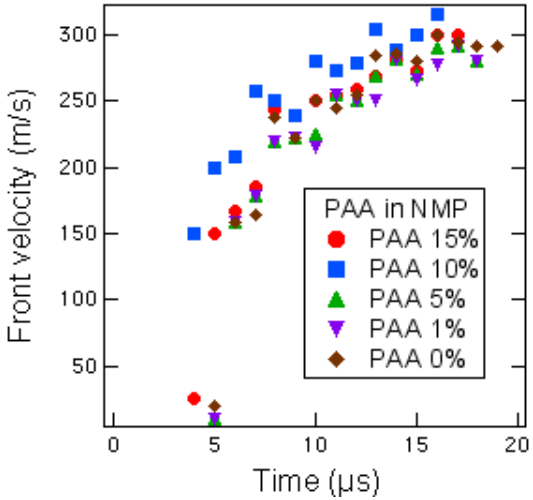


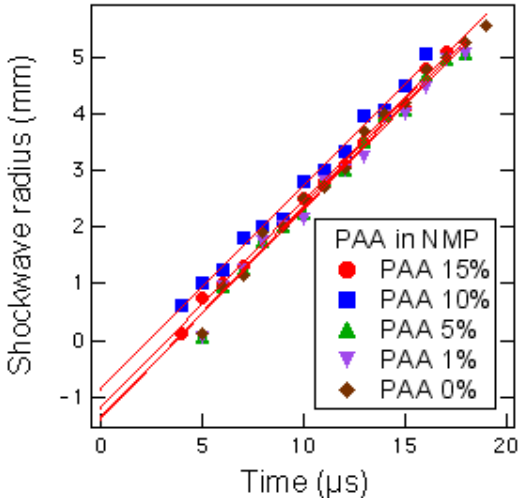


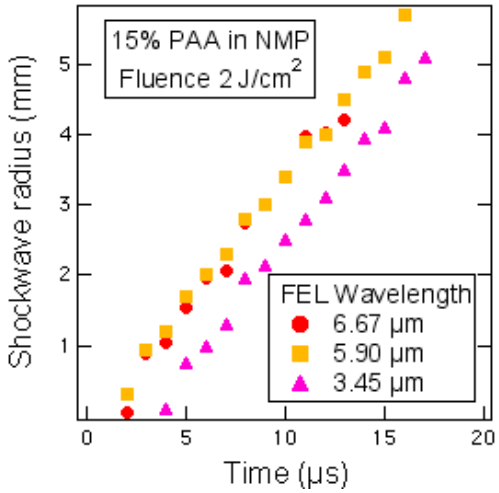
RIR-PLD in vacuum

- Threshold for deposition is ~0.5 J/cm^2 in vacuum and in air. (Scale bar above is 200 µm.)
- Photomicrographs show string (only in vacuum) and droplet (in air and vacuum) morphologies.
- Droplet size and relative abundance depend on fluence.
- Post-deposition methanol wash removed PAA-NMP.
- Curing of the PAA only occurred following heating!

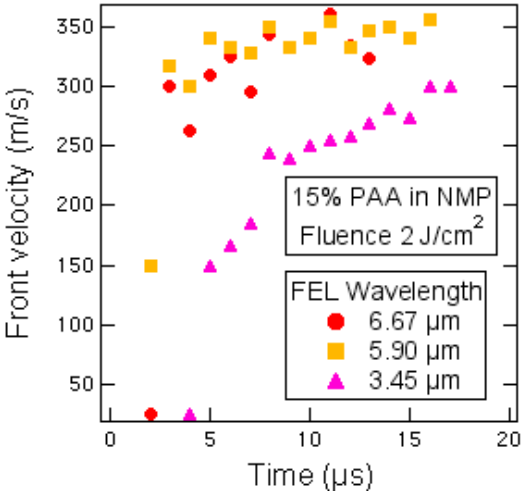
Shock-wave data at 2 J·cm^2



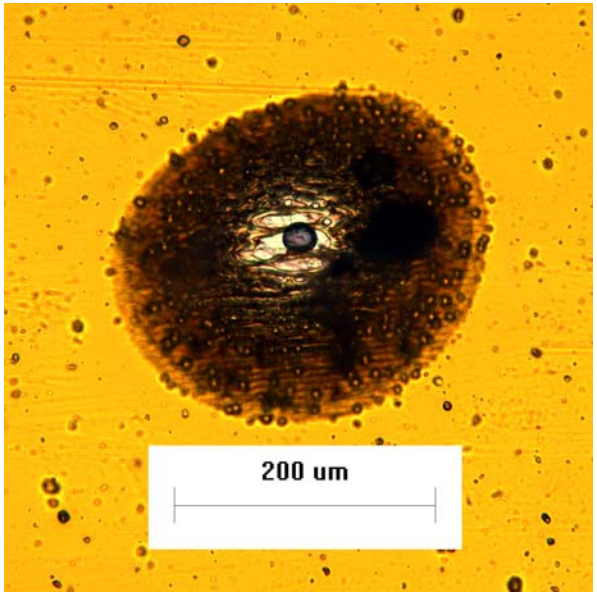


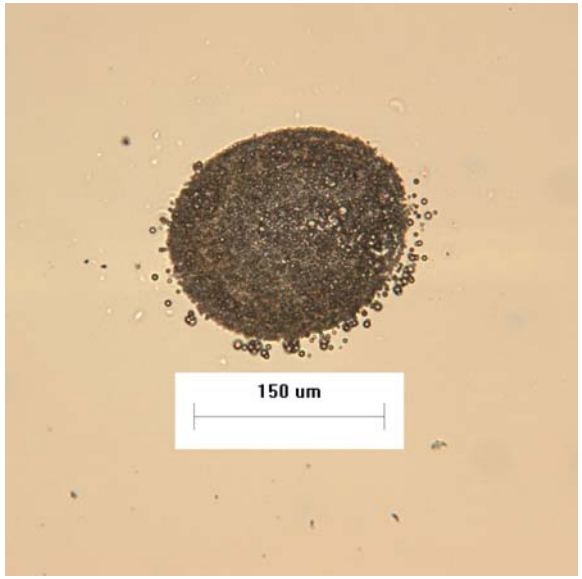


- Data from shadowgraph experiments carried out in air as function of delay time
- Shadowgraph apparatus calibrated by machinist's ruler
- At any given wavelength, shockwave velocity is relatively independent of PAA concentration
- Clear dependence of velocity on wavelength; note that 3.45 μm ablation produces slower shock wave.



Ablation of Kapton® film





- Attempts at conventional RIR-PLD on solid polyimide (Kapton®) film (left) and vacuum-dried PAA film (right) result only in damage.
- Droplet formation threshold is 3 J/cm^2 in Kapton and 1.5 J/cm^2 on PAA film.

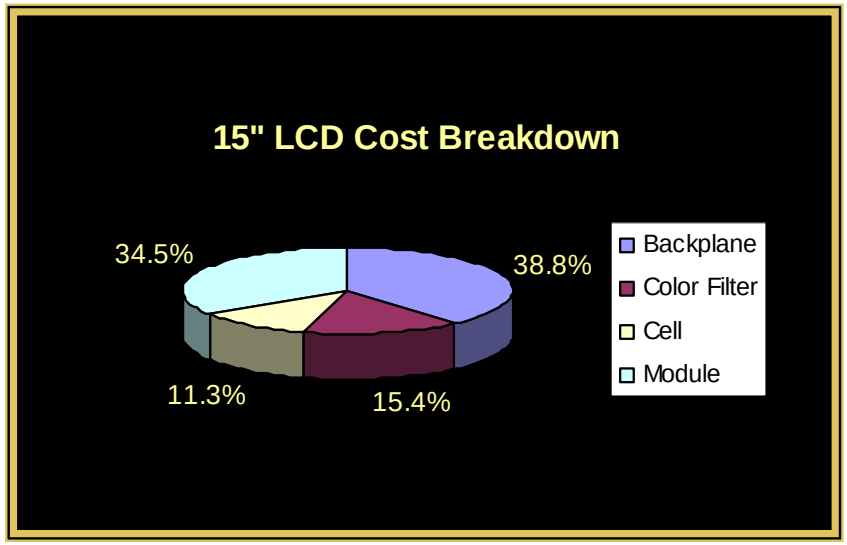
OLED Manufacturing

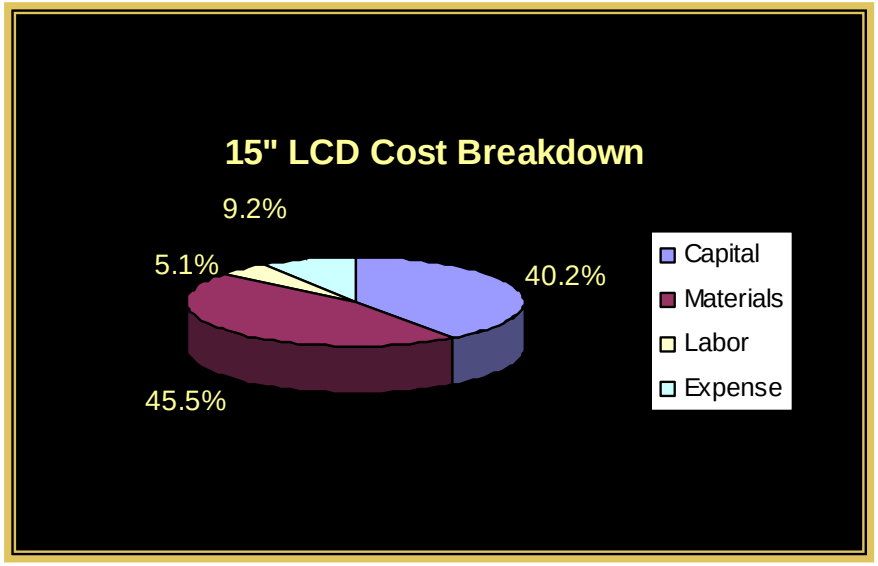
- Cost Driver

Year	2004	2007	2010
Fab cost ($/sq in)	5.00	1.00	0.50

  - Source: U.S. Display Consortium Roadmap

- Cost Breakdown

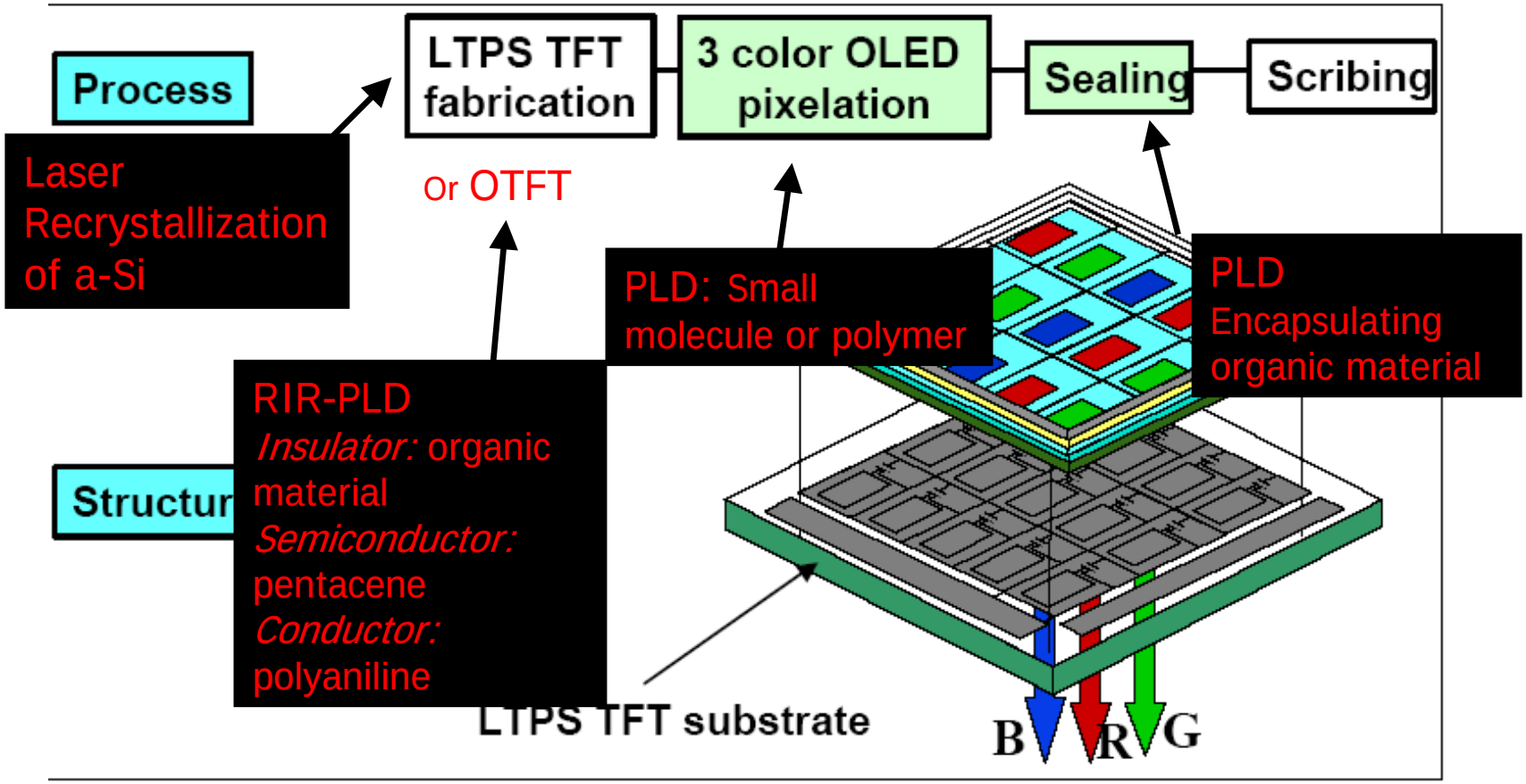




  - Source: a-SiNet

- Conclusion: Improvements that focus on (1) simpler fabrication process and (2) reduced material consumption will very likely be of interest to industry.

RIR-PLD for OLED processing …

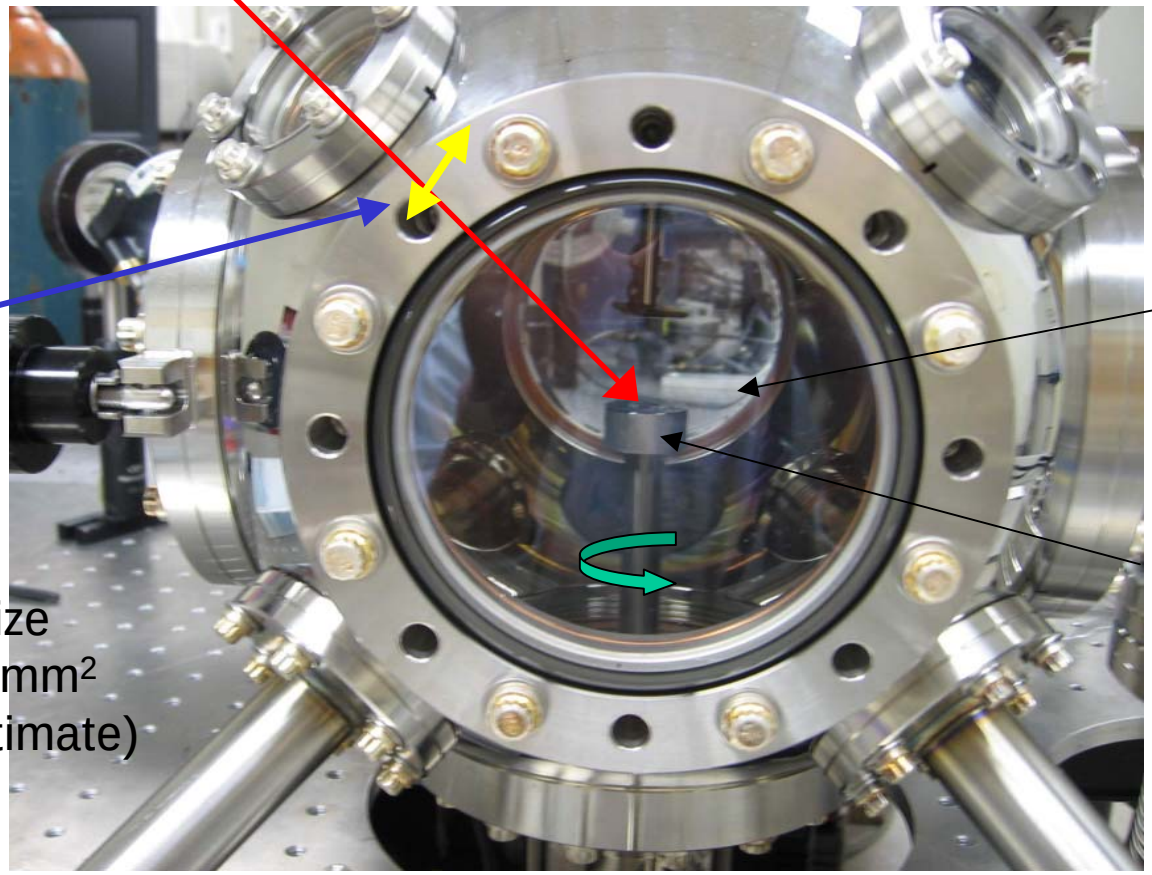


Process comparisons

	Thermal Evaporation	OVPD	Spin Coating	Ink Jet	RIR-PLD
Materials	Small organic molecules	Small organic molecules	Polymers only	Polymers only	Organics, polymers
Players	Ulvac, Tokki	Aixtron	Many, e.g. Rite Track	Seiko-Epson, Litrex	N/A
Status	Production	Pilot plant	Production	Engineering development	Prototype
Pluses	Market ready	A little faster	Atmosphere	Atmosphere, roll-to-roll	Fast, flexible
Minuses	Slow, UHV, thermal	Still slow, heating	Fab comp-atibility	Slow, ink formulation alignment	Vacuum-compatible

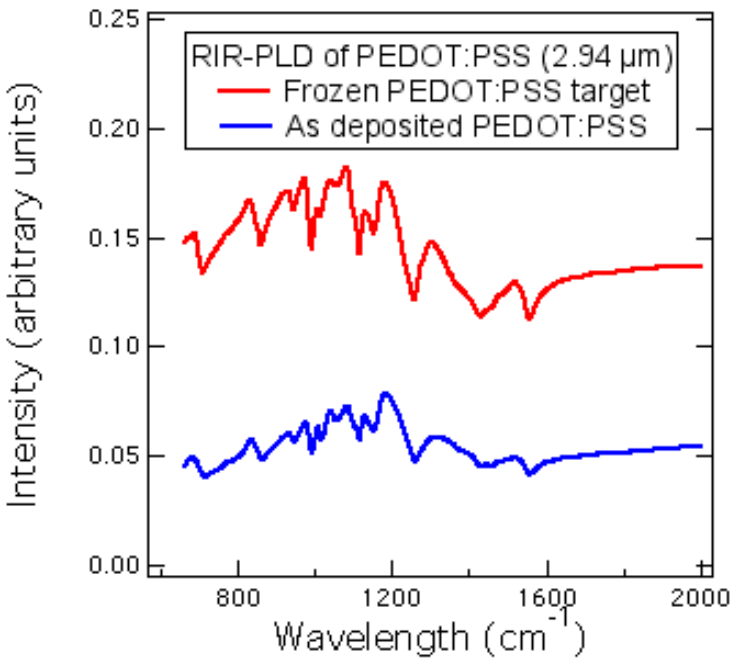
Experimental geometry

Deposition of poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) — that's PEDOT:PSS for physicists. Hole-transport layer in OLEDs



IR spectra of deposited PEDOT:PSS

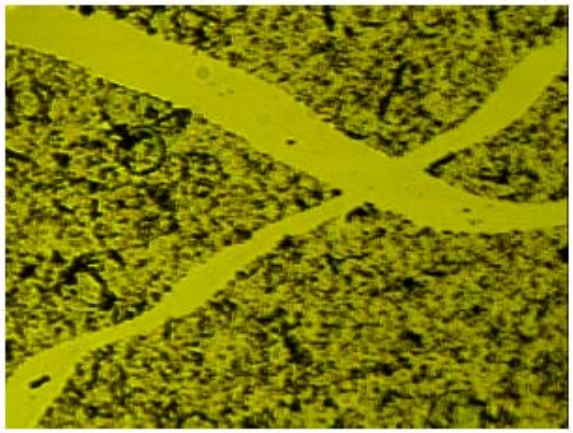
Vibrational mode	Wave number	Neat Target
Doping-induced	1303 cm^{-1}	—
C=C stretch of thiophene ring	1186	Present
Alkylene dioxy-group vibration	1080	—
Doping-induced	1039	Present
Doping-induced	1011	Present
Doping-induced	972	—
C-S stretch of thiophene ring	873	—
C-S stretch of thiophene ring	827	Weak

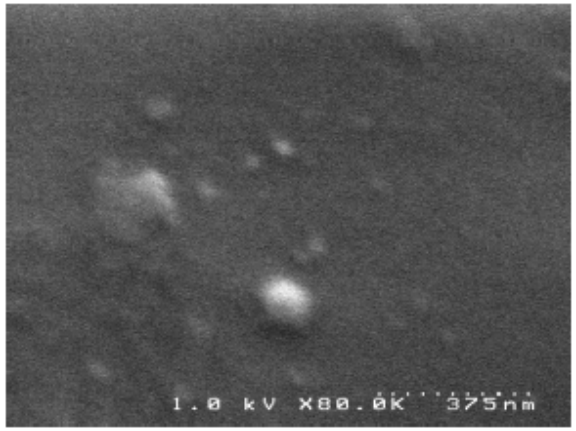


- FTIR of PEDOT:PSS in frozen target and after RIR-PLD are essentially identical to each other
- Also virtually identical to p-doped PEDOT:PSS spectra in the literature.

- FTIR data acquired on NaCl plates for IR transparency
- Water from PEDOT:PSS matrix probably dissolves some NaCl, producing *p*-doped PEDOT:PSS

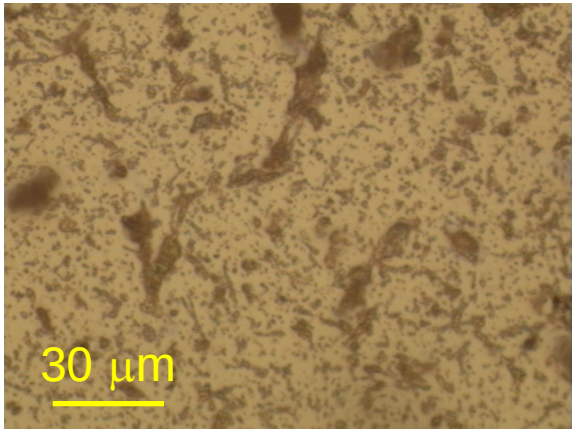
Film morphology

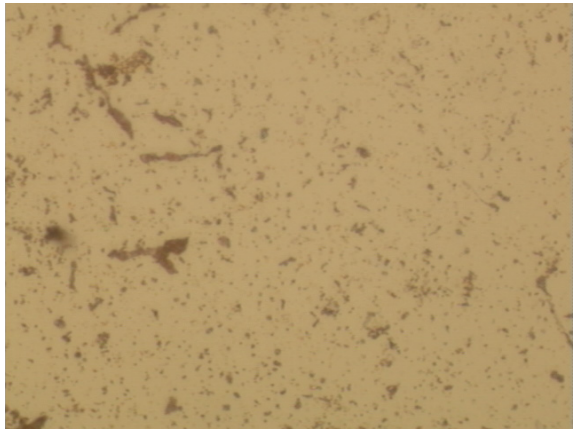


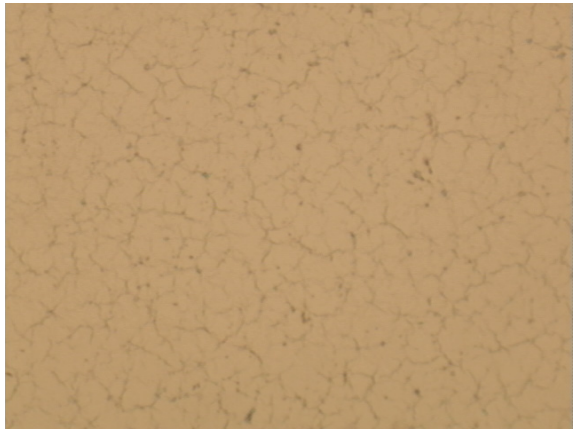


- λ = 2.95 μm on frozen PEDOT:PSS target
- "Stringy" particles form at low laser power.

High laser power | Medium laser power | Just above threshold



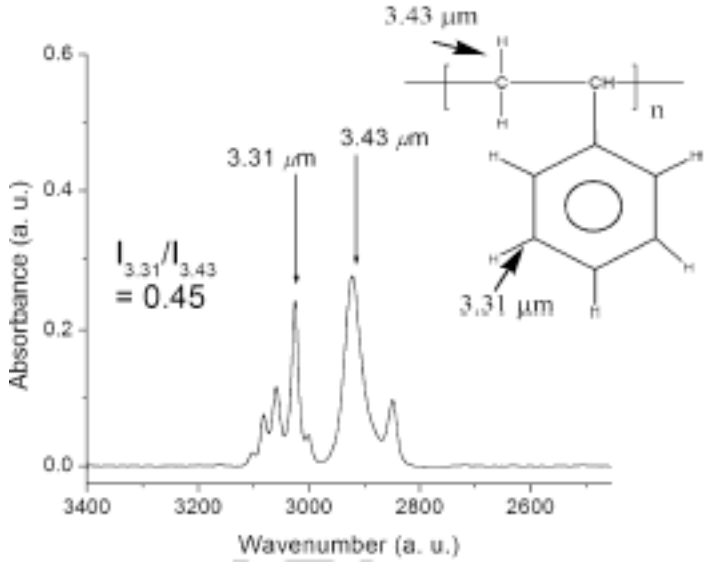


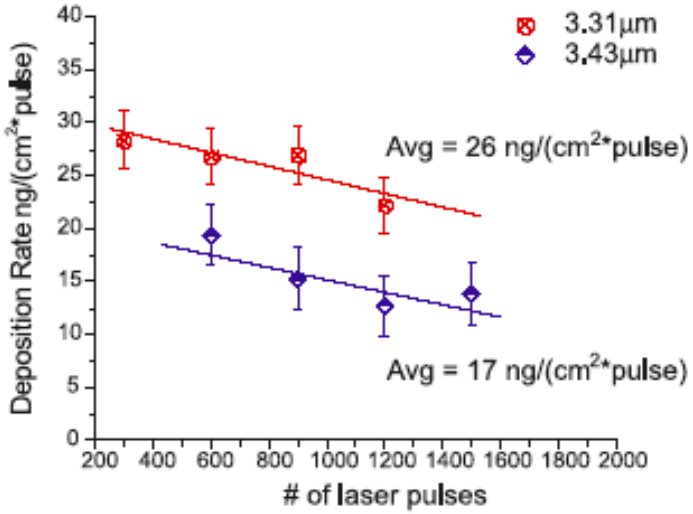


What you are about to hear …

- A new paradigm: resonant infrared pulsed laser deposition (RIR-PLD) of polymer films
- Two case studies …
  - Successful deposition of thermoset polymer: polyamic acid in *n*-methyl pyrrolidinone
  - Successful deposition of a hole-transport polymer: 3,4 poly(ethylene dioxythiophene):poly(styrene sulfonate) … PEDOT:PSS
- New evidence for low-temperature, non-thermal character of RIR-PLD … and some new thoughts about the mechanism

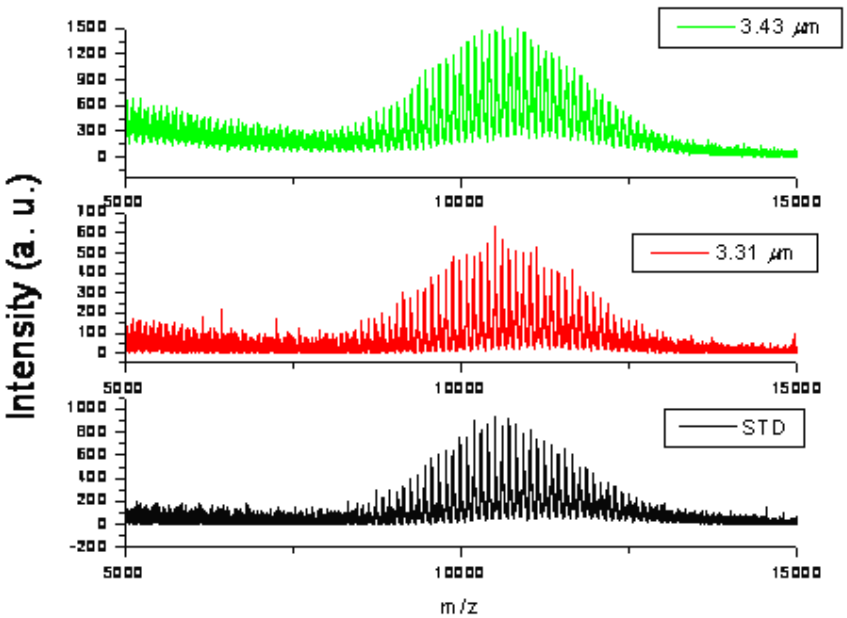
Ablation of poly(styrene)





- FEL macropulse ablation, fluence ~ 5 J/cm^2
- Molecular weight ~10 kDa
- Chain length ~100 monomer chain
- τ(3.31)~450 fs, τ(3.43)~150 fs
- *Applied Physics A* **83**, 147 (2006)

What's happening?



	3.31 μm	3.43 μm
α (cm^{-1})	1280	1450
L_p (μm)	7.8	6.9
$D_{thermal}$ (cm^2/s)	10^{-4}	10^{-4}
c_{sound} (m/s)	2200	2200
$\tau_{thermal}=(L_p)^2$ (ms)	5.7	4.5
$\tau_{pressure}=L_p/c_s$ (ns)	3.5	3.1
η/η_0	10^{-2}	10^{-2}

- Fragmentation usually from backbone modes
- Gentle bond-breaking from side-chain stretch
- Thermally, but not pressure, confined
- Dramatic decrease in viscosity (Vogler-Fulcher)
- Hydrogen bond-breaking between polymers

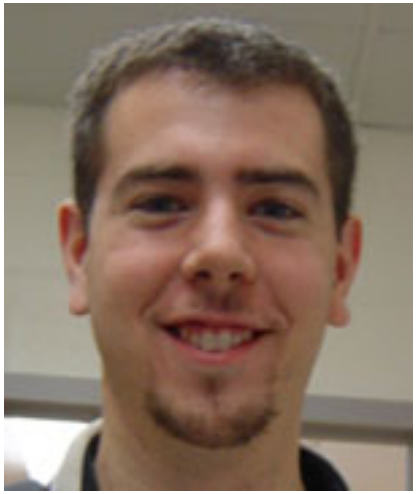
… Conclusions …

- Polyimide precursor deposition … without curing
  - much higher concentrations, much lower velocity than MAPLE
  - FTIR data (not shown) indicate wavelength selectivity
  - Thermal curing, or laser/shadow-mask patterning!!
- Deposition of PEDOT:PSS
  - First demonstration of non-liquid-phase deposition
  - Measurement of electrical transport properties in progress
  - Possible applications interest in multilayer OLED devices
- RIR-PLD is intrinsically a low-temperature process
  - Poly(amic acid) does not cure during ablation
  - Modest temperature rise, but large viscosity change
  - Mode selection influences fragmentation
- Next steps: photoacoustic measurements, more detailed characterization of transport properties, ellipsometry, hardness, patterning, integrating with plasmonics …

Thanks to the heavy lifters …

Nicole Dygert

Stephen Johnson



Ron Belmont

Ken Schriver

$$upported by the Naval Research Laboratory, the Medical Free-Electron Laser Program administered by the Air Force Office of Scientific Research and the National Science Foundation (IGERT)

And about the Doorknob Principle: "It warn't so much what I didn't know what hurt me, but what I knowed that warn't so."

(Huck Finn)